



## Quality Assurance Project Plan

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# Chlorinated Pesticides, PCBs, and Dioxins in Yakima River Fish - 2006: Assessing Progress Toward TMDL Targets and Updating the Fish Consumption Advisory

by  
Art Johnson

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

September 2006

Publication Number 06-03-111

This plan is available on the Department of Ecology home page on the  
World Wide Web at [www.ecy.wa.gov/biblio/0603111.html](http://www.ecy.wa.gov/biblio/0603111.html).

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September 2006

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

Keechelus Lake (WA-39-9050) PCBs, dioxin Yakima River (WA-39-1010) Chlordane, PCBs, dioxin Cowiche Creek (WA-38-1015) 4,4'-DDE Yakima River (WA-37-1040) 4,4'-DDE, 4,4'-DDD, alpha-BHC, PCBs Yakima River (WA-37-1020) 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, dieldrin, PCBs Yakima River (WA-37-1010) 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, dieldrin, chlordane, alpha-BHC, PCBs, dioxin.

Project Code: 07-078

#### Approvals

Approved by:	September 22, 2006
_____ Ryan Anderson, Central Regional Office	_____ Date
Approved by:	September 22, 2006
_____ Denise Mills, Section Manager, Central Regional Office	_____ Date
Approved by:	September 22, 2006
_____ John Merz, Watershed Unit Supervisor, Central Regional Office	_____ Date
Approved by:	September 12, 2006
_____ Art Johnson, Toxics Studies Unit	_____ Date
Approved by:	September 13, 2006
_____ Kristin Kinney, EIM Data Engineer, Watershed Ecology Section	_____ Date
Approved by:	September 12, 2006
_____ Dale Norton, Unit Supervisor, Toxics Studies Unit	_____ Date
Approved by:	September 13, 2006
_____ Will Kendra, Section Manager, Watershed Ecology Section	_____ Date
Approved by:	September 14, 2006
_____ Stuart Magoon, Director, Manchester Environmental Laboratory	_____ Date
Approved by:	September 13, 2006
_____ Bill Kammin, Ecology Quality Assurance Officer	_____ Date

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## Appendices

A. Chemicals to be Analyzed for the 2006 Yakima River Fish Tissue Study

## Abstract

A Quality Assurance Project Plan is provided for measuring levels of chlorinated pesticides, polychlorinated biphenyls (PCBs), and polychlorinated dioxins and furans (PCDDs/PCDFs) in fish from the Yakima River drainage. The river is on the Federal Clean Water Act Section 303(d) List for exceeding human health criteria for these compounds in edible fish tissue samples. The study will assess progress toward meeting Total Maximum Daily Load targets that have been established for the chlorinated pesticides DDT and dieldrin, assess compliance with human health criteria for all listed chemicals, and provide data to update the 1993 fish consumption advisory for DDT. Field work for the study will be conducted during the late summer and fall of 2006. A draft technical report for stakeholder review is planned for April 2007.

## Background

As required by the Clean Water Act, Total Maximum Daily Loads (TMDLs) have been established for suspended sediment in the Yakima River to bring it into compliance with Washington State water quality standards for chlorinated pesticides and turbidity. A TMDL establishes the maximum pollutant load a waterbody can assimilate without violating standards.

The basic premise behind the Yakima TMDLs was that suspended sediment from erosion of farm soils is the primary vehicle by which DDT, dieldrin, and other chlorinated pesticides were being introduced to the river at levels that adversely affected aquatic life and caused an increased health risk to people consuming fish. These pesticides were banned in the 1970s and 1980s, but persist in soil and aquatic habitats. The Washington State Department of Health (WDOH) issued a fish consumption advisory for DDT in the lower Yakima River in 1993.

([www.doh.wa.gov/ehp/oehas/EHA\\_fish\\_adv.htm](http://www.doh.wa.gov/ehp/oehas/EHA_fish_adv.htm)).

Suspended sediments (as total suspended solids or TSS) also caused excessive turbidity in the Yakima River and its tributaries. The combined effects of high TSS, turbidity, and chlorinated pesticides degrade fish and wildlife habitat. Threatened and endangered salmonids are a particular concern.

The technical study for the Lower Yakima River Suspended Sediment/DDT TMDL was conducted by the Washington State Department of Ecology (Ecology) during 1994-1995 (Joy and Patterson, 1997). [In this context, the Lower Yakima River extends downstream from approximately the town of Selah, just above the city of Yakima.] Field work for Ecology's Upper Yakima River Suspended Sediment/Organochlorine Pesticide TMDL was conducted in 1999 (Joy, 2002). The schedules adopted for meeting water quality targets developed through this work are shown below. Targets that apply directly to the present study are in bold.

### Lower Yakima River TMDL Schedule

Year	Target	Applies To
2002	≤ 5 NTU increase above background	Mainstem
2002	25 NTU	Mouths of all tributaries and drains
2007	25 NTU	All points within tributaries and drains
<b>2007</b>	<b>Develop strategy to meet DDT human health criteria</b>	<b>All tributaries, drains, and the mainstem</b>
2012	7 mg/L TSS	All tributaries, drains, and the mainstem
<b>2015</b>	<b>DDT human health criteria to be met in fish and water</b>	<b>All tributaries, drains, and the mainstem</b>

## Upper Yakima River TMDL Schedule

Year	Target	Applies To
2006	DDT compounds and dieldrin to meet aquatic life criteria	Cherry Creek and Whipple Wasteway
<b>2006</b>	<b>DDT compounds to meet human health criteria in fish fillets</b>	<b>Mainstem</b>
<b>2006</b>	<b>Monitor dieldrin in fish fillets to gauge progress toward meeting human health criteria</b>	<b>Mainstem</b>
2006	90 <sup>th</sup> percentile turbidity $\leq$ 10 NTU over background	Mainstem (r.m. 121.7 – 139.8) and mouths of selected tributaries
2011	DDT compounds and dieldrin to meet human health criteria in water	Mouths of Cherry Creek and Whipple Wasteway
<b>2011</b>	<b>Substantial progress made toward meeting human health target for dieldrin in fish fillets</b>	<b>Upper Yakima Basin</b>
2011	90 <sup>th</sup> percentile turbidity $\leq$ 5 NTU over background	Mainstem (r.m. 121.7 – 139.8) and mouths of selected tributaries

Many farmers in the Yakima basin have adopted contemporary soil erosion control Best Management Practices (BMPs) in order to meet the 5- and 10-year targets (2002/2007) for the Lower Yakima River and the 5-year targets (2006) for the Upper Yakima River. TMDL effectiveness monitoring by Ecology has shown dramatic reductions in lower river turbidities as a result (Figure 1).



Figure 1. Turbidity Improvement in the Mainstem Lower Yakima River, 1995 - 2003. [Unpublished data provided by Ryan Anderson, Ecology Central Regional Office.]

Waterbodies that exceed standards and thus require TMDLs are identified on the Federal Clean Water Act Section 303(d) List. The U.S. Environmental Protection Agency (EPA) requires states to compile a new list every two-to-four years. The Lower Yakima River was first listed for DDT, dieldrin, and other chlorinated pesticides in 1994, based on water and fish tissue samples analyzed by Ecology and the U.S. Geological Survey. The Upper Yakima River was listed for DDT compounds and dieldrin in 1996.

Washington State's 303(d) List for 2002/2004 has Yakima River fish tissue listings for a number of additional organochlorine compounds including polychlorinated biphenyls (PCBs), polychlorinated dioxins and -furans (PCDDs/PCDFs\*), chlordane, and alpha-BHC ([www.ecy.wa.gov/programs/wq/303d/index.html](http://www.ecy.wa.gov/programs/wq/303d/index.html)). PCBs were used in closed industrial systems such as electrical transformers and capacitors, plasticizers, lubricants, and hydraulic fluids. PCDDs/PCDFs are unintended byproducts found in association with certain industrial sites and waste incinerators. Chlordane and alpha-BHC are chlorinated pesticides. Uses of PCBs, chlordane, and alpha-BHC were also banned in the 1970s/1980s. These chemicals have not yet been addressed through the TMDL process.

Table 1 shows all current 303(d) Category 5 toxics listings for edible fish tissue in the Yakima River drainage. TMDLs are required for all waterbodies in Category 5. The Yakima is presently listed for DDT compounds (4,4'-DDT and breakdown products 4,4'-DDE and 4,4'-DDD), dieldrin, chlordane, alpha-BHC, PCBs, and dioxin TEQs in fish tissue. The Lower Yakima River remains on the 303(d) list for DDT and dieldrin because, unlike the Upper Yakima River, the TMDL did not specify measures to achieve human health criteria for these pesticides.

Ecology's 303(d) listing criteria for the chemicals of concern in Yakima River fish are shown in Table 2. The criteria are derived from EPA bioconcentration factors (BCFs<sup>†</sup>) and human health water column criteria established for fish consumption under the EPA National Toxics Rule (40 CFR Part 131; Federal Register Vol. 57, No. 246, and as updated). The criteria are for a 10<sup>-6</sup> (one-in-one million) excess life-time cancer risk for average fish consumers among the general public. Washington has adopted the NTR criteria as state human health water quality standards.

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\* The PCDD/PCDF listings are for dioxin (2,3,7,8-TCDD) Toxicity Equivalents (TEQs). TEQs are a measure of the combined toxicity of a mixture of PCDDs and PCDFs, based on the toxicity of dioxin, the most toxic compound.

<sup>†</sup>BCF=  $C_t/C_w$ , where  $C_t$  is the contaminant concentration in fish or shellfish tissue (wet weight) and  $C_w$  is the concentration in water (from the EPA 1980 Ambient Water Quality Criteria documents, ([www.epa.gov/waterscience/criteria/1980docs.htm](http://www.epa.gov/waterscience/criteria/1980docs.htm))).

Table 1. 303(d) Category 5 Toxics Listings for Edible Fish Tissue in the Yakima River Drainage

Listing ID	WRIA	Water Body	Parameter	Approximate Location
Upper Yakima River				
43146	39	Keechelus Lake	Total PCBs	Near inlet
43128	39	Keechelus Lake	Dioxin	Near inlet
20182	39	Yakima River	Chlordane	Umtanum
20219	39	Yakima River	Total PCBs	Umtanum
34889	39	Yakima River	Dioxin	Umtanum
17214	38	Cowiche Creek	4,4'-DDE	Near mouth
Lower Yakima River				
14257	37	Yakima River	4,4'-DDE	Union Gap
14255	37	Yakima River	4,4'-DDD	Union Gap
14259	37	Yakima River	Alpha-BHC	Union Gap
14261	37	Yakima River	Total PCBs	Union Gap
7351	37	Yakima River	4,4'-DDT	Zillah
8874	37	Yakima River	4,4'-DDE	Zillah
8875	37	Yakima River	Dieldrin	Zillah
19595	37	Yakima River	4,4'-DDE	Granger
19597	37	Yakima River	4,4'-DDE	Granger
20047	37	Yakima River	Total PCBs	Granger
20045	37	Yakima River	Total PCBs	Granger
16430	37	Yakima River	4,4'-DDD	Grandview
19598	37	Yakima River	4,4'-DDE	Prosser
19705	37	Yakima River	Chlordane	Prosser
34887	37	Yakima River	Dioxin	Prosser
8897	37	Yakima River	4,4'-DDT	Benton City
19602	37	Yakima River	4,4'-DDE	Benton City
14256	37	Yakima River	4,4'-DDE	Benton City
8893	37	Yakima River	4,4'-DDE	Benton City
14254	37	Yakima River	4,4'-DDD	Benton City
14258	37	Yakima River	Alpha-BHC	Benton City
7350	37	Yakima River	Total PCBs	Benton City
19622	37	Yakima River	4,4'-DDT	Horn Rapids
19601	37	Yakima River	4,4'-DDE	Horn Rapids
8861	37	Yakima River	4,4'-DDE	Horn Rapids
8902	37	Yakima River	Dieldrin	Horn Rapids
8864	37	Yakima River	Total PCBs	Horn Rapids
8863	37	Yakima River	Total PCBs	Horn Rapids
19614	37	Yakima River	4,4'-DDT	Near mouth
19592	37	Yakima River	4,4'-DDE	Near mouth



Table 2. National Toxics Rule Human Health Criteria for Category 5 Toxics in Yakima River Fish (ug/Kg wet weight; parts per billion)

Chemical	Edible Fish Tissue Criteria
Chlorinated Pesticides:	
4,4'-DDT	32
4,4'-DDE	32
4,4'-DDD	45
Dieldrin	0.65
Chlordane	8.3
alpha-BHC	1.7
Total PCBs	5.3
Dioxin (2,3,7,8-TCDD)	0.00007

## Project Description

In light of the human health TMDL targets for 2006/2007 and the recent 303(d) listings for other chemicals, the Ecology Central Regional Office (CRO) requested an intensive study to determine current levels of organochlorine compounds in fish throughout the Yakima River. The study will be conducted by the Ecology Environmental Assessment (EA) Program during 2006.

The objectives of the 2006 Yakima River fish tissue study will be to:

- 1) Determine if chlorinated pesticide levels have decreased in resident fish species as a result of the reduction in suspended sediment loading.
- 2) Evaluate compliance with the human health criteria for DDT compounds, dieldrin, and other 303(d) listed compounds.
- 3) Provide data to WDOH to update their fish consumption advisory.

The data obtained during this study will also be used in designing a technical TMDL study for meeting human health criteria in the Yakima River. This study is required to meet the current TMDL schedules and will set targets (loading capacity, numerical targets, load/wasteload allocations) for all 303(d) listed organochlorine compounds. Field work for the human health TMDL is scheduled to begin in the spring of 2007. In a related but separate effort, the EA Program's Freshwater Monitoring Unit will conduct effectiveness monitoring in the Wilson Creek drainage (Cherry Creek and Whipple Wasteway) to determine if the 2006 aquatic life targets for DDT compounds, dieldrin, and turbidity have been achieved. Effectiveness monitoring will also begin in the spring of 2007.

The study area boundaries for the 2006 fish tissue study will extend from the storage reservoirs in the upper watershed to Horn Rapids Dam near the river mouth and include the lower Naches River, the major Yakima tributary. Samples will also be collected in Cowiche Creek, a Naches tributary which is on the 2002/2004 303(d) list for DDE in edible fish tissue. Dieldrin and PCB exceedances have been reported in Cowiche Creek fish (Davis et al., 1998) but these findings were overlooked in preparing the 2002/2004 303(d) list. The Naches River is not listed for toxics.

Fish will be collected from nine sites in the drainage. The field work will be conducted during the late summer and fall of 2006. An effort will be made to enlist the help of biologists from the Yakama Nation and Washington Department of Fish and Wildlife (WDFW) in the fish collection. Up to 114 composite samples will be analyzed by the Ecology Manchester Environmental Laboratory (MEL) for all 303(d) listed pesticides, PCBs, and PCDDs/PCDFs. Efforts will be made to ensure that ESA listed species are not harmed by the study; this may be a constraint to obtaining the desired sample size.

The study will be limited to resident fish species. Levels of chemical contaminants in returning migratory species largely reflect residues accumulated elsewhere and would have little bearing on the TMDLs. Recent contaminant data already exist for Yakima River steelhead and chinook from the EPA Columbia River Basin Fish Contaminant Survey (EPA, 2002). Although the EPA survey also analyzed resident species, the number of samples and species were limited for most of their Yakima River collection sites.

## Organization, Schedule, and Lab Budget

### Organization

Name	Ecology Affiliation	Role	Contact Information
Ryan Anderson	CRO	Client	509-575-2642 <a href="mailto:rand461@ecy.wa.gov">rand461@ecy.wa.gov</a>
Art Johnson	EAP-TSU	Project Lead	360-407-6766 <a href="mailto:arjo461@ecy.wa.gov">arjo461@ecy.wa.gov</a>
Randy Coots	EAP-TSU	Field Lead	360-407-6690 <a href="mailto:rcoo461@ecy.wa.gov">rcoo461@ecy.wa.gov</a>
Brandee Era-Miller	EAP-TSU	Field Assistance	360-407-6771 <a href="mailto:bera461@ecy.wa.gov">bera461@ecy.wa.gov</a>
Kristin Kinney	EAP-TSU	Field Assistance EIM Data Engineer Data Report to WDOH	360-407-7168 <a href="mailto:kkin461@ecy.wa.gov">kkin461@ecy.wa.gov</a>
Dale Norton	EAP-TSU	Unit Supervisor	360-407-6765 <a href="mailto:dnor461@ecy.wa.gov">dnor461@ecy.wa.gov</a>
Stuart Magoon	Manchester Lab	Director	360-871-8801 <a href="mailto:smag461@ecy.wa.gov">smag461@ecy.wa.gov</a>
Dean Momohara	Manchester Lab	Units Supervisor	360-871-8808 <a href="mailto:dmomo461@ecy.wa.gov">dmomo461@ecy.wa.gov</a>
Pam Covey	Manchester Lab	Sample Scheduling/Receipt	360-871-8827 <a href="mailto:pcov461@ecy.wa.gov">pcov461@ecy.wa.gov</a>
Bill Kammin	EAP	Quality Assurance Officer	360-407-6964 <a href="mailto:wkam461@ecy.wa.gov">wkam461@ecy.wa.gov</a>

## Schedule

<b>Field Work and Laboratory Analyses</b>	
Fish Collection	August – October 2006
Chemical Analyses Completed	December 2006
<b>Final Report</b>	
Report Author Lead	Art Johnson
Schedule:	
Report Supervisor Draft Due	February 2007
Report Client/Peer Draft Due	March 2007
Report External Draft Due	April 2007
Report Final Due (Original)	June 2007
<b>Environmental Information System (EIM) Data Set</b>	
EIM Data Engineer	Kristin Kinney
EIM User Study ID	AJOH0050
EIM Study Name	Yakima River 2006 Fish Tissue Study
EIM Completion Due	June 2007

A completion date for a revision to the WDOH fish consumption advisory has yet to be determined.

## Lab Budget Estimate

The laboratory budget for this project is estimated at \$73,900 (see Table 6). The costs include a 50% discount for MEL analyses and MEL's 25% surcharge for contract laboratory work.

## Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality so that uncertainties are minimized and results are comparable to existing data from other studies. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this plan.

### Measurement Quality Objectives

MEL and their contractors are expected to meet all QC requirements of the analytical methods being used for this project. Measurement quality objectives (MQOs) are shown in Table 3. These MQOs correspond to MEL's QC limits.

Table 3. Measurement Quality Objectives for 2006 Yakima River Fish Tissue Study

Analysis	Check Stds./ Lab Control Samples (% recov.)	Laboratory Duplicates (RPD)	Matrix Spikes (% recov.)	Surrogates (% recov.)	Lowest Concentration of Interest
Chlorinated pesticides	50 - 150	≤ 50	50 - 150	30 - 150	0.5 ug/Kg ww
PCBs	50 - 150	≤ 50	50 - 150	30 - 150	4 ug/Kg ww
PCDDs/PCDFs	50 - 150	≤ 50	50 - 150	25 - 150*	0.1-1 ng/Kg ww
Percent lipids	NA	≤ 20	NA	NA	0.1 %

\*recovery of labeled congeners

NA = not applicable

Check standards and laboratory control samples (LCS) contain known amounts of analyte and indicate bias due to sample preparation and/or calibration. Results on laboratory duplicates (split samples) provide estimates of analytical precision. Matrix spikes may indicate bias due to matrix effects and provide an estimate of the precision of the results. Surrogates are compounds with characteristics similar to target compounds and are added to all samples prior to extraction. Recovery of surrogate spikes can be used to estimate the recovery of target compounds in the sample. The PCDD/PCDF analysis will be done by an isotopic dilution method and each sample is spiked with labeled congeners. The lowest concentrations of interest shown in Table 3 are those practically attainable within budget constraints of this project and are low enough to compare to human health criteria (Table 2).

## Sampling Design

Table 4 has a summary of the Yakima River fish tissue samples that have been analyzed historically for 303(d) listed pesticides, PCBs, and PCDDs/PCDFs, arranged by location, sample type, and date of collection.

Nine sampling sites are proposed for the 2006 Yakima River fish tissue study (Figure 2). Starting at the uppermost part of the drainage, fish samples will be analyzed from Keechelus Lake and Kachess Lake, two of the three storage reservoirs. Keechelus is listed for PCBs and dioxin TEQs, based on the EPA National Study of Chemical Residues in Lake Fish Tissue (unpublished data). Chlorinated pesticide concentrations were low in these samples and met human health criteria. Kachess Lake lacks the development around Keechelus and is proposed for sampling to give a more representative assessment of upstream conditions and to put the Keechelus results in perspective. Cle Elum Lake, the third reservoir, is similar to Kachess with respect to development, is also not on the 303(d) list, and will not be sampled.

Table 4. Sources of Data on Organochlorines in Fillet and Whole Body Samples of Yakima River Fish

Reach	Location	Date	Species	Chlor. Pest.	PCBs	Dioxins	Type	N* =	Reference
Keechelus Lake	Keechelus Lake	2001	MWF	✓	✓	✓	F	1	EPA Nat. Lakes Study
Keechelus Lake	Keechelus Lake	2001	LSS	✓	✓	✓	W	1	EPA Nat. Lakes Study
Cle Elum	Cle Elum	1985	MWF, RBT	✓	✓		F	3	Johnson et al. (1986)
Cle Elum	Cle Elum	Oct-99	MWF, RBT	✓			F	3	Rogowski (2000)
Cle Elum	Cle Elum	8-9/85	MWF, MUSS	✓	✓		W	2	Johnson et al. (1986)
Cle Elum	Cle Elum	1989-90	MWF	✓	✓		W	2	Rinella et al. (1992)
Yakima Canyon	Wymer	8-9/85	MWF, BLS, NPM, RBT	✓	✓		F	5	Johnson et al. (1986)
Yakima Canyon	Rosa Dam	5-7/85	CHNK	✓	✓		F	4	Johnson et al. (1986)
Yakima Canyon	Umtanum	1991	MWF, LSS	✓	✓		F	?	Rinella et al. (1992)
Yakima Canyon	Nr. Umtanum	Sep-96	LSS, RBT, CAT	✓	✓	✓	F	9	EPA (2002)
Yakima Canyon	Wymer	Oct-99	RBT, LSS	✓			F	2	Rogowski (2000)
Yakima Canyon	Rosa Dam	5-7/85	CHNK (smolts)	✓	✓		W	2	Johnson et al. (1986)
Yakima Canyon	Wymer	8-9/85	MWF, BLS, NPM, MUSS	✓	✓		W	4	Johnson et al. (1986)
Yakima Canyon	Umtanum	1990	MWF, LSS, BLS	✓	✓		W	3	Rinella et al. (1992)
Yakima Canyon	Nr. Umtanum	Sep-96	LSS, RBT, CAT	✓	✓	✓	W	9	EPA (2002)
Yakima-Parker	Bw. Birchfield Drain	Sep-83	BLS, MWF	✓	✓		F	2	Hopkins et al. (1985)
Yakima-Parker	Parker	1989-90	MWF, LSS	✓	✓		F	?	Rinella et al. (1992)
Yakima-Parker	Bw. Birchfield Drain	Sep-83	BLS, MWF, NPM	✓	✓		W	3	Hopkins et al. (1985)
Yakima-Parker	Parker	1989-90	LSS	✓	✓		W	1	Rinella et al. (1992)
Buena	Buena	8/85	MWF, SCK, NMP	✓	✓		F	5	Johnson et al. (1986)
Buena	Buena	8/85	MWF, SCK, NMP	✓	✓		W	5	Johnson et al. (1986)
Granger - Grandview	Grandview	Sep-95	SMB, CRP	✓	✓		F	2	Davis et al. (1998)
Granger - Grandview	Granger	Apr-98	LSS	✓	✓	✓	F	1	EPA (2002)
Granger - Grandview	Granger	1970-74	3 Species	✓	✓		W	9	Schmitt et al., (1981)
Granger - Grandview	Granger	1976	BCR, LSS	✓	✓		W	3	Schmitt et al., (1983)
Granger - Grandview	Granger	1978	WCR, CRP	✓	✓		W	3	Schmitt et al., (1983)
Granger - Grandview	Granger	1980	BCR, LSS	✓	✓		W	3	Schmitt et al., (1985)
Granger - Grandview	Granger	1984	BCR, LSS	✓	✓		W	3	Schmitt et al., (1990)
Granger - Grandview	Sunnyside	1989	MWF, LSS, CRP	✓	✓		W	3	Rinella et al. (1992)
Granger - Grandview	Grandview	1989-90	LSS	✓	✓		W	2	Rinella et al. (1992)



Reach	Location	Date	Species	Chlor. Pest.	PCBs	Dioxins	Type	N* =	Reference
Granger - Grandview	Granger	1990	LSS	✓	✓		W	1	Rinella et al. (1992)
Granger - Grandview	Grandview	Sep-95	LSS	✓	✓		W	3	Davis et al. (1998)
Granger - Grandview	Granger	1997	CRP, NPM, LMB, SMB	✓	✓		WB	6	Hinck et al. (2004)
Granger - Grandview	Bw. Granger	Apr-98	LSS	✓	✓	✓	W	2	EPA (2002)
Granger - Grandview	Granger	Apr-98	LSS	✓	✓	✓	W	1	EPA (2002)
Prosser Area	Chandler Canal Entrance	5-10/97	CHNK	✓	✓	✓	F	4	EPA (2002)
Prosser Area	Chandler Canal Entrance	Mar-98	STHD	✓	✓	✓	F	3	EPA (2002)
Prosser Area	Chandler Canal Entrance	Mar-98	MWF	✓	✓	✓	F	3	EPA (2002)
Prosser Area	Prosser	Mar-98?	MWF	✓	✓	✓	F	3	EPA (2002)
Prosser Area	Chandler Canal Entrance	Jul-96	BLS, LSS, MWF	✓	✓	✓	W	9	EPA (2002)
Prosser Area	Chandler Canal Entrance	5-10/97	CHNK	✓	✓	✓	W	3	EPA (2002)
Prosser Area	Chandler Canal Entrance	Mar-98	STHD	✓	✓	✓	W	3	EPA (2002)
Prosser Area	Prosser	Mar-98?	MWF	✓	✓	✓	W	3	EPA (2002)
Horn Rapids-Kiona	Kiona	8/85	LSS, NMP, SMB, CAT	✓	✓		F	4	Johnson et al. (1986)
Horn Rapids-Kiona	Horn Rapids	1987	SMB	✓	✓	✓	F?	1	EPA (1992)
Horn Rapids-Kiona	Kiona	1989-90	MWF, LSS	✓	✓		F	?	Rinella et al. (1992)
Horn Rapids-Kiona	Horn Rapids	Sep-92	SMB	✓	✓		F	2	Davis & Johnson (1994)
Horn Rapids-Kiona	1/2 mi ab. Horn Rapids	Apr-98	SMB	✓	✓	✓	F	1	EPA (2002)
Horn Rapids-Kiona	2 mi. ab. Horn Rapids	Apr-98	SMB	✓	✓	✓	F	3	EPA (2002)
Horn Rapids-Kiona	Kiona	Sep-80	SMB, BLS	✓	✓		W	2	Hopkins et al. (1985)
Horn Rapids-Kiona	Kiona	Aug-81	NPM, LSS	✓	✓		W	2	Hopkins et al. (1985)
Horn Rapids-Kiona	Bw. Kiona	Sep-82	BLS, MWF	✓	✓		W	2	Hopkins et al. (1985)
Horn Rapids-Kiona	Bw. Kiona	Sep-83	BLS, CAT	✓	✓		W	2	Hopkins et al. (1985)
Horn Rapids-Kiona	Kiona	8/85	LSS, NMP	✓	✓		W	2	Johnson et al. (1986)
Horn Rapids-Kiona	Horn Rapids	1987	CRP	✓	✓	✓	W	1	EPA (1992)
Horn Rapids-Kiona	Kiona	1989-90	MWF, LSS	✓	✓		W	5	Rinella et al. (1992)
Horn Rapids-Kiona	Horn Rapids	Sep-92	LSS	✓	✓		W	2	Davis & Johnson (1994)
Horn Rapids-Kiona	1/2 mi ab. Horn Rapids	Apr-98	SMB	✓	✓	✓	W	1	EPA (2002)
Horn Rapids-Kiona	Kiona	Apr-98	SMB	✓	✓	✓	W	1	EPA (2002)
Horn Rapids-Kiona	2 mi. ab. Horn Rapids	Apr-98	SMB	✓	✓	✓	W	1	EPA (2002)
Yakima @ mouth	Yakima @ mouth	May-98	CAT	✓	✓	✓	F	3	EPA (2002)
Yakima @ mouth	Yakima @ mouth	May-98	CAT	✓	✓	✓	W	3	EPA (2002)

Reach	Location	Date	Species	Chlor. Pest.	PCBs	Dioxins	Type	N* =	Reference
Naches River	Naches River	1990	MWF, LSS	✓	✓		W	2	Rinella et al. (1992)
Yakima Tributary	Cowiche Creek	Sep-95	RBT	✓	✓		F	1	Davis et al. (1998)
Yakima Tributary	Marion Drain, mouth	Apr-98	LSS	✓	✓		F	2	EPA (2002)
Yakima Tributary	Wide Hollow Cr.	1989	LSS, BLS	✓	✓		W	3	Rinella et al. (1992)
Yakima Tributary	Moxee Drain	1989	MWF, LSS	✓	✓		W	2	Rinella et al. (1992)
Yakima Tributary	Granger Drain, mouth	1989	LSS, BLS	✓	✓		W	2	Rinella et al. (1992)
Yakima Tributary	Toppenish Cr.	1989	LSS	✓	✓		W	1	Rinella et al. (1992)
Yakima Tributary	Sulphur Cr.	1989	LSS	✓	✓		W	1	Rinella et al. (1992)
Yakima Tributary	Cherry Cr.	1990	BLS	✓	✓		W	1	Rinella et al. (1992)

\*total number of samples, all species

BCR = black crappie

BLS = bridgelip sucker

CAT = channel catfish

CHNK = chinook

CRAY = crayfish

CRP = common carp

F = fillet

LSS = largescale sucker

MB = largemouth bass

MUSS = mussel

MWF = mountain whitefish

NPM = northern pikeminnow

RBT = rainbow trout

SCK = sucker

SMB = smallmouth bass

W = whole body

WCR = white crappie

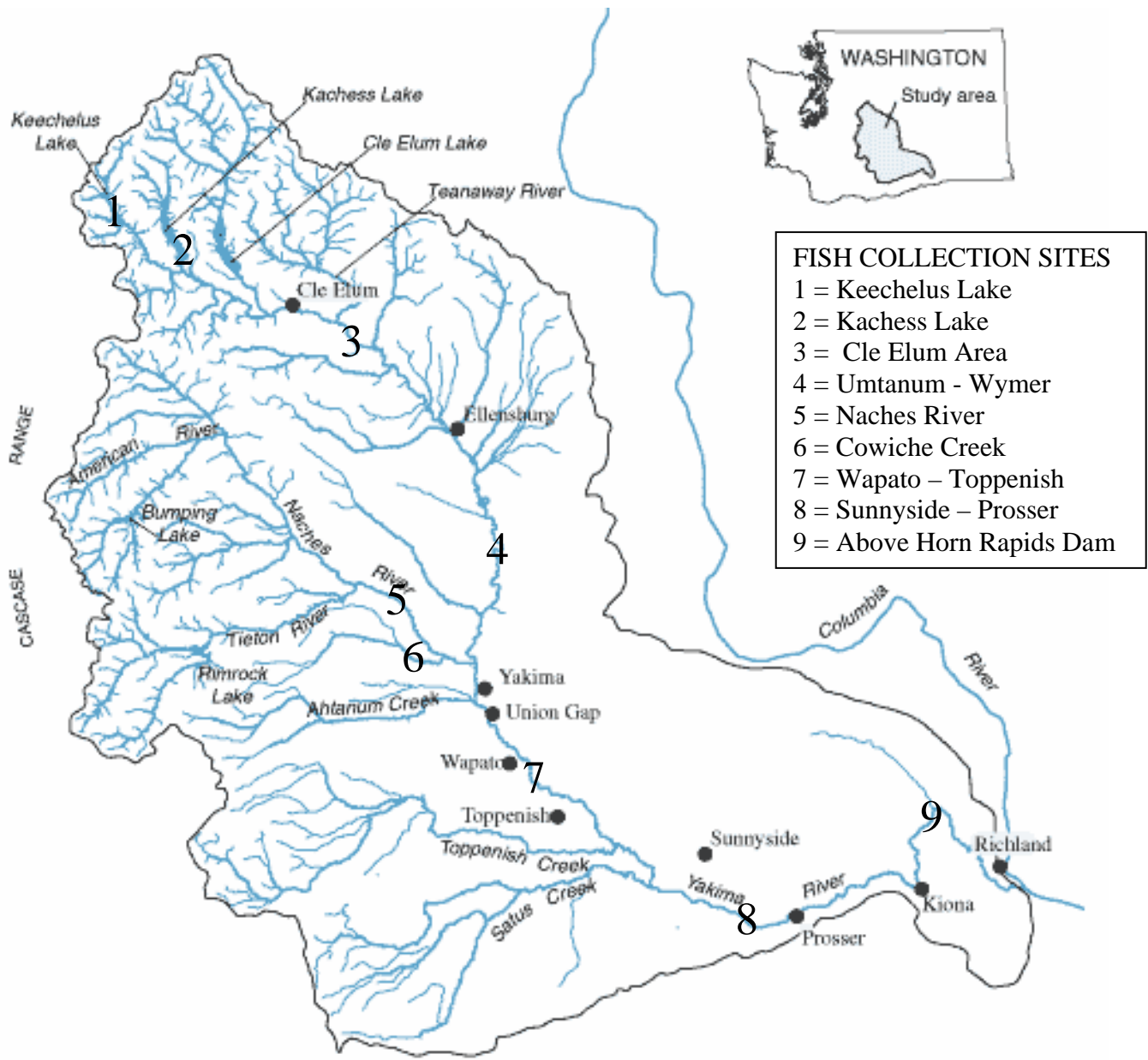


Figure 2. Sampling Sites Proposed for 2006 Yakima River Fish Tissue Study.

Five fish collection areas are proposed for the mainstem Yakima River: Cle Elum, Umtanum–Wymer (Yakima Canyon), Wapato–Toppenish, Sunnyside–Prosser, and above Horn Rapids Dam. These reaches have been the focus of historical fish tissue studies and are positioned below major tributary, irrigation, and urban inputs. Fish tissue will also be analyzed from one site each on the Naches River and Cowiche Creek, for reasons previously explained.

The numbers and types of fish tissue samples to be analyzed are shown in Table 5. Based on previous experience, it is anticipated that between two-to-four species of interest could be

collected at each site, depending on location. Species diversity is generally greatest in the mid- and lower Yakima mainstem. The species most frequently analyzed historically have been largescale suckers (*Catostomus macrocheilus*), mountain whitefish (*Prosopium williamsoni*), smallmouth bass (*Micropterus dolomieu*), and pike minnow (*Ptychocheilus oregonensis*). These will be the target species for the new study, supplemented by less common species such as common carp (*Cyprinus carpio*), crappie (*Pomoxis* spp.), and channel catfish (*Ictalurus punctatus*). Rainbow trout cannot be taken because steelhead (a sea-going rainbow) are listed under ESA.

Table 5. Number of Samples\* Proposed for 2006 Yakima River Fish Tissue Study

Sampling Site	Fillet Samples			Whole Body Samples			Totals
	Species	Per Species	Subtotals	Species	Per Species	Subtotals	
Keechelus Lake	2	3	6				6
Kachess Lake	2	3	6				6
Cle Elum	3	3	9				9
Umtanum-Wymer	4	3	12	2	3	6	18
Naches River	3	3	9				9
Cowiche Creek	2	3	6				6
Wapato-Toppenish	4	3	12	2	3	6	18
Sunnyside-Prosser	4	3	12	3	3	9	21
Ab. Horn Rapids Dam	4	3	12	3	3	9	21
			84			30	114

\*composites of five fish each, resident species only

Fillet samples will be analyzed for all fish samples. Limited numbers of whole body samples will be analyzed for comparison with the historical data. The whole body samples will be from those reaches with the most historical data: Yakima Canyon, Granger-Prosser, and Kiona-Horn Rapids Dam. Whole body may also be considered a worst-case sample for human health. Each fillet and whole fish sample will consist of a composite of pooled tissues from five individual fish. Composite samples provide a more cost efficient estimate of mean contaminant concentrations than single fish samples.

A sufficient number of samples need to be analyzed to draw conclusions about progress toward achieving the TMDL targets, compliance with human health criteria, and the health implications of consuming Yakima River fish. WDOH has recommended that at least three composite fillet samples be analyzed for each species at each collection site for a human health evaluation (Dave McBride, Office of Environmental Health Assessments, personal communication). A sample size of three composites each for fillets and whole fish should also be sufficient to meet other project objectives, as discussed below.

There has been no organized effort to collect data for detecting trends in contaminant levels in Yakima River fish and the number of data points that establish chlorinated pesticide levels at or near the time BMPs were first initiated is limited (Table 4). Therefore, conclusions about progress toward TMDL targets will be based on a weight-of-evidence approach. The historical fish tissue data against which progress will be judged are for sample sizes of three or less (most often one or two) for any given species and site. Sample size for the present study will be equivalent to or better than the historical data.

Specific quantitative criteria for determining the success of a TMDL are based on the approved targets within the TMDL itself (Ecology, 2002). Once a TMDL is approved, Ecology assumes that the analysis and implementation measures included in it will be successful in bringing about improvements to water quality as needed to reach compliance within the time period scheduled in the TMDL. The Yakima TMDLs do not specify exactly how it will be determined that compliance with human health criteria has been achieved.

Ecology's 303(d) policy has pertinent guidance on sample size (Ecology, 2002). The current policy requires at least one composite sample made up of at least five separate fish of the same species to list a waterbody for toxics under Category 5. Past practice has been to move waterbodies out of Category 5 based on evidence of compliance from a larger or higher quality data set than used for listing. Therefore, a sample size of three composites is consistent with 303(d) policy and should be sufficient to make the determination that human health criteria have been achieved, based on a simple comparison with average values.

The statistical power associated with a sample size of three will be low, but analyzing enough samples to statistically demonstrate compliance with criteria would be prohibitively expensive. Results from the present study will show if and where such an effort may be useful in the future and provide variance estimates that can be used to select the appropriate sample size.

Appendix A lists all the chemicals to be analyzed for this project. All samples will be analyzed for chlorinated pesticides, PCBs (as Aroclor-equivalents\*), and percent lipids. Lipids data may be useful for normalizing contaminant concentrations between samples, since fat content is sometimes correlated with organochlorine residues.

Relatively high dioxin TEQs - up to 1 ng/Kg (parts per trillion) - have been reported in fish from the mid- to lower Yakima River (EPA, 2002). To reduce laboratory cost (\$750/sample) it is proposed the PCDD/PCDF analysis be limited to one sample per species per location. Aliquots from all 15 fish used in the associated pesticide/PCB sample will be composited to give representative PCDD/PCDF data.

No analyses are planned for PCB congeners or for PCDDs/PCDFs in whole fish, since this information is available in EPA (2002). The same EPA study also obtained data on arsenic and

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\* In the United States, PCBs were primarily manufactured and sold under the trade name Aroclors. PCBs are typically analyzed as equivalent concentrations of commercial Aroclor mixtures (e.g., PCB-1254) or as individual compounds, referred to as PCB congeners. Congener data can sometimes be useful in assessing the toxicity of a PCB mixture.

mercury, two other contaminants that WDOH may consider in evaluating human health implications of eating Yakima River fish.

Fish collections for past studies in the Yakima have occurred as early as March and as late as October. Most of the sampling has been during the late spring, summer, and fall, which is also the period sport and subsistence fishing is most active. Due to the time required to obtain collection permits and permit requirements that water temperatures must be lower than 18°C when fish sampling is conducted, the field work for the present study will get underway in late August 2006 and should be completed by the end of October 2006. The irrigation season extends from approximately March 15 through October 15.

Table 6 has an estimate of laboratory costs for this project.

Table 6. Laboratory Cost Estimate for 2006 Yakima River Fish Tissue Study

Sample Type / Analysis	No. of Samples	Cost per Sample	Cost Subtotals
<b>Fillet Samples</b>			
Chlorinated Pesticides & PCBs	84	325	27,300
PCDDs/PCDFs*	28	750	21,000
Percent Lipids	84	31	2,604
			<u>\$50,904</u>
<b>Whole Body Samples</b>			
Chlorinated Pesticides & PCBs	30	325	9,750
Percent Lipids	30	31	930
			<u>\$10,680</u>
Total Lab Cost (+20% QC) =			\$73,901

\*one sample per species per location

## Sampling Procedures

Fish will be collected by electroshocking, beach seines, fyke nets, or hook and line. Only legal size fish will be taken for chemical analysis. For species with no size limits, only those large enough to reasonably be retained for consumption will be taken. The latitude and longitude of the sampling sites will be recorded from a GPS.

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 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 guidance in EPA (2000). Techniques to minimize potential for 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 deionized 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 or Hobart commercial blender. The fillets will be scaled and analyzed skin-on, except skin-off for catfish since the skin is not eaten. Whole fish will be homogenized in a Hobart blender. The sex of each fish will be recorded and hard structures saved for age determination (scales, otoliths, opercles, dorsal, and/or pectoral spines as appropriate for each species). Aging will be done by WDFW or a private lab.

Five individual fish will be used for each composite sample, except 15 fish for the PCDD/PCDF analysis. 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 4 - 8 oz. glass jars with Teflon lid liners, cleaned to EPA (1990) QA/QC specifications.

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.

The tissue samples will be refrozen for shipment with chain-of-custody record to MEL. The samples will be stored frozen at MEL until analyzed. Excess samples will be stored frozen at Ecology HQ. The holding time for tissue samples being analyzed for organochlorines is up to one year (PSWQAT, 1997; Method 1668A).

## Measurement Procedures

Table 7 shows the numbers of samples to be analyzed, expected range of results, required reporting limits, and sample preparation and analysis methods. To the extent possible, methods were chosen that give reporting limits equal to or less than the lowest concentrations of interest. Other methods may be used by MEL after consulting with the project lead.

Table 7. Laboratory Procedures for 2006 Yakima River Fish Tissue Study

Analysis	Field Samples	Number of Expected Range of Results	Reporting Limit	Sample Prep Method*	Analytical Method*
Chlor. Pesticides	114	1-500 ug/Kg wet	0.4 ug/Kg wet	EPA 3540/3620/3665	EPA 8081
PCBs (Aroclors)	114	10-500 ug/Kg wet	4 ug/Kg wet	EPA 3540	EPA 8082
PCDDs/PCDFs	28	<0.1 - 2 ng/Kg wet	0.01 - 0.1 ng/Kg wet	NA	EPA 1613B
Percent lipids	114	0.1-10%	0.1%	extraction	EPA608.5

NA = not applicable

\*and corresponding Manchester SOPs and modifications



# Quality Control Procedures

## Field

No field QC samples are planned for this project.

## Laboratory

The QC procedures routinely followed by MEL or required of its contractors will be satisfactory for purposes of this project. Laboratory QC samples to be analyzed are shown in Table 8.

Table 8. Laboratory Quality Control Samples for 2006 Yakima River Fish Tissue Study

Analysis	Method Blanks	Check Std./ LCS	Surrogate Spikes	MS/MSD	OPR Stds./ Labelled Cmpds.	Duplicates
Pesticides/PCBs	1/batch*	1/batch	all samples	1/batch	NA	1/batch
PCDDs/PCDFs	1/batch	1/batch	NA	1/batch	all samples	1/batch
Percent Lipids	1/batch	NA	NA	NA	NA	1/batch

\*One batch is  $\leq 20$  samples

LCS = laboratory control sample

MS/MSD = matrix spike and matrix spike duplicate

OPR = Ongoing precision and recovery

NA = not applicable

Laboratory duplicates (split samples) will be used to help assess the analytical precision associated with the fish tissue data. One composite will be split and analyzed in duplicate with each batch of samples. The split samples will be selected to represent a range of contaminant levels, include both fillets and whole fish, and be submitted blind to the laboratory.

## Data Management Procedures

Field data and data from preparation of the tissue samples will be recorded in a bound notebook of waterproof paper.

The data package from the laboratory will include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. This should include results for all blanks, check standards/LCS samples, surrogate compounds, labeled compounds, matrix spikes, and analytical duplicates included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual on the project team.

All project data will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal Data Validation Review Procedure where data is reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

# Audits and Reports

## Audits

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

The PCDD/PCDF analysis will be done by a laboratory accredited by Ecology. On-site assessments are required every three years to maintain accreditation.

## Reports

The following reports will be prepared for this project:

- 1) A fish tissue data report for WDOH for their use in conducting a human health assessment. The tentative date for this report is January 2007. The responsible staff member is Kristin Kinney.
- 2) A draft technical report for review by CRO, stakeholders, and other interested parties. The tentative dates are March 2007 for the CRO draft and April 2007 for the stakeholder draft. The responsible staff members are Art Johnson, Kristin Kinney, and Brandee Era-Miller.
- 3) A final technical report is anticipated in June 2007. The responsible staff members are Art Johnson, Kristin Kinney, and Brandee Era-Miller.
- 4) The project data will be entered into Ecology's Environmental Information Management System on or before June 2007. The responsible staff member is Kristin Kinney.

## Data Verification and Validation

MEL will conduct a review of all laboratory data and case narratives. MEL will verify that methods and protocols specified in this Quality Assurance Project Plan were followed; that all calibrations, checks on quality control, 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, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary can meet the requirements for a data verification report.

To determine if project MQOs have been met, results for check standards/LCS, matrix spikes, surrogates, labeled compounds, and duplicate samples will be compared to QC limits. The method blanks 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.

The project lead will review the laboratory data packages and MEL’s data verification report and validate the data. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

## **Data Quality (Usability) Assessment**

Once the data have been verified and validated, 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 results are satisfactory, data analysis will proceed.

Summary statistics will be tabulated for each parameter. The data will be plotted to identify exceedances of human health criteria and to compare contaminant concentrations between sampling sites and species. If a correlation exists between chemical concentrations and lipid content, the data will be normalized to percent lipid and re-examined for site and species differences.

Comparable data will be compiled by sampling site and species, and examined for evidence of trends over time. Because there has been no systematic effort to collect a consistent data set appropriate for statistical testing, conclusion regarding the presence or absence of trends will be based primarily on a weight-of-evidence approach, as previously noted. Conclusions regarding progress toward meeting TMDL targets will be based on evidence of time trends in the data and comparison with human health criteria.

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## Appendices

### Appendix A. Chemicals to be Analyzed for the 2006 Yakima River Fish Tissue Study

#### Chlorinated Pesticides

4,4'-DDT  
4,4'-DDE  
4,4'-DDD  
gamma-BHC (Lindane)  
alpha-BHC  
beta-BHC  
delta-BHC  
dieldrin  
endrin  
endrin aldehyde  
endrin ketone  
aldrin  
heptachlor  
heptachlor epoxide  
endosulfan I  
endosulfan II  
endosulfan sulfate  
hexachlorobenzene  
trans-chlordane  
cis-chlordane  
trans-nonachlor  
cis-nonachlor  
oxychlordane  
methoxychlor

#### PCDDs/PCDFs

2,3,7,8-TCDD  
1,2,3,7,8-PeCDD  
1,2,3,7,8,9-HxCDD  
1,2,3,6,7,8-HxCDD  
1,2,3,4,7,8-HxCDD  
1,2,3,4,6,7,8-HpCDD  
1,2,3,4,6,7,8,9-OCDD  
2,3,7,8-TCDF  
1,2,3,7,8-PeCDF  
2,3,4,7,8-PeCDF  
2,3,4,6,7,8-HxCDF  
1,2,3,7,8,9-HxCDF  
1,2,3,6,7,8-HxCDF  
1,2,3,4,7,8-HxCDF  
1,2,3,4,7,8,9-HpCDF  
1,2,3,4,6,7,8-HpCDF  
1,2,3,4,6,7,8,9-OCDF

#### PCBs

PCB-1016  
PCB-1221  
PCB-1232  
PCB-1242  
PCB-1248  
PCB-1254  
PCB-1260  
PCB-1268