

Quality Assurance Project Plan

Status Monitoring for Upper Yakima River Suspended Sediments and Organochlorine Pesticides

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Data for this project will be available on Ecology's Environmental Information Management (EIM) website at <u>www.ecy.wa.gov/eim/index.htm</u>. Search Study ID mifr0001.

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April 2014

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Abstract

A Suspended Sediment and Organochlorine Pesticide Total Maximum Daily Load (TMDL) was established for the Upper Yakima River in 1999 (Creech and Joy, 2002). TMDL effectiveness monitoring for total suspended solids and turbidity followed in 2006 (Anderson, 2008). This Quality Assurance Project Plan (QAPP) is provided to describe status monitoring of chlorinated pesticides and breakdown products as called for in the TMDL schedule. Samples will be collected every two weeks from March through November 2014. This sampling period brackets the 2014 irrigation season. Analysis will target DDT compounds, dieldrin, total suspended solids (TSS) and turbidity. Samples will be collected from Cherry Creek and Wipple Wasteway (also known as Badger Creek), in the Wilson Creek drainage near Ellensburg, WA.

Background

The Yakima River basin is located in south-central Washington State (Figure 1). The Yakima River flows 214.5 miles from the outlet of Keechelus Dam, southeasterly to its confluence with the Columbia River. The basin drains nearly half of Washington's eastern slope of the Cascade Mountains (6,155 square miles). Land use in the basin varies from forestland, range, and intensively irrigated agriculture to urban and suburban areas. Past studies and monitoring data have shown that each of these uses contributes to suspended sediment loads in the Yakima River and many of its tributaries (Joy, 2002).





http://wa.water.usgs.gov/projects/yakimawarsmp/maps.htm

A suspended sediment and organochlorine pesticide TMDL is underway in the Upper Yakima River (Joy, 2002; Creech and Joy, 2002). This study defines the Upper Yakima River as the reach from the headwaters to river mile (R.M.) 121.7, just above the city of Yakima (Figure 1). The major water quality impacts to the upper Yakima are from Wilson Creek, which drains the Kittitas Valley, an area around Ellensburg devoted primarily to hay, cereal crops, and irrigated pasture (Anderson, 2008). Cherry Creek and Wipple Wasteway will be sampled for this study as both of these tributaries contribute turbid water to Wilson Creek from agricultural lands (Anderson, 2008).

DDT and dieldrin are legacy pesticides no longer produced or used in the United States. Suspended sediment is considered the main transport mechanism for these pesticides (Creech and Joy, 2002). Efforts to reduce agricultural runoff and erosion have been underway in the Upper Yakima basin since the TMDL implementation began in 2003 (Creech, 2003). Riparian fencing and re-vegetation, changes to irrigation practices, outreach and education, and road improvements by the forestry industry have all helped reduce erosion in the Yakima Basin (Anderson, 2008). These best management practices (BMPs) have been implemented to reduce erosion and the organochlorine pesticides associated with suspended sediment.

The upper river TMDL schedule (Creech and Joy, 2002) called for effectiveness monitoring for turbidity, DDT, and dieldrin in 2006. The Ecology Freshwater Monitoring Unit (FMU) led the effort of monitoring turbidity and total suspended solids (TSS) during the 2006 irrigation season, as prescribed in the schedule. The Water Quality Effectiveness Monitoring Report describes TSS and turbidity results from 2006 (Anderson, 2008). This report concludes that "implementation of the TMDL is successful so far". TSS and turbidity values were lower than in 1999, but not all targets of the TMDL were met. Pesticide samples were not collected at Cherry Creek or Wipple Wasteway in 2006.

Ecology conducted a water quality study in the Yakima River basin during 2007-8 to assist in developing a TMDL for 303(d) listed chemicals not addressed in other Yakima River TMDLs (Johnson et al., 2010). Pesticide data for Cherry Creek and Wipple Wasteway from that study will be compared to 1999 results to evaluate progress towards TMDL targets established in the Upper Yakima River TMDL (Creech and Joy, 2002).

The targets that were set in the TMDL compliance schedule for Cherry Creek and Wipple Wasteway are for DDT compounds, total DDT (all DDT compounds) and dieldrin (Table 1). The 2006 target was based on aquatic toxicity criteria (1.0 ng/L DDT compounds, or total DDT, and 1.9 ng/L dieldrin; WAC 173-201A). The 2011 target was based on human health criteria, back calculated from fish consumption criteria using average bioaccumulation factors and lipid contents (Joy, 2002). Concentrations below 0.59 ug/L for DDT or DDE compounds, 0.83 ug/L for only DDD, and 0.14 ug/L dieldrin would meet the 2011 target (Creech and Joy, 2002).

TMDL targets	DDT	DDE	DDD (exclusively*)	Total DDT†	Dieldrin
2006 Targets	n/a	n/a	n/a	1.0 ng/L	1.9 ng/L
(aquatic toxicity criteria)					
2011 Targets	0.59 ng/L	0.59 ng/L	0.83 ng/L		0.14 ng/L
(human health criteria)					

Table 1. 2006 and 2011 TMDL Targets for Cherry Creek and Wipple Wasteway.

*Human health criteria is 0.83 ng/L for *only* DDD (when no DDE or DDT are present) [†]Total DDT is the sum of DDT and its metabolites, DDD and DDE

--- No criteria exist

Study Area

This study will be conducted in the Upper Yakima Basin, located in south central Washington (Figure 1). Samples will be collected at Cherry Creek and Wipple Wasteway (Figure 2). These waterways are tributaries to Wilson Creek which drains into the Yakima River, southeast of Ellensburg. These two sites are being targeted because the initial TMDL evaluation found Cherry Creek exceeded chronic toxicity criteria for 4,4'-DDE, total DDT and dieldrin and Wipple Wasteway exceeded chronic toxicity criteria for 4,4'-DDE and total DDT (Joy, 2002).



Figure 2. Sites to be sampled for Upper Yakima Status Monitoring; Cherry Creek at Moe Rd. and Wipple Wasteway at Moe Rd.

Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area

WRIAs

• Cherry Creek and Wipple Wasteway are located in WRIA 39- Upper Yakima.

HUC numbers

• The HUC for the study area is 17030001- Wilson Creek- Cherry Creek.

Project Description

DDT compounds, dieldrin, TSS, and turbidity will be monitored at Cherry Creek and Wipple Wasteway every other week from March to November 2014. The sampling schedule will include the months before and after irrigation season to characterize non-irrigation season waterbody conditions. The results will be compared to data from the TMDL technical study conducted in 1999 and effectiveness monitoring data collected in 2006. The primary objective of this study is to evaluate progress in meeting water quality targets established in the Upper Yakima River TMDL. Status monitoring will be conducted by the Toxics Studies Unit (TSU) with assistance from Environmental Assessment Program (EAP) staff stationed at the Central Regional Office (CRO). The samples will be analyzed by the Ecology Manchester Environmental Laboratory (MEL).

Organization and Schedule

Table 2 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 3 presents the proposed schedule for this project.

Staff (all are EAP except client)	Title	Responsibilities
Michael Friese Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6737	Principal Investigator	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Jane Creech Watershed Unit Central Regional Office Phone: (509) 454-7860	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Chris Coffin Central Regional Office Phone: (509) 575-2821	Unit Supervisor for the Client	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Kristin Carmack and Evan Newell Central Regional Office Phone: (509) 454-4243 (509) 575-2825	Field Assistants	Help collect samples and record field information.
Tom Mackie Eastern Operations Section Phone: 509-454-4244	Section Manager for Project Study Area	Reviews and approves the QAPP, staffing plan, technical study budget, and the technical sections of the report.
Dale Norton Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Lab Phone: (360) 871-8801	MEL Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

Table 2.	Organization	of project s	staff and resp	onsibilities.
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EAP: Environmental Assessment Program

EIM: Environmental Information Management database

QAPP: Quality Assurance Project Plan

Field and laboratory work	Due date	Lead staff
Field work completed	November 2014	Michael Friese
Laboratory analyses completed	January 2015	
Environmental Information System (EIM)	database	
EIM Study ID	MIFR0001	
Product	Due date	Lead staff
EIM data loaded	May 2015	Michael Friese
EIM QA	June 2015	Melissa McCall
EIM complete	July 2015	Michael Friese
Final report		
Author lead / Support staff	Michael Friese	
Schedule		
Draft due to supervisor	April 2015	
Draft due to client/peer reviewer May 2015		
Final (all reviews done) due to publications coordinator (Joan)	June 2015	
Final report due on web	July 2015	

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Quality Objectives

TSS and turbidity samples will be analyzed by MEL. DDT and dieldrin samples will be analyzed by a commercial analytical laboratory. It is expected that both labs will meet the QC requirements for the analytical methods that are used for this study. Measurement quality objectives (MQO) for this project are defined in Table 4.

Table 4. Measurement Quality Objectives.

Analysis	Lab Control Samples (% recov.)	Duplicates (RPD)	Surrogates (% recov.)
DDT, DDE, Dieldrin	50 - 120%	NA*	70 - 130%
DDD	42 - 120%	NA*	70 - 130%
TSS	80 - 120%	±20%	NA
Turbidity	90 - 110%	±20%	NA

NA= not analyzed

*Field replicates will be analyzed.

Laboratory control samples contain known amounts of analyte and indicate bias due to sample preparation and calibration. Results on duplicate (split) samples provide estimates of analytical precision. The precision of the organics data for the present study will be assessed with field replicates to estimate the total variability in the data (i.e., field + laboratory). As a cost savings measure, additional laboratory duplicates will not be requested for organic compounds.

Surrogates are compounds with characteristics similar to target compounds and are added to all organics' samples prior to extraction. Recovery of surrogate spikes is used to estimate recovery of target compounds in the sample.

Sampling Design

The Submittal Report for the Upper Yakima River Organochlorine TMDL (Creech and Joy, 2002) established load allocations for total DDT and dieldrin. The interim targets for these pesticides (see Table 1) at the Cherry and Wipple sites (originally scheduled for October, 2006) calls for "...water column concentrations of individual DDT compounds, or total DDT, and dieldrin will not exceed aquatic toxic criteria (0.001 ug/L DDT compounds, or total DDT, and 0.0014 ug/L dieldrin)." This project will provide data to determine if the presence and concentrations of these pesticides meets the specified interim targets for this established TMDL. Pesticide concentrations will also be compared to the final target, defined in the submittal report: "Cherry Creek and Wipple Wasteway water column concentrations of individual DDT compounds, total DDT, and dieldrin will not exceed human health criteria (0.00059 ug/L DDT or DDE compounds, 0.00083 ug/L DDD, and 0.00014 ug/L dieldrin)". The final targets that pesticide concentrations will be compared to are also displayed in Table 1.

Ecology field staff will measure flow using a Marsh-McBirney flow meter. Depending on water levels and velocities, the flow meter will be attached to a sounding reel and a bridgeboard, as described in the Ecology Standard Operating Procedure (SOP) for Measuring Streamflow from a Bridge (Holt, 2010) or to a top-setting wading rod as described in the Ecology SOP, Estimating Streamflow (Kardouni, 2013). A reference point for a tape-down measurement will be established at each of the sampling sites and measurements will be recorded on the field data sheet. Flows will be used to convert pesticide and sediment concentrations into estimated daily and seasonal loads.

Sampling Procedures

Ecology staff will collect samples every other week from March through November 2014. Depth integrated samplers such as the DH-81 will not be used for this study. Ecology has established that pesticide samples collected using quarter-point transect simple grabs show no significant statistical difference from depth-integrated samples collected from quarter-point transects with the DH-81 (Sargeant, 2011). Potential cross contamination of samples is another reason that depth integrating equipment will not be used. Water samples will be collected by simple grab from quarter-point transects following the procedures described in the SOP, Sampling Pesticides in Surface Waters (Anderson, 2011). Pesticide samples will be collected in appropriately cleaned, single- use, 1-liter transfer bottles and composited into appropriately cleaned 1-liter

amber bottles. TSS and turbidity samples will be simple grab samples collected from the thalweg of the waterway being sampled. Sample containers and holding times are described in Table 5.

Parameter	Min. Sample Size	Container*	Preservation	Holding Time
Chlorinated Pesticides	1 Liter (L)	1 L amber	Cool to 4° C	7 days
TSS	1,000 mL	1 L poly bottle	Cool to 4° C	7 days
Turbidity	100 mL	500 mL poly bottle	Cool to 4° C	48 hours

Table 5. Field Procedures for Water Samples.

*Sample containers will be obtained from MEL

Measurement Procedures

Analytical methods for this project are described in Table 6. Pesticides will be analyzed by highresolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). This analytical instrumentation will be used to achieve detection limits in the sub-parts per trillion range for comparison with human health criteria. All DDT and dieldrin analyses will be conducted by the contract lab. MEL will analyze the TSS and turbidity samples.

Table 6. Laboratory Procedures.

Analyte	Sample Matrix	Expected Number of Samples*	Expected Range of Results	Quantitation Limit	Analytical Method
4,4'-DDD	Surface water	45	0.01 - 100 ng/l	0.2 ng/L	EPA 1699 [†]
4,4'-DDE	Surface water	45	0.01 - 100 ng/l	0.2 ng/L	EPA 1699 [†]
4,4'-DDT	Surface water	45	0.01 - 100 ng/l	0.2 ng/L	EPA 1699 [†]
Dieldrin	Surface water	45	0.01 - 100 ng/l	0.1 ng/L	EPA 1699 [†]
TSS	Surface water	40	1 - 200 mg/l	1 mg/l	EPA 160.2
Turbidity	Surface water	40	1 - 200 NTU	0.5 NTU	EPA 180.1

*including field replicate and QA/QC samples

[†]Laboratory modification of EPA method

ng/L = parts per trillion

mg/L = parts per million

The estimated total cost of analyzing samples for this project is \$28,332 (Table 7).

Analysis	# of Samples	Cost per Sample	Total cost
Pest by 1669	36	\$700	\$25,200
Pesticide QC*	9(3**)	\$700	\$2,100
TSS †	43	\$12	\$516
Turbidity†	43	\$12	\$516
	•	•	\$28,332

Table 7. Laboratory Budget.

* Pesticide QC includes 3 transfer blanks, and 6 field replicates

**4 replicates and 2 transfer blanks analyzed free of charge

† Number of TSS and turbidity samples includes field replicates and blanks

Quality Control Procedures

Field

Field replicates will be collected for all parameters during March, May, July, August, and September, alternating between Cherry Creek and Wipple Wasteway. A replicate pesticide sample will be collected during March to verify pre-irrigation season concentrations. Initial sampling will be immediately followed by replicate sampling, using identical methods, equipment, and personnel. Ten percent or more of the total number of pesticide samples collected for this project will be replicated in order to assess variability in field sampling and laboratory analysis.

Transfer blanks will be prepared during March, August, and October sampling events. The contract lab will provide ultra-pure blank water in the same quart glass bottles that will be used for grab sampling. Ecology field staff will transfer blank water from the sampling jar into a clean 1-liter amber jar normally used for compositing samples. Transfer blanks will be prepared on site in the field and submitted blind to MEL. Potential contamination during sampling procedures will be assessed using transfer blank results.

Samples that will be collected for QA and QC are documented in Table 8.

QA/QC Sample	# of Samples	Month of QA/QC Sample Collection				
Transfer Blank	3	March	Aug.	Oct.		
Field Replicate	6	March	May	July	Aug.(2)	Sept.

Table 8. QA/QC Samples to be Collected for the Upper Yakima Project.

Laboratory

Laboratory QC samples will follow routine procedures, with two exceptions:

1. Laboratory duplicates will not be requested for the organics analyses. Field replicate samples will be submitted in their place.

2. Matrix spikes (MS) and matrix spike duplicates (MSD) will not be collected for this project. The analytical method that will be used (EPA 1699) requires that samples are spiked with isotopically labeled analogs. Analysis of spiked samples evaluates and documents data quality and also may identify matrix interference and assess laboratory variability. Spiked samples will take the place of MS/MSDs.

The contract lab will provide analysis on 4 field replicate samples and 2 transfer blanks, free of charge. A method blank will be analyzed with each batch of samples.

Data Management Procedures

All field measurements will be recorded on data sheets during sample collection. Data sheets include date, time, location, staff, and water quality parameters being collected. Notes will be recorded for weather conditions, streamside vegetation, and any other specific information needed for sample analysis or data interpretation. Data will be stored in spreadsheet format on a PC using Microsoft Excel[®]. The original field data sheets and photo copies will be preserved and kept on file by Ecology. The data will be analyzed and summarized accordingly as required to complete reports.

Audits

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

Reports

A draft report on results and analysis of data from this project will be prepared for review by CRO and EAP. The Principal Investigator (PI) will be lead author. This report will include results from status monitoring conducted in 2014. The tentative date for this report is May, 2015. Based on review comments, a revised draft will be prepared for external review. The tentative date for this report is June 2015.

A final report will be completed by July 2015.

All project data will be entered into Ecology's Environmental Information Management System on or before August 2015.

Data Verification

Data Verification

All field data will be reviewed internally by the PI. Data input into the database will be compared to data on field sheets to ensure that:

- Information has been accurately transcribed.
- Any qualifiers with the data are identified.
- Corrections and adjustments are made as required.
- Established protocols have been followed.

MEL will verify all data before reporting the results to the PI. The PI will review lab data and narratives for errors or omissions. Data verification will be completed by the PI using professional judgment as to whether the lab followed the procedures in this QAPP and the laboratory Quality Assurance Manual (MEL, 2012) and that the requirements for this project have been met.

Data verification involves examining the data for errors, omissions, and compliance with QC acceptance criteria. MEL's SOPs for data reduction, review, and reporting will meet the needs of the project. Data packages, including QC results for analyses conducted by MEL, will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review.

MEL staff will provide a written report of their data review which will include a discussion of whether (1) MQOs were met, (2) proper analytical methods and protocols were followed, (3) calibrations and controls were within limits, and (4) data were consistent, correct, and complete, without errors or omissions.

Data Quality (Usability) Assessment

After data are verified and before the final report is prepared, data quality will be assessed by:

- Reviewing data quality objectives
- Conducting a preliminary data review
- Applying statistical tests as needed to assess quality assurance

After the project data have been reviewed and verified, the PI will determine if the data are of sufficient quality to make determinations and decisions for which the study was conducted. The data from the laboratory's QC procedures, as well as results from field replicates, and surrogate recoveries will provide information to determine if MQOs have been met. A review of sample results will be performed following each sampling event to assess the need for modifications to the sampling or analysis program. Laboratory and QA staff familiar with assessment of data quality may be consulted. The project's 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 may be reported near the detection capability of the selected methods. MQOs may be difficult to achieve for these results. MEL's SOP for data qualification and best professional judgment will be used in the final determination of whether to accept, reject, or accept the results with qualification. The assessment will be based on a review of field replicates, along with laboratory QC results. This will include assessment of laboratory precision, contamination (blanks), accuracy, matrix interferences, and the success of laboratory QC samples meeting control limits.

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Appendixes

Appendix 1. Glossary, Acronyms, and Abbreviations

Glossary

Organochlorine: Chlorinated hydrocarbons, especially pesticides such as DDT or dieldrin.

Streamflow: Discharge of water in a surface stream (river or creek).

Thalweg: the line of lowest elevation in a waterway or valley.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standard and are not expected to improve within the next two years.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

BMP	Best management practices
CRO	Central Regional Office
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlordiphenyltrichloroethane
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FMU	Freshwater Monitoring Unit
HRGC/HRMS	High Resolution Gas Chromatography/ High Resolution Mass Spectrometry
HUC	Hydrologic unit code
MEL	Manchester Environmental Laboratory
MS	Matrix spike
MSD	Matrix spike duplicate
MQO	Measurement quality objective
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
SRM	Standard reference materials
TMDL	(See Glossary above)
TOC	Total organic carbon
TSS	(See Glossary above)
TSU	Toxics Studies Unit
USGS	U.S. Geological Survey
WRIA	Water Resource Inventory Area

Units of Measurement

g	gram, a unit of mass
mg	milligram
mg/L	milligrams per liter (parts per million)
mĹ	milliliter
ng/g	nanograms per gram (parts per billion)
ng/Kg	nanograms per kilogram (parts per trillion)
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
ug/L	micrograms per liter (parts per billion)
°C	degrees Celsius