Quality Assurance Project Plan

Assessing Current Levels of 303(d) Listed Pesticides and PCBs in Palouse River Fish

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May 2005

303(d) Listings Addressed in this Study:

Palouse River (WRIA 34) – 4,4'-DDE, dieldrin, heptachlor epoxide, alpha-BHC, PCB-1260

Waterbody Numbers: Palouse River (WA-34-1010); S.F. Palouse River (WA-34-1020); N.F. Palouse River (WA-34-1030)

User Study ID Number: AJOH0046

Approvals

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Abstract

The Palouse River has been listed by the state of Washington under Section 303(d) of the Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for 4,4'-DDE, dieldrin, heptachlor epoxide, alpha-BHC, and PCB-1260 in edible fish tissue. The listing is based on sampling done by the Washington State Department of Ecology in 1984 and 1994.

EPA requires the states to set priorities for cleaning up 303(d) listed waters and to establish a Total Maximum Daily Load (TMDL) for each. A TMDL entails an analysis of how much of a pollutant load a waterbody can assimilate without violating water quality standards. Because the Palouse listings are based on older data and because very few samples were analyzed, an intensive study is proposed to more accurately determine current levels of these contaminants in Palouse River fish. Results will be used to determine the appropriate level of effort and focus for the TMDL.

Background

303(d) Listings

The Palouse River has been listed by the state of Washington under Section 303(d) of the Clean Water Act for non-attainment of the U.S. Environmental Protection Agency (EPA) human health criteria for 4,4'-DDE, dieldrin, heptachlor epoxide, alpha-BHC, and PCB-1260 in edible fish tissue. The listings (Table 1) are based on sampling done by the Washington State Department of Ecology (Ecology) in 1984 and 1994.

Table 1. Palouse River 303(d) Listings for Fish Tissue (draft 2002/2004 list)

Listing ID	Parameter	Township Range Section	Water Course/ Grid #	Lower Route #	Listing Basis
14190	4,4'-DDE	15N-37E-26	NX00WG	29.009	Hopkins et al. (1985). Excursions beyond the National Toxic Rule criterion in a multiple fish composite of edible tissue of largescale sucker and northern squawfish samples at RM 19.5 in 1984.
8819	4,4'-DDE	17N-40E-20	NX00WG	75.039	Davis and Serdar (1996) Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.
14191	alpha-BHC	15N-37E-26	NX00WG	29.009	Hopkins et al. (1985). Excursions beyond the National Toxic Rule criterion in a multiple fish composite of edible tissue of largescale sucker and northern squawfish samples at RM 19.5 in 1984.
8818	Dieldrin	17N-40E-20	NX00WG	75.039	Davis and Serdar (1996). Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.
8822	Heptachlor epoxide	17N-40E-20	NX00WG	75.039	Davis and Serdar (1996). Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.
8820	PCB-1260	17N-40E-20	NX00WG	75.039	Davis and Serdar (1996). Excursions beyond the criterion in edible squawfish tissue at RM 40.8 in 1994.

These chlorinated pesticides, breakdown products, and polychlorinated biphenyls (PCBs) are no longer used in the United States, having been banned in the 1970s and 1980s for ecological and human health concerns. They are now classed by EPA as probable human carcinogens. Detailed profiles including use, regulations, environmental occurrence, and health effects have been prepared by the Agency for Toxic Substances & Disease Registry and are available at www.atsdr.cdc.gov/toxpro2.html.

EPA requires the states to set priorities for cleaning up 303(d) listed waters and to establish a Total Maximum Daily Load (TMDL) for each. A TMDL entails an analysis of how much pollutant loading a waterbody can assimilate without violating water quality standards. Because the Palouse listings are based on older data and because very few samples were analyzed, an

intensive study is proposed to more accurately determine current levels of these contaminants in Palouse River fish. The results will be used to determine the appropriate level of effort and focus for the TMDL. The study will be conducted by the Ecology Environmental Assessment (EA) Program.

Basin Description

The Palouse River drains approximately 3,300 square miles of the Columbia Plateau in Southeastern Washington and the Idaho Panhandle (Figure 1). Eighty-three percent of the basin is in Washington State, primarily Whitman County.

The headwaters of the Palouse River originate in the forested mountains of Idaho at an elevation of 5,300 feet. It flows for over 165 miles through dryland farming in the central part of the basin and barren rangeland to the west, before its confluence with the Snake River at an elevation of about 500 feet. Major tributaries to the Palouse are Paradise, Rebel Flat, Rock, Union Flat, and Cow Creeks.

The segment of the river between the Washington-Idaho state line and the town of Colfax is locally referred to as the North Fork. The North and South forks merge at Colfax to form the lower mainstem of the Palouse River. The North Fork contributes about 83% of the annual mean flow of the Palouse River at Colfax (Ahmed, 2004).

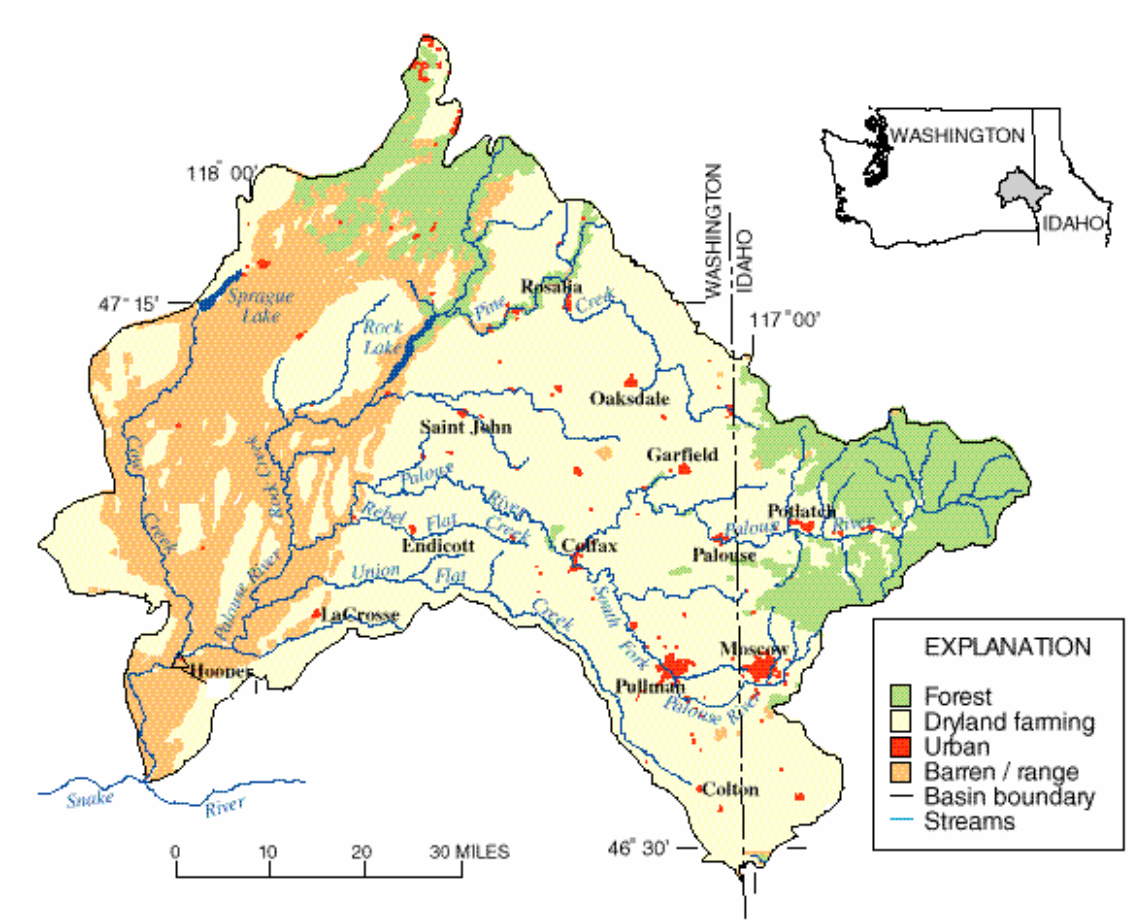

Figure 1. Palouse River Basin (from Ebbert and Roe, 1998)

The primary land use is dryland agriculture (67%), with some rangeland (26%) and forested areas (6%) (Ecology, 2003). Wheat, barley, lentils, and peas are the major crops. Irrigated farming along the Palouse River and its tributaries contributes less than 1% of land use (Wagner and Roberts, 1998).

With a population of only about 47,000, urban areas make up less than 1% of the basin in Washington (Ecology, 2003). The major cities are Pullman (population 26,779), Moscow (population 21,674), Colfax (population 4,124), Palouse (population 1,408), and Potlatch (population 773).

The South Fork of the Palouse River is particularly influenced by urban pollution, a potential source of both chlorinated pesticides and PCBs. The Moscow Wastewater Treatment Plant (WWTP) discharges to Paradise Creek, and the Pullman WWTP discharges to the South Fork about two miles below the Paradise Creek confluence. Pelletier (1993) conducted a TMDL for ammonia in South Fork. He concluded that "during periods of low flow, the Moscow WWTP comprises nearly the entire flow of Paradise Creek and the South Fork Palouse River until

confluence with the Pullman WWTP discharge. WWTP flows have the potential to account for most of the total river flow during any month of the year."

Soil erosion is a major problem in the Palouse Basin. Farming began in the late 1800s. Erosion became particularly acute in the early 1900s when steep lands, once used for hay and pasture, were converted to grain production (Ebbert and Roe, 1998; USDA, 1978). About 40% of the rich Palouse soils have been lost in the last century because of erosion by water (Pimentel et al., 1995). Erosion of agricultural soils is often a major route through which chlorinated pesticides reach surface waters.

Many farmers have voluntarily implemented erosion control practices in the basin. Since the late 1970s, erosion from cropland has been reduced by at least 10% (Ebbert and Roe, 1998). Evidence of resulting water quality improvements, however, has been equivocal. USGS and Ecology have analyzed the TSS data for Hooper (Hallock and Ebbert, 1996; Ebbert and Roe, 1998). Although there were indications of improvement, the data were considered inconclusive because the recent period of record was short and because large storm events skewed some of the older data.

Fish Tissue Data

The Ecology fish tissue data that resulted in 303(d) listings for the Palouse River are summarized in Table 2 and compared to the listing criteria. Each of these samples was a composite formed by pooling tissues from five individual fish. In order for data to be considered for the 303(d) list, Ecology required at least two single-fish samples or one composite of at least five fish that exceeded 303(d) human health criteria. The criteria apply to edible tissues only.

The 303(d) criteria shown in Table 2 are based on EPA bioconcentration factors (BCF*) and water column criteria established under the EPA National Toxics Rule (NTR; 40 CFR Part 131). The NTR water column criteria have been adopted as human health criteria by the state of Washington (WAC 173-210A).

Ecology's fish samples were collected in the lower Palouse River at Hooper in 1984 (river mile 19.5) and near Winona in 1994 (river mile 40.8). The analyses included up to 43 chlorinated pesticides, breakdown products, and PCB mixtures; only detected compounds are shown in Table 2.

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*BCF= C_t/C_w, where C_t is the contaminant concentration in tissue (wet weight) and C_w is the concentration in water.

Table 2. Ecology Data on Chlorinated Pesticides and PCBs Detected in Palouse River Fish (ug/Kg wet weight; parts per billion)

Location:	Palouse R. nr Winona		Palouse R. @ Hooper		
Species:	Largescale Sucker	N. Pike Minnow	Bridgelip Sucker	N. Pike Minnow	303(d) Human
Tissue:	Whole Body	Fillet	Fillet	Fillet	Health
Date:	Sep-94	Sep-94	Sep-84	Sep-84	Criteria
4,4'-DDE	170	**73**	**92**	**130**	32
4,4'-DDD	18	nd	10	5	45
4,4'-DDT	12 J	nd	23	2	32
Total DDT	200	**73**	**125**	**137**	32
Cis-Chlordane	5.7	1.2 J	na	na	
Trans-Chlordane	14	nd	na	na	
Oxychlordane	7.2	2.4 J	na	na	
Cis-Nonachlor	1.7 J	0.75 J	na	na	
Trans-Nonachlor	4.7 J	2.1 J	na	na	
Total Chlordane	33	6.5	na	na	8.3
Dieldrin	13	**7 NJ**	na	na	0.65
alpha-BHC	nd	nd	**37**	**16**	1.7
gamma-BHC (Lindane)	0.27 NJ	0.44 J	na	na	8.2
Heptachlor epoxide	14	**6.3**	na	na	1.2
Hexachlorobenzene	10	3.6	na	na	6.7
DDMU	2.7 J	nd	na	na	
PCB - 1254	13 J	nd	nd	nd	5.3
PCB - 1260	18 J	**11 J**	<10	<10	5.3
Total PCBs	31	**11**	<10	<10	5.3

Data from: Davis and Serdar (1996) and Hopkins et al. (1985)
Note: Values in bold exceed 303(d) criteria for edible tissue
J = The analyte was postively identified. The associated numerical value is an estimate.
NJ = There is evidence that the analyte is present. The associated numerical value is an estimate.
nd = not detected
na = not analyzed or not reported

Fillets were analyzed from two species – bridgelip sucker (*Catostomus columbianus*) and northern pike minnow (*Ptychocheilus oregonensis*, a.k.a. northern squawfish). The compounds that exceeded 303(d) criteria were DDE, dieldrin, alpha-BHC, heptachlor epoxide, and PCBs.

The 1984 data are too old to be considered representative of contaminant levels in the Palouse River. The more recent fillet sample from1994 showed modest exceedances for DDE and total PCBs, by about a factor of 2. Dieldrin and heptachlor epoxide exceeded criteria by factors of 5 – 10. The dieldrin concentration, however, was an estimate. Although alpha-BHC was reported as being detected in 1984, it was not detected in either the fillet or whole fish sample from 1994.

USGS analyzed chlorinated pesticides and PCBs in whole body fish samples from the Palouse Basin as part of their National Water Quality Assessment Program (Table 3). The Palouse samples were collected in 1992 and 1994. Whole body data are not comparable to 303(d) criteria.

Table 3. USGS Data on Chlorinated Pesticides and PCBs Detected in Whole Body Samples of Largscale Suckers Collected from the Palouse River Basin in 1992 and 1994 (ug/Kg wet weight; parts per billion)

Location	4,4'-DDD	4,4'-DDE	4,4'-DDT	Total DDT	Hexachloro-benzene	Dieldrin	Endrin	Total Chlordane	Total PCBs
Palouse R. @ Harvard (ID)	nd	nd	nd	nd	nd	nd	nd	nd	nd
N.F. Palouse R. @ Colfax	nd	160	24	180	26	32	nd	nd	nd
"	22	400	29	450	33	22	nd	53	70
Palouse R. @ Hooper	5.1	87	7.0	99	14	7.8	9.2	nd	nd
Pine Creek	6.9	120	8.6	140	27	21	10	14	nd
Paradise Creek	58	120	nd	180	11	nd	nd	nd	820
S.F. Palouse @ Colfax	nd	340	nd	340	16	nd	nd	nd	nd

Data from Munn and Gruber (1997)
nd = not detected

USGS collected one sample each of largescale suckers from the Upper Palouse River in Idaho, the North and South Forks, the Lower Mainstem, Paradise Creek, and Pine Creek (Munn and Gruber, 1997). DDT, DDE, DDD, hexachlorobenzene, and dieldrin were detected in most samples. The highest total DDT concentrations (DDT+DDE+DDD) were found in the North and South forks, 340 – 450 ug/Kg. PCBs were only detected in fish from the North Fork and Paradise Creek (5.0 ug/Kg detection limit). The PCB concentration in the Paradise Creek fish sample was relatively high at 820 ug/Kg. No pesticides or PCBs were detected in fish from the Upper Palouse River in Idaho.

The limited nature of the available data on contaminant levels in Palouse River fish raises questions about the most appropriate course of action for the TMDL dictated by the 303(d) listings. The Palouse listings are based on older Ecology data and few samples were analyzed--only one relatively recently and none in the North or South Forks. For three of the five 303(d) listed compounds, the exceedances were modest or, in one case, questionable. The USGS data suggest that higher concentrations occur further upstream, but these results are also more than 10 years old and did not include edible tissue samples.

Problem Statement

The problem to be addressed in this study is to determine the current levels of 303(d) listed pesticides and PCBs in edible tissues of Palouse River fish and implications for the TMDL.

Project Description

The goal of this study will be to determine if, and where, chlorinated pesticides and PCBs exceed 303(d) listing criteria in edible tissues of Palouse River fish. The Washington State Department of Health (WDOH) will be requested to analyze the resulting data and determine if there is need for a fish consumption advisory.

The study area will include the Mainstem Lower Palouse River, the North Fork, and the South Fork. Approximately 17 composite fish fillet samples will be analyzed from each of these three areas. The field work will be conducted during May and June 2005. A thorough analysis will be conducted for chlorinated pesticides, breakdown products, and PCBs, including all compounds previously detected in Palouse River fish.

Specific objectives of the study will be to:

1) Obtain a reliable estimate of mean concentrations of chlorinated pesticide, breakdown products, PCBs, and percent lipids in fillets from mainstem, North Fork, and South Fork fish species.
2) Screen a subset of samples for a broader range of bioaccumulative chemicals.
3) Obtain ancillary data on fish age, length, weight, and sex.
4) Determine if 303(d)/NTR criteria are exceeded and where.
5) Make TMDL recommendations for those chemicals that exceed criteria.

Organization and Schedule

Responsibilities

Ecology Eastern Regional Office Client – Elaine Snouwaert (509-329-3503)
EA Program Project Lead – Art Johnson (360-407-6766)
EA Program Field Leads – Brandee Era-Miller (360-407-6771) Kristin Kinney (360-407-7168)
EA Program Toxics Studies Unit Supervisor – Dale Norton (360-407-6765)
Manchester Environmental Laboratory Director – Stuart Magoon (360-871-8813)
Manchester Laboratory Organics Unit Supervisor – Dean Momohara (360-871-8808)
Manchester Laboratory QC & Sample Management – Karin Feddersen (360-871-8829)
Ecology Quality Assurance Officer – Cliff Kirchmer (360-407-6455)
Ecology Environmental Information Management System (EIM) Data Entry – Brandee Era-Miller (360-407-6771)

Schedule

Field Work	May – June 2005
Laboratory Analyses Completed	September 2005
Fish Tissue Data Report to WDOH	October 2005
Draft Project Report	December 2005
Final Project Report	February 2006
EIM Data Entry Completed	February 2006

Quality Objectives

Manchester Laboratory and their contract laboratories are expected to meet all quality control (QC) requirements of the analytical methods being used for this project. Recoveries of surrogate compounds have been selected as the significant, bottom-line measurement quality objectives for estimating the accuracy of the pesticides and PCB analyses. The MQOs for this project are shown below in Table 4.

Table 4. Measurement Quality Objectives for Fish Tissue Samples

Analysis	MQO
Chlorinated pesticides	50-150% surrogate recovery
PCB Aroclors	50-150% surrogate recovery
Percent lipids	0-20% precision, 80-100% bias

The lowest concentrations of interest for project samples are listed in Table 5. These are the lowest concentrations practically attainable within budget constraints of this project and should be low enough to compare to 303(d) criteria, given the concentrations anticipated in the fish tissue samples (Tables 2 and 3).

Table 5. Lowest Concentrations of Interest in Fish Tissue Samples

Analysis	Lowest Concentration of Interest
Chlorinated pesticides	0.5 ug/Kg, wet
PCB Aroclors	5 ug/Kg, wet
Percent lipid	0.1%

Study Design

Washington State Department of Fish & Wildlife (WDFW) biologists in the Palouse area were contacted for information on sport and subsistence fishing in the river. Results of these discussions, supplemented with information from Gilmore (2004), are summarized in Table 6.

Table 6. Fisheries Information on the Palouse River (Washington portion, above Palouse Falls)

Species	Range	Fishery	Spawning Season	Size and Bag Limits
Smallmouth Bass	Throughout Palouse River	Fished in late Spring and Summer	May	Slot limit – 5 per day under 12" and only 1 above 17"
Northern Pike Minnow	Throughout Palouse River	Fished in late Spring and Summer	Spring	No min. size or limit
Largescale Suckers	Throughout Palouse River	Unknown	Spring	No min. size or limit
Redside Shiner	Throughout Palouse River	Unknown	Spring	No min. size or limit
Chiselmouth	Throughout Palouse River	Unknown	Spring	No min. size or limit
Rainbow Trout	Rock Creek and Union Flat Creek	Specialty fished	Spring	Min. size 8" – 2 per day from rivers and streams
Brown Trout	Rock Creek and Union Flat Creek	Specialty fished	Fall/winter	Min. size 8" – 2 per day from rivers and streams
Brook Trout	Upper headwater streams	Unknown	Fall	No min. size – 5 per day
Channel Catfish	Throughout Palouse River, but sparse	Unknown	Spring	No min. size – 5 per day
Common Carp	Cow Creek and mainstem Palouse below the Cow Creek Confluence	Unknown	Spring	No min. size or limit

According to WDFW, there is a low diversity of fish species in the Palouse River above Palouse Falls (r.m. 7.0). The two species most frequently fished for are smallmouth bass (*Micropterus dolomieui*) and northern pike minnow (*Ptychocheilus oregonensis*). Largescale suckers (*Catostomus macrocheilus*), chiselmouth (*Arcocheilus alutaceus*), and redside shiner (*Richardsonius balteatus*) are also found throughout the basin. It is not known the extent to which suckers, chiselmouth, or shiners are consumed. Channel catfish (*Ictalurus punctatus*) are taken, but are uncommon above the falls. Carp are primarily restricted to the reach below Cow Creek. Subsistence fishing is minimal in the Palouse River.

Rainbow trout (*Oncorynchus mykiss*) and brown trout (*Salmo trutta*) are found in and near the confluence of Rock Creek and in Union Flat Creek. Brook trout (*Salvelinus fontinalis*) are found in the uppermost tributaries of the Palouse River. Trout, in general, can be found where stream temperatures are cooler, such as near natural springs, for example.

The Palouse River has high flows in the spring and is dark and muddy. The water generally clears up towards the end of May. Fishing is best in the late spring through early summer months.

Fish sampling for the present study will focus on the mainstem species most likely to be consumed, i.e., smallmouth bass, channel catfish, and carp. Trout will be collected if encountered. It appears likely, however, that the fish collection will have to rely heavily on northern pike minnow and largescale suckers. Although pike minnow and suckers may not be eaten to any significant extent, the results can be extrapolated to other more desirable species.

Fish will be collected from three reaches of the Palouse River--one each for the Mainstem, North Fork, and South Fork--as highlighted in Figure 2. These areas were selected to give results that are representative of the waterbody in question, avoiding samples in the upper and lower parts of each reach. Specific collection sites will depend on access, which is limited. Individual tributaries will not be sampled. The fish collection will be done in May and June of 2005.

Composite sampling will be used to obtain a cost efficient estimate of mean pesticide/PCB concentrations. For a given number of fish to be analyzed as composites, greater statistical power is achieved by increasing the number of replicate composites as opposed to increasing the number of fish per composite (EPA, 2000).

A sample size of 25 fish is proposed for each of the three most abundant species from each location, analyzed in composites of five fish each, for a total of 15 samples per location. The laboratory budget assumes six additional composites from other species will be obtained during the study. To the extent possible, the composites will be formed using fish having similar lengths, in keeping with EPA (2000) guidance.

A composite size of five was selected to balance the need for confidence in estimating contaminant concentrations against the cost of sample analysis. Figure 3 shows the confidence intervals around the median for the case where 25 fish are analyzed in groups of five. The geometric standard deviation (x-axis) is a measure of how variable the samples are: a value near 1 indicating results are relatively close and a value of 5 indicating the results are highly dispersed. In Ecology surveys similar to the one proposed for the Palouse, this value has been around 2. A log-normal distribution of the data is assumed.

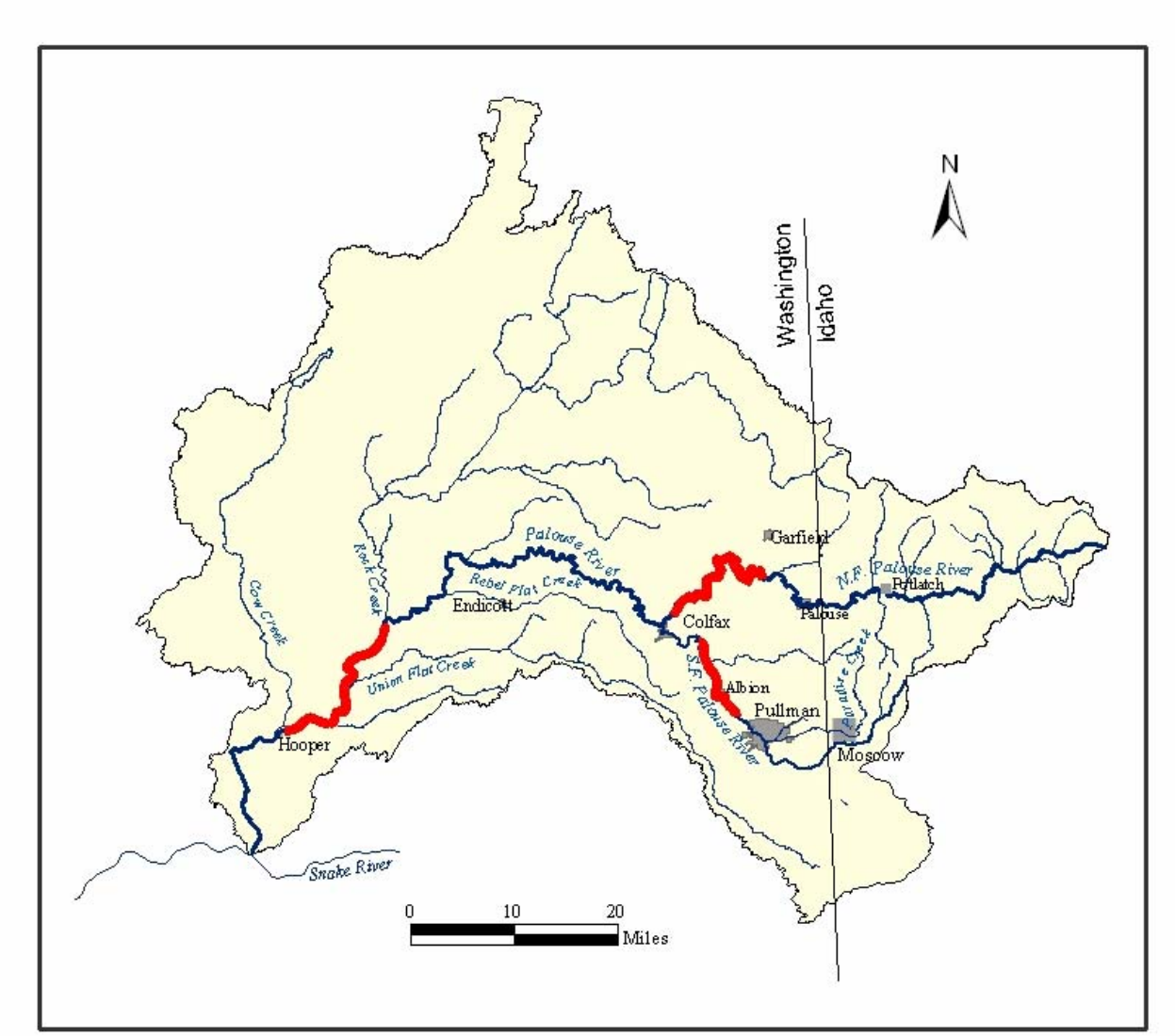

Figure 2. General Areas Where Fish Samples will be Collected in the Palouse River Drainage.

Fillets will be analyzed for chlorinated pesticides, PCBs, and percent lipids (Appendix A). Lipid data may be useful for between-species or between-site comparisons, since these compounds accumulate in fat. PCBs will be analyzed as Aroclor-equivalents.

At the request of the Ecology Eastern Regional Office (ERO), a subset of the fish samples will be analyzed for a broader range of bioaccumulative contaminants through the Washington State Toxics Monitoring Program (Seiders and Kinney, 2004). The target analytes for this program are listed in Appendix B. These data will not be available until March 2006.

This sampling design has been provided to WDOH for their review and approval as meeting their requirements for conducting a human health assessment.

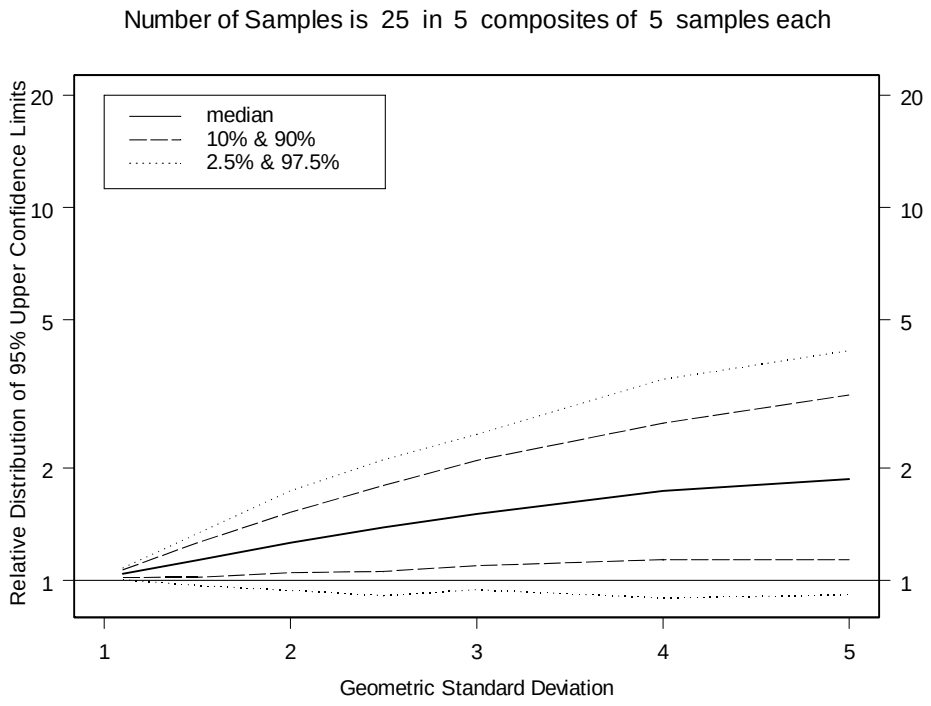

Figure 3. Confidence Intervals for 25 Fish Analyzed in Composites of 5 Fish Each (prep. by Bill Griffith, University of Washington, Department of Environmental Health).

Sampling Procedures

Fish will be collected by electroshocking or with beach seines or gill nets. Only legal size fish will be taken for chemical analysis (Table 6). 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 Magellan 320 GPS (NAD 84).

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. Preparation of tissue samples will 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 side 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. 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, Olympia.

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 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 Manchester Laboratory. The samples will be stored frozen at Manchester until analyzed. Separate containers with excess samples will be stored frozen at Ecology HQ. The holding time for tissue samples being analyzed for chlorinated pesticides and PCBs 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 to give reporting limits equal to or less than the lowest concentrations of interest. Other methods may by used by Manchester after consulting with the project lead.

Table 7. Laboratory Procedures for Fish Tissue Samples

Analysis	Number of Field Samples*	Expected Range of Results	Reporting Limit	Sample Prep Method†	Analytical Method†
Chlor. Pesticides	54	1-500 ug/Kg, wet	0.5 ug/Kg wet	EPA 3540/3620/3665	EPA 8081
PCB Aroclors	54	10-500 ug/Kg, wet	5 ug/Kg wet	EPA 3540	EPA 8082
Percent lipid	54	0.1-10%	0.1%	extraction	EPA608.5

*including blind duplicates

†and corresponding Manchester SOPs and modifications (Appendix B)

Achieving low detection limits is important to the success of this study. Manchester will conduct the chemical analyses in a manner consistent with the required reporting limits.

The laboratories will re-mix all fish tissue samples by stirring thoroughly prior to subsampling for analysis.

Excess sample extracts and excess fish tissue will be saved by the laboratories for a period of 60 days after reporting the data to the project lead. A turn-around time of 30 - 45 days is required for this project.

The cost of analyzing samples for this project is estimated at $21,000.*

*The cost for analyses conducted by Manchester Laboratory is the 50% discounted price; true cost is 2X.

Quality Control

Field

No field QC samples are planned for this project.

Laboratory

The laboratory QC samples to be analyzed for this project are shown in Table 8.

Table 8. Laboratory Quality Control Samples for Fish Tissue Samples

Analysis	Method Blanks	Check Stnds/ LCS	SRM	Surrogate Spikes	MS/MSD	Duplicates
Pesticides/PCBs	2/batch	1/batch	1/batch	all samples	2/batch	3/project
Lipids	2/batch	1/batch		- -	- -	- -

A Standard Reference Material (SRM) for chlorinated pesticides will be analyzed with each batch of samples. The SRM will be National Institute of Standards SRM 1946 - Lake Superior Fish Tissue (Appendix C). No similar SRMs are available for PCBs.

The analytical precision associated with the fish tissue data will be assessed with duplicate (split) samples. Three tissue composites will be analyzed in duplicate for the project. These will be selected to represent a range of contaminant levels and submitted blind to the laboratory.

Data Management Procedures

Field data and observations 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, surrogate compounds, and check standards included in the sample batch, as well as results for analytical duplicates and matrix spikes.

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

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

Reports

The following reports are planned for this project:

1) A fish tissue data report will be prepared for WDOH to conduct their human health assessment. The tentative date for this report is October 2005. Responsible staff: Brandee Era-Miller and Kristin Kinney.

2) A draft technical report will be prepared for review by ERO, stakeholders, and other interested parties. The tentative date for this report is December 2005. Responsible staff: Art Johnson, Brandee Era-Miller, and Kristin Kinney.

3) A final technical report is anticipated on, or about, February 2006. Responsible staff: Art Johnson, Brandee Era-Miller, and Kristin Kinney.

4) The project data will be entered into Ecology's Environmental Information Management System on, or before, February 2006. Responsible staff: Brandee Era-Miller.

5) Manchester's data report on the WSTMP data from the chemical screening of selected Palouse River fish samples will be provided to the ERO on, or about, March 2006, along with a cover memo highlighting findings of interest. The draft WSTPMP report for the Palouse and other samples analyzed in 2005 is anticipated in June 2007 and will be prepared by the investigators in that monitoring program.

Data Verification and Validation

Manchester will conduct a review of all laboratory data and case narratives. Manchester will verify that methods and protocols specified in the Quality Assurance (QA) 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. Manchester 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 surrogate recoveries in pesticide and PCB analyses will be compared to QC limits. These MQO limits correspond to the laboratory's QC limits for this project. 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 Manchester'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 the data 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.

Dot density plots and box-and-whisker plots will be prepared to identify exceedances of 303(d)/NTR criteria and to compare pesticide/PCB concentrations between species and sampling sites. If a correlation exists between chemical concentrations and lipid content, the data will be normalized to percent lipid and re-examined for species and site differences.

Based on the levels and patterns shown in the data, recommendations will be made as to the appropriate level of effort and focus for the TMDL.

References

Ahmed, A. 2004. North Fork Palouse River Fecal Coliform Bacteria Total Maximum Daily Load Recommendations. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-022. www.ecy.wa.gov/biblio/0403022.html.

Davis, D. and D. Serdar. 1996. Washington State Pesticide Monitoring Program: 1994 Fish Tissue and Sediment Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 96-352. www.ecy.wa.gov/biblio/96352.html.

Ebbert, J. C. and R. D. Roe. 1998. Soil Erosion in the Palouse River Basin: Indications of Improvement. USGS Fact Sheet FS-069-98.

Ecology. 2003. Final Environmental Impact Statement for Watershed Planning Under Chapter 90.82 RCW. Shorelands and Environmental Assistance Program. Washington State Dept of Ecology, Olympia, WA. Publication No. 03-06-013. www.ecy.wa.gov/biblio/0306013.html.

EPA. 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. OSWER Directive #93240.0-05.

EPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Vol. 1, Fish Sampling and Analysis. Office of Water. EPA-823-B-00-007.

Gilmore, S. 2004. Palouse Subbasin Management Plan. Prep. for Palouse-Rock Lake Conservation District, Trevor Cook Project Manager. Resource Planning Unlimited, Inc Moscow, ID.

Hallock, D. and J. C. Ebbert. 1996. Long-Term Trends in Concentrations of Suspended Sediment and Differences in Sediment Loads (1960-1995) in the Palouse River. Agriculture and Water Quality in the Pacific Northwest (WA, OR, ID): Understanding Each Other and Working Together; October 22-23, 1996; Yakima Convention Center, Yakima, WA. Washington State Department of Ecology and U.S. Geological Survey.

Hopkins, B. S., D. K. Clark, M. Schlender, and M. Stinson. 1985. Basic Water Monitoring Program: Fish Tissue and Sediment Sampling for 1984. Washington State Department of Ecology, Olympia, WA. Pub. No. 85-7. www.ecy.wa.gov/biblio/857.html.

Munn, M. D. and S. J. Gruber. 1997. The Relationship Between Land Use and Organochlorine Compounds in Streambed Sediment and Fish in the Central Columbia Plateau, Washington, and Idaho, USA. Environ. Toxicol.Chem. 16(9):1877-1887.

Pelletier, G. 1993. South Fork Palouse River Total Maximum Daily Load of Ammonia. Washington State Department of Ecology, Olympia, WA. Publication No. 93-e48.

Pimentel, D., C. Harvey, P. Resosudarmo, K. Sinclair, D. Kurz, M. McNair, S. Crist, L. Shpritz, L. Fitton, R. Saffouri, and R. Blair. 1995. Environmental and Economic Costs of Soil Erosion and Conservation Benefits. Science 267:1117-1123.

PSWQAT. 1997. Recommended Guidelines for Measuring Organic Compounds in Puget Sound Water, Sediment, and Tissue Samples. EPA Region 10 and Puget Sound Water Quality Action Team, Seattle, WA.

Seiders, K. and K. Kinney. 2004. Washington State Toxics Monitoring Program: Toxics Contaminants in Fish Tissue and Surface Water in Freshwater Environments, 2002. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-040. www.ecy.wa.gov/biblio/0403040.html.

U.S. Dept. of Agriculture. 1978. Palouse Co-Operative River Basin Study. USDA, Soil Conservation Service, Forest Service, Economics, Statistics, and Cooperatives Service. US Government Printing Office, 1979-797-658.

Appendices

Appendix A

Pesticides and PCBs to be Analyzed for the Palouse River Fish Tissue Study

4,4'-DDE
4,4'-DDT
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
oxychlordane
trans-chlordane
trans-nonachlor
cis-chlordane
cis-nonachlor
methoxychlor
PCB-1016
PCB-1221
PCB-1232
PCB-1242
PCB-1248
PCB-1254
PCB-1260
PCB-1268

Appendix B

Target Analytes for Ecology's 2005 WSTMP Fish Tissue Samples

Chlorinated Pesticides
alpha-BHC
beta-BHC
gamma-BHC (lindane)
delta- BHC
Heptachlor
Aldrin
Heptachlor epoxide
trans-chlordane (gamma)
cis-Chlordane (alpha)
Endosulfan I (Alpha-endosulfan)
Dieldrin
Endrin
Endrin Ketone
Endosulfan II (Beta-endosulfan)
Endrin Aldehyde
Endosulfan Sulfate
4,4'-DDD
4,4'-DDE
4,4'-DDT
2,4'-DDE
2,4'-DDD
2,4'-DDT
methoxychlor
Oxychlordane
DDMU
Cis-nonachlor
Toxaphene
Trans-nonachlor
Mirex
Chlordane (technical)
Hexachlorobenzene
Dacthal (DCPA)
Pentachloroanisole
Chlorpyrifos (OP pesticide)

Metals
mercury (total)

PCB Congeners (all 209 compounds)
PCB 001 - PCB 209

Other
Lipids (%)

PCB Aroclors (polychlorinated biphenyls)
PCB 1016
PCB 1221
PCB 1232
PCB 1242
PCB 1248
PCB 1254
PCB 1260
PCB 1262
PCB 1268

PBDEs (polybrominated diphenyl ethers)
PBDE 047
PBDE 100
PBDE 099
PBDE 154
PBDE 153
PBDE 066
PBDE 071
PBDE 183
PBDE 138
PBDE 190
PBDE 209

PCDD/Fs (polychlorinated dibenzo-p-dioxins and -furans)
1,2,3,4,6,7,8,9-OCDD
1,2,3,4,6,7,8,9-OCDF
1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
1,2,3,4,7,8-HxCDD
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD
1,2,3,7,8,9-HxCDF
1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF
2,3,4,6,7,8-HxCDF
2,3,4,7,8-PeCDF
2,3,7,8-TCDD
2,3,7,8-TCDF

Appendix C

Certified Pesticide Concentrations for SRM 1946 – Lake Superior Fish Tissue

Chemical	ug/Kg
Hexaclorobenzene	7.25
a-BHC	5.72
g-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