Quality Assurance Project Plan

Pesticide Monitoring in the Mission Creek Basin

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303(d) listings addressed in this study:

Waterbody Number: DQ04NW
Ecology EIM Number: DSER0005

Approvals

Mike Rikel, Chelan County Conservation District	Date
Ray Latham, Water Quality Program, Central Regional Office	Date
Will Kendra, Section Manager, Watershed Ecology Section	Date
Dave Serdar, Project Manager, Watershed Ecology Section	Date
Dale Norton, Unit Supervisor, Contaminant Studies Unit	Date
Stuart Magoon, Director, Manchester Environmental Laboratory	Date
Cliff Kirchmer, Ecology Quality Assurance Officer	Date

Project Description

Background

In 1992, the Department of Ecology (Ecology) detected several pesticides in Mission Creek during monitoring performed as part of the Washington State Pesticide Monitoring Program (WSPMP; Davis, 1993). WSPMP sampling during the subsequent two years included analysis of seven water samples and one composite rainbow trout fillet from Mission Creek (Davis and Johnson, 1994, Davis *et al*., 1995, Davis, 1996). In all, eleven pesticides were detected in water samples during WSPMP monitoring, including six above criteria or recommendations to protect aquatic life (Table 1). Two pesticides were detected in rainbow trout fillet, with the total DDT concentration above the human health criterion and guidelines to protect piscivorous (fish-eating) wildlife. As a result of these findings, Mission Creek is on Ecology's candidate 303(d) list for DDT and azinphos-methyl.

Table 1. Pesticides Detected in Mission Creek by Ecology's WSPMP, 1992-1994.

Water (μg/L)	5/92	4/93	6/93	8/93	10/93	4/94	6/94	10/94
Azinphos-methyl	**0.033**	(0.16)u	**0.13**	(0.16)u	**0.012**	**0.004**	**0.027**	(0.16)u
Glyphosate	**1.13**	(1.0)u	(1.0)u	na	na	na	na	na
Pentachlorophenol	**0.002**	(0.01)u	(0.01)u	(0.01)u	(0.01)u	(0.02)u	(0.02)u	(0.02)u
Simazine	**0.041**	(0.08)u	(0.08)u	(0.08)u	(0.08)u	**0.25**	(0.08)u	**0.011**
Total DDT	(0.05)u	**0.004**	**0.018**	(0.05)u	(0.05)u	(0.05)u	**0.025**	(0.05)u
Chlorpyriphos	(0.05)u	**0.14**	(0.05)u	(0.05)u	(0.05)u	(0.06)u	(0.06)u	**0.02**
Diazinon	(0.07)u	(0.07)u	(0.07)u	(0.07)u	**0.007**	(0.07)u	(0.07)u	**0.031**
Total endosulfan	(0.05)u	**0.048**	(0.05)u	(0.05)u	(0.05)u	(0.05)u	(0.05)u	(0.05)u
3-Hydroxycarbofuran	(2.5)u	(0.15)u	(0.15)u	(0.15)u	(0.15)u	(0.04)u	(0.04)u	**0.421**
Carbaryl	(2.5)u	(0.3)u	(0.3)u	(0.3)u	(0.3)u	(0.04)u	**0.059**	(0.04)u
Bromacil	(0.50)u	(0.50)u	(0.50)u	(0.50)u	(0.50)u	(0.50)u	**0.022**	**0.044**

Fish Tissue (μg/kg)	9/93
Total DDT	**363**
Endosulfan sulfate	8

Concentrations exceeding water quality criteria, guidelines, or recommended maximum concentrations to protect aquatic life, wildlife, and human health

Detected compounds in **bold**

u=undetected at concentration in parentheses

na=not analyzed

Based on WSPMP findings, Ecology recommended conducting an intensive survey of streams flowing through orchards to assess the impacts of multiple pesticides on stream biota and associated wildlife (Ehinger *et al*., 1995). More recently, the Wenatchee River Watershed Action Plan rated pesticide contamination of Mission Creek as one of the most important pollution problems in the watershed (WRWSC, 1998).

Objectives of the Proposed Study

The primary objectives of this project will be to: 1) assess the current types and concentrations of pesticides in Mission Creek and its tributaries and 2) help determine which drainages are contributing pesticides to Mission Creek. To the extent possible, the results of this study will be used to assess the relationship between the application of pesticides and their presence in streams. The relationships between pesticide concentrations, streamflow, and suspended solids will also be examined. The study will ultimately help guide management practices designed to reduce pesticides in Mission Creek.

Project Organization and Responsibility

Schedule/Completion Dates

Field Sampling - April - October 2000
Final Data Received from Laboratory and Quality Assurance Review - January 2001
Draft Report of Findings - March 2001
Final Report of Findings - May 2001
EIM Data Entry - June 2001

Contacts

Project Officer - Dave Serdar (360) 407-6772
Supervisor - Dale Norton (360) 407-6765
Field Assistance - Katina Kapantais (360) 407-6458
Contract Officer - Stuart Magoon (360) 871-8813
Clients - Ray Latham (509) 575-2807 and Mike Rikel (509) 664-0266

Project Cost

Estimated Lab Cost = $ 25,300
Estimated Staff Time = 0.25 FTE

Sampling Design

Site Selection

Water samples will be collected from two Mission Creek sites and two tributary streams on five occasions between April 2000 and October 2000. Sample site selection was based on a review of land use/land cover in the watershed and site reconnaissance during September, 1999 (Figure 1). Brender Creek and the Yaxon Canyon drainage provide the greatest contributrion to flows in the orchard lands of lower Mission Creek. Mission Creek itself will be sampled near the mouth just upstream of the Brender Creek confluence. Sampling will also be done at Mission Creek upstream of the U.S. Forest Service boundary to determine pesticide concentrations before the stream reaches private lands. Stations correspond to those developed during the Wenatchee Watershed Ranking Project (WRWSC, 1998) and are described in Appendix A.

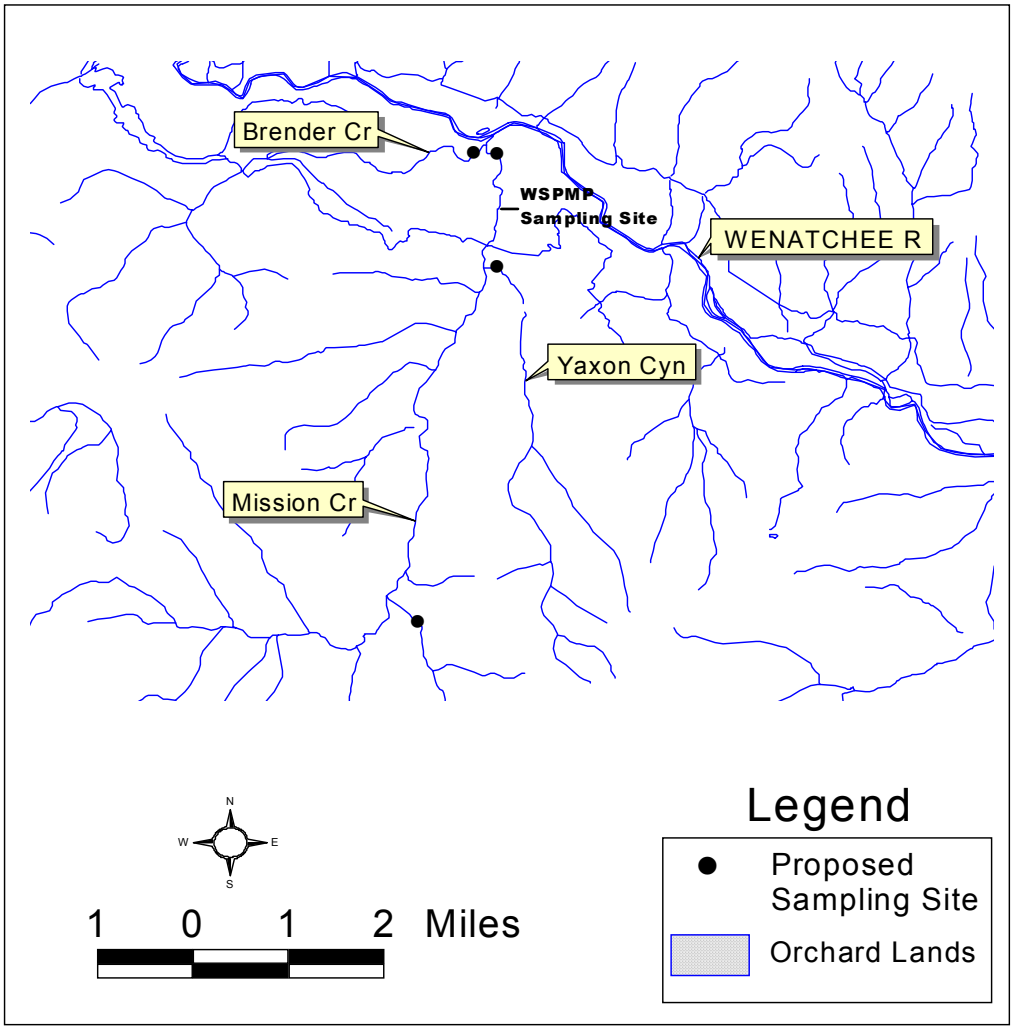

Figure 1. Proposed Sample Locations for Pesticide Sampling in the Mission Creek Drainage.

Analyte Selection

Water samples will be analyzed for five classes of pesticides: nitrogen, organophosphorous, chlorinated, chlorophenoxy (herbicides), and carbamates. This suite of pesticide analyses was chosen on the basis of previous detections during WSPMP monitoring (Table 1). Although glyphosate was previously detected in Mission Creek, it was not selected for this project because it requires a separate method for this single analyte, at relatively high cost. Glyphosate was dropped from the WSPMP due to difficulty in obtaining low detection limits (Davis and Johnson, 1994).

Samples will also be analyzed for total suspended solids (TSS) and total organic carbon (TOC). Measurements of flow, pH, temperature, and specific conductance will be made in the field.

Methods

Sample Collection and Field Procedures

Samples will be collected using a U.S. Geological Survey (USGS) depth-integrating sampler or a hand held bottle for water less than one foot deep. The depth-integrating sampler consists of a DH-81 adapter with a D-77 cap and priority pollutant-cleaned 1-L jar assembled so that water contacts only Teflon or glass. Samples will be collected by slowly lowering the sampler to the bottom and immediately raising the sampler at the same rate from three points (quarter point transect) across each site. Water will be split into sample containers, filling each container one-third full from each quarter point. The depth-integrating samplers will be cleaned prior to sampling by scrubbing with Liquinox® detergent followed by sequential rinses with tap water, deionized water, pesticide-grade acetone, and spectro-grade hexane.

Recommended sample bottles, preservatives, and holding times are listed in Table 2. All water samples will be immediately put on ice and delivered to the Manchester Environmental Laboratory within 24 hours of collection.

Stream flow will be measured using USGS Stream Gaging Procedure (196) and a Swoffer Model 2100 TSR or a Marsh-McBirney, Inc. Model 201 flow meter. Temperature will be measured with a long-line thermometer. pH will be measured using an Orion Model 250 temperature compensating pH meter. Specific conductance will be measured using a YSI Model 33 S-C-T meter. Sample location coordinates will be recorded using a Magellan NAV 5000 global positioning receiver.

Table 2. Summary of Recommended Sample Containers and Preservation.

Parameter	Sample Container	Preservation	Holding Time
Pesticides	glass/teflon lid liner, 1 gal.	4°C	7 days
Total Suspended Solids	polyethylene, 1 L	4 °C	7 days
Total Organic Carbon	polyethylene, 60 mL	4°C, H_2SO_4, <pH 2	28 days

Laboratory Analysis and Data Quality

Table 3 shows a summary of analytical methods and target detection limits for pesticides and conventionals. All classes of pesticides except carbamates will be analyzed using gas chromatography with atomic emission detection (GC/AED). Carbamates will be analyzed by high performance liquid chromatography with fluoresence detection (HPLC/FD). TSS and TOC will be analyzed using standard EPA methods. Sample analyses will be conducted at the Ecology/EPA Manchester Environmental Laboratory (MEL).

Table 3. Analytical Methods and Required Detection Limits.

Parameter	Target Detection Limit	Expected Range of Results	Method	Laboratory
Nitrogen Pesticides	0.01 μg/L	0.01-0.5 μg/L	GC/AED - EPA 8085	MEL
Organophosphorous Pesticides	0.005 μg/L	0.005-0.2 μg/L	GC/AED - EPA 8085	MEL
Chlorinated Pesticides	0.004 μg/L	0.004-0.1 μg/L	GC/AED - EPA 8085	MEL
Chlorophenoxy Herbicides	0.002 μg/L	0.002-0.1 μg/L	GC/AED - EPA 8085	MEL
Carbamate Pesticides	0.04 μg/L	0.04-0.5 μg/L	HPLC/FD - EPA 8318	MEL
Total Suspended Solids	1.0 mg/L	1-2,000 mg/L	Gravimetric - EPA 160.2	MEL
Total Organic Carbon	1.0 mg/L	1-20 mg/L	Combustion IR - EPA 415.1	MEL

The target detection limits and expected range of results are derived from the WSPMP data. Historically, most of the pesticides detected by WSPMP in water samples are below quantitation limits. Appendix B shows expected quantitation limits for pesticide analysis at MEL.

Bias of the data will be assessed through analysis of matrix spikes. Surrogate recoveries will also be used as an indication of systematic error. The data quality objective for bias is 50% - 150% recovery of matrix spikes. ***Precision*** of the data will be assessed through the analysis of matrix spike duplicates. The data quality objective for precision is relative percent differences (RPDs) <25%. Matrix spike/spike duplicate analyses conducted by MEL for recent pesticide projects (e.g. Davis, 1998; Serdar *et al*., 1999) indicate that objectives for bias and precision will be easily achievable.

Representativeness of the samples will be enhanced by sampling streams at their mouths, integrating and capturing pesticide sources for each particular stream. The sample collection methods (depth integration, quarter-point transects) are designed to increase the likelihood that samples collected for analysis offer a true representation of the water column.

The probability of attaining 100% ***completeness*** will be improved by detailed field preparation, following sample collection methods outlined previously, and using care in transporting samples. All samples stored in one-gallon glass jars will be jacketed in bubble wrap before being placed in coolers. MEL and the laboratory courier will be notified in advance of a sampling event to ensure recommended holding times are met.

Comparability of project data with other pesticide data should be excellent. Sample collection and field procedures are consistent with those used currently and historically by the WSPMP. The laboratory analyses are EPA methods. Achieving the data quality objectives described here should guarantee useable and representative data.

Data Reduction, Review, and Reporting

Data received from the MEL will be accompanied by narrative quality assurance reviews. A draft report will be peer-reviewed within EA Program and by the project clients. The project officer will prepare a final report for the clients which, at a minimum, will contain the following elements:

- Description of the project
- Summary of the findings
- Detailed description of the sampling methods and sampling stations
- Map and coordinates (lat/long) of the sampling stations
- Discussion of the analytical methods and data quality
- Tables of the chemical data
- Discussion of pesticide contributions from tributaries and stream segments
- Comparison to WSPMP and any other data in the Mission Creek watershed
- Comparison to water quality criteria, guidelines, and recommended maximum concentrations to protect aquatic life, wildlife, and human health
- Recommendations for further action (if warranted)

Results will also be entered into the Ecology Environmental Information Management (EIM) database.

References

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Davis, D., A. Johnson, and D. Serdar, 1995. *Washington State Pesticide Monitoring Program - 1993 Fish Tissue Sampling Report*. Ecology Publication Number 95-356, Washington State Department of Ecology, Olympia, Washington.

Ehinger, W., R. Cusimano, D. Davis, R. Garrigues, and S. Golding, 1995. *Watershed Briefing Paper for the Wenatchee Basin Water Resources Inventory Area*. Ecology Publication Number 95-348, Washington State Department of Ecology, Olympia, Washington.

Serdar, D., D. Davis, and J. Hirsch, 1999. *Lake Whatcom Watershed Cooperative Drinking Water Protection Project - Results of 1998 Water, Sediment and Fish Tissue Sampling*. Ecology Publication Number 99-337, Washington State Department of Ecology, Olympia, Washington.

Wenatchee River Watershed Steering Committee (WRWSC), 1998. *Wenatchee River Watershed Action Plan*.

Appendix A

Sampling Locations

Mission Creek near Mouth

Located just above the Brender Creek confluence and approximately 750 feet from Wenatchee River entry. This station corresponds to Wenatchee Watershed Ranking Project Station 2MC.

Brender Creek near Mouth

Located just above the Mission Creek confluence and approximately 700 feet from Wenatchee River entry. This station corresponds to Wenatchee Watershed Ranking Project Station 3MC.

Yaxon Canyon (Yaksum Creek) near Mouth

Located just above the Mission Creek confluence at Coates Road crossing. This station corresponds to Wenatchee Watershed Ranking Project Station 7MC.

Mission Creek on USFS Land

Located just inside U.S. Forest Service boundary off FSR 2204. This station corresponds to Wenatchee Watershed Ranking Project Station 11MC.

Appendix B

Quantitation Limits for Pesticide Analyses

Nitrogen Pesticides (ug/L)					
Alachlor	0.071	Diuron	0.12	Pendimethalin	0.03
Ametryn	0.02	Eptam	0.039	Profluralin	0.047
Atraton	0.03	Ethalfluralin (Sonalan)	0.03	Prometon (Pramitol 5p)	0.02
Atrazine	0.02	Fenarimol	0.059	Prometryn	0.02
Benefin	0.03	Fluridone	0.12	Pronamide (Kerb)	0.079
Bromacil	0.079	Hexazinone	0.03	Propachlor (Ramrod)	0.047
Butachlor	0.12	Metalaxyl	0.12	Propazine	0.02
Butylate	0.039	Metolachlor	0.079	Simazine	0.02
Carboxin	0.12	Metribuzin	0.02	Tebuthiuron	0.03
Chlorothalonil (Daconil)	0.047	MGK-264	0.16	Terbacil	0.059
Chlorpropham	0.079	Molinate	0.039	Terbutryn Igran)	0.02
Cyanazine	0.03	Napropamide	0.059	Triadimefon	0.051
Cycloate	0.039	Norflurazon	0.039	Triallate	0.059
Diallate (Avadex)	0.14	Oxyfluorfen	0.079	Trifluralin (Treflan)	0.03
Dichlobenil	0.039	Pebulate	0.039	Vernolate	0.039
Diphenamid	0.059				

Organophosphorous Pesticides (ug/L)					
Azinphos-ethyl	0.031	EPN	0.02	Paraoxon-methyl	0.035
Azinphos-methyl (Guthion)	0.031	Ethion	0.014	Parathion	0.016
Carbophenothion	0.02	Ethoprop	0.016	Parathion-Methyl	0.014
Chlorpyrifos	0.016	Fenamiphos	0.03	Phorate	0.014
Chlorpyrifos-methyl	0.016	Fenitrothion	0.014	Phosphamidan	0.047
Coumaphos	0.024	Fensulfothion	0.02	Propetamphos	0.039
Demeton-O	0.014	Fenthion	0.014	Ronnel	0.014
Demeton-S	0.014	Fonophos	0.012	Sulfotepp	0.012
Diazinon	0.016	Imidan	0.022	Sulprofos (Bolstar)	0.014
Dichlorvos (DDVP)	0.016	Malathion	0.016	Temephos (Abate)	0.12
Dimethoate	0.016	Merphos (1 & 2)	0.024	Tetrachlorvinphos (Gardona)	0.039
Dioxathion	0.033	Mevinphos	0.02	Tribufos (DEF)	0.028
Disulfoton (Di-Syston)	0.012				

Chlorinated Pesticides (ug/L)					
2,4'-DDT	0.035	captan	0.14	Endosulfan II	0.035
2,4'-DDE	0.035	captafol	0.21	Endosulfan Sulfate	0.035
2,4'-DDD	0.035	Cis-Chlordane	0.035	Endrin	0.035
4,4'-DDT	0.035	Trans-Chlordane	0.035	Endrin Aldehyde	0.035
4,4'-DDE	0.035	Alpha-Chlordene	0.043	Endrin Ketone	0.035
4,4'-DDD	0.035	Gamma-Chlordene	0.035	Heptachlor	0.035
DDMU	0.035	Cis-Nonachlor	0.035	Heptachlor Epoxide	0.035
Aldrin	0.035	Trans-Nonachlor	0.035	Methoxychlor	0.035
Alpha-BHC	0.035	Oxychlordane	0.035	Mirex	0.035
Beta-BHC	0.035	Dicofol (Kelthane)	0.17	Pentachloroanisole	0.035
Delta-BHC	0.035	Dieldrin	0.035	Toxaphene	0.85
Gamma-BHC (Lindane)	0.035	Endosulfan I	0.035		

Chlorophenoxy Herbicides (ug/L)					
2,3,4,5-Tetrachlorophenol	0.042	3,5-Dichlorobenzoic acid	0.076	Diclofop-methyl	0.11
2,3,4,6-Tetrachlorophenol	0.042	4-Nitrophenol	0.13	Dinoseb	0.11
2,4,5-T	0.061	Acifluorfen (Blazer)	0.3	Ioxynil	0.076
2,4,5-TB	0.068	Bentazon	0.11	MCPA	0.15
2,4,5-TP (Silvex)	0.061	Bromoxynil	0.076	MCPP (Mecoprop)	0.15
2,4,5-Trichlorophenol	0.046	DCPA (Dacthal)	0.061	Pentachlorophenol	0.038
2,4,6-Trichlorophenol	0.046	Dicamba	0.076	Picloram	0.076
2,4-D	0.076	Dichlorprop	0.083	Triclopyr	0.064
2,4-DB	0.091				

Carbamate Pesticides (ug/L)					
3-Hydroxycarbofuran	0.12	Carbaryl	0.12	Methomyl	0.12
Aldicarb	0.12	Carbofuran	0.12	Oxamyl (Vydate)	0.12
Aldicarb Sulfone	0.12	Methiocarb	0.12	Propoxur (Baygon)	0.12
Aldicarb Sulfoxide	0.12				