

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2010 Data Summary

A Cooperative Study by the Washington State Departments of Ecology and Agriculture





April 2011 Publication No. 11-03-021

Publication and Contact Information

This report is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/1103021.html

Data for this project are available at Ecology's Environmental Information Management (EIM) website <u>www.ecy.wa.gov/eim/index.htm</u>. Search User Study ID, DSAR0006.

Activity Tracker Code for this study is 11-084.

For more information contact:

Publications Coordinator Environmental Assessment Program P.O. Box 47600, Olympia, WA 98504-7600 Phone: (360) 407-6764

Washington State Department of Ecology - www.ecy.wa.gov/

- o Headquarters, Olympia (360) 407-6000
- o Northwest Regional Office, Bellevue (425) 649-7000
- o Southwest Regional Office, Olympia (360) 407-6300
- o Central Regional Office, Yakima (509) 575-2490
- o Eastern Regional Office, Spokane (509) 329-3400

Cover photo:

- Left: Trellised apple orchard in the Brender Creek subbasin (photo by Dan Dugger).
- Right: Dan Dugger, Department of Ecology employee, sampling for pesticides at Peshastin Creek (photo by Evan Newell).

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

If you need this document in a format for the visually impaired, call 360-407-6764. Persons with hearing loss can call 711 for Washington Relay Service. Persons with a speech disability can call 877-833-6341.

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2010 Data Summary

A Cooperative Study by the Washington State Departments of Ecology and Agriculture

by Debby Sargeant, Dan Dugger, Paul Anderson, and Evan Newell

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

Waterbody Number(s): WA-03-2010, WA-03-3100, WA-03-4000, WA-08-1020, WA-09-1000, WA-37-1014, WA-37-1025, WA-37-1030, WA-45-1010, WA-45-1011, WA-45-1013, WA-45-1100, WA-46-1010 This page is purposely left blank

Table of Contents

	Page
List of Figures and Tables	4
Abstract	7
Acknowledgements	8
Introduction	9
Study Area	11
Basins Monitored During 2010	11
Study Design and Methods	13
Sampling Sites and Sampling Frequency	13
Field Procedures and Laboratory Analyses	13
Data Quality	15
Laboratory Data Quality	15
Field Data Quality	17
Data Analysis and Reporting Methods	17
EPA Assessment Criteria and Washington State Water Quality Standards	19
EPA Pesticide Registration Toxicity Criteria	19
EPA National Recommended Water Quality Criteria	21
Washington State Water Quality Standards	21
Pesticides	21
Water Quality Standards for Temperature, Dissolved Oxygen, and pH	21
Results	25
Western Washington	25
Cedar-Sammamish Basin (WRIA 8): Thornton Creek, 2010	25
Green-Duwamish Basin (WRIA 9): Longfellow Creek, 2010	28
Lower Skagit-Samish Basin (WRIA 3), 2010	30
Eastern Washington	
Lower Yakima Basin (WRIA 37), 2010	
Wenatchee-Entiat Basins (WRIAs 45 and 46), 2010	44
Summary for 2010	49
Findings	49
Monitoring Program Changes	49
Planned Program Changes for 2011	50
References	51
Appendices	55
Appendix A. Glossary, Acronyms, and Abbreviations	57
Appendix B. Monitoring Sites and Duration of Sampling	61

Appendices C-E are in a separate electronic file on the web.

List of Figures and Tables

Figures

Figure 1.	State map showing the six urban and agricultural basins monitored during	
U	2010	12
Figure 2.	Pesticide detections by week and type for Thornton Creek, 2010.	26
Figure 3.	Pesticide detections by week and type for Longfellow Creek, 2010	28
Figure 4.	Pesticide detections by week and type for the upstream Big Ditch site, 2010	31
Figure 5.	Pesticide detections by week and type for the downstream Big Ditch site, 2010	31
Figure 6.	Pesticide detections by week and type for Indian Slough, 2010.	33
Figure 7.	Pesticide detections by week and type for Browns Slough, 2010	34
Figure 8.	Pesticide detections by week and type for the Samish River, 2010.	35
Figure 9.	Pesticide detections by week and type for upstream Spring Creek, 2010	39
Figure 10	Pesticide detections by week and type for downstream Spring Creek, 2010	39
Figure 11	. Pesticide detections by week and type for Marion Drain, 2010	41
Figure 12	. Pesticide detections by week and type for Sulphur Creek Wasteway, 2010	42
Figure 13	. Pesticide detections by week and type for Brender Creek, 2010.	45

Tables

Table 1.	Summary of laboratory methods, 2010	. 14
Table 2.	Laboratory blank detections, 2010	. 16
Table 3.	Definitions of data qualifiers.	. 18
Table 4.	Risk quotient criteria for direct and indirect effects of pesticides on aquatic organisms.	. 20
Table 5.	Freshwater water quality standards for temperature, dissolved oxygen, and pH for <i>Core Summer Salmonid Habitat</i> use and <i>Extraordinary Primary Contact Recreation</i> use.	. 22
Table 6.	Freshwater water quality standards for temperature, dissolved oxygen, and pH for <i>Salmonid Spawning, Rearing, and Migration Habitat</i> use and <i>Primary Contact Recreation</i> use.	. 23
Table 7.	Marine water quality standards for temperature, dissolved oxygen, and pH for <i>Aquatic Life Excellent</i> use.	. 23
Table 8.	Most frequently detected pesticides for Thornton Creek, 2010	. 25

Table 9. 1	Pesticide detections for Thornton Creek, 2010	. 26
Table 10.	Mean, minimum, and maximum for discrete conventional parameter measurements for Thornton Creek, 2010	. 27
Table 11.	Most frequently detected pesticides for Longfellow Creek, 2010	. 28
Table 12.	Pesticide detections in Longfellow Creek, 2010.	. 29
Table 13.	Mean, minimum, and maximum for discrete conventional parameter measurements for Longfellow Creek, 2010	. 29
Table 14.	Most frequently detected pesticides for the Skagit-Samish sites, 2010	. 30
Table 15.	Most frequently detected pesticides for the Big Ditch sites, 2010.	. 32
Table 16.	Most frequently detected pesticides for Indian Creek, 2010.	. 33
Table 17.	Most frequently detected pesticides for Browns Slough, 2010.	. 34
Table 18.	Mean, minimum, and maximum for discrete conventional parameter measurements for the Skagit-Samish sites, 2010	. 36
Table 19.	Periods of water temperature exceedance for the Skagit-Samish sites, 2010	. 37
Table 20.	Most frequently detected pesticides for the lower Yakima sites, 2010.	. 38
Table 21.	Most frequently detected pesticides for the Spring Creek sites, 2010	. 40
Table 22.	Most frequently detected pesticides for Marion Drain, 2010.	. 40
Table 23.	Most frequently detected pesticides for Sulphur Creek Wasteway, 2010.	. 41
Table 24.	Mean, minimum, and maximum for discrete conventional parameter measurements for the lower Yakima sites, 2010.	. 43
Table 25.	Periods of water temperature exceedance for the lower Yakima sites, 2010	. 43
Table 26.	Most frequently detected pesticides for the Wenatchee-Entiat sites, 2010	. 44
Table 27.	Most frequently detected pesticides for Brender Creek, 2010	. 45
Table 28.	Arithmetic mean and range for conventional parameters (grabs) for the Wenatchee-Entiat sites, 2010.	. 47
Table 29.	Periods of water temperature exceedance for the Wenatchee - Entiat sites, 2010	. 48

This page is purposely left blank

.

Abstract

Since 2003 the Washington State Departments of Agriculture and Ecology have been conducting a multi-year monitoring study to characterize pesticide concentrations in selected salmon-bearing streams during a typical pesticide-use period.

Monitoring is conducted in six basins:

- Thornton Creek in the Cedar-Sammamish basin and Longfellow Creek in the Green-Duwamish basin, representing urban land use.
- Lower Skagit-Samish basin, representing western Washington agriculture.
- Lower Yakima basin, representing eastern Washington irrigated agriculture.
- Wenatchee and Entiat basins, representing central Washington tree fruit agriculture.

This report summarizes data collected during the 2010 monitoring season. In 2010 surface water samples were analyzed for over 170 pesticides and pesticide degradates, as well as total suspended solids. Field measurements were collected for streamflow, temperature, pH, conductivity, and dissolved oxygen.

During 2010 only a few pesticide detections did not meet water quality criteria or standards:

- The urban sites and the Skagit-Samish sites met all available pesticide criteria.
- In the lower Yakima basins, one chlorpyrifos detection and one malathion did not meet a chronic pesticide criteria.
- In the Wenatchee-Entiat basins, the Wenatchee River and Mission Creek pesticide detections met all available criteria. One endosulfan detection in Peshastin Creek and in Brender Creek did not meet the endangered species level of concern for fish. The Entiat River had one detection of a legacy DDT degradate that did not meet chronic criteria. As in previous years, Brender Creek also had a number of detections of DDT and degradates that did not meet chronic criteria.

An intensive triennial review of pesticide results will be conducted after the 2011 monitoring season.

Acknowledgements

The authors of this report thank the following people for their contribution to this study:

- Jim Cowles, Washington State Department of Agriculture, for technical assistance and peer review of this report.
- Moses Squeochs, Joanne Cornwall, Scott Ladd, and James Thomas, members and staff of the Yakama Nation, for permission to sample Marion Drain, technical expertise, historical and operational knowledge, and ecological insight.
- John Clemens, U.S. Geological Survey, for Wenatchee-Monitor station streamflow data.
- Andrew Murdoch and Chad Herring, Washington State Department of Fish and Wildlife, for temperature data.
- Andrew Booker and Richard Woodsmith, U.S. Department of Agriculture Forest Service, for data sharing.
- Mike Jurgens for permission to access the Mission Creek site.
- Elaine Brouillard, Rosa-Sunnyside Board of Joint Control, for cooperative sampling and data sharing.
- Nina Horne, intern with the Chelan County Natural Resources Department, for field assistance.
- Washington State Department of Ecology staff:
 - For field assistance: Mike Anderson, Caitlin Bonner, Kristin Carmack, Jenna Durkee, Brandee Era-Miller, Michael Friese, Zack Holt, Sean Hopkins, Trevor Hutton, James Kardouni, Callie Meredith, Nicole Murphy, Janice Sloan, Kurt Walker, and Maiko Yasu.
 - Tyler Burks for flow data on Peshastin Creek.
 - Manchester Environmental Laboratory staff for sample processing, sample analysis, review of results, and technical assistance: Stuart Magoon, John Weakland, Jeff Westerlund, Nancy Rosenbower, Bob Carrell, Dickey Huntamer, Kamilee Ginder, Dean Momohara, Stuart Magoon, Karin Feddersen, Leon Weiks, and others.
 - Dale Norton for review of this report.
 - o Joan LeTourneau and Cindy Cook for document review and publication.

Introduction

The Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) are conducting a multi-year monitoring study to evaluate pesticide concentrations in surface waters. The study assesses pesticide presence in salmon-bearing streams during a typical pesticide-use season (e.g., March through October).

WSDA, the U.S. Environmental Protection Agency (EPA), the National Atmospheric and Oceanic Administration (NOAA) National Marine Fisheries Service, and the U.S. Fish and Wildlife Service (USFWS) use the data from this study to refine exposure assessments for pesticides that are registered for use in Washington State. Understanding the fate and transport of pesticides allows regulators to assess the potential effects of pesticides on endangered salmon species while minimizing the economic impacts to agriculture.

The purpose of this data report is to provide results from monitoring conducted during 2010 in six basins and to document any changes that occurred in the monitoring program during the year.

This page is purposely left blank

Study Area

This pesticide monitoring project has been ongoing since 2003. As the project has progressed, additional sampling areas have been added.

Basins Monitored During 2010

The six basins monitored in 2010 are presented in Figure 1: two urban and four agricultural basins. The urban basins were chosen due to land-use characteristics, history of pesticide detections, and habitat use by salmon. The agricultural basins were chosen because they support several salmonid populations, produce a variety of agricultural commodities, and have a high percentage of cultivated areas.

Monitoring areas and timeframes are:

- Thornton Creek, located in the Cedar-Sammamish basin (WRIA¹ 8), represents an urban land-use area. Two to four sites have been sampled on this creek from 2003-2008. Starting in 2009 only one site, at the mouth of Thornton Creek, was sampled.
- Longfellow Creek, located in the Green-Duwamish basin (WRIA 9), represents an urban land-use area. Sampling started on this creek at one site in 2009.
- Four sub-basins of the lower Skagit-Samish basin (WRIA 3) were selected to represent western Washington agricultural land-use practices. The Samish River, Big Ditch Slough, Browns Slough, and Indian Slough have been sampled since 2006.
- Three sub-basins of the Lower Yakima basin (WRIA 37) were selected to represent eastern Washington irrigated crop-land agricultural practices. Marion Drain, Sulphur Creek Wasteway, and Spring Creek have been sampled since the start of the project in 2003.
- Four sub-basins of the Wenatchee basin (WRIA 45) and Entiat basin (WRIA 46) were selected to represent central Washington agricultural tree fruit practices. Peshastin Creek, Mission Creek, Brender Creek, and the Wenatchee River (WRIA 45) and the Entiat River (WRIA 46) have been sampled since 2007.

Site locations and duration of sampling during 2010 are described in Appendix B.

Detailed descriptions of sites, including basin description, site map, climate, agricultural landuse, and the salmon fishery, are included in the last triennial report (Sargeant et al., 2010) and the 2009 data report (Sargeant et al., 2011).

¹ Water Resource Inventory Area



Figure 1. State map showing the six urban and agricultural basins monitored during 2010.

Study Design and Methods

Sampling was designed to address pesticide presence in salmonid-bearing streams during a typical pesticide-use period (e.g., March through September). The focus of monitoring is on currently registered pesticides, but laboratory analysis also included some historically used pesticides. Conventional water quality parameters were measured: total suspended solids (TSS), pH, conductivity, temperature, dissolved oxygen, and streamflow. The conventional parameters provide information to help better determine the factors influencing pesticide toxicity, fate and transport, and general water quality.

Detailed information on study design and methods are described in the Quality Assurance (QA) Project Plan (Johnson and Cowles, 2003), subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009), and the triennial reports (Burke et al., 2006; Sargeant et al., 2010).

During 2010 samples were collected for analysis of over 170 pesticides and degradates including: 74 insecticides, 59 herbicides, 30 degradate pesticides, 10 fungicides, 2 synergistic compounds, and one wood preservative.

Sampling Sites and Sampling Frequency

In 2010, 27 sampling events were conducted. Sampling began the second week in March and continued through the second week in September at all sites except Marion Drain. As in previous years, Marion Drain sampling continued through the end of October (for a total of 34 sampling events) for organophosphate pesticides and TSS. The upstream Spring Creek site in the lower Yakima basin was sampled every other week for a total of 14 sampling events.

Field Procedures and Laboratory Analyses

A full description of field procedures and laboratory analysis is included in Sargeant et al. (2010). Field methods for grab sampling are a direct application or modification of United States Geological Survey (USGS) or EPA procedures. Surface water samples were collected by hand-compositing grab samples from quarter-point transects across each stream. In situations where streamflow was vertically integrated, a one-liter transfer container was used to dip and pour water from the stream into sample containers. Otherwise samples were collected using depth integrating equipment. Sample/transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA, 1990). After collection, all samples were labeled and preserved according to the QA Project Plan (Johnson and Cowles, 2003).

Field meters were calibrated at the beginning of the field day according to manufacturers' specifications, using Ecology standard operating procedures (SOPs) (Swanson, 2007). Meters were post-checked at the end of the field day using known standards. Conventional parameters measured in the field were replicated once per sample day. Dissolved oxygen meter results were compared to grab samples that were analyzed by Winkler Titration for dissolved oxygen following Ecology SOPs (Ward, 2007). Two to three Winkler grab samples were obtained

during each sample day. Continuous, 30-minute interval, temperature data were collected yearround in 2010. Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Wagner et al., 2000). Data quality objectives for field meters are described in Anderson and Sargeant (2009).

Discharge for sites other than Sulphur Creek Wasteway, Wenatchee River, Peshastin Creek, and Entiat River were measured using a Marsh-McBirney flow meter and top-setting wading rod, as described in the USGS method (Rantz et al., 1983). Discharge data for Sulphur Creek Wasteway were obtained from an adjacent U.S. Bureau of Reclamation gaging station, "SUCW – Sulphur Creek Wasteway at Holaday Road near Sunnyside". Wenatchee and Entiat River discharge data were obtained from USGS at the Wenatchee River at Monitor (Station 12462500) and Entiat River near Entiat (Station 12452990). Discharge data for Peshastin Creek were obtained from an Ecology gaging station located at Green Bridge Road (Station 45F070). Fifteen-minute discharges were available during the sampling period. The recorded flow closest to the actual sampling time was used in lieu of field measurements.

Ecology's Manchester Environmental Laboratory (MEL) analyzed all pesticide and TSS samples. Laboratory methods are presented in Table 1. A list of target analytes for this study is presented in Appendix C, Table C-3.

Analyta	Analytical Methods ¹			
Anaryte	Extraction	Analysis	Reference	
Pesticides ²	3510	GC/MS	8270	
Herbicides	8151	GC/MS	8270 and 8251	
Carbamates	3535M	LCMS/MS	8321A	
Total Suspended Solids	n/a	Gravimetric	EPA 160.2	

Table 1. Summary of laboratory methods, 2010.

¹ All analytical methods refer to EPA SW 846, unless otherwise noted.

² Pesticides refers to all forms tested unless indicated otherwise.

GC: gas chromatograph.

MS: mass spectrometry.

LC: Liquid chromatography.

n/a: not applicable.

In 2010 MEL purchased a new instrument for carbamate analysis. With the new instrument, all analytes have at least one confirmation ion in addition to the quant ion. In addition, the new instrument improved sensitivity for all analytes. These improvements significantly reduced identification uncertainty, thus decreasing the potential for false positive and negatives.

Laboratory methods are discussed in the QA Project Plan (Anderson and Sargeant, 2009); previous QA Project Plan (Johnson and Cowles, 2003) and the QA Project Plan addendum (Burke and Anderson, 2006); and the SOP for the *Pesticides in Salmonid Streams Project* (Anderson and Sargeant, 2010).

Data Quality

Laboratory Data Quality

Performance of laboratory analyses is governed by QA and quality control (QC) protocols. The QA/QC protocol employs application of blanks, replicates, surrogates, and laboratory control samples, as well as matrix spike/matrix spike duplicates (MS/MSDs). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. A summary of laboratory and field data quality are presented below. For a detailed discussion of 2010 data quality, refer to Appendix C.

At a minimum, during each week there was at least one replicate, one blank, and one MS/MSD covering at least one of the four laboratory analyses (PESTMS, HERBS, CARBAMLL, and TSS). QA/QC samples were concentrated during April, May, and June to cover the intensive application period for most pesticides. Sites were randomly selected for application of QA/QC samples.

From 2006-2009 there was an anomaly in the carbamate pesticide analytical method that caused false positive identification of 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl (2009 only). In 2010 MEL purchased a new instrument that greatly improved the identification of all analytes included in the carbamate analysis. In addition sensitivity also improved. The improvements combined to significantly reduce identification uncertainty, thus decreasing the potential for false positives.

Because of the increased sensitivity of the new instrument, detections of select analytes in the carbamate analysis suite increased. One notable increase in detections was for the neonicotinoid insecticide, imidacloprid. In 2009 there were 15 detections of imidacloprid, and in 2010 there were 114 detections of imidacloprid; detections occurred in all of the project sampling areas.

Laboratory Blanks

Laboratory blank detections for 2010 are presented in Table 2. For all lab blank detections, any analyte found in associated samples below 5 times the lab blank detection were reported at the level detected but qualified as not detected at an estimated detection limit (UJ).

Analysis	Chemical	Analysis Date	Value	
	2,4'-DDT		0.015 J	
	4,4'-DDD		0.012 J	
	4,4'-DDE		0.007 J	
GCMS	4,4'-DDT	6/11/2010	0.018 J	
	cis-Chlordane		0.002 J	
	Mirex		0.012 J	
	Trans-Chlordane		0.002 J	
LCMS\MS	Imidaalanrid	4/14/2010	0.001 J	
	militaciopi la	9/28/2010	0.002 J	
	Carboral	6/11/2010	0.003 J	
	Carbaryr	7/23/2010	0.004 J	

Table 2. Laboratory blank detections, 2010 (µg/L).

Field Blanks

Field blank detections indicate the potential for sample contamination in the field and laboratory and the potential for false detections due to analytical error.

In 2010 there were no field blank detections for the pesticide analysis. There was one TSS field blank detection of 3 mg/L on July 20, 2010 for the Samish River site. The reporting limit for TSS was 1 mg/L. All TSS values collected on that day (July 20, 2010) that are less than 9 mg/L will be qualified as estimates.

Replicate Results

Replicate sampling tests the reproducibility or precision of sampling results. During 2010 field replicate sampling frequency for pesticides was 7.6%, and for TSS was 7.7%. Precision between replicate pairs was calculated using relative percent difference (RPD).

Excluding TSS, 77 analytes were consistently identified, and 19 analytes were inconsistently identified in 97 replicate pairs. The average RPD of consistent field replicate pairs was low, 8.4%. This is an improvement over previous years and is likely due to improvements in the carbamate analysis instrumentation.

TSS was consistently detected in 33 replicate pairs. The average RPD of all replicates was 12.4%. A total of 81% of the replicate pairs were within the RPD criterion (20%).

Surrogates, Matrix Spikes, and Laboratory Control Samples

Surrogates are used to evaluate recovery for a group of compounds. The majority of surrogate recoveries fell within the control limits established by MEL. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

MS/MSDs provide an indication of bias due to interferences from components of the sample matrix. The duplicate spike can be used to estimate analytical precision at the concentration of the spiked samples. The average recovery of the MS/MSD was 97%, and the average RPD between MS/MSD pairs was 7.8%. For most compounds, recovery and RPDs of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Sample results were qualified as estimates if the MS/MSD recoveries did not meet MEL QC criteria.

Laboratory control samples (LCS) are analyte compounds spiked into deionized water at known concentrations and subjected to analysis. They are used to evaluate accuracy of pesticide residue recovery for a specific analyte. The average percent recovery for the LCS and the LCS duplicates was 92%, and the average RPD between the LCS and duplicate pairs was 12%. For most compounds, recovery and RPDs of LCS and LCS duplicates showed acceptable performance and were within limits for the project. Sample results were qualified as estimates if the LCS recoveries did not meet MEL QC criteria.

Field Data Quality

A detailed discussion of 2010 field data quality is included in Appendix C. In 2010 the field meter for the lower Yakima and Wenatchee-Entiat sites (eastside sites) met QC objectives including post-checks and Winkler comparisons for most sample events. On July 7, August 9 and 25, and October 20, conductivity measurements for the eastside sites were qualified as estimates due to meter post-checks not meeting QC limits.

At Indian Slough, a westside site, two replicate measures for dissolved oxygen and one for conductivity did not meet QC objectives. This site is influenced by incoming marine water; temperature, dissolved oxygen, and conductivity values vary by depth. Differences in the replicates were likely due to environmental factors and not due to data quality issues. Indian Slough dissolved oxygen and conductivity results for these days were qualified as estimates.

Two field audits were conducted in 2010. The purpose of the field audit is to ensure that sampling methodologies are consistent. Details of the audits are presented in Appendix C. The findings of the field audits include that both Ecology sampling teams are conducting field operations using consistent sampling methodologies that results in comparable data.

Data Analysis and Reporting Methods

The 2010 field and laboratory data were compiled and organized using Excel[®] spreadsheet software and Access[®] database software (Microsoft Corporation, 2007). Water quality results from field and laboratory work were also entered into Ecology's Environmental Information Management (EIM) database (www.ecy.wa.gov/eim).

Graphs, plots, mass balance calculations, and some statistical analyses were made using Excel® software. The following guidelines were used in reporting and analyzing data for this report.

Laboratory data were qualified as needed, and qualifiers are described in Table 3. A positive pesticide detection included unqualified values and values qualified with a J or E. Values qualified with NJ, U, or UJ were considered non-detects.

Qualifier	Definition
No qualifier	The analyte was detected at the reported concentration. Data are not qualified.
Е	Reported result is an estimate because it exceeds the calibration range.
J	The analyte was positively identified; the associated numeric value is the approximate concentration of the analyte in the sample.
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified," and the associated numeric value represents its approximate concentration.
NAF	Not analyzed for.
NC	Not calculated.
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.
U	The analyte was not detected at or above the reported sample quantitation limit.
UJ	The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

Table J. Deminions of data dualitiers.
--

MEL, 2000, 2008; EPA, 1999, 2007.

Comparison to Assessment Criteria and Water Quality Standards

Non-detect values (U, UJ, N, NJ) were not used for comparison to *assessment criteria* or *water quality standards*. When summing compound totals (such as total DDT, total endosulfan), the Toxic Studies Unit Guidance was used (Ecology, 2008). Non-detects (U, UJ) were assigned a value of zero (as in the guidance). Unlike the guidance, NJ values (tentatively identified compounds) were also assigned a value of zero.

Replicate Values

Field and laboratory replicates were obtained to determine data quality. Field and laboratory replicates were arithmetically averaged for comparisons to *assessment criteria* and *water quality standards*. For data analysis purposes, field and laboratory replicates were arithmetically averaged. If the sample or the replicate was a non-detect value while the other (either sample or replicate) was a detection, then the detected value was used.

When a laboratory replicate was performed on a field replicate, the laboratory replicate mean was calculated before the field replicate mean.

For select statistical analysis, NJ qualified data were used when detected pesticide values were not available. When this occurred, it is specified in the statistical test description.

EPA Assessment Criteria and Washington State Water Quality Standards

Assessment of pesticide effects on endangered salmonid species is evaluated by comparing detected pesticide concentrations against three criteria:

- EPA Federal Insecticide Fungicide and Rodenticide Act (FIFRA) Pesticide Registration Toxicity Criteria.
- EPA National Recommended Water Quality Criteria (NRWQC).
- Washington State Water Quality Standards for the Protection of Aquatic Life (WAC 173-201A).

The EPA and Washington State aquatic life criteria are based on evaluating the effects of a single chemical on a wide array of families, including at least one fish species from the family *Salmonidae* and a second species in the class *Osteichthys*. The criteria and standards do not account for the effects of multiple chemicals or pesticide mixtures on an organism. Many of the pesticides included in this study do not have EPA or Washington State criteria.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix D. Measured concentrations higher than criteria concentrations do not necessarily indicate that the water quality criteria have not been met. Numeric water quality criteria contain concentration values and duration of exposure components; both must be compared to the measured concentrations to assess compliance with the criteria.

In this report, EPA FIFRA Pesticide Registration Toxicity Criteria and EPA NRWQC will be referred to as *assessment criteria*. Washington State numeric water quality standards for pesticides will be referred to as *water quality standards*. For a description of these criteria and standards for pesticides, refer to Appendix D.

EPA Pesticide Registration Toxicity Criteria

EPA uses risk quotients (RQ) to assess the potential risk of a pesticide to non-target organisms. A RQ is calculated by dividing the environmental concentration by either an acute or chronic toxicity value, which gives an evaluation of exposure over toxicity. The resulting RQ is a unitless value that is compared to Levels of Concern (LOC). The LOC set by EPA are presented in Table 4. These LOC are used to assess the potential risk of a pesticide to non-target organisms.

The endangered species LOC (0.05 for aquatic species) is used as a comparative value to assess potential risk to threatened or endangered salmonids. The endangered species RQ can also be expressed as $1/20^{\text{th}}$ of the acute Lethal Concentration 50 (LC₅₀) for aquatic organisms. To assess the potential risk of a pesticide to salmonids, the LC₅₀ for rainbow trout is commonly used as a surrogate species. Thus the endangered species LOC presented in subsequent tables are $1/20^{\text{th}}$ of

the rainbow trout LC_{50} . When available, the endangered species LOC for specific salmonids is also presented.

Test Data	Risk Quotient	Presumption
	>0.5	Potentially high acute risk.
Acute LC ₅₀	>0.1	Risk that may be mitigated through restricted use classification.
	>0.05	Endangered species may be affected acutely, including sublethal effects.
Chronic NOEC	>1	Chronic risk; endangered species may be affected chronically, including reproduction and effects on progeny.
Acute invertebrate LC ₅₀	>0.5	May be indirect effects on T&E fish through food supply reduction.
Aquatic plant acute LC ₅₀	>1	May be indirect effects on aquatic vegetative cover for T&E fish.

Table 4. Risk quotient criteria for direct and indirect effects of pesticides on aquatic organisms.

Turner, 2003.

NOEC: No observable effect concentration.

T&E: Threatened and endangered.

Acute toxicity is calculated by standardized toxicity tests using lethality as the measured criteria. A properly conducted test will use a sensitive (representative) species at a susceptible life stage (usually young, though not immature). The test also will subject the test species to a pesticide under a range of concentrations (minimum: no effect, 50% and 100% mortality). The dose response curve may be calculated, and the LC₅₀ lethal concentration to cause mortality in 50% of test species will be derived. For fish, the lethality test is conducted over 96 hours at a constant concentration. Acute invertebrate toxicity is normally calculated over 48 hours, with the criteria being mortality or immobility (LC_{50} , or Effective Concentration - EC_{50} for immobility). Acute toxicity testing for aquatic plants is conducted over 96 hours; the criterion is based on reduction in aquatic plant growth (EC_{50}) .

Chronic fish tests normally use reproductive effects, or effects to offspring, as the measured effect. The dose response curve is evaluated to determine a no observable effect concentration (NOEC). The chronic toxicity test is longer than the 96-hour acute test (21 day for fish, 14 days for invertebrates, 5 to 60 days for plants) to simulate exposure resulting from a persistent chemical or effect of repeated applications.

Toxicity values such as those used for pesticide registration are determined from continuous exposure over time (e.g., LC₅₀ freshwater fish acute toxicity tests are run for 96 hours at a constant concentration). When comparing the monitoring data to either the aquatic life criteria or directly to the toxicity criteria, one must consider the duration of exposure as well as the numeric toxicity value. For pesticide registration criteria, it is not possible to determine if an aquatic life criterion has been met based solely on an individual sample because the sampling frequency is usually weekly. Weekly sampling does not allow for assessment of the temporal component of the criteria.

EPA National Recommended Water Quality Criteria

The NRWQC are established by the EPA Office of Water for the protection of aquatic life, as established under the federal Clean Water Act (33 U.S.C. 1251 et. seq.). The pesticide criteria established under the Act are based on vertebrate and invertebrate acute and chronic toxicological data. States often adopt the NRWQC as their promulgated (legal) standards. The NRWQC was updated in 2006, and those criteria are used in this report (EPA, 2006).

Washington State Water Quality Standards

Pesticides

Washington State water quality standards are established in the Washington Administrative Code (WAC), Chapter 173-201A. These standards include numeric pesticide criteria for the protection of aquatic life.

The aquatic life criteria are designed to protect for both short-term (acute) and long-term (chronic) effects of chemical exposure. The criteria are primarily intended to avoid direct lethality, and growth and reproductive effects, to fish and other aquatic life within the specified exposure periods. The chronic criteria for a number of the chlorinated pesticides are based on protection of fish-eating wildlife from adverse effects due to bioaccumulation.

The exposure periods assigned to the acute criteria are expressed as: (1) an instantaneous concentration not to be exceeded at any time or (2) a one-hour average concentration not to be exceeded more than once every three years on average. The exposure periods for the chronic criteria are either: (1) a 24-hour average not to be exceeded at any time or (2) a four-day average concentration not to be exceeded more than once every three years on average. For Clean Water Act section 303(d) listing purposes, measurements of instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards for both acute and chronic criteria, unless additional measurements are available to calculate averages (Ecology, 2006).

Because few water quality criteria for pesticides have been developed, the majority of comparisons to measured pesticide concentrations contained in this report are made using pesticide registration toxicity criteria.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix D.

Water Quality Standards for Temperature, Dissolved Oxygen, and pH

Washington State water quality standards for conventional water quality parameters are set forth in Chapter 173-201A of the WAC. Waterbodies are required to meet numeric water quality standards based on the beneficial uses of the waterbody. Conventional parameters including temperature, dissolved oxygen, and pH were measured in this study. Sargeant et al. (2010)

provides a full description of the water quality standards and also explains why parameters such as temperature, dissolved oxygen, and pH are important for fish health.

Numeric Water Quality Standards

Thornton Creek subbasin

Beneficial uses for Thornton Creek are *Core Summer Salmonid Habitat* and *Extraordinary Primary Contact Recreation*. The numeric water quality standards for temperature, dissolved oxygen, and pH in Thornton Creek are described in Table 5.

Table 5. Freshwater water quality standards for temperature, dissolved oxygen, and pH for *Core Summer Salmonid Habitat* use and *Extraordinary Primary Contact Recreation* use.

Parameter	Condition	Value
Temperature	Highest 7- DADMax	16° C. Thornton Creek also has <i>Supplemental Spawning</i> <i>and Incubation</i> criteria: during Sept 15 - May 15, highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	9.5 mg/L.
pН		Range within $6.5 - 8.5$, with a human-caused variation within the above range of < 0.2 units.

DADMax: Daily average of the daily maximum temperature.

Longfellow Creek subbasin

Beneficial uses for Longfellow Creek include *Salmonid Spawning, Rearing, and Migration* habitat and *Primary Contact Recreation*. The numeric water quality standards for temperature, dissolved oxygen, and pH for Longfellow Creek (freshwater) are described in Table 6.

Skagit-Samish basin

Beneficial uses for the Samish River, Indian Slough, Big Ditch, and Browns Slough are *Salmonid Spawning, Rearing, and Migration Habitat* and *Primary Contact Recreation*. The Samish River, Indian Slough, and Big Ditch sites are freshwater and must meet the water quality standards described in Table 6. The site on Browns Slough is marine water and must meet the water quality standards described in Table 7.

Lower Yakima basin

Beneficial uses for Marion Drain, Sulphur Creek Wasteway, and Spring Creek are *Salmonid Spawning, Rearing, and Migration Habitat*. The freshwater water quality standard described in Table 6 applies to these sites.

Wenatchee-Entiat basins

Beneficial uses for the Mission Creek, Brender Creek, Wenatchee River, and Entiat River are *Salmonid Spawning, Rearing, and Migration*. The water quality standard described in Table 6 applies to these sites.

Table 6. Freshwater water quality standards for temperature, dissolved oxygen, and pH for *Salmonid Spawning, Rearing, and Migration Habitat* use and *Primary Contact Recreation* use.

Parameter	Condition	Value
Temperature	Highest 7- DADMax	17.5° C. The Wenatchee River site also has <i>Supplemental Spawning and Incubation</i> criteria: during Oct 1 - May 15, highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	8.0 mg/L
pН		Range within $6.5 - 8.5$, with a human-caused variation within the above range of < 0.5 units.

Table 7.	Marine water	quality standar	rds for temperature	, dissolved	oxygen,	and pH for
Aquatic I	Life Excellent u	use.				

Parameter	Condition	Value
Temperature	Highest 7- DADMax	16°C (60.8°F).
Dissolved Oxygen	Lowest 1-day minimum	6.0 mg/L.
рН		Range within $7.0 - 8.5$, with a human-caused variation within the above range of < 0.5 units.

This page is purposely left blank

Results

Results from the 2010 monitoring season are summarized by basin in the following sections. All results for the 2010 season are available through Ecology's EIM system, <u>www.ecy.wa.gov/eim/</u>.

Pesticide calendars for 2010 are included in Appendix E. The calendars provide a chronological overview of concentrations and detections during 2010. The calendars also compare EPA Pesticide Registration Toxicity Criteria and EPA National Recommended Water Quality Criteria *(assessment criteria)* to numeric Washington State Water Quality Standards *(water quality standards)*. Refer to Appendix D, Assessment Criteria and Water Quality Standards, in this report for information on assessment criteria development.

Western Washington

Cedar-Sammamish Basin (WRIA 8): Thornton Creek, 2010

Pesticide Detections and Concentrations

A total of 27 sampling events were conducted on Thornton Creek between March 8 and September 8, 2010. During this period, there were 58 detections of ten pesticides.

Of the 10 types of compounds detected, there were three insecticides (7 detections), six herbicides (42 detections), and a wood preservative (9 detections).

The number and types of pesticide detections are presented in Figure 2. The maximum number of pesticides detected during a sampling event was seven (Figure 2). The most frequently detected pesticides are described in Table 8.

Pesticide	Pesticide Type	Number of Detections
Dichlobenil	Herbicide	24
Pentachlorophenol	Wood Preservative	9
2,4-D	Herbicide	7

Table 8. Most frequently detected pesticides for Thornton Creek, 2010.



Figure 2. Pesticide detections by week and type for Thornton Creek, 2010.

Table 9 presents a pesticide calendar for Thornton Creek. This pesticide calendar is included as an example; the rest of the calendars are included in Appendix E. The calendar provides a chronological overview of concentrations and detections during 2010 and compares pesticide concentrations to *assessment criteria* and *water quality standards*. In the calendars, the number below the months indicate sample week. Numbers below Appendix E, Table E-1, present the color codes used to compare detected pesticide concentrations to assessment criteria.

In 2010, pesticide concentrations in Thornton Creek met (did not exceed) any available *assessment criteria* or *water quality standard* (Appendix D).

Table 9. Pesticide detections for Thornton Creek, 2010.

Pesticide resul	ts are in μg/L,	and TSS results	are in mg/L.
-----------------	-----------------	-----------------	--------------

Month			Ma	rch			Ap	oril			Μ	lay				June				Ju	ly			Aug	gust		S	ep
Chemical	Туре	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
2,4-D	Н				0.073				0.110	0.056										0.095						0.087	0.033	0.067
Carbaryl	I-C								0.005																			
Dichlobenil	Н	0.017	0.008	0.013	0.027	0.011	0.009	0.009	0.044	0.014	0.010		0.008	0.021	0.012	0.014	0.014	0.007	0.001	0.002		0.012	0.012	0.016	0.012	0.015	0.008	
Diuron	Н								0.039					0.053												0.028		
Imidacloprid	I-N											0.005		0.005							0.004	0.003	0.003					
MCPA	Н																										0.031	
MCPP	Н								0.050																		0.022	
Pentachlorophenol	WP		0.018	0.032			0.019	0.021	0.031					0.021				0.018									0.024	0.049
Propoxur	I-C								0.008																			
Triclopyr	Н													0.035						0.063						0.064	0.150	0.210
Total Suspended Solids	NA	6.0	2.0	13.0	9.0	5.0	6.0	6.0	15.0	7.0	5.0	8.0	18.5	5.0	6.0	9.0	6.0	4.3	4.0	8.0	11.0	7.3	5.0	5.0	6.0	4.0	5.0	12.0

C: Carbamate, H: Herbicide, I: Insecticide, N: Neonicotinoid, NA: Not applicable, WP: Wood Preservative

Conventional Parameters

Conventional water quality parameters were measured in Thornton Creek. All summaries are based on point (discrete) measurements obtained during the time of sampling. Table 10 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen.

PH levels met water quality standards during 2010. Dissolved oxygen dropped below the 9.5 mg/L water quality standard nine times during July 13 – September 8, 2010.

Table 10. Mean, minimum, and maximum for discrete conventional parameter measurements for Thornton Creek, 2010.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	27	7	2	19
Discharge (cfs)	27	8.0	4.0	20.0
pH (s.u.)	27	7.8	7.2	8.0
Conductivity (umhos/cm)	27	218	132	247
Dissolved Oxygen (mg/L)	27	9.9	8.3	11.6

In addition to discrete measurements for stream temperature, continuous (30-minute interval) measurements were collected year-round. During September 15 - May 15, the highest 7-Daily Average Daily Maximum (DADMax) should not exceed 13° C; during the rest of the year, the highest 7-DADMax should not exceed 16°C.

In 2010, stream temperatures did not meet (exceeded) the standard during the following periods:

- May 12-15, >13°C.
- July 6-August 27, >16°C.
- September 14, >16°C.
- September 15-October 13, >13°C.

Green-Duwamish Basin (WRIA 9): Longfellow Creek, 2010

Pesticide Detections and Concentrations

A total of 27 sampling events were conducted on Longfellow Creek between March 8 and September 8, 2010. During this period, there were 78 detections of 15 pesticides and degradates. The 15 compounds included five insecticides (13 detections), seven herbicides (58 detections), one insecticide degradate (1 detection), a fungicide (1 detection), and a wood preservative (5 detections).

The maximum number of pesticides detected during a sampling event was eight, and most of the pesticides detected were herbicide compounds (Figure 3). The most frequently detected pesticides were herbicides (Table 11).



Figure 3. Pesticide detections by week and type for Longfellow Creek, 2010.

Table 11. Most frequently detected pesticides for Longfellow Creek, 2010.

Postigida	Pesticide	Number of			
resticide	Туре	Detections			
Dichlobenil	Herbicide	22			
Triclopyr	Herbicide	19			
2,4 - D	Herbicide	12			

Table 12 presents a pesticide calendar for Longfellow Creek. This calendar is included as an example; the rest of the calendars are included in Appendix E. The calendar provides a chronological overview of concentrations and detections during 2010 and compares pesticide

concentrations to *assessment criteria* and *water quality standards*. In the calendars, the number below the months indicate sample week. Appendix E, Table E-1, presents the color codes used to compare detected pesticide concentrations to *assessment criteria* and *water quality standards*.

In 2010, pesticide concentrations in Longfellow Creek met (did not exceed) any available *assessment criteria* and *water quality standards* (Appendix D).

Table 12. Pesticide detections in Longfellow Creek, 2010.

Pesticide results are in $\mu g/L$, and TSS results are in mg/L.



C: Carbamate, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, NA: Not applicable, WP: Wood Preservative

Conventional Parameters

Conventional water quality parameters were measured in Longfellow Creek. Table 13 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling.

All field data collected met the pH water quality standard (between 6.5-8.5 s.u.) and the 8.0 mg/L minimum dissolved oxygen water quality standard.

Table 13. Mean, minimum, and maximum for discrete conventional parameter measurements for Longfellow Creek, 2010.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	27	4	2	17
Discharge (cfs)	27	1.6	0.7	5.8
pH (s.u.)	27	8.0	7.5	8.2
Conductivity (umhos/cm)	27	284	167	328
Dissolved Oxygen (mg/L)	27	10.3	9.2	11.9

In addition to discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature standard for Longfellow Creek is: the 7-DADMax should not exceed 17.5° C. During 2010 temperature did not meet (exceeded) the standard during the following periods:

- July 9-10, >17.5 °C.
- August 14-16, >17.5 °C.

Lower Skagit-Samish Basin (WRIA 3), 2010

Pesticide Detections and Concentrations

The lower Skagit-Samish sites were sampled for 27 consecutive weeks from March 8 to September 8, 2010. The lower Skagit-Samish sites are: upstream and downstream Big Ditch, Indian Slough, Browns Slough, and the Samish River. Browns Slough is classified as marine water; the other four sites are classified freshwater.

For the five Skagit-Samish sites combined, there were a total of 39 compounds detected: eight insecticides, 26 herbicides, two fungicides, one degradate, a wood preservative, and a synergistic compound. The most frequently detected pesticides found at the Skagit-Samish sites are described in Table 14.

Pesticide	Pesticide Type	Number of Detections
Dichlobenil	Herbicide	65
Bromacil	Herbicide	47
Imidacloprid	Insecticide	42
Triclopyr	Herbicide	38
Metolachlor	Herbicide	37
Pentachlorophenol	Wood preservative	24
Carbofuran	Insecticide	19

Table 14. Most frequently detected pesticides for the Skagit-Samish sites, 2010.

For the Skagit-Samish sites, Indian Slough had the greatest number of pesticide detections, with 145 detections. The upstream Big Ditch site had 140 detections and the downstream site 136 detections. Browns Slough had 76 detections and the Samish River nine detections. The Big Ditch site had 89 detections, Browns Slough had 46 detections, and the Samish River had 20 detections. The greatest number of pesticide detections during a sample event occurred on June 1, 2010, with 14 pesticide detections in both Indian Slough and Browns Slough.

Big Ditch

Two sites on Big Ditch were sampled in 2010. Water quality at the upstream site is influenced by industrial land use and stormwater, while the downstream site is influenced by agricultural land use. In 2010, 30 compounds were detected in Big Ditch: 22 at the upstream site and 26 at the downstream site. Eighteen of these compounds were found in common between the two sites.

At the upstream site, the maximum number of pesticides detected during a sampling event was 10; this occurred during three sample events (Figure 4). At the downstream site, the maximum number of pesticides detected during a sample event was 13 (Figure 5).



Figure 4. Pesticide detections by week and type for the upstream Big Ditch site, 2010.



Figure 5. Pesticide detections by week and type for the downstream Big Ditch site, 2010.

Most of the pesticides detected were herbicide compounds. At the upstream site, pesticides were detected during every sampling event. At the downstream site, the greatest number of detections occurred from March through June. The most frequently detected pesticides during 2010 for both the upstream and downstream Big Ditch sites are presented in Table 15.

Pesticide	Pesticide Type	Number of Detections		
Upstream Big D	vitch			
Dichlobenil	Herbicide	25		
Bromacil	Herbicide	22		
Imidacloprid	Insecticide	22		
Downstream Big	g Ditch			
Metolachlor	Herbicide	18		
Dichlobenil	Herbicide	15		
Imidacloprid	Insecticide	13		

Table 15. Most frequently detected pesticides for the Big Ditch sites, 2010.

Tables E-4 and E-5 in Appendix E present the pesticide calendars for 2010 for the upstream and downstream Big Ditch sites, respectively. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards*. Both Big Ditch sites met (did not exceed) any available *assessment criteria* or *water quality standard* (Appendix D).

Indian Slough

During 2010 there were 145 detections of 23 compounds. These 23 compounds were 17 herbicides, four insecticides, one fungicide, and a wood preservative. The number and types of pesticide detections are presented in Figure 6. The maximum number of pesticides detected during a sampling event was 13 (Figure 6). Of the 145 pesticide detections, 129 were herbicides.



Figure 6. Pesticide detections by week and type for Indian Slough, 2010.

In Indian Slough the most frequently detected pesticides were herbicides (Table 16).

Pesticide	Pesticide Type	Number of Detections		
Bromacil	Herbicide	24		
Dichlobenil	Herbicide	17		
Hexazinone	Herbicide	15		
Triclopyr	Herbicide	14		
Diphenamid	Herbicide	12		

Table 16. Most frequently detected pesticides for Indian Creek, 2010.

During the 2006-09 monitoring, the herbicide diphenamid was detected 68 times in Indian Slough. Diphenamid has not been registered for use by EPA since 1991 (EPA, 2002). It is not known why diphenamid is detected so frequently in Indian Slough. Data quality for herbicide parameters is excellent, and detections are not likely due to field or laboratory error.

Appendix E, Table E-6, presents the pesticide calendar for 2010 for Indian Slough. The calendar provides a chronological overview of concentrations and detections and compares pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D). In 2010, pesticide concentrations in Indian Slough met (did not exceed) any available marine *assessment criteria* or *water quality standards* (Appendix D).

Browns Slough

Browns Slough is sampled downstream of a tidegate. Due to higher salinity at this site, marine *assessment criteria* and *water quality standards* are used for evaluating water quality. During

2010 there were 76 detections of 15 pesticides. The 15 pesticides were 12 herbicides, two insecticides, and a fungicide. The number and types of pesticide detections are presented in Figure 7. The maximum number of pesticides detected during a sampling event was 14 (Figure 7).



Figure 7. Pesticide detections by week and type for Browns Slough, 2010.

Most of the pesticides detected were herbicides (64 of 76). The most frequently detected pesticides are described in Table 17.

Table 17. Most frequently detected pesticides for Browns Slough, 2010.

Pesticide	Pesticide Type	Number of Detections
DCPA (dacthal)	Herbicide	20
Metolachlor	Herbicide	9
Carbofuran	Insecticide	6
Dichlobenil	Herbicide	6

Appendix E, Table E-7, presents the pesticide calendar for 2010 for Browns Slough. The calendar provides a chronological overview of concentrations and detections and compares pesticide concentrations to *assessment criteria* and *water quality standards*. In 2010, pesticide concentrations in Browns Slough met (did not exceed) any available marine *assessment criteria* or *water quality standards* (Appendix D).

Samish River

A total of 27 sampling events were conducted on the Samish River between March 8 and September 8, 2010. There were very few pesticide detections (9 detections total); these were four herbicides (eight detections) and an insecticide (one detection). The number and types of pesticide detections are presented in Figure 8. The maximum number of pesticides detected during a sampling event was two (Figure 8). The most commonly detected pesticide was the herbicide 2,4-D, with three detections.



Figure 8. Pesticide detections by week and type for the Samish River, 2010.

Appendix E, Table E-8, presents a pesticide calendar for 2010 for the Samish River. The calendar provides a chronological overview of concentrations and detections and compares pesticide concentrations to *assessment criteria* and *water quality standards*. The Samish River met (did not exceed) any available *assessment criteria* or *water quality standards* (Appendix D).

Conventional Parameters

Conventional water quality parameters were measured at the Skagit-Samish sites. Table 18 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling. Browns Slough is a marine site and must meet marine water quality standards; all the other Skagit-Samish sites must meet freshwater quality standards.

During 2010 dissolved oxygen levels did not meet the 8.0 mg/L minimum freshwater quality standard in upper Big Ditch (10 times), lower Big Ditch (6 times), and Indian Slough (17 times). The Samish River met dissolved oxygen water quality standards during all sampling events.

Browns Slough did not meet the 6.0 mg/L minimum marine water quality standard for four sampling events.

Upper Big Ditch, Indian Slough, and Samish River met pH water quality standards. Both Browns Slough (marine) and lower Big Ditch (freshwater) did not meet the pH standard once during the sample period with pH levels of 8.8 and 9.4 s.u., respectively.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)					
Big Ditch (upstream)										
number	27	27	26	27	27					
mean	7	2.3	7.0	319	8.5					
minimum	3	0.5	6.8	213	6.1					
maximum	16	6.2	7.3	448	10.3					
Big Ditch (downs	tream)									
number	27	24	26	27	27					
mean	7	13.3	7.6	475	10.6					
minimum	< 1	2.4	6.8	50	6.1					
maximum	25	34	9.4	925	16.0					
Indian Slough										
number	27	27	26	27	27					
mean	8	26.5	7.0	1040	7.4					
minimum	2	0.7	6.6	268	4.4					
maximum	22	56	7.5	7400	11.2					
Brown Slough										
number	27	27	26	27	27					
mean	7	4.7	7.6	10083	10.3					
minimum	2	< 0.1	7.1	90	2.8					
maximum	17	13	8.7	19106	20.1					
Samish River										
number	27	27	26	27	27					
mean	15	196	7.5	99	10.7					
minimum	2	34	6.9	54	9.8					
maximum	151	859	8.4	135	12.8					

Table 18. Mean, minimum, and maximum for discrete conventional parameter measurements for the Skagit-Samish sites, 2010.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature standard for the freshwater sites is that the 7-DADMax should not exceed 17.5° C; and for the marine water site is that the 7-DADMax should not exceed 16.0° C. Table 19 describes the periods that temperature did not meet (exceeded) the standard.

Site	Periods When Temperature Did Not Meet Standards		
Big Ditch (upstream) >17.5°C	Aug 12-21.		
Big Ditch (downstream) >17.5°C	May 10-19, June 3-29, July 4-Sept 9, Sept 15-18.		
Indian Slough >17.5°C	June 21-28, July 4-Sept 2, Sept 5-25.		
Browns Slough >16.0°C	Apr 13-21, Apr 25-May 1, May 6-Oct 8.		
Samish River >17.5°C	July 8-14, July 22-Aug 6, Aug 11-19.		

Table 19. Periods of water temperature exceedance for the Skagit-Samish sites, 2010.

Eastern Washington

Lower Yakima Basin (WRIA 37), 2010

Pesticide Detections and Concentrations

In the lower Yakima River basin, downstream Spring Creek, Marion Drain, and Sulphur Creek Wasteway were sampled for 27 consecutive weeks from March 10 to September 8, 2010. The upstream Spring Creek site was sampled every other week during the same period for a total of 14 sampling events. In Marion Drain, weekly sampling for organophosphates continued from September 13 through October 26, 2010. Historically, Marion Drain sampling for organophosphates has continued through the end of October.

For the four sites combined, there were a total of 368 detections of 35 types of pesticides and degradates. These 35 compounds were 12 insecticides, 21 herbicides, and two insecticide degradates. Marion Drain had the greatest number of detections, 162, and the greatest number of sampling events. Sulphur Creek Wasteway had 115 detections. The downstream Spring Creek site had 62 detections. The upstream Spring Creek site had 29 detections and the least number of sampling events.

The most frequently detected pesticides found at the lower Yakima sites are described in Table 20.

Destinida	Destinida Tura	Number of	
resticide	resucide Type	Detections	
2,4-D	Herbicide	67	
Imidacloprid	Insecticide	49	
Dicamba I	Herbicide	38	
Terbacil	Herbicide	28	
Carbaryl	Insecticide	24	
Bromacil	Herbicide	19	
Diuron	Herbicide	17	
Bentazon	Herbicide	16	

Table 20. Most frequently detected pesticides for the lower Yakima sites, 2010.

Spring Creek

Two sites on Spring Creek were sampled in 2010. The upstream site was sampled every two weeks, and the downstream site was sampled weekly. A total of 17 pesticide and degradate types were detected in Spring Creek: 11 herbicides, five insecticides, and one insecticide degradate. A total of 12 pesticides were detected in common between the upstream and downstream sites. A total of 14 pesticides were found upstream, and 15 were found downstream. The number and types of pesticide detections are presented in Figure 9 for the upstream site and Figure 10 for the downstream site. The maximum number of pesticides detected during a sampling event at the upstream site was five (Figure 9) and at the downstream site was six (Figure 10).



Figure 9. Pesticide detections by week and type for upstream Spring Creek, 2010.



Figure 10. Pesticide detections by week and type for downstream Spring Creek, 2010.

The most frequently detected pesticides at the upstream and downstream sites were similar. Table 21 describes the most frequently detected pesticides for the upstream and downstream Spring Creek sites in 2010.

Pesticide	Pesticide Type	Number of Detections		
Upstream Spring Creek				
Imidacloprid	Insecticide	7		
2,4-D	Herbicide	5		
Downstream Spring Creek				
2,4-D	Herbicide	19		
Imidacloprid	Insecticide	11		

Table 21. Most frequently detected pesticides for the Spring Creek sites, 2010.

Appendix E, Tables E-9 and E-10, present the pesticide calendars for 2010 for the upstream and downstream Spring Creek sites, respectively. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

At the downstream site, a March 30 detection of chlorpyrifos did not meet (exceeded) the chronic *water quality standard* and EPA's chronic invertebrate *criteria*. This single event met (did not exceed) the 21-day time component of the chronic invertebrate criteria.

Marion Drain

An additional seven weeks of sampling for organophosphates was conducted on Marion Drain after September 8, 2010. No pesticides were detected during the last two sampling events in late October. In addition only one pesticide, the insecticide imidacloprid, was detected between March 10 and April 13.

During 2010 there were 162 detections of 22 pesticides and a degradate. These 23 compounds were 14 herbicides, eight insecticides, and one insecticide degradate. The number and types of pesticide detections are presented in Figure 11. The maximum number of pesticides detected during a sampling event was 12 (Figure 11).

The most frequently detected pesticides in Marion Drain are described in Table 22.

Pesticide	Pesticide Type	Number of Detections
Terbacil	Herbicide	25
2,4-D	Herbicide	20
Dicamba I	Herbicide	18
Imidacloprid	Insecticide	17
Pendimethalin	Herbicide	12

Table 22. Most frequently detected pesticides for Marion Drain, 2010.



Figure 11. Pesticide detections by week and type for Marion Drain, 2010.

The pesticide calendar in Appendix E, Table E-11, provides a chronological overview of pesticide concentrations and detections during 2010 and compares concentrations to *assessment criteria* and *water quality standards* (Appendix D).

One detection of malathion on May 17 did not meet (exceeded) the registration criteria for chronic invertebrates. This single event met (did not exceed) the 21-day time component of the chronic invertebrate criteria.

Sulphur Creek Wasteway

During 2010 there were 115 detections of 21 pesticides and a degradate. These 22 compounds were 14 herbicides, seven insecticides, and one insecticide degradate. The number and types of pesticide detections are presented in Figure 12. The maximum number of pesticides detected during a sampling event was nine (Figure 12).

The the most frequently detected pesticides in Sulphur Creek Wasteway are described in Table 23.

Table 23. Most frequently detected pesticides for Sulphur Creek Wasteway, 2010.

Pesticide	Pesticide Type	Number of
		Detections
2,4-D	Herbicide	23
Imidacloprid	Insecticide	14
Bromacil	Herbicide	12
Dicamba I	Herbicide	12
Carbaryl	Insecticide	11



Figure 12. Pesticide detections by week and type for Sulphur Creek Wasteway, 2010.

The pesticide calendar in Appendix E, Table E-12, provides a chronological overview of pesticide concentrations and detections during 2010 and compares concentrations to *assessment criteria* and *water quality standards* (Appendix D).

In March there were two consecutive detections of chlorpyrifos that did not meet (were above) the chronic water quality standard and EPA's chronic invertebrate criteria. In addition, one of these detections also did not meet (was above) the acute water quality standard and EPA's acute invertebrate criteria.

Conventional Parameters

Conventional water quality parameters were measured at the four lower Yakima sites. Table 24 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling. All sites must meet freshwater quality standards.

With the exception of the upstream Spring Creek site, all sites did not meet (exceeded) the pH water quality standard of 8.5 s.u. The downstream Spring Creek site exceeded the standard 17 times, Marion Drain five times, and Sulphur Creek Wasteway six times. Maximum pH values are described in Table 15.

All sites met the dissolved oxygen standard with the exception of the upstream Spring Creek site. On August 9, a dissolved oxygen value of 7.8 did not meet (fell below) the minimum water quality standard of 8.0 mg/L.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)				
Spring Creek (up	Spring Creek (upstream)								
Number	14	14	14	14	14				
Mean	30	5.9	8.1	462	9.6				
Minimum	7	2.3	7.8	334	7.8				
maximum	143	11.3	8.3	656	11.2				
Spring Creek (do	wnstream)								
Number	27	27	27	27	27				
Mean	9	12.0	8.7	407	10.3				
Minimum	2	1.9	8.4	190	8.7				
maximum	30	57.2	9.5	624	12.4				
Marion Drain									
Number	34	33	34	34	34				
Mean	13	158	8.1	262	12.0				
Minimum	1	24.1	7.5	191	8.8				
maximum	48	324	8.9	368	16.6				
Sulphur Creek Wasteway									
Number	27	27	27	27	27				
Mean	44	233	8.4	311	10.6				
Minimum	7	51.4	8.1	193	9.2				
maximum	251	493	8.8	775	12.1				

Table 24. Mean, minimum, and maximum for discrete conventional parameter measurements for the lower Yakima sites, 2010.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature thermistor for Sulphur Creek was lost; data for January 20-March 15 are not available.

The temperature standard for the freshwater sites is that the 7-DADMax should not exceed 17.5°C. None of the sites met temperature standards during all periods. Table 25 describes the periods that temperature did not meet the standard.

Table 25. Periods of water temperature exceedance for the lower Yakima sites, 2010.

Site	Periods When Temperature Did Not Meet Standards		
Spring Creek (upstream) >17.5°C	Apr 17-28, May 11-Sept 24, Sept 28-Oct 5		
Spring Creek (downstream) >17.5°C	May 17-21, June 9-19, June 23-Aug 30, Sept 16-22		
Marion Drain >17.5°C	May 18, June 22-Sept 1, Sept 7-9, Sept 17-21, Oct 2-3		
Sulphur Creek Wasteway >17.5°C	May 15-21, June 10-Sept 23, Oct 1-5		

Wenatchee-Entiat Basins (WRIAs 45 and 46), 2010

Pesticide Detections and Concentrations

In the Wenatchee and Entiat basins, Peshastin, Mission, and Brender Creeks and the Wenatchee and Entiat Rivers were sampled for 27 consecutive weeks from March 9 to September 8, 2010. For the five sites combined, there was a total of 128 detections of 20 types of pesticides including degradates, a wood preservative, and a synergist. These 20 compounds were seven insecticides, seven herbicides, four degradates, a wood preservative, and a synergist.

The most frequently detected pesticides are described in Table 26. Very few pesticides were detected in the Wenatchee and Entiat Rivers and Peshastin and Mission Creeks. Detections presented in Table 26 are reflective of pesticide detections in Brender Creek (Table 27). Brender Creek had the greatest number of detections, 109. The other four sites had less than eight detections during the 2010 sampling period.

Table 26.	Most frequently	detected pes	ticides for th	e Wenato	chee-Entiat sites	, 2010.
The major	rity of detections	included in t	his table are	Brender	Creek pesticide	detections.

Pesticide	Pesticide Type ¹	Number of Detections
Endosulfan Sulfate	Endosulfan degradate	21
4,4'-DDT	Legacy Insecticide	16
4,4'-DDE	DDT (legacy) degradate	15
4,4'-DDD	DDT (legacy) degradate	10
Carbaryl	Insecticide	10

¹ Legacy pesticides are no longer allowed for use, and detections are due to historic applications.

Peshastin Creek

During 2010 very few pesticides were detected in Peshastin Creek. During 27 sample events, there were four detections: two herbicides, one insecticide, and one insecticide degradate. The maximum number of pesticides detected during a sampling event was one.

Appendix E, Table E-13, presents pesticide calendars for 2010 for Peshastin Creek. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D). On March 24, there was one detection of endosulfan that did not meet (was above) the endangered species level of concern (ESLOC) criteria for fish.

Mission Creek

During 2010 very few pesticide were detected in Mission Creek. During 27 sample events, there were three detections: one detection of the synergist compound, piperonyl butoxide, and two detections of the carbamate insecticide, carbaryl. The maximum number of pesticides detected during a sampling event was one.

Appendix E, Table E-14, presents the pesticide calendars for 2010 for Peshastin Creek. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D). Pesticide concentrations in Mission Creek met (did not exceed) any available *assessment criteria* or *water quality standards* (Appendix D).

Brender Creek

During 2010 there were 109 detections of 15 compounds: seven insecticides, three insecticide degradates, four herbicides, and a wood preservative. The number and types of pesticide detections are presented in Figure 13. The maximum number of pesticides detected during a sampling event was nine (Figure 13).



Figure 13. Pesticide detections by week and type for Brender Creek, 2010.

The most frequently detected pesticides in Brender Creek are described in Table 27.

Pesticide	Pesticide Type	Number of Detections
Endosulfan Sulfate	Endosulfan degradate	21
4,4'DDT	Legacy ¹ insecticide	15
4,4'DDE	DDT (legacy ¹) degradate	15
4,4'DDD	DDT (legacy ¹) degradate	10

¹ Legacy pesticides are no longer allowed for use, and detections are due to historic applications.

Appendix E, Table E-15, presents a pesticide calendar for 2010. The calendar provides a chronological overview of pesticide concentrations and detections and compares concentrations to *assessment criteria* and *water quality standards* (Appendix D).

There was one total endosulfan detection on March 24 that did not meet (was above) the ESLOC for fish and the chronic water quality standard.

One detection of chlorpyrifos on April 12 was above the acute and chronic water quality standard and EPA criteria.

On September 8, one detection of diazinon was above EPA's acute and chronic criteria.

DDT and DDT degradates were detected consistently throughout 2010. DDT and degradate detections were less than in previous years. In 2010 there were 18 sample events out of 27 where total DDT concentrations were above the chronic water quality standard.

Wenatchee River

During 2010 there were very few pesticides detected at the Wenatchee River site. During 27 sample events, there were five detections: three herbicides and two insecticides. The maximum number of pesticides detected during a sampling event was three on September 8.

Appendix E, Table E-16, presents the pesticide calendar for 2010 for the Wenatchee River. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards*. During 2010 pesticide concentration met all *assessment criteria* and *water quality standards* (Appendix D).

Entiat River

During 2010 there were very few pesticides detected at the Entiat River site. During 27 sample events, there were five detections: three insecticides, one herbicide, and a synergist. The maximum number of pesticides detected during a sampling event was one.

Appendix E, Table E-17, present the pesticide calendars for 2010 for the Entiat River. The calendars provide a chronological overview of concentrations and detections and compare pesticide concentrations to *assessment criteria* and *water quality standards*.

On September 1, there was one detection of DDT that was above the chronic water quality standard and EPA criteria (Appendix D).

Conventional Parameters

Conventional water quality parameters were measured at all Wenatchee and Entiat sites. Table 17 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling. All sites must meet freshwater quality standards. Brender and Peshastin Creeks met the pH standard of 8.5 s.u., but the pH standard was not met nine times for the Wenatchee River, six times for the Entiat River, and twice for Mission Creek. Maximum pH values are described in Table 28. All sites met the dissolved oxygen standard.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)	
Peshastin Cre	ek					
number	27	27	27	27	27	
mean	9	266	8.0	127	11.5	
minimum	<1	18.3	7.6	80	9.3	
maximum	55	887	8.4	199	13.3	
Mission Creek	Σ.					
number	27	27	27	27	27	
mean	202	24.2	8.3	214	11.5	
minimum	2	1.5	7.9	134	9.7	
maximum	4180	87.8	8.7	270	13.6	
Brender Cree	k _			• 		
number	27	27	27	27	27	
mean	52	3.1	8.1	256	10.7	
minimum	7	0.5	7.7	146	9.5	
maximum	249	9.7	8.4	416	12.0	
Wenatchee Ri	ver			-		
number	27	27	27	27	27	
mean	10	4485	8.2	54	11.9	
minimum	2	766	7.1	31	9.9	
maximum	70	13000	9.3	84	14.2	
Entiat River						
number	27	27	27	27	27	
mean	8	806	8.1	63	11.4	
minimum	2	157	7.2	31	9.7	
maximum	31	2440	9.0	111	12.7	

Table 28. Arithmetic mean and range for conventional parameters (grabs) for the Wenatchee-Entiat sites, 2010.

Mean: Arithmetic mean.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature thermistor for Brender Creek was lost; therefore, data for October 28-December 31, 2010 are not available.

The temperature standard for the freshwater sites is that the 7-DADMax should not exceed 17.5°C. The Wenatchee River has an additional temperature standard: the 7-DADMax should not exceed 13.0°C from October 1 – May 15. None of the sites met temperature standards during all periods. Table 29 describes the periods that temperature did not meet the standard.

Site	Periods When Temperature Did Not Meet Standards
Peshastin Creek >17.5°C	July 21-Aug 31
Mission Creek >17.5°C	July 28-Aug 12, Aug 14-23
Brender Creek >17.5°C	July 29-Aug 2
Wenatchee River >17.5°C	July 24-Sept 8
Wenatchee River >13.0°C	Oct 1-10
Entiat River >17.5°C	July 30-Aug 30

Table 29. Periods of water temperature exceedance for the Wenatchee - Entiat sites, 2010.

Summary for 2010

Findings

In 2010 the most commonly detected pesticide for the urban sites and the Skagit-Samish agricultural sites was the herbicide dichlobenil. At the urban sites, the herbicide 2,4-D was also frequently detected. For the Skagit-Samish sites, the herbicide bromacil and the neonicotinoid insecticide imidacloprid were also frequent detections.

For the lower Yakima sites, representing irrigated agriculture, the most commonly detected pesticides were the herbicide 2,4-D, followed by imidacloprid.

For the Wenatchee-Entiat sites, representing tree fruit agricultural, the most common detections were insecticide degradates, including the degradates for the legacy insecticide DDT and the endosulfan degradate.

Increases in imidacloprid detections were seen in 2010. This is likely due to increased sensitivity in the laboratory analysis because there were improvements in laboratory instrumentation during 2010.

Monitoring Program Changes

The following changes were made during the 2010 monitoring of the six basins across Washington State.

To improve data quality, Manchester Laboratory purchased a new instrument for carbamate analysis. The instrument enabled improvements to the identification criteria for all analytes in the carbamate analysis suite. All analytes now have at least one confirmation ion in addition to the quant ion. Sensitivity also improved with a drastic increase in the signal-to-noise ratio at the low end of the calibration curve. The maximum detection limit on the instrument demonstrates improved sensitivity for all analytes. These improvements have significantly reduced identification uncertainty, thus decreasing the potential for false positive and negatives.

Sampling for the following pesticides or degradates was added for all basins:

- Fenitrothion (fungicide).
- Phosmet oxygen analog (organophosphate phosmet degradate).
- Ronnel (organophosphate insecticide).

Planned Program Changes for 2011

Manchester Laboratory is planning to make the following changes during 2011:

1. Modify the carbamate analysis method used for this project. Eliminate the SE procedure and go to a DI method for the LCMS/MS carbamate analysis.

In previous years, samples for the carbamate analysis underwent a sample extraction procedure before analysis. In 2010 the laboratory conducted a comparison study of two methods: the sample extraction (SE) procedure and a direct injection (DI) method before analysis. Results of the study showed that both methods were comparable (Weakland, 2011).

Benefits of DI include higher spike recoveries for some analytes, closer to 100% recovery. During the SE process, there are losses which affect recovery rates. Another benefit of more consistent recoveries is less qualification of reported data and less rejected data.

Changing to DI will also mean that solvents used during the SE process will no longer be needed. This will reduce the total solvent use at the laboratory, lessening toxic waste by-products.

2. Conduct a comparison study of DI versus the SE procedure for herbicide analysis.

The laboratory will conduct a side-by-side study using both methods during the first four weeks of sampling. After the study is complete, the laboratory will compare results and make a recommendation about switching to DI for herbicide analysis.

References

Anderson, P. and D. Sargeant, 2009. Addendum 3 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD3. <u>www.ecy.wa.gov/biblio/0303104add3.html</u>.

Anderson, P. and D. Sargeant, 2010. Standard Operating Procedures for Sampling of Pesticides in Surface Waters, Version 2.0 Revised: April 21, 2010. Washington State Department of Ecology, Olympia, WA. SOP Number EAP003. <u>www.ecy.wa.gov/programs/eap/quality.html</u>.

Burke, C. and P. Anderson, 2006. Addendum to the Quality Assurance Project Plan: Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, Addition of the Skagit-Samish Watersheds and Extension of the Program Through June 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD. www.ecy.wa.gov/biblio/0303104add.html.

Burke, C. and P. Anderson, 2006. Addendum to the Quality Assurance Project Plan for the Pesticides in Salmonid-Bearing Streams, Addition of the Skagit-Samish Watersheds and Extension of the Program Through June 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104add. <u>www.ecy.wa.gov/bibio/0303104add.html</u>.

Ecology, 2006. Water Quality Program Policy 1-11, Revised: September, 2006, Assessment of Water Quality for the Clean Water Act Sections 303(d) and 305(b) Integrated Report. Water Quality Program, Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/programs/wq/303d/wqp01-11-ch1Final2006.pdf.

Ecology, 2008. Excel spreadsheet entitled 'Guidance for Calculating "Total" Values of Selected Analytes for the EAP Toxics Studies Unit and EIM Parameters to Use. November 3, 2008. Toxics Studies Unit SharePoint site, Environmental Assessment Program, Washington State Department of Ecology, Olympia, WA.

EPA, 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. U.S. Environmental Protection Agency. OSWER Directive #93240.0-05.

EPA, 1999. Contract laboratory Program National Functional Guidelines for Organic Data Review. U.S. Environmental Protection Agency. EPA 540/R-99/008. www.epa.gov/superfund/programs/clp/download/fgorg.pdf.

EPA, 2002. Atrazine, Bensulide, Diphenamid; Imazalil, 6-Methyl-1,3-dithiolo[4,5-b] quinoxalin-2-one, Phosphamidon S-Propyl dipropylthiocarbamate, and Trimethacarb; Tolerance Revocations. U.S. Environmental Protection Agency docket ID: EPA-HQ-OPP-2002-0085-0001. <u>http://pmep.cce.cornell.edu/profiles/herb-growthreg/dalapon-ethephon/diphenamid_tol_602.html</u>.

EPA, 2006. National Recommended Water Quality Criteria listings. U.S. Environmental Protection Agency. Accessed May 2008. <u>www.epa.gov/waterscience/criteria/wqcriteria.html</u>.

EPA, 2007. USEPA Contract Laboratory Program. National Functional Guidelines for Superfund Organic Methods Data Review. U.S. Environmental Protection Agency. EPA-540-R-04-009. <u>www.epa.gov/superfund/programs/clp/download/somnfg.pdf</u>.

Johnson, A. and J. Cowles, 2003. Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds: A Study for the Washington State Department of Agriculture Conducted by the Washington State Department of Ecology. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104. www.ecy.wa.gov/biblio/0303104.html.

Mathieu, N., 2006. Replicate Precision for 12 TMDL Studies and Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-044. www.ecy.wa.gov/biblio/0603044.html.

MEL, 2000. Standard Operating Procedure for Pesticides Screening and Compound Independent Elemental Quantitation by Gas Chromatography with Atomic Emission Detection (AED), Method 8085, version 2.0. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2008. Manchester Environmental Laboratory: Lab Users Manual, Ninth Edition. Washington State Department of Ecology, Manchester, WA.

Microsoft Corporation, 2007. Microsoft Office XP Professional, Version 10.0 Microsoft Corporation.

Rantz et al., 1983. Measurement and Computation of Streamflow. Volume 1: Measurement of Stage and Discharge. Volume 2: Computation of Discharge. Water Supply Paper 2175. http://pubs.er.usgs.gov/usgspubs/wsp/wsp2175.

Sargeant, D., D. Dugger, E. Newell, P. Anderson, and J. Cowles, 2010. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Stream, 2006-2008 Triennial Report. Washington State Departments of Agriculture and Ecology, Olympia, WA. Publication No. 10-03-008. <u>www.ecy.wa.gov/biblio/1003008.html</u>.

Sargeant, D., D. Dugger, P. Anderson, and E. Newell, 2011. Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Stream, 2009 Data Summary. Washington State Departments of Agriculture and Ecology, Olympia, WA. Publication No. 11-03-004. www.ecy.wa.gov/biblio/1103004.html.

Swanson, T., 2007. Standard Operating Procedure (SOP) for Hydrolab DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. <u>www.ecy.wa.gov/programs/eap/quality.html</u>.

Turner, L., 2003. Chlorpyrifos: Analysis of Risks to Endangered and Threatened Salmon and Steelhead. U.S. Environmental Protection Agency, Office of Pesticide Programs, Environmental Field Branch. <u>www.epa.gov/espp/litstatus/effects/chlorpyrifos-analysis.pdf</u>.

Wagner, R.J., H.C. Mattraw, G.F. Ritz, and B.A. Smith, 2000. Guidelines and standard procedures for continuous water-quality monitors: site selection, field operation, calibration, record computation, and reporting. U.S. Geological Survey Water Resources Investigations Report 00-4252.

Ward, W., 2007. Standard Operating Procedures (SOP) for the Collection and Analysis of Dissolved Oxygen (Winkler Method). Washington State Department of Ecology, Olympia, WA. <u>www.ecy.wa.gov/programs/eap/quality.html</u>.

Weakland, J., 2011. Memorandum dated January 24, 2011 from John Weakland, Organics Supervisor, Manchester Environmental Laboratory to Stuart Magoon, Laboratory Director. Method comparison between extraction and direct injection of carbamate pesticides. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA. This page is purposely left blank

Appendices

This page is purposely left blank

Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Analyte: Water quality constituent being measured (parameter).

Assessment criteria: Assessment criteria in this report are numeric criteria included in the EPA FIFRA Pesticide Registration Toxicity Criteria and endpoints; and the EPA National Recommended Water Quality Criteria (NRWQC).

Basin: Watershed. A drainage area 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.

Bioaccumulation: Progressive increase in the amount of a substance in an organism or part of an organism which occurs because the rate of intake exceeds the organism's ability to remove the substance from the body.

Carbamate insecticide: N-methyl carbamate insecticides are similar to organophosphate insecticides in that they are nerve agents that inhibit cholinesterase enzymes. However they differ in action from the organophosphate compounds in that the inhibitory effect on cholinesterase is brief.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Degradate: Pesticide breakdown product.

Dissolved oxygen: A measure of the amount of oxygen dissolved in water.

Endosulfan: Endosulfan is an organochlorine insecticide that is registered for use on a number of agricultural commodities. In 2010, EPA signed an agreement with the registrants of endosulfan that will result in voluntary cancellation and phase out of all existing endosulfan uses in the United States. Under this agreement, all endosulfan uses will be phased out by July 2016. EPA is terminating uses of endosulfan to address its unacceptable risks to agricultural workers and wildlife (EPA, 2010).

Exceeded criteria: Did not meet criteria.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Herbicide: A substance used to kill plants or inhibit their growth.

Legacy pesticide: Banned pesticides no longer used but that persist in the environment.

Loading: The input of pollutants into a waterbody.

Marine water (seawater): Salt water.

Organophosphate pesticide: Organophosphate pesticides are derived from phosphoric acid and are highly neurotoxic, typically inhibiting cholinesterase.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Pesticide: A pesticide is any substance or mixture of substances intended for killing, repelling or mitigating any pest. Pests include nuisance microbes, plants, fungus, and animals.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salmonid: Any fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. <u>www.fws.gov/le/ImpExp/FactSheetSalmonids.htm</u>

Suspended sediment: Solid fragmented material (soil and organic matter) in the water column.

Synergistic: A synergistic effect occurs when the combined effects of two chemicals are greater than the predicted sum of each chemical's effects.

Thermistor: An electronic device that uses semiconductors to measure temperature. A data logger.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from 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): The suspended particulate matter in a water sample as retained by a filter.

Water quality standards: Washington State water quality standards.

Watershed: Basin. A drainage area 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 periodically to 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 Washington State surface water quality standards and are not expected to improve within the next two years.

7-DADMax or 7-day average of the daily maximum temperatures: The arithmetic average of seven consecutive measures of daily maximum temperatures. The 7-DADMax for any individual day is calculated by averaging that day's daily maximum temperature with the daily maximum temperatures of the three days prior and the three days after that date.

Acronyms and Abbreviations

DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management (Ecology)
EPA	United States Environmental Protection Agency
ESLOC	Endangered species level of concern (EPA)
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
GCMS	Gas chromatograph coupled with mass spectrometer
LC ₅₀	Lethal concentration to cause mortality in 50% of test species
LCMS	Liquid chromatograph coupled with mass spectrometer
LCS	Laboratory control sample
LOC	Level of concern
LPQL	Lower practical quantitation limit
MEL	Manchester Environmental Laboratory
MS	Mass spectrometer
MS/MSD	Matrix spike/matrix spike duplicate
n	Number
NAD	North American Datum
NRWQC	National Recommended Water Quality Criteria (EPA)
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOEC	No observable effect concentration
QA	Quality assurance
QC	Quality control
RQ	Risk quotient
RPD	Relative percent difference
RSD	Relative standard deviation

SOP	Standard operation procedures
TMDL	(See Glossary above)
TSS	(See Glossary above)
TSU	Toxics Studies Unit
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area
WSDA	Washington State Department of Agriculture
7-DADMax	(See Glossary above)

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
m	meter
mg	milligrams
mg/L	milligrams per liter (parts per million)
s.u.	standard units
umhos/cm	micromhos per centimeter

Appendix B. Monitoring Sites and Duration of Sampling

Site	Duration	Latitude	Longitude	Location Description	
Cedar-Sammamish Watershed					
TC-3	Mar 8– Sept 8	47.6958	122.2757	Downstream of pedestrian footbridge near Mathews Beach Park.	
Green-I	Duwamish Watershee	d			
LC-1	Mar 8– Sept 8	47.5625	122.367	Upstream of the culvert under the 12th Fairway on the West Seattle Golf Course.	
Skagit-S	Samish Watershed				
BD-1	Mar 8 – Sept 8	48.3086	122.3473	Upstream side of bridge at Milltown Road.	
BD-2	Mar 8 – Sept 8	48.3887	122.3329	Upstream side of bridge at Lenor Lane.	
BS-1	Mar 8 – Sept 8	48.3406	122.4140	Downstream of tidegate on Fir Island Road.	
IS-1	Mar 8 – Sept 8	48.4506	122.4651	Inside upstream side of tidegate at Bayview-Edison Road.	
SR-1	Mar 8 – Sept 8	48.5209	122.4113	Upstream side of bridge at Thomas Road.	
Lower Y	Yakima Watershed				
MA-2	Mar 10 – Oct 26	46.3306	120.1989	Approximately 15 meters upstream of bridge at Indian Church Rd.	
SP-2	Mar 10 – Sept 8	46.2583	119.7101	Downstream side of culvert on McCready Road.	
SP-3	Mar 10 – Sept 8	46.2344	119.6845	Approximately 3 meters downstream of Chandler Canal overpass.	
SU-1	Mar 10 – Sept 8	46.2509	120.0202	Downstream side of bridge at Holaday Road.	
Wenatchee Watershed					
WE-1	Mar 9 – Sept 8	47.4721	120.3710	Upstream side of Sleepy Hollow bridge.	
MI-1	Mar 9 – Sept 8	47.4893	120.4815	Above Woodring Canyon Road and Mission Creek Road.	
PE-1	Mar 9 – Sept 8	47.5570	120.5825	Approximately 30 meters downstream of bridge at Saunders Road.	
BR-1	Mar 9 – Sept 8	47.5211	120.4862	Upstream side of culvert at Evergreen Drive.	
Entiat Watershed					
EN-1	Mar 9 – Sept 8	47.6633	120.2506	Upstream side of bridge at Keystone Road.	
Datum in	Datum in NAD 83.				

Table B-1. Station locations, duration of monitoring, and site location descriptions for 2010.

Page 61