

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2012 Data Summary

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

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Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2012 Data Summary

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

by

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

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

WRIAs

- 3 Lower Skagit/Samish
- 8 Cedar/Sammamish
- 9 Duwamish/Green
- 37 Lower Yakima
- 45 Wenatchee
- 46 Entiat

HUC numbers

- 17110002 Samish
- 17110007 Skagit
- 17110012 Cedar/Sammamish
- 17110013 Duwamish/Green
- 17030003 Yakima
- 17020011 Wenatchee
- 17020010 Entiat

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Abstract

Since 2003 the Washington State Departments of Ecology and Agriculture have been conducting a multi-year monitoring study to characterize pesticide concentrations in selected salmon-bearing streams during the typical application season (March - September) in Washington.

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 2012 monitoring season. In 2012, surface water samples were analyzed for 170 pesticides and pesticide-related compounds, as well as total suspended solids. Field measurements were collected for streamflow, temperature, pH, conductivity, and dissolved oxygen.

During 2012, there were 1,095 detections of 58 pesticides or pesticide-related compounds for the 15 sites sampled statewide. Herbicides were the most frequently detected pesticide, followed by insecticides, and then pesticide degradates.

The urban sites (Thornton and Longfellow Creeks) met (were below) all available pesticide assessment criteria and standards in 2012. Several pesticides were detected that did not meet (were above) aquatic life criteria or standards in the following areas:

- Skagit Samish basin: metolachlor (herbicide) and diazinon (insecticide).
- Lower Yakima basin: bifenthrin, malathion, chlorpyrifos (insecticides); 4,4'-DDE (legacy insecticide degradate); and 2,4-D (herbicide).
- Wenatchee-Entiat basin: Total endosulfan, chlorpyrifos (insecticides); endosulfan sulfate (endosulfan degradate); and DDT and DDT degradates (legacy insecticide and degradates).

Recommendations are provided for changes to the program for the 2013 monitoring season. They include: discontinuing monitoring at the Entiat River site and adding three new sites:

- Stemilt Creek in the Alkali-Squilchuck basin (WRIA 40)
- Two sites on Bertrand Creek in the Nooksack basin (WRIA 1)

In addition the extended sampling season on Marion Drain will be reduced by two weeks, ending mid-October.

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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 the typical pesticide-use season (March through September) in Washington.

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 2012 and to document any changes in the monitoring program during the year.

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Study Area

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

Basins Monitored During 2012

The six basins monitored in 2012 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 acres in agricultural production.



Figure 1. State map showing the six urban and agricultural basins monitored in 2012.

Monitoring areas and timeframes are:

- Thornton Creek subbasin is located in the Cedar-Sammamish basin (WRIA¹ 8), and represents an urban land-use area. One to four sites have been sampled on this creek from 2003-2011. One of those sites, at the mouth of Thornton Creek, was sampled during 2012 (Figure 2).
- Longfellow Creek subbasin is located in the Green-Duwamish basin (WRIA 9), and represents an urban land-use area. One site near the mouth of the basin has been sampled from 2009-2012 (Figure 3).
- Four subbasins of the lower Skagit-Samish basin (WRIA 3) were selected to represent western Washington agricultural land-use practices. Five sites, one on the Samish River, two on Big Ditch Slough, one on Browns Slough, and one on Indian Slough have been sampled from 2006-2012 (Figure 4).
- Three subbasins of the Lower Yakima basin (WRIA 37) were selected to represent eastern Washington irrigated crop-land agricultural practices. Three sites—one on Marion Drain, one on Sulphur Creek Wasteway, and one on Spring Creek—have been sampled from 2003-2012 (Figure 5).
- Four subbasins of the Wenatchee basin (WRIA 45) and Entiat basin (WRIA 46) were selected to represent central Washington agricultural tree fruit practices. Five sites have been sampled from 2007-2012 near the mouth of the following waterways: Peshastin Creek, Mission Creek, Brender Creek, the Wenatchee River (WRIA 45), and the Entiat River (WRIA 46) (Figure 6).

Site locations and sampling duration are described in Appendix A.

The monitoring sites are described in previous reports, and include maps of monitoring sites, land use, salmon fishery, and climate (Sargeant et al., 2011 and 2013).

¹ Water Resource Inventory Area



Figure 2. Thornton Creek sampling location in the Cedar-Sammamish basin, 2009-2011.



Figure 3. Longfellow Creek sampling location in the Green-Duwamish basin, 2009-2011.



Figure 4. Lower Skagit-Samish basin sampling locations, 2009-2011.



Figure 5. Lower Yakima basin sampling locations, 2009-2011.



Figure 6. Wenatchee and Entiat basins sampling locations, 2009-2011.

Study Design and Methods

Sampling was designed to address pesticide presence in salmonid-bearing streams during a typical pesticide-use period of March through September. The focus of monitoring is on currently registered pesticides, but laboratory analysis also included some historically used pesticides. Several conventional water quality parameters were measured: total suspended solids (TSS), pH, conductivity, temperature, dissolved oxygen, and streamflow. The conventional parameters provide information to help 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; Anderson, 2011; Anderson, 2012), and the triennial reports (Burke et al., 2006; Sargeant et al., 2010; Sargeant et al., 2013).

During 2012, samples collected for analysis of 170 pesticides and pesticide-related compounds included: 71 insecticides, 59 herbicides, 30 pesticide degradates, seven fungicides, two pesticide synergists, and one wood preservative.

The following copper and copper-related parameters were added to the analyte list at select sites in 2012: total and dissolved copper, calcium, magnesium, sodium, potassium, hardness, dissolved organic carbon, sulfate, chloride and alkalinity. The goal of the copper sampling was to evaluate copper concentrations at urban and agricultural sites. Results of this sampling are included in a separate report, Copper in Agricultural and Urban Waterways, which will be available in November 2013.

Sampling Sites and Sampling Frequency

In 2012, sampling was conducted weekly for 27 consecutive weeks, beginning the second week in March and continued through the first 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, to capture a late season pesticide application period in that drainage. Sampling at the upstream Spring Creek site in the lower Yakima basin was discontinued in 2012.

Field Procedures and Laboratory Analyses

A full description of field procedures and laboratory analysis is included in the QA Project Plan and subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009; Anderson, 2011; Anderson, 2012).

Field methods for surface water 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 following Ecology's Standard Operating Procedure for Sampling of Pesticides in Surface Waters, SOP

EAP003 (Anderson and Sargeant, 2010). 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.

Wenatchee River site samples were collected using depth integrating sampling 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).

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 Ecology SOP EAP056 (Shedd, 2011).

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 B, Table B-3.

Analyte	Analyti	Reference	
Tillaryte	Extraction	Analysis	Reference
Pesticides	3535	GC/MS	8270
Herbicide Analysis	3535/8151	GC/MS	8270
Carbamates	n/a	HPLC/MS/MS	8321B
TSS	n/a	Gravimetric	EPA 160.2

Table 1. Summary of laboratory methods, 2012.

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

n/a: not applicable

TSS: total suspended solids

GC/MS: gas chromatography/mass spectrometry

HPLC/MS/MS: high performance liquid chromatography/triple quadrupole mass spectrometry

Laboratory and Field Data Quality

Laboratory Data Quality

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. The QA/QC protocol employs the use of blanks, replicates, and surrogate recoveries. Laboratory surrogate recovery, blanks, replicates, and laboratory control samples (LCS) and LCS duplicates are analyzed as the laboratory component of QA/QC. Field blanks, field replicates, and matrix spikes (MS) and MS duplicates (MSD) integrate field and laboratory components.

Fourteen percent of field samples analyzed in 2012 were for QA samples. Highlights of laboratory and field data quality are presented below; for a detailed discussion refer to Appendix B.

Field and Laboratory 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. There were no field blank detections for the pesticide analyses in 2012. There was one TSS field blank detection of 2 mg/L on March 20, 2012 for the Sulphur Creek Wasteway site. The reporting limit for TSS was 1 mg/L. TSS values for the lower Yakima sites on March 20, 2012 were qualified as estimates at concentrations ≤ 6 mg/L.

Laboratory blanks assess the precision of equipment and the potential for internal laboratory contamination. There were no laboratory blank detections reported in 2012.

Replicate Results

Table 2 shows average pooled results for pesticide field replicates by analysis type. Precision between replicate pairs was calculated using relative percent difference (RPD). The RPD is calculated by dividing the absolute value of the difference between the replicates by their mean and then multiplying by 100 for a percent value.

Table 2. Pooled average RPD of consistent field replicate pairs by analysis type, including NJ and J qualified data, in 2012.

Analysis	Pooled Average RPD	Number of Replicate Pairs
Herbicides	8.8%	47
Carbamates	13.0%	12
Pesticide GCMS	6.4%	41
TSS	7.6%	31

The average RPD for each of the analytical methods was excellent. Of the consistently identified replicate pairs, only two of the 100 consistently identified pairs exceeded the 40% RPD criterion for the three types of pesticide analysis. On April 23, 2012, a pentachlorophenol replicate pair had an RPD of 43%, and on May 16, a replicate pair for carbaryl had an RPD of 62%.

For TSS a total of 87% of the replicates were within the 20% RPD criterion. Four replicates were slightly above the criterion at 25-33% RPD. Results for three out of four of these replicate pairs were close to the detection limit, and RPD statistic has limited effectiveness in assessing variability at low levels (Mathieu, 2006).

All pesticide and TSS data for replicates are of acceptable data quality.

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 (2012). The percentage of time a surrogate recovery did not meet the quality control limits is described in Table B-8 of Appendix B. 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. Table B-9 in Appendix B shows the average recovery of the MS/MSD as well as the RPD for the MS/MSD pairs. 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 deionized water spiked with analytes at known concentrations and subjected to analysis. They are used to evaluate accuracy of pesticide residue recovery for a specific analyte. Table B-11 in Appendix B shows the average percent recovery for the LCS and the LCS duplicates; it also shows the average RPD between the LCS and duplicate pairs. 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

Field meters were calibrated at the beginning of the field day according to the manufacturer's specifications using Ecology SOP EAP033 *Standard Operating Procedure for Hydrolab DataSonde*® *and MiniSonde*® *Multiprobes* (Swanson, 2010). Field meters were post-checked at the end of the field day using known standards. Dissolved oxygen meter results were compared to results from grab samples analyzed using the Winkler laboratory titration method. Dissolved oxygen grab samples and Winkler titrations were collected and analyzed according to the SOP (Ward, 2007). Two to three Winkler grab samples were obtained during each sample week. Measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler dissolved oxygen comparisons are described by Anderson and Sargeant (2009).

2012 Field Data Quality Results

The Hydrolab field meter for the Lower Yakima and Wenatchee-Entiat (eastern Washington) sites met MQOs including post-checks and Winkler comparisons (Table 3) with the following exceptions:

• On August 6 and 8, 2012, Hydrolab field meter and Winkler dissolved oxygen values did not meet MQOs. Hydrolab dissolved oxygen field meter results for these days are qualified as estimates.

The Hydrolab field meter for the urban sites and the Lower Skagit-Samish (western Washington) sites met all QC objectives including post-checks and Winkler comparisons (Table 3) with the following exceptions:

- On April 17, 2012, conductivity did not meet the MQOs for the Hydrolab field meter postcheck. Conductivity results for this day were qualified as estimates.
- On June 19, 2012, pH did not meet the MQOs for the Hydrolab field meter post-check. pH results for this day were qualified as estimates.

Table 3. Quality control results (%RSD) for field meter and Winkler dissolved oxygen replicates and flow meter replicates, 2012.

	Western W	Vashington	Eastern Washington		
Replicate Meter Parameter	Sites		Sites		
	Average	Maximum	Average	Maximum	
Winkler and meter DO	1.2%	4.2%	1.2%	4.6%	
Replicate Winklers for DO	0.4%	1.6%	0.1%	0.6%	
Meter flow	2.6%	15.9%	3.1%	17.8%	

DO: dissolved oxygen.

For 2012 flow replicates, two replicate flows exceeded MQOs: one flow on Brender Creek and one at the upstream Big Ditch site. Both of these flow replicates occurred during low-flow conditions when the percent RSD statistic produces higher variability (Mathieu, 2006). Flow results for these days were acceptable.

To determine comparability of field methods, a side-by-side field audit was conducted on April 23, 2012. Comparability of the two teams was excellent; results of the field audit are described in Appendix B.

Field data quality for 2012 was very good, with most data meeting MQOs as described in Anderson and Sargeant (2009). Data that did not meet MQOs were qualified as described in Anderson and Sargeant (2009).

Reporting Methods and Data Analysis

The 2012 field and laboratory data were compiled and organized using Excel[®] spreadsheet software and Access[®] database software (Microsoft Corporation, 2007). Field and laboratory data 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.

Laboratory data were qualified as discussed in the data quality section, and qualifiers are described in Table B-1 in Appendix B. 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.

Comparison to Assessment Criteria and Water Quality Standards

Laboratory results qualified as either non-detect or tentative detection (U, UJ, N, NJ) were not used for comparison to pesticide 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 assess precision.

- In cases where both laboratory replicates yielded detections of equal laboratory confidence as indicated by data qualifiers, the arithmetic average of the replicates was used for criteria comparisons or statistical analysis.
- In cases where one of the two laboratory replicates yielded data with higher laboratory confidence as indicated by data qualifiers, then the higher confidence value was used for criteria comparisons or statistical analysis.
- In cases where only one of the two laboratory replicates yielded a detection, the detected value was used for criteria comparison or statistical analysis.
- Field replicates were arithmetically averaged for use in criteria comparisons and statistical analysis.

All laboratory replicates were arithmetically averaged prior to averaging field replicates.

Statistical Analysis

For the majority of analytes, concentrations were below the analytical reporting limit of the laboratory and were reported as "less than" the reporting limit. Statistical analysis of pesticide data, including non-detect values, was conducted using a non-detect data analysis method as described in Helsel (2005).

For calculating summary statistics on data sets with non-detect values, the following statistical tests were used based on the number of non-detects:

- For data sets with < 50% non-detects the nonparametric Kaplan-Meier test was used.
- For data sets with 50 80% non-detects the robust "regression on order statistics" (ROS) was used because it is more appropriate for smaller data sets than is the maximum likelihood estimation test (Helsel, 2005).

For ROS, data was assumed to follow a log-normal distribution. Both tests accept variable reporting limits. For all non-detects, the method detection limit value was used for data analysis rather than the reporting limit value as recommended in Helsel (2005). J and NJ qualified data were treated as detected data for statistical tests.

Toxic Units

For this report, toxic units (TUs) were used to estimate the additive effects of pesticide mixtures, as described by Faust et al. in 1993 (Lydy et al., 2004). For example, TUs are calculated for a two-component mixture using the formula and the LC_{50} (lethal concentration to cause mortality in 50% of test species) as an assessment endpoint:

$$x_1/LC_{50}(X_1) + x_2/LC_{50}(X_2) = TU$$

In this equation, x_1 and x_2 are the concentrations of the pesticide mixture components. X_1 and X_2 , $LC_{50}(X_1)$ and $LC_{50}(X_2)$, are the concentrations where acute effects of the individual pesticide compounds are observed. Equivalent measures of effects are compared: for example, acute effects for fish or invertebrates, or chronic effects for fish or invertebrates.

Because the example above uses an acute measure, a TU value ≥ 1 means 50% or more of the organisms tested may experience lethality. For chronic measures, effects represent sublethal assessment endpoints and may include reproductive, growth and development effects if exposed for a period of time (21 days for fish, 14 days for invertebrates). Toxic units are calculated for acute and chronic fish and invertebrate exposure assessment concentrations described in Appendix C.

Assessment Criteria and Washington State Water Quality Standards

Pesticide effects to endangered salmonid species are assessed by comparing detected pesticide concentrations against three criteria:

- Pesticide registration toxicity and risk assessment 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 specific species (often non-salmonid) and do not take into account the effects of multiple chemicals or pesticide mixtures on an organism.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix C. Numeric exceedances of values in Appendix C do not necessarily indicate that the water quality criteria have been exceeded. There is typically a temporal duration of exposure criteria in addition to numeric criteria for a water quality standard. In this report, pesticide registration toxicity, risk assessment 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.

Pesticide Registration Toxicity Criteria

The EPA uses risk quotients (RQ) to assess the potential risk of a pesticide to non-target organisms. An 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 LOCs set by EPA are presented in Table 4 and 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 LC₅₀. When available, the endangered species LOC for specific salmonids is also presented.

Test Data	Risk Quotient	Presumption
	>0.5	Potentially high acute risk to aquatic species.
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 indirectly affect T&E fish through food supply reduction.
Aquatic plant acute LC ₅₀	>1	May indirectly affect aquatic vegetative cover for T&E fish.

Table 4.	Risk quotient	criteria for	direct and	d indirect	effects on	aquatic	organisms.
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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. The no observed effects concentration (NOEC) is the highest concentration in toxicity test which does not show a statistically significant difference from the control. The LOEC is the lowest concentration in a toxicity test which shows a statistically significant difference from the control. The NOEC is by definition the next concentration below the LOEC in the concentration series. The dose response curve may be plotted graphically or fitted to a mathematical equation and the LC₅₀, lethal concentration to cause mortality in 50% of test species can 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, and the biological endpoint is reduction in growth (EC_{50}).

Chronic fish tests normally use growth or developmental effects as the biological endpoint. A chronic toxicity test may assess a sublethal biological endpoint such as reproduction, growth, or development. It is generally longer than the 96-hour (21 days for fish, 14 days for invertebrates, 4 to 60 days for plants) to simulate exposure resulting from a persistent chemical or the effect of repeated applications.

Toxicity values such as those used for pesticide registration are determined from continuous exposure over time (e.g., LC_{50} freshwater fish acute toxicity tests are commonly run for 96 hours at a constant concentration). When comparing the monitoring data either to 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 exceeded based solely on an individual sample because the

sampling frequency is usually weekly; this does not allow for assessment of the temporal component of the criteria.

Pollutant concentrations in streams are constantly changing and may occur above aquatic life criteria for durations of time that are less than or greater than the test durations used to set the aquatic life criteria. If the stream concentration of a pollutant is above its aquatic life criterion for less time than the test duration, then comparison to the criterion overestimates risk. If the concentration for a pollutant is above its aquatic life criterion for a longer time than the test duration, then comparison to the criterion for a longer time than the test duration, then comparison to the criterion for a longer time than the test duration, then comparison to the criterion for a longer time than the test duration.

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 Clean Water Act (33 U.S.C. 1251 et. seq.). The pesticide criteria established under the Clean Water Act are closely aligned with invertebrate acute and chronic toxicity criteria. 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), and presented in Appendix C.

Washington State Water Quality Standards

Pesticides

Washington State water quality standards are established in the Washington Administrative Code (WAC), Chapter 173-201A. Washington State water quality 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 to fish and other aquatic life within the specified exposure periods. The chronic criteria for some of the chlorinated pesticides are to protect 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 the average. For 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, 2012).

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

Water Quality Standards for Temperature, pH, and Dissolved Oxygen

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.

Numeric Water Quality Standards

Thornton Creek subbasin in the Cedar-Sammamish basin

Thornton Creek beneficial uses include *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. This table also includes supplemental spawning and incubation criteria for temperature during September 15 - May 15.

Table 5. Freshwater *water quality standard* for temperature, dissolved oxygen, and pH for core summer salmonid habitat use and *Extraordinary Primary Contact Recreation*.

Parameter	Condition	Value
Temperature	Highest 7- DADMax	16° C. Thornton Creek has <i>Supplemental Spawning and</i> <i>Incubation</i> criteria: during September 15 - May 15, the highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	9.5 mg/L.
рН		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 in the Green-Duwamish basin

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 in Longfellow Creek 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 standards 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 standards 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 October 1 - May 15, highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	8 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 standard* for temperature, dissolved oxygen, and pH for *Aquatic Life Excellent* use.

Temperature (highest 7- DADMax)	Dissolved Oxygen (lowest 1-day minimum)	pH (must be within the range)
16°C (60.8°F).	6.0 mg/L.	7.0 - 8.5, with a human-caused variation within the above range of < 0.5 units.

Results

Results from the 2012 monitoring season are summarized by basin in the following sections. Monitoring results for all sites are available through Ecology's Environmental Information Management (EIM) system, <u>www.ecy.wa.gov/eim/</u>.

Pesticide calendars for 2012 are included in Appendix D. The calendars provide a chronological overview of concentrations and detections during 2012. The calendars also compare pesticide concentrations to EPA Pesticide Registration Toxicity Criteria and EPA National Recommended Water Quality Criteria (NRWQC) (assessment criteria) and to numeric Washington State Water Quality Standards (water quality standards). Refer to Appendix C, Assessment Criteria and Water Quality Standards, in this report for information on assessment criteria development.

King County Urban Sites: WRIAs 8 and 9

Two urban sites in King County were sampled for 27 consecutive weeks from March 9 to September 4, 2013. The two urban streams include Thornton Creek in the Cedar-Sammamish basin, and Longfellow Creek in the Green-Duwamish basin.

For the two sites combined, there were a total of 123 pesticide detections of 12 types of pesticides including:

- Two insecticides (10 detections)
- Nine herbicides (99 detections)
- One wood preservative (14 detections)

The most commonly detected type of pesticides was herbicides:

- Dichlobenil, 50 detections
- 2,4-D, 17 detections

At both the urban sites dichlobenil is detected consistently during the sample season.

Herbicides are detected most frequently between mid-April (week 16) through late-July (week 30), Figure 7. The wood preservative, pentachlorophenol is detected mid-March (week 11) through late-July (week 30). Insecticides are rarely detected at the urban sites but they were most frequently detected from mid-July (week 29) through the end of the sample season, September 4, 2012. Pesticide degradates and fungicides were not detected at the urban sites.



Figure 7. Types of pesticides detected at the urban sites by week in 2012.

Cedar-Sammamish WRIA 8: Thornton Creek

Pesticides

Thornton Creek is an urban stream in King County in the Cedar-Sammamish Basin (Figure 2). During the sample period, 60 pesticides were detected, including:

- One type of insecticide (1 detection)
- Eight types of herbicides (51 detections)
- One wood preservative (8 detections)

The most frequently detected pesticides for Thornton Creek are described in Table 8. For the past four years these three pesticides have been the most frequently detected pesticides at this site.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
Dichlobenil	Herbicide	25	0.014	0.017	0.037
2,4-D	Herbicide	11	0.009	0.034	0.170
Pentachlorophenol	Wood Preservative	12	0.007	0.012	0.041 J

Table 8. Most frequently detected pesticides for Thornton Creek, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was seven on March 13, 2012. Toxic units (TUs) were used to predict toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). During 2012, all TU values were < 1.0, a TU value \geq 1.0 may indicate a risk to aquatic life.

The number and type of pesticide detections are presented in the Thornton Creek pesticide calendar in Appendix D, Table D-2. In 2012, all Thornton Creek pesticide detections met available pesticide assessment criteria and water quality standards.

Conventional Parameters

Conventional water quality parameters were measured in Thornton Creek. Table 9 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling.

Dissolved oxygen levels did not meet the water quality standard dropping below the 9.5 mg/L standard five times during July and August. pH values met water quality standards during all sample events.

Table 9. Mean, minimum, and maximum for discrete conventional parameter measurements for Thornton Creek, 2012.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	27	10	3	116
Discharge (cfs)	27	8.5	3.5	28.1
pH (s.u.)	27	7.9	7.5	8.3
Conductivity (umhos/cm)	27	226	161	249
Dissolved Oxygen (mg/L)	27	10.1	7.8	11.9

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 2012, periods when stream temperatures were above (did not meet) the applicable water quality standards are shown in Table 10.

Table 10. Thornton Creek periods of water temperature exceedance, 2012.

Temperature > 13°C (Sept 15-May 15)	Maximum Temperature during Period	Temperature > 16°C (May 16-Sept 14)	Maximum Temperature during Period
April 21-26	15.0°C	July 5-August 28	19.6°C
May 9-15	15.0°C	September 5-7	16.7°C
September 15-October 1	15.5°C		
October 13-17	14.6°C		
November 1-3	14.6°C		

Green-Duwamish Basin (WRIA 9): Longfellow Creek

Pesticides

Longfellow Creek is an urban stream in King County, west Seattle, in the Green-Duwamish Basin (Figure 3). During the sample period, 63 pesticides were detected, including:

- Two types of insecticides (9 detections)
- Eight types of herbicides (48 detections)
- One wood preservative (6 detections)

The most frequently detected pesticides for Longfellow Creek are described in Table 11. As with the other urban site, dichlobenil is the most frequently detected pesticide.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
Dichlobenil	Herbicide	26	0.015	0.024	0.096
Triclopyr	Herbicide	14	0.013	0.023	0.135
Imidacloprid	Insecticide	8	0.018	0.020	0.037

Table 11. Most frequently detected pesticides for Longfellow Creek, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was seven on May 21, 2012. Toxic units (TUs) were used to predict toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). During 2012, all TU values were < 1.0, a TU value \geq 1.0 may indicate a risk to aquatic life.

The number and type of pesticide detections are presented in the Longfellow Creek pesticide calendar in Appendix D, Table D-4. In 2012, all Longfellow Creek pesticide detections met available pesticide assessment criteria and water quality standards.

Conventional Parameters

Conventional water quality parameters were measured in Longfellow Creek. Table 12 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling.

Dissolved oxygen levels, pH, and temperature met water quality standards during sampling.

In addition to discrete measurements for stream temperature, 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. In 2012, stream temperatures met the water quality standard throughout the year.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	27	8.4	2.0	73
Discharge (cfs)	27	1.9	0.8	9.8
pH (s.u.)	27	7.8	7.3	8.3
Conductivity (umhos/cm)	27	285	110	400
Dissolved Oxygen (mg/L)	27	10.4	9.3	12.2

Table 12. Mean, minimum, and maximum for discrete conventional parameter measurements for Longfellow Creek, 2012.

Lower-Skagit-Samish Basin (WRIA 3)

The five lower Skagit-Samish sites were sampled for 27 consecutive weeks from March 9 to September 4, 2013. The lower Skagit-Samish basin sites are: upstream and downstream Big Ditch, Indian Slough, Browns Slough, and the Samish River (Figure 4). 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 554 pesticide detections of 34 compounds including:

- Seven insecticides (36 detections)
- 27 herbicides (462 detections)
- Two fungicides (14 detections)
- One pesticide degradate (1 detection)
- One wood preservative (41 detections)

The most commonly detected type of pesticide was herbicides:

- Diuron, 73 detections
- Dichlobenil, 68 detections
- Metolachlor, 62 detections

The wood preservative pentachlorophenol was detected frequently with 41 detections.

The most commonly detected insecticides were:

- Imidacloprid (15 detections)
- Diazinon (11 detections)

The downstream Big Ditch sites had the most pesticide detections (177 detections) followed by Indian Slough (134 detections), Browns Slough (114 detections), upstream Big Ditch (112 detections), then the Samish River (17 detections).

Herbicides and the wood preservative pentachlorophenol were detected most frequently from mid-April (week 16) through late-July (week 30), Figure 8. Insecticides were detected most frequently from May (week 18) through June (week 26). Fungicides were detected fairly consistently throughout the sample period.



Figure 8. Types of pesticides detected at the Skagit-Samish sites by week in 2012.

Big Ditch

Two sites on big Ditch were sampled in 2012. Water quality at the upstream site is influenced by commercial/industrial land use, while the downstream site is influenced by agricultural use. About 52% of the Big Ditch drainage is in agricultural production. Potatoes, wheat, grass hay, and corn are the major crops.

In 2012, there were 112 pesticides detected at the upstream Big Ditch site, including:

- Two types of insecticides (10 detections)
- 11 types of herbicides (78 detections)
- Two types of fungicides (6 detections)
- One wood preservative (18 detections)

At the downstream site there were 177 pesticide detections including:

- Six types of insecticides (15 detections)
- 19 types of herbicides (144 detections)
- One fungicide (2 detections)
- One wood preservative (16 detections)
The most frequently detected pesticides for both Big Ditch sites are described in Table 13. The herbicide, dichlobenil has been a frequently detected pesticide in Big Ditch for the past several years.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L		
Upstream Big Ditch							
Dichlobenil	Herbicide	25	0.018	0.032	0.220		
Pentachlorophenol	Wood Preservative	20	0.024	0.038	0.290		
2,4-D	Herbicide	14	0.014	0.091	0.780		
Downstream Big D	Downstream Big Ditch						
Metolachlor	Herbicide	22	0.051	0.164	1.60		
Diuron	Herbicide	20	0.029	0.124	1.35		
Dichlobenil	Herbicide	18	0.011	0.018	0.125		
Pentachlorophenol	Wood Preservative	19	0.012	0.017	0.046 J		

Table 13. Most frequently detected pesticides for the Big Ditch sites, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was nine at the upstream site on May 4, 2012. At the downstream site the maximum number of pesticides detected during a sample event was 19 pesticides on June 25, 2012, including five insecticides, 12 herbicides, a fungicide, and a wood preservative. Four of the five insecticides detected that day were acetylcholinesterase (AChE) inhibiting insecticides. While none of the insecticide concentrations were above an assessment criteria or water quality standard, AChE inhibiting insecticides have been shown to work synergistically, thus having a greater than additive effect on exposed juvenile Coho (Laetz et al., 2009).

Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). At the upstream Big Ditch site TU values were < 1.0, a TU value ≥ 1.0 may indicate a risk to aquatic life. At the downstream Big Ditch site TU values were ≥ 1.0 for the chronic invertebrate assessment endpoint TU (Table 14). A TU value of ≥ 1.0 means a lethal or sublethal (for chronic criteria) effect may occur with increasing likelihood depending on the degree to which TUs exceed 1.0.

Table 14. Downstream Big Ditch dates, chronic assessment endpoint TU, and contributing pesticides where TU values were ≥ 1.0 during 2012.

Date	Chronic Invertebrate Assessment Endpoint TU	Pesticides Representing a Significant Contribution to the TU Values (≥ 0.01 TU)	Number of Pesticides in Mixture
6/5/2012	1.1	diazinon, metolachlor	10
6/19/2012	2.6	metolachlor, diazinon, ethoprop	14
6/25/2012	1.3	metolachlor, diazinon, alachlor	10

The number and type of pesticide detections for the Big Ditch sites are presented in pesticide calendar in Appendix D, Tables D-4 and D-5. In 2012, all upstream Big Ditch pesticide detections met available pesticide assessment criteria and water quality standards.

At the downstream site most pesticide detections met available pesticide assessment criteria and water quality standards, with the exception of one detection of the herbicide, metolachlor. On June 19, 2012 a metolachlor concentration was above the chronic assessment criterion for aquatic macroinvertebrates. Metolachlor is an herbicide that can be used on corn and potatoes, which are major crops grown in the Big Ditch drainage.

Indian Slough

About 53% of the Indian Slough drainage is in agricultural production. Potatoes, grass hay, wheat, and blueberries are the major crops.

In 2012, there were 134 pesticides detected, including:

- Two types of insecticides (2 detections)
- 15 types of herbicides (120 detections)
- Two types of fungicides (6 detections)
- One wood preservative (6 detections)

In Indian Slough the most frequently detected pesticides are herbicides. The most commonly detected herbicides are described in Table 15.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
Diuron	Herbicide	20	0.014	0.040	0.392
Dichlobenil	Herbicide	20	0.011	0.019	0.100
Metolachlor	Herbicide	20	0.026	0.033	0.140
Triclopyr	Herbicide	20	0.027	0.121	1.30

Table 15. Most frequently detected pesticides for Indian Slough, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was 10 on April 17, 2012. Toxic units (TUs) were used to predict toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). In 2012, all TU values were < 1.0.

The number and type of pesticide detections are presented in the Indian Slough pesticide calendar in Appendix D, Table D-6. In 2012, all Indian Slough pesticide detections met available pesticide assessment criteria and water quality standards.

Browns Slough

About 92% of the Browns Slough drainage is in agricultural production. Potatoes, corn, wheat, and spinach seed are the major crops.

Browns Slough is sampled downstream of a tidegate. Due to higher salinity at this site, marine and freshwater pesticide assessment criteria and water quality standards are used for evaluating water quality at this site. During 2012, there were 114 pesticides detected, including:

- Four types of insecticides (9 detections)
- 16 types of herbicides (104 detections)
- One pesticide degradate (1 detection)

In Browns Slough the most frequently detected pesticides were herbicides. The most commonly detected herbicides are described in Table 16.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
Diuron	Herbicide	23	0.020	0.101	0.600
DCPA	Herbicide	21	0.150	0.159	0.150
Metolachlor	Herbicide	21	0.032	0.138	2.30

Table 16. Most frequently detected pesticides for Browns Slough, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was 10 on June 19, 2012. Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). In Browns Slough TU, two sample events had pesticide mixtures with TU values ≥ 1.0 for chronic invertebrate assessment endpoint TU (Table 17).

Table 17. Browns Slough dates, chronic assessment endpoint TU (marine and freshwater), and contributing pesticides where TU values were ≥ 1.0 during 2012.

Date	Chronic Inv Assessment E Freshwater		Pesticides Representing a Significant Contribution to the TU Values (≥ 0.01 TU)	Number of Pesticides in Mixture
5/4/2012	2.3		metolachlor	6
5/21/2012	1.4		diazinon, metolachlor	7
5/21/2012		1.0	diazinon	7

The number and type of pesticide detections are presented in the Browns Slough pesticide calendar in Appendix D, Table D-7. Browns Slough pesticide concentrations are compared to both fresh and marine water assessment criteria. In Browns Slough two pesticide detections did not meet pesticide assessment criteria. On May 4, 2012, a metolachlor detection of 2.3 ug/L was above the chronic assessment criteria for freshwater invertebrates and marine plants. On May 21, 2012, a diazinon detection exceeded the acute and chronic NRWQC and the freshwater invertebrate criterion.

Samish River

Of the Skagit-Samish sites, Samish River has the least percentage of the basin in agricultural production, approximately 10%. Major crops include grass hay, potatoes, pasture, and corn. The Samish River has the highest flow of any of the sites.

Samish River had the lowest number of pesticide detections. During 2012, there were 17 pesticides detected, including:

- Six types of herbicides (16 detections)
- One pesticide degradate (1 detection)

The most frequently detected herbicide was 2,4-D with 6 detections followed by triclopyr with five detections.

The maximum number of pesticides detected during a sample event was three which occurred on April 17 and June 19, 2012. In 2012, all TU values were < 1.0. A TU value ≥ 1.0 may indicate a risk to aquatic life.

The number and type of pesticide detections are presented in the Samish River pesticide calendar in Appendix D, Table D-8. In 2012, all Samish River pesticide detections met available pesticide assessment criteria and water quality standards.

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 2012, dissolved oxygen levels did not meet the 8.0 mg/L minimum freshwater quality standard in upstream Big Ditch (14 times), downstream Big Ditch (16 times), and Indian Slough (24 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 two sample events.

Upstream Big Ditch met pH water quality standards. Downstream Big Ditch exceeded the pH range (6.5 - 8.5 s.u.) twice, and Browns Slough (marine) exceeded the pH range once during 2012. Samish River dropped below the pH range twice, and Indian Slough dropped below the pH range once in 2012.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)
Big Ditch (upstr	ream)				
number	27	27	27	27	27
mean	10	5.1	7.0	291	8.1
minimum	4	0.6	6.7	129	5.7
maximum	45	31	7.4	383	11.4
Big Ditch (down	nstream)			•	
number	27	24	27	27	27
mean	19	18.9	7.3	480	8.1
minimum	2	1.9	6.7	48	4.5
maximum	131	> 34	9.6	865	15.2
Indian Slough	•			•	
number	27	26	27	27	27
mean	10.4	35	6.8	1722	6.3
minimum	5.0	8.3	6.3	251	4.3
maximum	30.0	80	7.3	7150	10.6
Brown Slough	•			•	
number	27	27	27	27	27
mean	12	9.2	7.6	6641	9.6
minimum	4	2.9	7.1	766	4.3
maximum	112	35	8.8	23780	15.7
Samish River					
number	27	27	27	27	27
mean	15	223	7.3	90	10.7
minimum	2	36	6.3	62	9.5
maximum	43	614 e	8.1	130	12.1

Table 18. Mean, minimum, and maximum for discrete conventional parameter measurements for the Skagit-Samish sites, 2012.

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; for the marine water site the 7-DADMax should not exceed 16.0° C. Upstream Big Ditch met temperature standards during 2012. Table 19 describes the periods when stream temperatures were above (did not meet) the applicable water quality standard at the other Skagit-Samish sites in 2012.

Site and Period of Temperature Exceedance	Maximum Temperature During Period
Big Ditch (downstream) >17.5°C	
May 12-18	20.0°C
May 27-29	18.9°C
June 9	18.1°C
June 19 – September 29	24.2°C
Indian Slough >17.5°C	
June 12- 14	18.2°C
June 16 – 23	20.3°C
June 27 – September 20	24.2°C
Browns Slough >16.0°C	
April 7-12	18.4°
April 19-26	21.8°
May 4 – July 20	26.9°
Samish River >17.5°C	
July 14-19	18.8°C
August 1-19	20.1°C

Table 19. Periods of water temperature exceedance for the Skagit-Samish sites, 2012.

Lower Yakima Basin (WRIA 37)

Monitoring sites in the lower Yakima basin represent irrigated agricultural practices. A wide variety of crops are grown in the lower Yakima basin.

Three sites in the lower Yakima basin were sampled in 2012, Spring Creek, Sulphur Creek Wasteway, and Marion Drain (Figure 5). Spring Creek and Sulphur Creek Wasteway were sampled for 27 consecutive weeks from March 6 to September 4, 2012. Marion Drain was sampled for 34 consecutive weeks from March 8 to October 24, 2012. An additional 7 weeks of sampling occurs in Marion Drain for organophosphate pesticides due to historical late season detections of chlorpyrifos.

For the three lower Yakima sites combined, there were a total of 294 pesticide detections of 34 compounds including:

- 10 insecticides (68 detections)
- 21 herbicides (221 detections)
- Two pesticide degradates (2 detections)
- One wood preservative (3 detections)

The most commonly detected pesticides were the herbicides:

- 2,4-D, 59 detections
- Diuron, 44 detections
- Terbacil, 29 detections

The most commonly detected insecticides were:

- Carbaryl, 19 detections
- Chlorpyrifos, 14 detections
- Imidacloprid, 12 detections

The Marion Drain site had the most pesticide detections (157 detections); it was also sampled for an additional seven weeks. For the 27-week period (March through September), Marion Drain still had the most pesticide detections (144 detections) followed by Sulphur Creek Wasteway (90 detections), then Spring Creek (47 detections).



Figure 9. Types of pesticides detected at the lower Yakima sites by week in 2012.

Herbicides were detected most frequently from late-April (week 17) through July (week 31), Figure 9. Insecticides were detected most frequently from May (week 18) through July (week 31). The wood preservative pentachlorophenol and pesticide degradates were rarely detected. Fungicides were not detected at the lower Yakima sites.

Marion Drain

About 76% of Marion Drain subbasin is in agricultural production. Corn, hops, apples, mint, and pasture are the major crops.

In 2012, there were 157 pesticides detected, including:

- Nine types of insecticides (32 detections)
- 17 types of herbicides (123 detections)
- One pesticide degradate (1 detection)
- One wood preservative (1 detection)

In Marion Drain the most frequently detected pesticides were herbicides. The most commonly detected herbicides are described in Table 20. The most commonly detected insecticide was imidacloprid (11 detections) followed by ethoprop (6 detections).

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
Terbacil	Herbicide	25	0.093	0.153	0.550
Diuron	Herbicide	20	0.013	0.019	0.099
2,4-D	Herbicide	20	0.026	0.041	0.170

Table 20. Most frequently detected pesticides for Marion Drain, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was 10 on July 9, 2012. Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). Table 21 describes the sample dates where Marion Drain pesticide mixtures had TU values ≥ 1.0 for Marion Drain.

Table 21. Marion Drain dates, chronic assessment endpoint TU (acute and chronic), and contributing pesticides where TU values were ≥ 1.0 during 2012.

Date	Chronic Fish Assessment Endpoint	Chronic Invertebrate Assessment Endpoint TU	Pesticides Representing a Significant Contribution to the TU Values (≥ 0.01 TU)	Number of Pesticides in Mixture
5/2/2012	1.1	33.9	bifenthrin	8
5/29/2012		1.2	malathion	8
6/12/2012		1.9	malathion	8
6/25/2012		1.0	malathion, methomyl, trifluralin	9

The number and type of pesticide detections are presented in the Marion Drain pesticide calendar in Appendix D, Table D-9. In Marion Drain three pesticide detections did not meet an assessment criteria or standard. On May 2, 2012 a detection of bifenthrin, a pyrethroid insecticide, exceeded the ESLOC for fish, and was above the chronic assessment criteria for fish and invertebrates. Malathion concentrations were above the chronic invertebrate assessment criterion on May 29, and exceeded both the chronic NRWQC and the chronic invertebrate assessment criterion on June 12, 2012.

Spring Creek

About 71% of the Spring Creek drainage is agricultural land use, with 24% of that area in conservation reserve status. Major crops include wheat, grapes, and apples.

In 2012, there were 47 pesticides detected, including:

- Four types of insecticides (13 detections)
- Nine types of herbicides (34 detections)

In Spring Creek the most frequently detected pesticides were herbicides. The most commonly detected herbicides and insecticides are described in Table 22.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
2,4-D	Herbicide	20	0.018	1.58	42
Diuron	Herbicide	7	0.004	0.007	0.034
Carbaryl	Insecticide	5	0.008^{2}	0.010^{2}	0.031
Chlorpyrifos	Insecticide	5	0.006^{2}	0.017^{2}	0.100

Table 22. Most frequently detected pesticides for Spring Creek, 2012.

¹ Statistically estimated median and mean.

²Estimates are tenuous, over 80% censored.

The maximum number of pesticides detected during a sampling event was four on April 2 and June 6, 2012. Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures. Table 23 describes the sample dates where pesticide mixtures had TU values ≥ 1.0 for Spring Creek.

Table 23. Spring Creek dates, chronic assessment endpoint TU (acute and chronic), and contributing pesticides where TU values were ≥ 1.0 during 2012.

Date	Acute Invertebrate Assessment Endpoint TU	Chronic Invertebrate Assessment Endpoint TU	Pesticides Representing a Significant Contribution to the TU Values (≥ 0.01 TU)	Number of Pesticides in Mixture
3/28/2012	1.0	2.5	chlorpyrifos	2
4/2/2012		2.0	chlorpyrifos	4
4/10/2012		2.0	chlorpyrifos	2
4/18/2012		1.0	chlorpyrifos	2
6/25/2012		9.7	malathion	3

The number and type of pesticide detections are presented in the Spring Creek pesticide calendar in Appendix D, Table D-10. While Spring Creek had the fewest pesticide detections, of the Yakima sites, a number of pesticide detections were above a pesticide assessment criteria or water quality standards.

For four consecutive weekly sampling events from March 28 through April 18, 2012 chlorpyrifos concentrations exceeded the chronic invertebrate assessment criterion; in addition for the first three weeks both the chronic water quality standard and the chronic NRWQC were exceeded.

On June 25, 2012 a malathion detection exceeded the Endangered Species Level of Concern (ESLOC) for fish, as well as the chronic NRWQC and the chronic invertebrate assessment criterion.

On September 4, 2012 a very high concentration of the herbicide 2,4-D (42 ug/L) exceeded the ESLOC for fish.

Sulphur Creek Wasteway

About 42% of the Sulphur Creek Wasteway drainage is agricultural land use. Major crops include corn, grapes, apples, and alfalfa hay.

In 2012, there were 90 pesticides detected, including:

- Four types of insecticides (23 detections)
- 12 types of herbicides (64 detections)
- One type of pesticide degradate (1 detection)
- One wood preservative (2 detections)

In Sulphur Creek Wasteway the most frequently detected pesticides were herbicides. The most commonly detected herbicides and insecticides are described in Table 24. The most commonly detected pesticides were similar for both the Spring Creek and Sulphur Creek Wasteway sites.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
2,4-D	Herbicide	25	0.050	0.118	1.30
Diuron	Herbicide	17	0.008	0.020	0.109
Carbaryl	Insecticide	12	0.005	0.012	0.077
Chlorpyrifos	Insecticide	7	0.008	0.019	0.100

Table 24. Most frequently detected pesticides for Sulphur Creek Wasteway, 2012.

¹ Statistically estimated median and mean.

The maximum number of pesticides detected during a sampling event was six on July 24 and 30, 2012. Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures, Table 25 describes the sample dates where pesticide mixtures had TU values ≥ 1.0 for Sulphur Creek Wasteway.

Date	Acute Invertebrate Assessment Endpoint TU	Chronic Invertebrate Assessment Endpoint TU	Pesticides Representing a Significant Contribution to the TU Values (≥ 0.01 TU)	Number of Pesticides in Mixture
3/20/2012		1.0	4,4'-DDE	3
3/28/2012	1.0	2.5	chlorpyrifos	2
4/2/2012		1.3	chlorpyrifos	3
4/10/2012		2.0	chlorpyrifos	3
7/5/2012		1.8	malathion	3
7/18/2012		1.4	chlorpyrifos	4
7/24/2012		1.6	chlorpyrifos, diazinon	6

Table 25. Sulphur Creek Wasteway dates, chronic assessment endpoint TU (acute and chronic), and contributing pesticides where TU values were ≥ 1.0 during 2012.

The number and type of pesticide detections are presented in the Sulphur Creek Wasteway pesticide calendar in Appendix D, Table D-11. A number of chlorpyrifos detections exceeded a pesticide assessment criteria or water quality standard. For three consecutive weekly sample events (March 28 through April 10, 2012), chlorpyrifos concentrations exceeded the chronic water quality standard, the chronic NRWQC, and the chronic invertebrate assessment criterion. For two consecutive weekly sample events in July (July 18 and 24, 2012), chlorpyrifos concentrations again exceeded the chronic water quality standard, the chronic invertebrate assessment criterion.

On July 5, 2012, a single malathion detection was above the chronic NRWQC and the chronic invertebrate assessment criterion.

On March 20, 2012, one detection of 4,4'-DDE, a degradate of the legacy insecticide DDT, which exceeded the chronic water quality standard for DDT (and metabolites).

Conventional Parameters

Conventional water quality parameters were measured at the lower Yakima sites. Table 26 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.

During 2012, all lower Yakima sites met the dissolved oxygen water quality standard ($\geq 8.0 \text{ mg/L}$) during daytime sample events.

All of the lower Yakima sites exceeded (did not meet) the pH standard (6.5-8.5 s.u.) during at least one period in 2012. In Marion Drain, pH levels exceeded the standard twice in 2012. Spring Creek exceeded pH standards 14 times, often for consecutive sample weeks. Sulphur Creek Wasteway exceeded pH standards nine times in 2012.

Table 26. Mean, minimum, and maximum for discrete conventional parameter measurements for the lower Yakima sites, 2012.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)			
Marion Drain								
number	34	31	34	33	34			
mean	22	144	8.0	249	11.7			
minimum	2	7.9	7.3	182	9.4			
maximum	118	366	8.7	371	15.5			
Spring Creek (d	lownstream)							
number	27	27	27	27	27			
mean	24	25.2	8.6	310	10.0			
minimum	1	2.2	8.1	133	8.6			
maximum	107	92.9	9.7	649	13.9			
Sulphur Creek	Sulphur Creek Wasteway							
number	27	27	27	27	27			
mean	39	244	8.5	308	10.6			
minimum	7	74.4	7.8	190	9.3			
maximum	286	812	9.0	746	12.0			

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature standard for the lower Yakima sites is that the 7-DADMax should not exceed 17.5° C. None of the lower Yakima sites met temperature standards during all periods. In 2012, periods when stream temperatures were above (did not meet) the applicable water quality standard are shown in Table 27.

Site and Period of Temperature Exceedance	Maximum Temperature During Period				
Marion Drain >17.5°C					
July 3-September 11	22.8°C				
September 17-19	22.0°C				
Spring Creek >17.5°C					
April 20-28	23.1°C				
May 6-20	25.4°C				
May 28-June 4	19.8°C				
June 10-September 30	25.3°C				
Sulphur Creek Wasteway >17.5°C					
May 10-18	20.3°C				
May 30-June 2	19.8°C				
June 12-September 24	24.0°C				

Table 27. Periods of water temperature exceedance for the lower Yakima sites, 2012.

Wenatchee-Entiat Basins (WRIA 45 and 46)

Monitoring sites in the Wenatchee-Entiat basins represent tree-fruit agricultural practices. Major crops include apples, pears, and cherries.

Four sites are sampled in the Wenatchee basin: Peshastin, Mission and Brender creeks; and the Wenatchee River (Figure 6). One site is sampled near the mouth of the Entiat River in the Entiat basin. All sites were sampled for 27 consecutive weeks from March 5 to September 6, 2012.

For the five Wenatchee-Entiat basin sites combined, there were a total of 124 pesticide detections of 17 compounds including:

- Seven insecticides (49 detections)
- Five herbicides (8 detections)
- Three pesticide degradates (58 detections)
- One pesticide synergist (8 detections)
- One wood preservative (1 detection)

Insecticides and insecticide degradates are the most commonly detected pesticide at the Wenatchee-Entiat sites. The most commonly detected pesticides were:

- 4,4'-DDT (legacy insecticide)
- 4,4'-DDE (a DDT degradate)
- Endosulfan sulfate (degradates of the insecticide endosulfan)

Most sites with the exception of Brender Creek had few pesticide detections. Brender Creek had the most pesticide detections (110 detections), and the most detections above a pesticide assessment criteria or water quality standard. The other Wenatchee-Entiat sites had either three or four pesticide detections during 2012.

Insecticides were detected most frequently from late-March (week 13) through April (week 17), Figure 10. Insecticide degradates were present throughout the sample season but were detected most frequently from May (week 19) through July (week 30). Pesticide synergists were not frequently detected, but they were present consistently from mid-March (week 12) through mid-April (week 15). The wood preservative, pentachlorophenol, was rarely detected. Fungicides were not detected at the Wenatchee-Entiat sites.



Figure 10. Types of pesticides detected at the lower Yakima sites by week in 2012.

Peshastin Creek

Less than 1 % of the Peshastin basin is in agricultural production. Only three pesticide detections occurred in Peshastin Creek, all on April 4, 2012. The pesticide synergist, piperonyl butoxide, and the insecticides endosulfan I and II were detected.

Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures (or pesticides that occurred during a single sample event). On April 4, 2012, the chronic fish assessment endpoint TU value was 3.2 due to endosulfan detections.

The number and type of pesticide detections are presented in the Peshastin Creek pesticide calendar in Appendix D, Table D-12. The April 4, 2012 endosulfan levels exceeded the ESLOC for fish, and the acute and chronic water quality standard and the chronic NRWQC for endosulfan.

Mission Creek

Approximately 1.3 % of the Mission Creek basin is in agricultural production. Only four compounds were detected on Mission Creek, two insecticides, one herbicide, and a pesticide synergist. The maximum number of pesticide detected during a sample event was one.

The number and type of pesticide detections are presented in the Mission Creek pesticide calendar in Appendix D, Table D-13. During 2012, pesticide detections met all available pesticide assessment criteria and water quality standards.

Wenatchee River

Approximately 1.1 % of the Wenatchee basin is in agricultural production. Only three pesticiderelated compounds were detected at the Wenatchee River site, two insecticides, and a pesticide synergist. The maximum number of detections that occurred during a sample event was two, on April 9, 2012 for the insecticide chlorpyrifos and the pesticide synergist, piperonyl butoxide. In 2012, all TU values were < 1.0.

The number and type of pesticide detections are presented in the Wenatchee River pesticide calendar in Appendix D, Table D-14. During 2012, pesticide detections met all available pesticide assessment criteria and water quality standards.

Brender Creek

Of the Wenatchee-Entiat sites, Brender Creek basin has the greatest percentage area in agricultural production: 13 %. Brender Creek also has the lowest average flow during the sample season: 4.0 cfs.

Brender Creek had the greatest number of pesticide detections of the Wenatchee-Entiat sites; 89% of pesticide detections occur in Brender Creek. Sixty percent of the Brender Creek pesticide detections are for the legacy pesticide DDT and DDT degradates. During 2012, 110 pesticide compounds were detected in Brender Creek including:

- Seven types of insecticides (42 detections)
- Five types of herbicides (7 detections)
- Three types of pesticide degradate compounds (58 detections)
- One pesticide synergist (3 detections)

The most commonly detected pesticides (insecticides and insecticide degradates) are described in Table 28.

Pesticide	Pesticide Type	Number of Detections	Median ¹ ug/L	Mean ¹ ug/L	Maximum ug/L
4,4'-DDT	Legacy Insecticide	26	0.025	0.029	0.091
4,4'-DDE	Legacy Insecticide Degradate	26	0.034	0.035	0.080
Endosulfan Sulfate	Insecticide	18	0.033	0.039	0.100
4,4'-DDD	Legacy Insecticide Degradate	16	0.020	0.022	0.083
Total Endosulfan	Insecticide	5	0.016 ²	0.026 ²	0.096

Table 28. Most frequently detected pesticides for Brender Creek, 2012.

¹ Statistically estimated median and mean.

²Estimates are tenuous, over 80% censored.

The maximum number of pesticides detected during a sampling event was seven on April 25, and May 15, 2012. Toxic units (TUs) were used to predict additive toxicity of pesticide mixtures, Table 29 describes the sample dates where pesticide mixtures had TU values ≥ 1.0 for Brender Creek. Due to the consistent DDT and DDT degradate detections on Brender Creek, TU values were > 1.0 for the chronic invertebrate endpoint TU for 26 of the 27 sample events.

The number and type of pesticide detections are presented in the Brender Creek pesticide calendar in Appendix D, Table D-15. Of the Wenatchee-Entiat sites, Brender Creek had the most pesticide detections above an assessment criteria or water quality standard.

DDT and DDT degradates (DDE and DDD) were found consistently during 2012. For all 27 sample events, total DDT did not meet the chronic water quality standard and the chronic NRWQC.

In April 2012, a single detection of chlorpyrifos was above the chronic invertebrate assessment criterion, the chronic water quality standard, and the chronic NRWQC.

Total endosulfan concentrations exceeded the ESLOC for fish during four sample events: three consecutive events, March 27, April 4, and April 9; and again on April 25, 2012. During all of these sample events, endosulfan concentrations also exceeded the chronic water quality standard and the chronic NRWQC.

	Assess	nent Endpoint	ГUs	Pesticides Representing a	Number of
Date	Acute	Chronic	Chronic	Significant Contribution to	Pesticides
	Invertebrate	Invertebrate	Fish	the TU Values (≥ 0.01 TU)	in Mixture
3/5/2012		2.7		total DDT	4
3/13/2012		1.6		total DDT	2
3/21/2012		1.5		total DDT	1
3/27/2012		3.0	1.1	endosulfan, total DDT	3
4/4/2012		5.0	1.7	endosulfan, total DDT	5
4/9/2012		4.8	1.4	endosulfan, total DDT	5
4/17/2012	1.0	7.1		chlorpyrifos, total DDT,	4
	110			diazinon	
4/25/2012		7.0	2.6	endosulfan, total DDT,	6
				chlorpyrifos, diazinon	
5/1/2012		3.9		total DDT	2
5/7/2012		5.8		total DDT	2
5/15/2012		3.5		total DDT	6
5/23/2012		5.0		total DDT	2
5/30/2012		4.3		total DDT	3
6/5/2012		7.0	1.0	total DDT	2
6/11/2012		15.9	2.3	total DDT	1
6/26/2012		4.9		total DDT	2
7/2/2012		4.3		total DDT	2
7/10/2012		5.4		total DDT	2
7/17/2012		5.4		total DDT	4
7/25/2012		4.1		total DDT	2
8/1/2012		4.3		total DDT, chlorpyrifos	2
8/6/2012		4.0		total DDT	1
8/14/2012		3.9		total DDT	2
8/21/2012		4.5		total DDT	2
8/27/2012		5.4		total DDT	1
9/5/2012		4.8		total DDT	2

Table 29. Brender Creek Wasteway dates, chronic assessment endpoint TU (acute and chronic), and contributing pesticides where TU values were ≥ 1.0 during 2012.

Entiat River

Less than 0.5 % of the Entiat basin is in agricultural production. Only four pesticide compounds were detected in 2012: one insecticide, one wood preservative, and two pesticide synergists. The maximum number of detections that occurred during a sample event was two - on August 14, 2012. In 2012, all TU values were < 1.0.

The number and type of pesticide detections are presented in the Entiat River pesticide calendar in Appendix D, Table D-16. During 2012, pesticide detections met all available pesticide assessment criteria and water quality standards.

Conventional Parameters

Conventional water quality parameters were measured at the Wenatchee-Entiat sites. Table 30 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.

During 2012, all of the Wenatchee-Entiat sites met the dissolved oxygen water quality standard ($\geq 8.0 \text{ mg/L}$).

Peshastin Creek was the only site to meet pH standards (6.5 - 8.5). Mission Creek pH levels exceeded 8.5 s.u. for all sample events from June 26 through September 5, 2012 (11 sample events). Wenatchee River had six sample events where pH levels exceeded the standard: one exceedance at Brender Creek and five at Entiat River.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)			
Peshastin Creek								
number	27	27	27	27	27			
mean	6	329	8.1	122	11.2			
minimum	1	16.3	7.8	66	8.8			
maximum	54	1450	8.5	220	12.7			
Mission Creek								
number	27	24	27	27	27			
mean	17	23	8.5	205	11.8			
minimum	1	0.7	8.1	138	10.2			
maximum	199	70	9.0	264	13.1			
Wenatchee Rive	er			• •				
number	27	27	27	27	27			
mean	10	5724	8.0	53	11.8			
minimum	1	694	7.4	24	9.5			
maximum	51	12300	9.1	97	14.5			
Brender Creek								
number	27	27	27	27	27			
mean	45	4.0	8.1	223	10.6			
minimum	6	0.4	7.7	108	9.4			
maximum	216	11	8.6	413	11.5			
Entiat River								
number	27	27	27	27	27			
mean	8	910	8.1	61	11.4			
minimum	2	147	7.6	27	9.2			
maximum	37	2260	9.2	118	13.6			

Table 30. Mean, minimum, and maximum for discrete conventional parameter measurements for the Wenatchee-Entiat sites, 2012.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. The temperature standard for the Wenatchee-Entiat 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.

Brender Creek met temperature standards, while the other sites had some periods where the temperature standard was not met. Table 31 shows the periods in 2012 when stream temperatures were above (did not meet) the applicable water quality standard.

Site	Periods When Temperature Did Not Meet Standards				
Peshastin Creek >17.5°C					
July 24 – September 8	22.7°C				
Mission Creek >17.5°C					
July 10 – 19	18.9°C				
July 27 – August 22	20.9°C				
Wenatchee River >17.5°C					
July 29 – September 9	21.1°C				
Wenatchee River > 13.0°C					
October 1 – 3	15.5°C				
Entiat River >17.5°C					
July 30 – September 8	20.9°C				

Table 31. Periods of water temperature exceedance for the Wenatchee-Entiat sites, 2012.

Summary of 2012 Findings

During 2012, 15 sites were sampled statewide: two urban sites and 13 agricultural sites. For all sites combined there were 1,095 pesticide detections of 58 pesticides or pesticide-related compounds. Herbicides were the most frequently detected pesticide, followed by insecticides, and pesticide degradates (Table 32).

Most of the pesticide degradates (60 detections) were detected at the Eastside sites. A total of 67% of the degradate pesticide detections were for degradates of the legacy pesticide DDT. The majority of DDT degradate detections occurred at Brender Creek. All of the fungicide detections occurred at the Skagit-Samish sites. All of the pesticide synergist detections occurred at the Wenatchee-Entiat sites.

Table 32. Cumulative total for types of pesticides or pesticide-related compounds detected, and the number of detections, for 15 sites, 2012.

Type of Pesticide	Number of Types of Compounds Detected	Number of Detections
Herbicides	35	790
Insecticides	14	163
Pesticide Degradates	5	61
Wood Preservative	1	59
Fungicides	2	14
Pesticide Synergist	1	8

The most commonly detected herbicides were:

- 2,4-D (125 detections)
- Diuron (124 detections)
- Dichlobenil (119 detections)
- Triclopyr (62 detections)
- Metolachlor (62 detections)

The most commonly detected insecticides were:

- Imidacloprid, neonicotinoid insecticide (38 detections)
- Carbaryl, carbamate insecticide (30 detections)
- 4,4'-DDT, legacy organochlorine insecticide (26 detections)
- Chlorpyrifos, organophosphate insecticide (19 detections)
- Diazinon, organophosphate insecticide (17 detections)

The most commonly detected pesticides for the sites west of the Cascades (urban and Skagit-Samish sites) were the herbicides:

- Dichlobenil (118 detections)
- Diuron (78 detections)

The most commonly detected pesticides for the sites east of the Cascades (Wenatchee-Entiat and lower Yakima sites) were the herbicides:

- 2,4-D (61 detections)
- Diuron (29 detections)

The sites that had the most pesticide detections were:

- Downstream Big Ditch (177 detections)
- Marion Drain (157 detections)
- Indian Slough (134 detections)

Sites that had the greatest number of pesticide detections above a pesticide assessment criteria or water quality standard were:

- Brender Creek (73 detections exceeded a pesticide assessment criteria or water quality standard; 66 of these exceedances were for the legacy pesticide DDT and DDT degradates).
- Sulphur Creek Wasteway (7 detections exceeded a pesticide assessment criteria or water quality standard).
- Spring Creek (6 detections exceeded a pesticide assessment criteria or water quality standard).

During 2012, all of the urban sites met available pesticide assessment criteria and standards. The following sites had pesticide detections above (did not meet) pesticide assessment criteria or water quality standards:

- Skagit Samish basin: metolachlor (herbicide) and diazinon (insecticide).
- Lower Yakima basin: bifenthrin, malathion, chlorpyrifos (insecticides); 4, 4'-DDE (legacy insecticide degradate); and 2,4-D (herbicide).
- Wenatchee-Entiat basins: Total endosulfan, chlorpyrifos (insecticides); endosulfan sulfate (endosulfan degradate); and DDT and DDT degradates (legacy insecticide and degradates).

With the exception of Longfellow and Brender creeks and upstream Big Ditch, there were periods when the rest of the sites did not meet (exceeded) the temperature standard in 2012. Maximum temperatures exceeded 25.0°C in Browns Slough and Spring Creek.

All the Eastside sites met dissolved oxygen standards. Of the Westside sites, only Longfellow Creek and Samish River met the dissolved oxygen standard.

The urban sites met pH standards. The Skagit-Samish sites both exceeded and dropped below the pH standard range at times. The lower Yakima and the Wenatchee-Entiat sites exceeded the pH standard at times during 2012.

Recommended Program Changes for 2013

Changes to be implemented for the 2013 pesticide monitoring program are fully described in Addendum 6 to the Quality Assurance Project Plan (Sargeant, 2013).

Changes in Timing

Due to late season organophosphate insecticide detections in Marion Drain, the sample season was extended through the end of October for 2003-2012. Since 2008, no pesticides have been detected after October 15. In addition the irrigation system is generally turned off mid-October. It is recommended that the current sampling season on Marion Drain be reduced by two weeks, ending mid-October to coincide with the end of the irrigation period.

Changes in Sites

Pesticide detections at the Entiat River site are rare. In six years, 17 pesticides and 6 pesticide synergists have been detected. Due to the infrequency of pesticide detections and the low percentage of area in tree-fruit production (0.35%), it is recommended that sampling of this site be discontinued and a site with greater area in tree-fruit production be added for 2013.

Washington State Department of Agriculture (WSDA) is interested in adding a surface water pesticide monitoring site in an area that represents berry growing agricultural land-use, and to capture changes in pesticide use with the emergence of new pest pressures. While berries are grown in the lower Skagit-Samish basin (another project monitoring area), WSDA is interested in capturing data on pesticide residues from a more intensely cultivated berry region.

Bertrand Creek in the Nooksack basin is recommended as a candidate watershed because a high percentage of the subbasin is in agricultural production (approximately 61% in the U.S. portion of the drainage). In addition, 20% of the U.S. portion of the basin is in berry production including blueberries, caneberries, strawberries, and grapes (WSDA, 2013).

Changes in Parameters

In 2012, copper and copper-related parameters were added to the sample regime. Copper was added because an Ecology report (Norton et al., 2011) identified urban lawn and garden use of copper as potentially the largest source of copper in the Puget Sound basin. In addition, not enough sampling data existed to accurately assess how much copper is entering Puget Sound from surface water that drains urban and agricultural lands. To aid in filling the data gap, copper and copper-related parameters were added to this existing project.

Copper and copper-related parameters will not be sampled in 2013. Funding was only available for one year of copper sampling. Copper results are being evaluated and a report will be available July 2013.

For 2013, added pesticide parameters include the insecticide cypermethrin; the insecticide degradate of malathion, malaoxon; and the fungicides cyprodinil and boscalid. Cypermethrin and malaoxon will be added to capture possible increased pesticide use of cypermethrin and malathion on berries for the pest, Spotted wing Drosophila. To better capture fungicide use, especially for the Westside sites, two fungicides were added.

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Appendices

Appendix A. Monitoring Sites and Duration of Sampling

ammamish Watershee March– September	1		
March- September			
	47.6958	122.2757	Downstream of pedestrian footbridge near Matthews Beach Park.
ouwamish Watershed			
March-September	47.5625	122.367	Upstream of the culvert under the 12th fairway on the West Seattle Golf Course.
amish Watershed			
March-September	48.3086	122.3473	Upstream side of bridge at Milltown Road.
March- September	48.3887	122.3329	Upstream side of bridge at Eleanor Lane.
March- September	48.3406	122.4140	Downstream of tidegate on Fir Island Road.
March– September	48.4506	122.4651	Inside upstream side of tidegate at Bayview-Edison Road.
March- September	48.5209	122.4113	Upstream side of bridge at Thomas Road.
akima Watershed			
March-October	46.3306	120.1989	Approximately 15 meters upstream of bridge at Indian Church Road.
March- September	46.2583	119.7101	Downstream side of culvert on McCreadie Road.
March- September	46.2344	119.6845	Approximately 3 meters downstream of Chandler Canal overpass.
March- September	46.2509	120.0202	Downstream side of bridge at Holaday Road.
nee Watershed			
March- September	47.4721	120.3710	Upstream side of Sleepy Hollow bridge.
March-September	47.4893	120.4815	Mission Creek Road off of Trip Canyon Road.
March- September	47.5570	120.5825	Approximately 30 meters downstream of bridge at Saunders Road.
March-September	47.5211	120.4862	Upstream side of culvert at Evergreen Drive.
Vatershed	•	•	
March-September	47.6633	120.2506	Downstream side of bridge at Keystone Road.
	amish Watershed March– September March– September March– September March– September March– September akima Watershed March– October March– September March– September March– September March– September March– September March– September March– September March– September	amish Watershed March– September 48.3086 March– September 48.3887 March– September 48.3406 March– September 48.3406 March– September 48.4506 March– September 48.5209 akima Watershed 48.5209 March– September 46.3306 March– October 46.2583 March– September 46.2509 March– September 46.2509 ee Watershed 46.2509 March– September 47.4721 March– September 47.4721 March– September 47.5570 March– September 47.5211 March– September 47.5211	Amish Watershed March– September 48.3086 122.3473 March– September 48.3887 122.3329 March– September 48.3887 122.4140 March– September 48.4506 122.4140 March– September 48.4506 122.4131 March– September 48.5209 122.4113 March– September 46.3306 120.1989 March– October 46.2583 119.7101 March– September 46.2509 120.0202 March– September 46.2509 120.0202 March– September 47.4721 120.3710 March– September 47.4893 120.4815 March– September 47.5570 120.5825 March– September 47.5211 120.4862 Vatershed 47.5211 120.4862

Table A-1. Site names, monitoring periods, and site descriptions for 2009-2011.

Datum in North American Datum (NAD) 83.

Appendix B. 2012 Quality Assurance

Laboratory Data Quality

Data may be qualified if one or more analytical factors affect confidence in the prescribed data value. Manchester Environmental Laboratory (MEL) qualifies data according to the National Functional Guidelines for Organic Data Review (EPA, 2008). Definitions of data qualifiers are presented in Table B-1.

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 numerical 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 numerical 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 quality control 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 B-1. Data qualification.

MEL, 2000, 2008; EPA, 2008.

Performance measures for quality assurance (QA) and quality control (QC) are presented in Table B-2. Lowest concentrations of interest for surface water grab samples are below reporting limits. Detections quantified below reporting limits are qualified as estimates.

Analysis Method ¹	Analysis ²	Field/Lab Replicates, MS/MSD ³ , and Lab Control Samples RPD ⁴	MS/MSD ³ , Surrogates, and Lab Control Samples % Recovery
GCMS	Pesticide-C-l	± 40	30-130
	Pesticide-N	± 40	30-130
	Pesticide-OP	± 40	30-130
	Pesticide-Py	± 40	30-130
GCMS-H	Herbicides	±50	40-130
LCMS/MS	Pesticide-C	± 40	50-150
TSS	TSS	±20	80-120

Table B-2. Performance measures for quality assurance and quality control.

¹ GCMS: Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M. GCMS-H: Derivitizable acid herbicides by GCMS, EPA method (modified) SW 846 3535M/8270M.

LCMS/MS: Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM. TSS: Total suspended solids, EPA method 2540D.

²C-l: chlorinated, N: nitrogen containing, OP: organophosphorus, Py: pyrethroid, C: carbamate.

³MS/MSD: Matrix spike and matrix spike duplicate.

⁴RPD: Relative percent difference.

Lower Practical Quantitation Limits

Lower practical quantitation limits (LPQLs) are the limits at which laboratories may report data without classifying the concentration as an estimate below the lowest calibration standard. The LPQL is determined by averaging the lower reporting values, per analyte, for all batches over each study period. LPQL data for 2012 are presented in Table B-3.

		I		
Chemical	¹ Use	Parent	² Analysis Method	LPQL 2012
1-Naphthol	D-C		GCMS	0.307
2,3,4,5-Tetrachlorophenol	D-M		GCMS-H	0.064
2,3,4,6-Tetrachlorophenol	D-M		GCMS-H	0.064
2,4,5-T	Н		GCMS-H	0.064
2,4,5-TP (Silvex)	Н		GCMS-H	0.064
2,4,5-Trichlorophenol	D-M		GCMS-H	0.064
2,4,6-Trichlorophenol	D-M		GCMS-H	0.064
2,4-D	H		GCMS-H	0.101 ³
2,4-DB	Н		GCMS-H	0.064
2,4'-DDD	D-OC	DDT	GCMS	0.034
2,4'-DDE	D-OC	DDT	GCMS	0.034
2,4'-DDT	D-OC	DDT	GCMS	0.034
3,5-Dichlorobenzoic Acid	D-M		GCMS-H	0.064
3-Hydroxycarbofuran	D-C	Carbofuran		0.010
4,4'-DDD	D-OC	DDT	GCMS	0.034
4,4'-DDE	D-OC	DDT	GCMS	0.034
4,4'-DDT	I-OC		GCMS	0.034
4,4'-Dichlorobenzophenone	D		GCMS	0.102
4-Nitrophenol	D-H		GCMS-H	0.064
Acetochlor	Н		GCMS	0.102
Acifluorfen, Sodium Salt	H		GCMS-H	0.064
Alachlor	Н		GCMS	0.034
Aldicarb	I-C			0.036
Aldicarb Sulfone	D-C	Aldicarb		0.024
Aldicarb Sulfoxide	D-C	Aldicarb		0.017
Aldrin	I-OC		GCMS	0.034
Alpha-BHC	I-OC		GCMS	0.034
Atrazine	H		GCMS	0.035
Azinphos Ethyl	I-OP		GCMS	0.034
Azinphos Methyl	I-OP		GCMS	0.034
Benfluralin (Benefin)	Н		GCMS	0.034
Bentazon	Н		GCMS-H	0.064
Beta-BHC	I-OC		GCMS	0.034
Beta-Cypermethrin	I-Py		GCMS	0.102
Bifenthrin	I-Py		GCMS	0.102
Bolstar (Sulprofos)	I-OP		GCMS	0.051
Bromacil	Н		GCMS	0.034
Bromoxynil	H		GCMS-H	0.064
Butachlor	Н		GCMS	0.307
Butylate	H		GCMS	0.034
Captan	F		GCMS	0.034
Carbaryl	I-C		LCMS/MS	0.014
Carbofuran	I-C I-C		LCMS/MS	0.014
Chlorothalonil	F		GCMS	0.034

Table B-3. Mean performance lower practical quantitation limits (LPQL) (ug/L), 2012.

Chemical	¹ Use	Parent	² Analysis	LPQL
<u> </u>			Method GCMS	2012
Chlorpropham	H		GCMS	0.035
Chlorpyrifos	I-OP		GCMS	0.034
Chlorpyrifos O.A.	D-OP			0.102
Cis-Chlordane	I-OC		GCMS	0.034
Cis-Nonachlor	I-OC		GCMS	0.051
Cis-Permethrin	I-Py		GCMS	0.051
Clopyralid	H		GCMS-H GCMS	0.064
Coumaphos	I-OP			0.051
Cyanazine	H		GCMS	0.034
Cycloate	H		GCMS	0.034
DCPA (Dacthal)	H		GCMS-H	0.064
DDVP	I-OP		GCMS	0.051
Delta-BHC	I-OC		GCMS	0.034
Deltamethrin	I-Py		GCMS	0.102
Diallate	Н		GCMS	0.034
Diazinon	I-OP		GCMS	0.034
Diazoxon	D-OP	Diazinon	GCMS	0.102
Dicamba I	Н		GCMS-H	0.064
Dichlobenil	Н		GCMS	0.034
Dichlorprop	Н		GCMS-H	0.064
Diclofop-Methyl	Н		GCMS-H	0.064
Dicofol (Kelthane)	I-OC		GCMS	0.307
Dieldrin	I-OC		GCMS	0.051
Dimethoate	I-OP		GCMS	0.034
Dinoseb	Н		GCMS-H	0.064
Diphenamid	Н		GCMS	0.034
Disulfoton Sulfone	I-OP		GCMS	0.102
Disulfoton Sulfoxide	D-OP		GCMS	0.102
Diuron	Н		LCMS\MS	0.013
Endosulfan I	I-OC		GCMS	0.051
Endosulfan II	I-OC		GCMS	0.051
Endosulfan Sulfate	D-OC	Endosulfan	GCMS	0.034
Endrin	I-OC		GCMS	0.051
Endrin Aldehyde	D-OC	Endrin	GCMS	0.051
Endrin Ketone	D-OC	Endrin	GCMS	0.034
EPN	I-OP		GCMS	0.034
Eptam	Н		GCMS	0.034
Ethalfluralin	H		GCMS	0.034
Ethion	I-OP		GCMS	0.034
Ethoprop	I-OP		GCMS	0.034
Fenamiphos	I-OP		GCMS	0.034
Fenamiphos Sulfone	D-OP		GCMS	0.034
Fenarimol	F		GCMS	0.102
Fenitrothion	I-OP		GCMS	
Fensulfothion	I-OP		GCMS	0.050
I CHSUIIOUIIOII	1-0P		001410	0.033

Chemical	¹ Use	Parent	² Analysis	LPQL
			Method	2012
Fenthion	I-OP		GCMS	0.033
Fenvalerate (2 isomers)	I-Py		GCMS	0.034
Fipronil	I-Pyra		GCMS	0.102
Fipronil Sulfide	D-Pyra		GCMS	0.102
Fipronil Sulfone	D-Pyra		GCMS	0.102
Fluridone	Н		GCMS	0.102
Fonofos	I-OP		GCMS	0.034
Heptachlor	I-OC		GCMS	0.034
Heptachlor Epoxide	D-OC	Heptachlor	GCMS	0.034
Hexachlorobenzene	F		GCMS	0.034
Hexazinone	Н		GCMS	0.051
Imidacloprid	I-N		LCMS\MS	0.014
Imidan (Phosmet)	I-OP		GCMS	0.034
Ioxynil	Н		GCMS-H	0.064
Lindane (BHC-gamma)	I-OC		GCMS	0.034
Linuron	Н		LCMS\MS	0.032
Malathion	I-OP		GCMS	0.034
MCPA	Н		GCMS-H	0.064
MCPP	Н		GCMS-H	0.064
Metalaxyl	F		GCMS	0.034
Methidathion	I-OP		GCMS	0.306
Methiocarb	I-C		LCMS\MS	0.026
Methomyl	I-C		LCMS\MS	0.010
Methomyl oxime	D-C	Thiodicarb	LCMS\MS	0.064
Methoxychlor	I-OC		GCMS	0.051
Methyl Chlorpyrifos	I-OP		GCMS	0.034
Methyl Paraoxon	D-OP	Methyl parathion	GCMS	0.102
Methyl Parathion	I-OP		GCMS	0.034
Metolachlor	Н		GCMS	0.035
Metribuzin	Н		GCMS	0.034
Mevinphos	I-OP		GCMS	0.051
MGK-264	Sy		GCMS	0.051
Mirex	I-OC		GCMS	0.034
Monocrotophos	I-OP		GCMS	0.051
Monuron	Н		LCMS\MS	0.010
Naled	I-OP		GCMS	0.034
Napropamide	Н		GCMS	0.051
Neburon	Н		LCMS\MS	0.024
Norflurazon	Н		GCMS	0.034
Oryzalin	Н		GCMS	0.102
Oxamyl	I-C		LCMS\MS	0.010
Oxamyl Oxime	D-C	Oxamyl		0.019
Oxychlordane	D-OC	Chlordane	GCMS	0.034
Oxyfluorfen	Н		GCMS	0.102
Parathion	I-OP		GCMS	0.034

Chemical	¹ Use	Parent	² Analysis	LPQL
Chemical	Use	Parent	Method	2012
Pebulate	Н		GCMS	0.034
Pendimethalin	Н		GCMS	0.034
Pentachlorophenol	WP		GCMS-H	0.064
Phenothrin	I-Py		GCMS	0.034
Phorate	I-OP		GCMS	0.306
Phorate O.A.	D-OP		GCMS	0.102
Picloram	Н		GCMS-H	0.064
Piperonyl Butoxide	Sy		GCMS	0.102
Promecarb	I-C		LCMS\MS	0.010
Prometon	Н		GCMS	0.034
Prometryn	Н		GCMS	0.034
Pronamide	Н		GCMS	0.034
Propachlor	Н		GCMS	0.034
Propargite	I-SE		GCMS	0.051
Propazine	Н		GCMS	0.034
Propoxur	I-C		LCMS\MS	0.010
Resmethrin	I-Py		GCMS	0.034
Ronnel	I-OP		GCMS	0.051
Simazine	Н		GCMS	0.034
Simetryn	Н		GCMS	0.102
Sulfotepp	I-OP		GCMS	0.034
Tebuthiuron	Н		GCMS	0.034
Terbacil	Н		GCMS	0.034
Tetrachlorvinphos	I-OP		GCMS	0.051
Thiobencarb (Benthiocarb)	Н		GCMS	0.102
Tokuthion (Prothiofos)	I-OP		GCMS	0.102
Total Suspended Solids			TSS	1.8 mg/L
Tralomethrin	I-Py		GCMS	0.102
Trans-Chlordane	I-OP		GCMS	0.034
Trans-Nonachlor	I-OC		GCMS	0.051
trans-Permethrin	I-Py		GCMS	0.102
Triadimefon	F		GCMS	0.034
Triallate	Н		GCMS	0.034
Trichloronat	I-OP		GCMS	0.051
Triclopyr	Н		GCMS-H	0.064
Tricyclazole	F		GCMS	0.102
Trifluralin	Н		GCMS	0.034

¹C: Carbamate, D: Degradate, F: Fungicide, I: Insecticide, H: Herbicide, OC: Organochlorine, OP: Organophosphorus, Py: Pyrethroid, SE: Sulfite Ester, Sy: Synergist, WP: Wood Preservative.

² GCMS: Gas chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8270M. GCMS-H: Derivitizable acid herbicides by GCMS, EPA method (modified) SW 846 3535M/8270M.

LCMS\MS: Liquid chromatography/mass spectroscopy, EPA method (modified) SW 846 3535M/8321AM.

³2,4-D average LPQLs are artificially high due to one reporting limit of 6.2 ug/L; without this result the average LPQL was 0.064 ug/L.
Quality Assurance Samples

QA samples were collected each year to assure consistency and accuracy of sample analysis.

For this project, QA samples included field replicates, field blanks, and matrix spike and matrix spike duplicates (MS/MSD). QA samples for the laboratory included split sample duplicates, laboratory control samples, surrogate spikes, and method blanks.

In 2012, 14% of the field samples obtained was for QA. In 2012, QA samples included 30-31 field replicates for carbamates, herbicides, pesticide GCMS, and total suspended solids (TSS) each. QA also included 15 field blanks for each of the following: carbamates, herbicides, pesticide gas chromatography/mass spectroscopy (GCMS), and TSS. There were also 15 MS/MSD samples each for carbamates, herbicides, and pesticide GCMS.

Results for each QA sample method are outlined in the sections below.

Field Replicates

Results for pesticide field replicates are presented in Tables B-4 - B-6. Table B-5 presents the data value, data qualification (if assigned), and relative percent difference (RPD) between the results for compounds which were consistently identified in both the grab sample and replicate.

Table B-4. Pooled average RPD of consistent field replicate pairs by analysis type, including NJ and J qualified data, 2012.

	Pooled	Number of
Analysis	Average	Replicate
	RPD	Pairs
Herbicides	8.8%	47
Carbamates	13.0%	12
Pesticide GCMS	6.4%	41
TSS	7.6%	31

Consistent identification refers to compounds which were identified in both the original sample and field replicate. Inconsistently identified replicate pairs are those in which the compound was identified in one sample but not the other. Consistently identified grab sample replicates are presented in Table B-5.

During 2012, field replicate sampling frequency for pesticides and TSS was 7.5%. Precision between replicate pairs was calculated using RPD. The RPD is calculated by dividing the absolute value of the difference between the replicates by their mean, then multiplying by 100 for a percent value.

Excluding TSS, there were 100 consistently identified analytes and 25 inconsistently identified analytes detected in 125 replicate pairs. The average RPD for each of the analytical methods was excellent (Table B-4). Of the consistently identified replicate pairs, only two of the 100 consistently identified pairs exceeded the 40% RPD criterion (Table B-5). On April 23, 2012, a

replicate pair for pentachlorophenol had a RPD of 43%, and on May 16, a replicate pair for carbaryl had a RPD of 62%.

	1		1		· •
Parameter	Sample	Q	Replicate	Q	RPD
	0.054	J	0.042	J	25.0
	0.170		0.150		12.5
	0.350		0.320		9.0
	0.020	J	0.023	J	14.0
	0.035	J	0.041	J	15.8
	0.035	J	0.035	J	0.0
2,4-D	0.620		0.560		10.2
2,4-D	0.043	J	0.051	J	17.0
	0.018	J	0.020	J	10.5
	0.660		0.580		12.9
	0.020	NJ	0.018	J	10.5
	0.064	J	0.071	J	10.4
	0.014	J	0.014	J	0.0
			Me	an =	11.4
	0.019	J	0.019	J	0.0
4,4'-DDD	0.019	J	0.019	J	0.0
			Me	an =	0.0
	0.041	J	0.046	J	11.5
4,4'-DDE	0.022	J	0.026	J	16.7
		14.1			
	0.029	J	0.030	J	3.4
4,4'-DDT	0.020	J	0.020	J	0.0
		1.7			
4-Nitrophenol	0.095	NJ	0.081	an = NJ	15.9
Atrazine	0.052		0.040		26.1
	0.046	J	0.043	J	6.7
D	0.035	J	0.037	J	5.6
Bentazon	0.043	J	0.052	J	18.9
	Mean =				10.4
Bifenthrin	0.086	NJ	0.089	NJ	3.4
Bromoxynil	0.018	J	0.019	NJ	5.4
Carbaryl	0.051		0.027	J	61.5
Chlorpropham	0.880		0.910		3.4
Cycloate	0.034	NJ	0.030	NJ	12.5
Dacthal (DCPA)	0.020	J	0.026	J	26.1
	0.044		0.045		2.3
Diazinon	0.033	J	0.03	J	9.5
			Me	an =	5.9
	0.017	J	0.017	J	0.0
	0.033	J	0.033	J	0.0
		J	0.033	J	11.4
	0.037				
Dicamba	0.037	J	0.029	J	3.5
Dicamba		J J	0.029	J J	3.5 3.3
Dicamba	0.028				
Dicamba	0.028 0.030	J	0.031 0.023	J	3.3

Table B-5. Detected pairs within field replicate results (ug/L).

Diphenamid Diphenamid Endosulfan Sulfate Imidacloprid MCPA	0.120 0.017 0.016 0.040 0.039 0.017 0.009 0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.0051 0.025 0.008 0.030 0.030	J J J J J J J J J J J	0.13 0.02 0.016 0.039 0.039 0.017 0.009 0.009 M 0.028 0.013 0.141 0.029 0.057 0.028	J J J J ean= NJ J	8.0 16.2 0.0 2.5 0.0 0.0 0.0 0.0 3.6 7.4 2.2 14.8
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.016 0.040 0.039 0.017 0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030	J J J J J J	0.016 0.039 0.039 0.017 0.009 0.009 0.009 Mo 0.028 0.013 0.141 0.029 0.057	J J J ean= NJ	0.0 2.5 0.0 0.0 0.0 0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.040 0.039 0.017 0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030	J J J J	0.039 0.039 0.017 0.009 0.009 0.009 Mo 0.028 0.013 0.141 0.029 0.057	J J J ean= NJ	2.5 0.0 0.0 0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.039 0.017 0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030	J J NJ J	0.039 0.017 0.009 0.009 0.028 0.013 0.141 0.029 0.057	J J ean= NJ	0.0 0.0 0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.017 0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030	J J NJ J	0.017 0.009 0.009 0.028 0.013 0.141 0.029 0.057	J J ean= NJ	0.0 0.0 0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.009 0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030	J J NJ J	0.009 0.009 0.028 0.013 0.141 0.029 0.057	J J ean= NJ	0.0 0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.009 0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030 0.030	J NJ J	0.009 M 0.028 0.013 0.141 0.029 0.057	J ean= NJ	0.0 3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.029 0.014 0.138 0.025 0.051 0.025 0.008 0.030 0.030	NJ J	Mo 0.028 0.013 0.141 0.029 0.057	ean= NJ	3.6 7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.014 0.138 0.025 0.051 0.025 0.008 0.030 0.030	J	0.028 0.013 0.141 0.029 0.057	NJ	7.4 2.2
Diuron Endosulfan Sulfate Eptam Imidacloprid	0.014 0.138 0.025 0.051 0.025 0.008 0.030 0.030	J	0.013 0.141 0.029 0.057		2.2
Endosulfan Sulfate	0.138 0.025 0.051 0.025 0.008 0.030 0.030		0.141 0.029 0.057	J	
Endosulfan Sulfate	0.025 0.051 0.025 0.008 0.030 0.030	J	0.029 0.057		1/1 &
Endosulfan Sulfate	0.051 0.025 0.008 0.030 0.030	J	0.057		
Endosulfan Sulfate	0.025 0.008 0.030 0.030	J			11.1
Endosulfan Sulfate	0.008 0.030 0.030	J	0 0 2 8		11.3
Endosulfan Sulfate	0.030 0.030	J			22.2
Eptam	0.030		0.01		20.9
Eptam			0.037		6.9
Eptam	0.030		0.028		15.4
Eptam		J	0.035		7.4
Eptam				an =	12.5
Eptam	0.033		0.034		3.0
Imidacloprid	0.036	NJ	0.025	NJ	36.1
Imidacloprid			Me	an =	19.5
-	0.024	J	0.023	NJ	4.3
-	0.058		0.074		24.2
MCPA	0.017		0.016		6.1
МСРА			M	ean=	15.2
	0.016	J	0.016	J	0.0
	0.037	NJ	0.038	NJ	2.7
	0.013	NJ	0.014	NJ	7.4
	0.031	J	0.029	J	6.7
			Me	an =	4.2
	0.027	J	0.023	J	16.0
	0.015	NJ	0.017	NJ	12.5
МСРР	0.100		0.100		0.0
	0.014	NJ	0.015	NJ	6.9
	0.100		0.110		9.5
			Μ	ean=	9.0
Metolachlor	0.360		0.380		5.4
	0.030	J	0.030	J	0.0
	0.026	J	0.025	J	3.9
	0.054		0.058		7.1
	0.053		0.053		0.0
	0.047	NJ	0.051		8.2
	0.300		0.290		3.4
	0.028	J	0.026	J	7.4
	<u> </u>				
Norflurazon	0.031	NJ	0.031	NJ	0.0
	0.031	- 10	0.051	2.10	17.4
Pendimethalin	0.012	J	0.028	J	3.6
		I -	0.020 M	-	2.0

Parameter	Sample	Q	Replicate	Q	RPD
	0.017	J	0.011	J	42.9
	0.009	J	0.009	J	0.0
	0.099		0.099		0.0
Pentachlorophenol	0.008	J	0.008	J	0.0
	0.110		0.110		0.0
	0.022	NJ	0.021	NJ	4.7
	Mean=				7.9
Prometryn	0.011	J	0.009	J	20.0
Simazine	0.210		0.210		0.0
	0.140		0.130		7.4
Terbacil	0.230		0.250		8.3
			M	ean=	7.9
Treflan (Trifluralin)	0.014	J	0.014	J	0.0
	0.069		0.064	J	7.5
	0.140		0.130		7.4
	0.068		0.062	J	9.2
	0.077		0.099		25.0
Triclopyr	0.290		0.260		10.9
	0.011	J	0.011	NJ	0.0
	0.740		0.690		7.0
	0.013	NJ	0.011	NJ	16.7
			Μ	ean=	10.5

Of the inconsistently identified replicate pairs (compound was identified in one sample but was qualified as below reporting limits in the other sample, U or UJ), 21 out of 25 of the detected results were qualified as estimates (J) because they were below reporting limits. Four out of 25 of the detected results were just above the reporting limit (Table B-6). All data for these replicates are of acceptable data quality.

TSS was consistently detected in 31 replicate pairs. The average RPD of all replicates was 7.6%. A total of 87% of the replicates were within the 20% RPD criterion.

Parameter	Sample replicate result below detection limit	Detected replicate result	Result below reporting limit
2,4-D	0.066 U	0.017 NJ	Yes
	0.010 U	0.017	No
Carbaryl	0.010 U	0.011	No
	0.010 UJ	0.010 J	Yes
Cycloate	0.034 U	0.033 J	Yes
Diazinon	0.034 U	0.020 NJ	Yes
	0.062 U	0.022 NJ	Yes
Dicamba	0.065 U	0.021 NJ	Yes
	0.063 U	0.021 J	Yes
Dichlobenil	0.034 U	0.007 J	Yes
Diuron	0.010 U	0.009 J	Yes
Diuton	0.030 U	0.014 J	Yes
Imidacloprid	0.010 U	0.016	No
Linuron	0.020 U	0.006 J	Yes
LINUION	0.010 U	0.007 J	Yes
МСРР	0.062 U	0.032 J	Yes
MCPP	0.065 U	0.018 J	Yes
Metalaxyl	0.035 U	0.074 NJ	No
	0.064 U	0.022 J	Yes
Pentachlorophenol	0.065 U	0.019 J	Yes
	0.066 U	0.018 J	Yes
Treflan (Trifluralin)	0.033 U	0.026 J	Yes
	0.066 U	0.013 NJ	Yes
Triclopyr	0.063 U	0.013 NJ	Yes
	0.063 U	0.008 NJ	Yes

Table B-6. Inconsistent field replicate detections (ug/L), 2012.

Laboratory Duplicates

MEL used laboratory split sample duplicates to ensure consistency of TSS analyses. In 2012, there were 128 laboratory replicate pairs. The pooled average RPD was 5.1%; the maximum RPD was 40%. Three out of 128 replicate pairs exceeded the 20% RPD criterion. For these replicates, results were low, and the RPD statistic has limited effectiveness in assessing variability at low levels (Mathieu, 2006).

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 2012, there were no field blank detections for the pesticide analysis. There was one TSS field blank detection of 2 mg/L on March 20, 2012 for the Sulphur Creek Wasteway site. The reporting limit for TSS was 1 mg/L. For March 20, 2012, at the lower Yakima sites, all TSS values analyzed that are less than 6 mg/L will be qualified as estimates.

Laboratory Blanks

MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. If lab blank detections occur, the sample LPQL may be increased, and detections may be qualified as estimates. For 2012, there were no laboratory blank detections reported.

Surrogates

Surrogates are compounds that are spiked into field samples at the laboratory. They are used to check recovery for a group of compounds. For instance, triphenyl phosphate is a surrogate for organophosphorus insecticides (Table B-7).

Surrogate Compound	Surrogate for			
2,4,6-tribromophenol	Acid-derivitizable herbicides			
2,4-dichlorophenylacetic acid	Acid-derivitizable herbicides			
Carbaryl C13	Carbamate pesticides			
4,4'-DDE-13C12	Chloringtod postigidas			
Decachlorobiphenyl (DCB)	Chlorinated pesticides			
Atrazine-D5	Chlorinated and nitrogen pesticides			
1,3-dimethyl-2-nitrobenzene	Nitrogan pastiaidas			
Trifluralin-D-14	Nitrogen pesticides			
Chlorpyrifos-D10	Organophosphorus posticidas			
Triphenyl phosphate	Organophosphorus pesticides			

Table B-7. Pesticide surrogates.

The majority of 2012 surrogate recoveries fell within the QC limits established by MEL for all compounds. The percentage of time a surrogate recovery did not meet the QC limits is described in Table 8. High pesticide surrogate recovery requires related detections to be qualified as estimates. Low pesticide surrogate recovery requires all related data to be qualified as estimates (qualified with a 'J').

Surrogate compound	Surrogate for	Percentage of surrogate compound results that did not meet surrogate recovery targets
2,4,6-tribromophenol 2,4-dichlorophenylacetic acid	Acid-derivitizable herbicides	0.5%
Carbaryl C13	Carbamate pesticides	3.5%
4,4'-DDE-13C12 Decachlorobiphenyl (DCB)	Chlorinated pesticides	1.3% 0.4%
Atrazine-D5	Chlorinated and nitrogen pesticides	0.2%
1,3-dimethyl-2-nitrobenzene Trifluralin-D-14	Nitrogen pesticides	0.4%
Chlorpyrifos-D10 Triphenyl phosphate	Organophosphorus pesticides	0.2% 3.8%

Table B-8. Percentage of surrogate compound results that did not meet data quality control limits, 2012.

Matrix Spike/Matrix Spike Duplicates (MS/MSD)

MS/MSD results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. This measure is the best overall indicator of accuracy and reproducibility of the entire sampling process.

Table B-9 presents the mean, minimum, and maximum percent recovery for the MS/MSD for the three types of analysis as well as the RPD between for the MS/MSD for 2012.

Table B-9. Mean, minimum, and maximum percent recovery for MS/MSD and MS/MSD RPD, 2012.

Analysis	MS\MSD Recovery]	RPD for MS\M	SD
Analysis	Mean	Minimum	Maximum	Mean	Minimum	Maximum
LCMS\MS	104%	36%	214%	12%	0%	73%
GCMS-Herbicides	85%	0%	318%	11%	0%	110%
GCMS-Pesticides	98%	0%	262%	7%	0%	200%

The MS\MSD percent recoveries were good for all three types of analysis. The percent recoveries that fell within the target range were:

- LCMS\MS analysis: 88% fell within the 40-130% target recovery range.
- GCMS-Herbicide analysis: 92% fell within the 40-130% target recovery range.
- GCMS-Pesticide analysis: 96% fell within the target recovery range.

Analytes that did not meet the target recovery range and the percentage of time this occurred are described in Table B-10. During 2012, there were no detections of 1-naphthol, 2,4,6-trichlorophenol, acifluorfen, aldicarb or aldicarb sulfone, aldicarb sulfoxide, beta-BHC, diclofopmethyl, dieldrin, dinoseb, EPN, ethion, fenvalerate, methiocarb, methomyl oxime, neburon, oxamyl oxime, oxyfluorfen, promecarb, propargite, resmethrin, and sulfotepp. If there were detections of analytes that did not meet MS/MSD target recoveries, analyte results for that day were qualified as estimates (qualified with a 'J').

Analysis	Analyte	Percentage of samples outside target limits	Fell below or exceeded target limits?	Pesticide detected in 2012?
	aldicarb	6.8%	Exceeded	No
	aldicarb sulfone	70%	Exceeded	No
	aldicarb sulfoxide	50%	Exceeded	No
	carbaryl	3%	Exceeded	Yes
LCMS\MS	diuron	7%	Exceeded	Yes
	imidacloprid	17%	Exceeded	Yes
	linuron	23%	Exceeded	Yes
	methiocarb	13%	Exceeded	No
	Methomyl oxime	10%	Exceeded	No
	neburon	10%	Both	No
	oxamyl oxime	13%	Exceeded	No
	promecarb	7%	Exceeded	No
	2,4,6-Trichlorophenol	14%	Exceeded	No
	4-nitrophenol	14%	Fell below	Yes
	acifluorfen	75%	Both	No
GCMS-Herbicides	clopyralid	32%	Fell below	Yes
	diclofop-methyl	75%	Exceeded	No
	dinoseb	50%	Both	No
	picloram	93%	Fell below	Yes
	1-naphthol	66%	Exceeded	No
	beta-BHC	11%	Fell below	No
	dieldrin	11%	Fell below	No
	endosulfan	3%	Fell below	Yes
	EPN	10%	Exceeded	No
	ethion	20%	Exceeded	No
GCMS-Pesticides	fenvalerate	29%	Exceeded	No
	metribuzin	72%	Exceeded	Yes
	monocrotophos	6%	Exceeded	Yes
	oxyfluorfen	6%	Exceeded	No
	propargite	93%	Fell below	No
	resmethrin	33%	Fell below	No
	sulfotepp	10%	Exceeded	No

Table B-10. Analytes outside of target limits and percentage of time this occurred, 2012.

Laboratory Control Samples

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. Detections may be qualified based on low recovery and/or high RPD between the paired LCS and LCS duplicate.

Table B-11 presents the mean, minimum, and maximum percent recovery for the LCS and LCS duplicate for the three types of analysis, as well as the RPD between the LCS and the paired LCS duplicate for 2012.

Table B-11. Mean, minimum, and maximum percent recovery for LCS and LCS duplicate and the LCS and LCS duplicate RPD.

Amalausia	LCS Recovery			% RPD for LCS\LCSD		
Analysis	Mean	Minimum	Maximum	Mean	Minimum	Maximum
LCMS\MS	100%	32%	199%	12%	0%	84%
GCMS-Herbicides	79%	0%	207%	18%	0%	200%
GCMS-Pesticides	96%	0%	275%	8%	0%	83%

The LCS and LCS duplicate percent recoveries were good for all three types of analysis. The percent recoveries that fell within the target range were:

- LCMS\MS analysis: 91% fell within the 40-130% target recovery range.
- GCMS-Herbicide analysis: 92.5% fell within the 40-130% target recovery range.
- GCMS-Pesticide analysis: 91% fell within the target recovery range.

Analytes that did not meet the target recovery range and the percentage of time this occurred are described in Table B-12. For the analytes that did not meet target ranges in 2012, the following analytes were not detected: 1-naphthol, 2,4,5-T, 2,4,6-trichlorophenol, aldicarb, aldicarb sulfoxide, diclofop-methyl, dinoseb, ethion, fenamiphos, fenvalerate, fluridone, methomyl oxime, napropamide, neburon, and oxamyl oxime, phenothrin, propargite, and resmethrin. If there were detections of analytes that did not meet LCS and paired LCS target recoveries, analyte results for that day were qualified as estimates.

Analysis	Analyte	Percentage of samples outside target limits	Fell below or exceeded target limits?	Pesticide detected in 2012?
	Aldicarb	10%	Both	No
	Aldicarb sulfone	49%	Exceeded	No
	Aldicarb sulfoxide	62%	Exceeded	No
	imidacloprid	3%	Exceeded	Yes
LCMS\MS	linuron	21%	Exceeded	Yes
	Methomyl oxime	5%	Exceeded	No
	neburon	3%	Exceeded	No
	Oxamyl	5%	Both	Yes
	Oxamyl oxime	10%	Exceeded	No
	2,4,5-T	10%	Fell below	No
	2,4,6-Trichlorophenol	7%	Exceeded	No
	2,4-D	15%	Fell below	Yes
	4-nitrophenol	2%	Fell below	Yes
CCMC Hashiaidan	acifluorfen	42%	Both	No
GCMS-Herbicides	clopyralid	5%	Fell below	Yes
	diclofop-methyl	54%	Exceeded	No
	dinoseb	24%	Both	No
	МСРА	2%	Fell below	Yes
	picloram	42%	Fell below	Yes
	1-naphthol	23%	Exceeded	No
	Endosulfan I and II	3%	Fell below	Yes
	Endosulfan sulfate	3%	Fell below	Yes
	ethion	6%	Exceeded	No
	fenamiphos	35%	Fell below	No
	fenvalerate	40%	Exceeded	No
	fluridone	5%	Exceeded	No
	malathion	3%	Fell below	Yes
GCMS-Pesticides	metribuzin	65%	Exceeded	No
	monocrotophos	3%	Exceeded	Yes
	napropamide	5%	Exceeded	No
	norflurazon	10%	Exceeded	Yes
	phenothrin	5%	Exceeded	No
	propargite	40%	Fell below	No
	resmethrin	40%	Fell below	No
	simazine	5%	Fell below	Yes
	tebuthiuron	22%	Exceeded	Yes

Table B-12. LCS and paired LCS analytes outside of target limits and percentage of time this occurred, 2012.

Field Data Quality

Quality Control Procedures

Field meters were calibrated at the beginning of the field day according to manufacturers' specifications, using Ecology SOP EAP033 *Standard Operating Procedure for Hydrolab DataSonde*® *and MiniSonde*® *Multiprobes* (Swanson, 2010). Field meters were post-checked at the end of the field day using known standards. Dissolved oxygen (DO) meter results were compared to results from grab samples analyzed using the Winkler laboratory titration method. DO grab samples and Winkler titrations were collected and analyzed according to the SOP (Ward, 2007). Two to three Winkler grab samples were obtained during each sample week. Measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler DO comparisons are described in Anderson and Sargeant (2009).

2012 Field Data Quality Results

The Hydrolab field meter for the Lower Yakima and Wenatchee-Entiat (eastern Washington) sites met MQOs including post-checks and Winkler comparisons (Table B-13) with the following exceptions:

• On August 6 and 8, 2012, Hydrolab field meter and Winkler DO values did not meet MQOs. Hydrolab field meter results for these days are qualified as estimates.

The Hydrolab field meter for the urban sites and the Lower Skagit-Samish (western Washington) sites met all QC objectives including post-checks and Winkler comparisons (Table 13) with the following exceptions:

- On April 17, 2012, conductivity did not meet the MQOs for the Hydrolab field meter postcheck. Conductivity results for this day will be qualified as estimates.
- On June 19, 2012, pH did not meet the MQOs for the Hydrolab field meter post-check. pH results for this day will be qualified as estimates.
- On August 10, 2012, Hydrolab field meter and the Winkler DO value for Longfellow Creek did not meet MQOs. All other meter and Winkler DO values for the day met MQOs. Only Longfellow Creek meter results for August 10, 2012 will be qualified as an estimate.

Replicate Meter Parameter	Western W Sit	ashington / ashington	Eastern Washington Sites	
· · · · · · · · · · · · · · · · · · ·	Average	Maximum	Average	Maximum
Winkler and meter DO	1.2%	4.2%	1.2%	4.6%
Replicate Winkler's for DO	0.4%	1.6%	0.1%	0.6%
Meter flow	2.6%	15.9%	3.1%	17.8%

Table B-13. Quality control results (%RSD) for field meter and Winkler replicates, 2012.

DO: dissolved oxygen.

For 2012 flow replicates, two replicate flows exceeded MQOs: one flow on Brender Creek and one at the upstream Big Ditch site. Both of these flow replicates occurred during low-flow conditions when the percent RSD statistic produces higher variability (Mathieu, 2006). Flow results for these days are acceptable.

2012 Field Audit

The purpose of the field audit is to ensure that sampling methodologies are consistent. For field audits, both the western and eastern Washington field teams met at a surface water location to measure Hydrolab field parameters and flow and to obtain samples for measuring Winkler DO. Results and methods are compared to ensure that field teams are using consistent sampling methodologies that result in comparable data.

On April 23, 2012, a field audit was conducted at Thornton Creek in King County. Both sampling teams met at the Department of Ecology Operations Center (OC) in Lacey to calibrate field meters before sampling. Meters were calibrated successfully. Both teams met at the Thornton Creek sample site to perform the field audit simultaneously. Results are described in Table B-14.

Meter or Method	Temp (°C)	pH (s.u.)	Conductivity (uS/cm)	DO (mg/L)	DO (% sat)
Western Washington Hydrolab Meter	11.79	8.06	236.6	10.77	100.2
Eastern Washington Hydrolab Meter	11.77	7.96	232.6	10.76	100.4
Winkler Dissolved Oxygen (Western Washington)	-	-	-	10.6/10.65	-
Winkler Dissolved Oxygen (Eastern Washington)	-	-	-	10.5/10.5	-
	Discharg	ge (cfs)			
Flow Discharge Results	Western Washington meter	Eastern Washington Meter			
Marsh McBirney Flow Meter	7.24	7.48			

Table B-14. Hydrolab meter readings, flow measurements, and Winkler results for dissolved oxygen from the field audit at Thornton Creek, April 23, 2012.

cfs: cubic feet per second .

All replicate meter results were acceptable based on the MQOs described in Anderson and Sargeant (2009). Post-checks of both meters were performed after the field audit. Post checks of both the Hydrolab meters met MQOs for all parameters.

Appendix C. Assessment Criteria and Water Quality Standards

EPA pesticide assessment documents were reviewed to determine the most comparable and up-to-date toxicity guidelines for freshwater (Table C-1) and marine species (Table C-2).

EPA Toxicity Criteria

Rainbow trout (*Oncorhynchus mykiss*) are a surrogate for freshwater endangered and threatened species. *Daphnia magna* (invertebrate) and *Pseudokirchneria subcapitata* (green algae formerly called *Selenastrum capricornutum*) represent components of the aquatic food web that may be affected by pesticide use. Alternative species are used only if no data are available for rainbow trout, *Daphnia magna*, or *Pseudokirchneria subcapitata*.

Marine toxicity criteria were evaluated for detections at Browns Slough in the Skagit watershed, a site with estuarine influence. Criteria were generated for marine species including (1) sheepshead minnow (*Cyprinodon variegatus*) and tidewater silverside (*Menidia beryllina*) for fish; (2) Pink shrimp (*Penaeus duorarum*), Eastern and Pacific Oysters (*Crassostrea virginica and gigas* respectively), Grass shrimp (*Palaemonetes pugio*), *Acartia tonsa* (copepod), and mysid (*Americamysis bahia*) for invertebrates; and (3) *Isochrysis galbana*, and a diatom, *Skeletonema costatum*.

EPA classifies a laboratory study as 'core' if it meets guidelines appropriate for inclusion in pesticide registration. Usually a core designation may be made if the study is appropriately designed, monitored, and conditions controlled, and duration of exposure is consistent with other studies. Core study criteria are used in the assessment table. Keeping with pesticide review precedent, the most toxic, acceptable criteria from core studies are used.

Water Quality Standards and Assessment Criteria

The most recent versions of Washington State water quality standards and EPA National Recommended Water Quality Criteria (NRWQC) were applied for this report. The NRWQC remained largely unchanged from the 2003 update through 2008.

The toxic standards for Washington State waters were also used. These remain essentially unchanged following the 1997 rule and 2003 updates (Washington Administrative Code (WAC), Chapter 173-201A).

				1 _{Encol}			:		Cuitan	. .				Freekrow	Ctor Jon Jr	and Criteria			m Conc.
Chemical			Fisheri		iwater .	TOXICOLOG	Invert	egistratio	I Criter		D	lant			ter Standards VAC		WOC	Limit for	S Biop
Chemicai	Acute	Chronic	ESLOC	es Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC		Acute	Ref.
1-Naphthol	1400	100	70	~ FF . RT-A; FM-C	10	700		DM	10	1100		SC	10						
2,4,6-Trichlorophenol				í í															
2,4-D (Acids, Salts, Amines) ^m	101000	14200	5050	RT; FM	1	25000	16050	DM	1	3880	1440	ND	1					100	91
2,4-D (BEE Ester) ^m	428		21.4	BS	1	4970	200	DM	1	1020	538	ND	1					100	91
2,4'-DDD														1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
2,4'-DDE														1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
2,4'-DDT														1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
3,5-Dichlorobenzoic Acid																			
	362	5.7	18.1	RT	54: 60	2.23	0.75	CD	54										
3-Hydroxycarbofuran	88		4.4	BS	54	29	9.8/27	DM	60				1				1		
4,4'-DDD	~~						,		<u> </u>				1	1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
4,4'-DDE													1	1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
4,4'-DDT														1.1 ^{a,b}	0.001 ^{a,c}	1.1 ^a	0.001 ^a		
4-Nitrophenol	4000		200	RT	69	5000		DM	69						0.001		0.001		
Acetochlor	380	130	19	RT	70	8200	22.10	DM	70	1.43		SC	70						
Alachlor	1800	130	90	RT	2	7700	110	DM	2	1.64	0.35	SC	2						
Aldicarb	52	0.46	2.6	BS	3	20	3	CT	3	>5000	0.55	MD	3						
Aldicarb Sulfone	42000	0.40	2100	RT	3	280	3	DM	3	>5000		MD	5						
Aldicarb Sulfoxide	7140		357	RT	3	43	3	DM	3				-						
Atrazine	5300	65	265	RT-A; BT-C	4	3500	140	DM	4	49		SC	4						
Azinphos Ethyl	20	0.5	1	RT-A, BI-C	71	4	140	DM	71	49		30	4						
Azilipilos Edityi	2.9	0.44	0.145	RT	5	1.13	0.25	DM	5				-				0.01		90
Azinphos Methyl	3.2	0.44	0.145	Coho	5	1.15	0.25	Divi	5				-				0.01		,0
Pantazon	>100000		>5000	RT	6	>100000		DM	6	4500		SC	6						
Bentazon Bifenthrin	0.15	0.04	0.0075	RT-A; FM-C	72	1.6	0.0013	DM	72	4500		<u>sc</u>	0						
	36000	3000	1800	RT-A; FM-C	7		8200	DM	7	6.8	1100	SC	7						
Bromacil	50	<u> </u>	2.5	RT-A; FM-C		121000		DM	8		1100	SC SC	83						
Bromoxynil	26.2	9	1.31	BrT-A; FM-C	8 73	11 8400	2.5 560	DM	73	80 1770		SC SC	73						91
Captan				,				DM			270	SC SC							89
	1200	210	60 120	RT-A; FM-C	9,10	5.6	1.5	DM	10	1100	370	SC	10						89
Carbaryl	2400		-	Chinook	9,10														
	2400	67	120	Coho	9,10	2.22		CD	54				-						00
Carbofuran	362	5.7	18.1	RT	54; 60	2.23	0.0	CD	54				-						89
Cashaarin	88		4.4	BS	54	29	9.8	DM	60	270	110	80	74						
Carboxin Chlamathalamil	2300		115	RT DT. EM	74	84400	20	DM	74	370	110	SC	74					1.05	01
Chlorothalonil	42.3	3	2.115	RT; FM	46	68	39	DM	46	190		SC	46				<u> </u>	1.05	91
Chlorpropham	5700	0.57	285	RT	47	3700	770	DM	47				+	0.002.1	0.041	0.002	0.041	1 100	00
Chlorpyrifos	3	0.57	0.15	RT; FM	11; 12	0.1	0.04	DM	11				+	0.083d	0.041e	0.083	0.041	1.122	88
	5	0.56	0.25	RT	58	1.04	0.039	DM	58				+						├───┤
cis-Permethrin ⁿ	17	1.11	0.85	Coho	58								+						├───┤
	0.79	0.30	0.0395	BS-A; FM-C	58	112000	NT/ 4	DM	64	(000		60	- 4						├───┤
Clopyralid	1968000	N/A	98400	BS	64	113000	N/A	DM	64	6900		SC	64				ł	+	\mid
Cycloate	4500	27/4	225	RT	87	24000	27/4	DM	87	10000		80					ł	+	\mid
DCPA	6600	N/A	330	RT	56	27000	N/A	DM	56	>12380		SC	56				l		└───┤
DDVP	183	5.2	9.15	LT-A;RT-C	75	0.07	0.0058	DM	75	14000		ND	75				l		
Di-allate (Avadex)	no criteri	a tound																	

Table C 1	Enchryston to visity	and manulatomy	and deline velues	All values reported in ug/I
Table C-L.	Freshwaler loxicity	and regulatory	guidenne values.	All values reported in ug/L.
			0	

				¹ Fres	hwater '	Foxicolog	ical and R	egistration	Criter	ria				Freshwater	Standards a	nd Criteria	·	Lim	ım Conc. iit for mon
Chemical			Fisherie	s			Inverte	brate			P	lant		W	AC	NRV	VOC	NMF	S Biop
	Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC	Acute	Ref.
Diazinon	90	0.8	4.5	RT; BT	13; 14	0.8	0.17	DM	13	3700		SC	13			0.17	0.17	1.122	88
Dicamba I	28000		1400	RT	15	34600	16400	DM	15	>3700	3700	SC	15						
Dichlobenil	4930	330	247	RT	16; 17	6200	560	DM	17	1500	160	SC	17						
Dichlorprop	214000	14700	10700	RT	76	558000	74900	DM	76	77	13	NP	76						
Dimethoate	6200	430	310	RT	29	3320	40	DM	29	36000		SC	29					60	90
Dinoseb																			
Diphenamid	97000		4850	RT	59	58000		DM	59										
Disulfoton (Di-Systo	1850	220	92.5	RT	19	13	0.037	DM	19										90
Disulfoton Sulfone	9200		460	RT	19	35	0.14	DM	19										
Disulfoton Sulfoxide	60000		3000	RT	19	64	1.53	DM	19										
Diuron	1950	26.4	97.5	RT-A; FM-C	21, 22	1400	200	DM	21, 22	2.4		SC	21, 22					5	91
Diuron	2400		120	Coho	21, 22														
Endosulfan I	0.8	0.1	0.04	RT	23	166	2	DM	23					0.22 ^{b,t}	0.056 ^{c,t}	0.22 ¹	0.056 ¹		
Endosulfan II	0.8	0.1	0.04	RT	23	166	2	DM	23					0.22 ^{b,f}	0.056 ^{c,t}	0.22 ⁱ	0.056 ⁱ		
Endosulfan Sulfate	3.6		0.18	BS	82	580		DM	23										
Endrin Aldehyde																			
EPN	143		7.15	RT	84														
Eptam (EPTC)	14000		700	BS	24	6500	810	DM	24	1400	900	SC	24						
Ethoprop	1020	180	51	RT; FM	25	44	0.8	DM	25									20	90
Fenamiphos	68	3.8	3.4	RT	77	1.3	0.12	DM	77										90
Fenarimol	2100	870	105	RT	67	6800	113	DM	67		100	SC	67						
Fipronil	246	6.6	12.3	RT	78	190	9.8	DM	78	140	<140	SC	78						
Fipronil Sulfide (MB4	83	6.6	4.15	ND	78	100	0.11	M-A; ND-	78	140	<140	ND							
Fipronil Sulfone (MB	39	0.67	1.95	RT-A; ND-C	78	29	0.037	M-A; ND-	78	140	<140	ND							
TT 11 1	30	3.68	1.5	RT	26	30	16	DM	26	30		SC	26						
Hexachlorobenzene	50000		2500	Coho	26														
	180000	17000	9000	RT; FM	27; 28	151600	20000	DM	27	7	4	SC	27						
	317000		15850	Chinook	27														
Hexazinone	246000		12300	Coho	27														
	317000		15850	Sockeye	27														
Imidacloprid	>83000	1200	>4150	RT	61	69	1300	T-A; DM-	61	10000		ND	61						
Imidian (Phosmet)	230	3	11.5	RT	79	6	0.8	DM	79	150		SC	79						
Ioxynil																			
Linuron	3000	5.58	150	RT	48	120	0.09	DM	48	67		SC	49						91
Malathian	4.1	21	0.205	RT	31	1	0.06	DM	31								0.1	1.122	88
Malathion	170		8.5	Coho	31														
MCPA Acid or Ester										950	9	SC	32						
MCPP salt and ester	124800	N/A	6240	RT	65	100000		DM	65										
Metalaxyl	18400	9100	920	RT-A; FM-C	51	12000	1270	DM	51	140000		SC	51						
Methiocarb	436	50	21.8	ND	30	7	0.1	ND	30										
Methomyl	860	57	43	RT-A; FM-C	57	5	0.7	DM	57										89
Methomyl Oxime																			
Metolachlor	3800	2500	190	RT	33	1100	1	DM	33	8	1.5	SC	33						
Metribuzin	42000	3000	2100	RT	52	4200	1290	DM	52	11.9	8.9	NP	52						
Monocrotophos																			
Monuron																			

Table C-1 (continued). Freshwater toxicity and regulatory guideline values. All values reported in ug/L

				¹ Fres	hwater '	Foxicolog	ical and Re	egistration	Criter	ia				Freshwater S	tandards and	l Criteria		Lim	ım Conc. iit for mon
Chemical			Fisherie	s			Inverte	brate			P	Plant		WA	C	NRW	VQC	NMF	S Biop
	Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC	Acute	Ref.
Napropamide	6400	1100	320	RT	80	14300	1100	DM	80	3400	71	SC-A, LM-C	80						
Norflurazon	8100	770	405	RT	34	15000	1000	DM	34	9.7	3.2	SC	34						
Oryzalin	3260	>460	163	RT	85	1500	358	DM	85	52	13.8	SC	85					10	92
Oxamyl	4200	770	210	RT	62	420	27	DM	62	120	30000	SC	62						
Oxamyl Oxime																			
Oxyfluorfen	250	38	12.5	RT-A; FM-C	35	80	13	DM	35	0.29	0.1	SC	35						
Pendimethalin	138	6.3	6.9	RT-A; FM-C	37	280	14.5	DM	37	5.4	3	SC	37					1	92
Pentachlorophenol	15	11	0.75	RT	38	450	240	DM	38	50		SC	38	8.2 to 41.0 ^{d,g}	5.2-25.9 ^{e,h}	7.9-107.6 ^j	6.1-82.6 ^k		
Phorate O.A.																			
Picloram	5500	N/A	275	RT	53	34400	N/A	DM	53										
Piperonyl butoxide	1900	40	95	RT	81	510	30	DM	81										
Promecarb																			
Prometon	12000	9500	600	RT-A; FM-C	68	25700	3500	DM	68	98	32	SC	68						
Pronamide (Kerb)	72000	7700	3600	RT	66	5600	600	DM	66	4000	390	AF	66						
Propargite	118	16	5.9	RT-A; FM-C	40	74	9	DM	40	66.2	5	SC	40						
Propazine		720		FM-C	20	5320	47	DM	20	29	12	SC	20						
Propoxur	3700		185	RT	63	11		DM	63										
Ronnel																			
Simazine	40500	2500	2025	RT	36, 41	1000		DM	41	36	5.4	SC	36						
Simetryn																			
Tebuthiuron	143000	26000	7150	RT	42	297000	21800	DM	42	50	13	SC	42						
Terbacil	46220	1200	2310	RT	43	65000	640	DM	43	11	7	NP	43						
Triadimefon	4100	41	205	RT	55	1600	52	DM	55	1710	100	SC	55						
Triclopyr	1900	19	95	RT	44	13400	25000	DM	44	2300	2	SC-A; NP-C	44						91
Trifluralin	43.6	2.18	2.18	RT	45	251	2.4	DM	45	7.52	5.37	SC	45					1	92

Table C-1 (continued). Freshwater toxicity and regulatory guideline values. All values reported in ug/L

*Values are not analytically qualified. Non-asterisk values have been J-qualified as estimates, normally below the practical quantitation limit.

¹Criteria identified in EPA reregistration and review documents or peer reviewed literature. References listed separately.

Time component of standards are explained in body of report.

ESLOC refers to Endangered Species Level of Concern: A refers to acute, and C refers to chronic.

Fish species abbreviated in table: BS-Bluegill Sunfish; BT-Brook Trout, BrT-Brown Trout, Coho-Coho Salmon, Chinook-Chinook salmon, FM- Fathead Minnow, LT-Lake Trout, RT-Rainbow Trout, ND-Not Described, Sockeye-Sockeye Salmon.

Invertebrate species abbreviated in table: CD-Ceriodaphnia dubia, CT-Chironomus tentans (midge), DM-Daphnia magna, ND-Not Described

Plant species abbreviated in table: AF-Anabaena flos-aquae, LM-Lemma minor, MD-marine diatom, NP-Navicula pelliculosa, ND-Not Described, SC-Pseudokirchneriella subcapitata formerly Selenastrum capricornutum (aka; Pseudokirchneria subcapitata),

²WAC: Promulgated standards according to Chapter 173-201A WAC.

³EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

(continued on next page)

a-Criteria applies to DDT and its metabolites (Σ DDT).

b-An instantaneous concentration not to be exceeded at any time.

c-A 24-hour average not to be exceeded.

d-A 1-hour average concentration not to be exceeded more than once every three years on average.

e-A 4-day average concentration not to be exceeded more than once every three years on average.

f-Chemical form of endosulfan is not defined in WAC 173-201A. Endosulfan sulfate may be applied in this instance.

 $g \le e[1.005(pH)-4.830]$, pH range of 6.9 to 9.5 shown.

 $h{\leq}\,e[1.005(pH){\text{-}}5.29],\,pH$ range of 6.9 to 9.5 shown.

i-Value refers to $\sum \alpha$ and β -endosulfan.

 $j \le e[1.005(pH)-4.869]$, pH range of 6.9 to 9.5 shown.

 $k \le e[1.005(pH)\text{-}5.134], pH$ range of 6.9 to 9.5 shown.

m-There are many forms of 2,4-D that include acids, salts, amines, and esters all of which have unique toxicity values. The criteria presented are in acid equivalents and are intended to provide a range of possible effects. Toxicity values for each form of 2,4-D are available in the referenced document.

n-Assessment criteria for permethrin are based on a formulation of cis and trans-permethrin isomers. Manchester Laboratory analysis includes only the cis-permethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for permethrin.

	EPA Marine Toxicological and Registration Criteria Fisheries Plant Acute Chronic Spp. Ref Acute Chronic Spp.														ine Standar	ds and C	riterion
Chemical	Fisheries Invertebrate Plant Acute Chronic ESLOC Spp. Ref Acute Chronic Spp. Ref Acute Chronic Spp. Ref Acute Chronic Spp. Ref Acute Chronic Spp. I <th>WAC</th> <th></th> <th>RWQC</th>														WAC		RWQC
	Acute			Spp.	Ref	Acute			Ref	Acute		Spp.	Ref		Chronic	CMC	CCC
1-Naphthol	1200		60		10	200			10								
•	>80,000																
2,4-D (Acids, Salts, Amines) ^m	(175,000																
	definitive)		4000	TS	1	57000		EO	1								
4-Nitrophenol																	
Aldicarb Sulfone																	
Aldicarb Sulfoxide																	
Atrazine	2000	1100	100	SM	4	94	100	AT-A; PO-C	4	22		IG	4				
Bentazon	136		6.8	SM	6	>132.5; >109		PS; EO	6								
Bromoxynil	170		8.5	SM	8	65		MS	8	140		SkC	83				
Captan																	
	2600		130	SM	9,10	5.7		MS	10								
Carbaryl	250		12.5	AS	9,10												
Carbofuran	33	2.6	1.65	AS-A; SM-C	54	4.6	0.4	PS-A; MS-C	54								
Chlorpropham				ĺ ĺ													
Chlorpyrifos	270	0.28	13.5	SM-A; AS-C	11	0.035	< 0.0046	MS	11					0.011 ^c	0.0056 ^d	0.011 ^G	0.0056 ^G
Cycloate																	
DCPA	>1000		50	SM	56	620		EO	56	>11000		SkC	56				
Diazinon	150	< 0.47	7.5	SM	14	25	0.23	MS	14							0.82	0.82
Dicamba I	>180000		>9000	SM	15												
	14000		700	SM	16	1630		EO	16								
Dichlobenil						>1000		PS	16								
Dimethoate	111000		5550	SM	18	15000		MS	18								
Diuron	6700	440	335	SM	21	4900	270	EO-A; MS-C	21								
Endosulfan Sulfate	3.1		0.155	SM	82		0.38	MS	82								
Eptam																	
Imidacloprid	163000		8150	SM	61	37	0.6	MS	61								
MCPA Acid or Ester	179000		8950	AS	32	150000	115000	EO	32	300	15	SkC	32				
MCPP salt and ester (Mecoprop)																	
						5980		MS	51								
Metalaxyl						4400		EO	51	1							
Mathemat	1160	260	58	SM	50	>140000;		EO	50								
Methomyl						230	29	MS	50								
Metolachlor	9800	3600	490	SM	33	1600	700	EO	33	61	1.7	SkC	33				
	85000		4250	SM	52	42000		EO	52	8.7	5.8	SkC	52			1	
Metribuzin						48300		PS	52								
Norflurazon																	
Oxamyl	2600		130	SM	62	400		EO	62								
Pentachlorophenol	240	64	12	SM	38	48		PO	38	27		SkC	38	13.0 ^c	7.9 ^d		
Simazine	>4300		215	SM	41	113000; >3700		PS-A; EO-C	41	600	250	SkC	36				

Table C-2. Marine toxicity and regulatory guideline values for the Browns Slough site. All values are reported in ug/L.

		·		EPA N	Marine	e Toxicological ar	nd Registra	tion Criteria					0 	Mari	ne Standar	ds and C	riterion
Chemical		1	Fisheries				Invertebra	ate			Plant			² V	VAC	³ NF	WQC
	Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
Tebuthiuron						180000		EO	42	31	50	SkC	42				
rebuthluron						62000		PS	42								
Terbacil	108500	2800	5425	SM	43	4900		EO	43								
Triclopyr	130000		6500	TS	86	58000		EO	86	6700	400	SkC	86				
Trifluralin	240	1.3	12	SM	45	136	138	MS-A; GS-C	45	28	4.6	SkC	45				

Table C-2 (continued). Marine toxicity and regulatory guideline values for the Browns Slough site. All values are reported in ug/L.

*Values are not analytically qualified. Non-asterisk values have been J-qualified as estimates, normally below the practical quantitation limit.

¹Criteria identified in EPA reregistration and review documents or peer reviewed literature. References listed separately.

Time component of standards are explained in body of report.

ESLOC refers to Endangered Species Level of Concern: A refers to acute, and C refers to chronic.

Fish species abbreviated in table: AS-Atlantic silverside, ND-Not Described, SM-Sheepshead Minnow, TS-Tidewater silverside.

Invertebrate species abbreviated in table: AT-Acartia tonsa (copepod), EO-Eastern Oyster, GS-Grass Shrimp, MS-Mysid shrimp, ND-Not Described, PO-Pacific Oyster, PS-Pink Shrimp.

Plant species abbreviated in table: IG-Isochrysis galbana, SkC-Skeletonema costatum

² WAC: Promulgated standards according to Chapter 173-201A WAC.

³ EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

a-Criteria applies to DDT and its metabolites (Σ DDT).

b-An instantaneous concentration not to be exceeded at any time.

c-A 24-hour average not to be exceeded.

d-A 1-hour average concentration not to be exceeded more than once every three years on average.

e-A 4-day average concentration not to be exceeded more than once every three years on average.

f-Chemical form of endosulfan is not defined in WAC 173-201A. Endosulfan sulfate may be applied in this instance.

 $g \le e[1.005(pH)-4.830]$, pH range of 6.9 to 9.5 shown.

 $h{\leq}\,e[1.005(pH){-}5.29],\,pH$ range of 6.9 to 9.5 shown.

i-Value refers to $\sum \alpha$ and β -endosulfan.

 $j \le e[1.005(pH)-4.869]$, pH range of 6.9 to 9.5 shown.

 $k{\leq}\,e[1.005(pH){-}5.134],\,pH$ range of 6.9 to 9.5 shown.

m-There are many forms of 2,4-D that include acids, salts, amines, and esters all of which have unique toxicity values. The criteria presented are in acid equivalents and are intended to provide a range of possible effects. Toxicity values for each form of 2,4-D are available in the referenced document.

n-Assessment criteria for permethrin are based on a formulation of cis- and trans-permethrin isomers. Manchester Laboratory analysis includes only the cis-permethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for permethrin.

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⁸⁸National Marine Fisheries Service Endangered Species Act Section 7 Consultation Biological Opinion Environmental Protection Agency Registration of Pesticides Containing Chlorpyrifos, Diazinon, Malathion (2008). NMFS. <u>www.epa.gov/oppfead1/endanger/litstatus/effects</u>.

⁸⁹National Marine Fisheries Service Endangered Species Act Section 7 Consultation Biological Opinion Environmental Protection Agency Registration of Pesticides Containing Carbaryl, Carbofuran, and Methomyl (2009). NMFS. <u>www.epa.gov/oppfead1/endanger/litstatus/effects</u>.

⁹⁰National Marine Fisheries Service Endangered Species Act Section 7 Consultation Biological Opinion Environmental Protection Agency Registration of Pesticides Containing Azinphos methyl, Bensulide, Dimethoate, Disulfoton, Ethoprop, Fenamiphos, Naled, Methamidophos, Methidathion, Methyl parathion, Phorate and Phosmet (2010). NMFS. www.epa.gov/oppfead1/endanger/litstatus/effects. ⁹¹National Marine Fisheries Service Endangered Species Act Section 7 Consultation Biological Opinion Environmental Protection Agency Registration of Pesticides 2,4-D, Triclopyr BEE, Diuron, Linuron, Captan, and Chlorothalonil (2011). NMFS. www.epa.gov/oppfead1/endanger/litstatus/effects.

⁹²DRAFT National Marine Fisheries Service Endangered Species Act Section 7 Consultation Draft Biological Opinion Environmental Protection Agency Registration of Pesticides Oryzalin, Pendimethalin, Trifluralin (2012). NMFS. <u>www.epa.gov/oppfead1/endanger/litstatus/effects</u>.

⁹³Reregistration Eligibility Decision (RED) for Mecoprop-p (mcpp) (2007) OPP, EPA, Document ID: EPA-738-R-07-009. www.epa.gov/oppsrrd1/REDs/mcpp_red.pdf .

Appendix D. 2012 Pesticide Calendars

To determine if water quality concentrations were healthy for aquatic life, monitoring data were compared to EPA pesticide registration toxicity criteria and EPA National Recommended Water Quality Criteria (NRWQC), referred to as assessment criteria in this report. Data were also compared to numeric Washington State water quality standards, referred to as water quality standards. Refer to Appendix C, Assessment Criteria and Water Quality Standards, in this report for information on assessment criteria development.

For this report pesticide registration toxicity and risk assessment criteria, NRWQC, and the water quality standards were reviewed for changes and additions to numeric criteria.

Table D-1 presents the color codes used in Tables D-2 to D-16 (calendars) to compare detected pesticide concentrations to assessment criteria and water quality standards. In the calendars, the number below the months indicate sample week. Each square in a calendar represents the period when a sample was taken.

Table D-1.	Color	codes for	comparison	to assessment	criteria in	n the	pesticide calendars.	

No pesticide residue detected.
Analysis not completed.
Pesticide residue detected. Assessment criteria not available.
Magnitude of detection below regulatory or toxicological criteria or standard.
Magnitude of detection above an EPA ¹ acute or chronic invertebrate registration criteria.
Magnitude of detection above a WAC^2 or $NRWQC^3$ acute or chronic regulatory standard.
Magnitude of detection above Endangered Species Level of Concern for fish, which is 1/20 th of the acute toxicity criteria.

¹ EPA: United States Environmental Protection Agency

² WAC: Washington Administrative Code

³ NRWQC: EPA's National Recommended Water Quality Criteria

Detection of a pesticide concentration above an assessment criteria does not indicate exceedance of (not meeting) the regulatory criteria. The temporal component of the criteria must also be exceeded. The Washington State Department of Agriculture (WSDA) advises pesticide user groups and other stakeholders on the results of this study and determines if assessment criteria are exceeded. If an exceedance is determined, WSDA advises stakeholders of appropriate measures to reduce pesticide concentrations.

For additional information on pesticide assessment criteria, contact the WSDA, Natural Resources Assessment Section, toll free at (877) 301-4555, #6 or (360) 902-2067, or e-mail: <u>nras@agr.wa.gov</u>. Their web site is <u>http://agr.wa.gov/PestFert/natresources/SWM/</u>.

Cedar-Sammamish Basin

Thornton Creek

Ten types of pesticide compounds were detected in Thornton Creek in 2012 (Table D-2). In 2012, all Thornton Creek pesticide detections met available pesticide assessment criteria and water quality standards.

Month			Μ	lar			A	pr			Μ	lay				Jun					Jul				A	ug		Sep
Calendar Week	Use	10	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
2,4-D	Н		0.024							0.077			0.160	0.047		0.023	0.170	0.018		0.140	0.051	0.110						
Carbaryl	I-C																			0.017								
Dicamba I	Н																0.039				0.027							
Dichlobenil	Н		0.037	0.014	0.012	0.013	0.014	0.015	0.008	0.019	0.020		0.034	0.021	0.017	0.037	0.018	0.018	0.012	0.037	0.012	0.016	0.009	0.010	0.011	0.010	0.009	
Dichlorprop	Н																								0.021			
Diuron	Н		0.012																	0.014		0.021						
MCPA	Н		0.052																									
Mecoprop (MCPP)	Н		0.018													0.017	0.059	0.018			0.032							
Pentachlorophenol	WP		0.014		0.002								0.040	0.019		0.018		0.019		0.035		0.041						
Triclopyr	Н		0.031							0.041			0.073	0.033								0.064						
Total Suspended Solids	NA	5.0	11.0	7.0	3.0	6.0	3.0	4.0	4.0	9.0	5.0	7.0	116.0	7.0	5.0	5.0	7.0	5.0	4.0	28.0	8.0	6.0	5.0	4.0	3.0	5.0	4.0	4.0
C: Carbamate, H: Herbici	ide, I: In	sectic	ide, NA	A: Not	applic	able, W	/P: Wo	ood Pre	eserva	tive																		

Table D-2. Thornton Creek (downstream), 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Green-Duwamish Basin

Longfellow Creek

Eleven types of pesticide compounds were detected in Longfellow Creek in 2012 (Table D-3). In 2012, all Thornton Creek pesticide detections met available pesticide assessment criteria and water quality standards.

Month			Μ	lar			Α	pr			Μ	ay				Jun					Jul				A	ug		Sep
Calendar Week	Use	10	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
2,4-D	Н		0.020					0.038		0.160			0.170	0.079			0.061					0.034						
Carbaryl	I-C												0.025															
Dicamba I	Н												0.039															
Dichlobenil	Н	0.016	0.096	0.035	0.018	0.029	0.014	0.026	0.014	0.042	0.036		0.058	0.044	0.015	0.037	0.017	0.031	0.013	0.011	0.010	0.014	0.010	0.011	0.011	0.010	0.010	0.010
Diuron	Н												0.025															0.022
Imidacloprid	I-N																			0.023	0.024		0.037	0.037	0.029	0.033	0.026	0.030
MCPA	Η	0.042																										
Mecoprop (MCPP)	Η							0.013						0.024														
Pentachlorophenol	WP		0.011							0.009			0.057						0.018	0.017		0.019						
Prometon	Н																					0.019						
Triclopyr	Н	0.021	0.037					0.029		0.135			0.100	0.050			0.044					0.021						
Total Suspended Solids	NA	8.0	15.0	5.0	3.0	3.0	2.0	3.0	3.0	11.0	4.0	4.0	73.0	6.0	4.0	3.0	5.0	4.0	6.0	5.0	7.0	3.0	7.0	6.0	5.0	6.0	7.0	19.0
C: Carbamate, H: Herbici	arbamate, H: Herbicide, I: Insecticide, N: Neonicotinoid, NA: Not applicable, WP: Wood Preservative																											

Table D-3. Longfellow Creek, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Skagit-Samish Basin

Big Ditch

A total of 31 pesticide compounds were detected in Big Ditch in 2012 (Tables D-4 and D-5). Of these, 16 were identified at the upstream Big Ditch site; and 27 were found at the downstream Big Ditch site.

In 2012, pesticide detections at the upstream Big Ditch site met available pesticide assessment criteria and water quality standards. At the downstream site on June 19, 2012 a metolachlor detection was above the chronic invertebrate assessment criterion.

Comparison of Upstream Big Ditch to Downstream Big Ditch

During the 2012 sample season, both Big Ditch sites were sampled weekly on the same day. During 2012, 12 pesticides were detected in common between the two sites: 2,4-D, carbaryl, dicamba, dichlobenil, diuron, imidacloprid, MCPA, mecoprop (MCPP), metalaxyl, metolachlor, pentachlorophenol, and triclopyr. Four pesticides were detected only at the upstream site: chlorothalonil, picloram, prometon, and tebuthiuron. Fifteen pesticides were detected only at the downstream site: alachlor, atrazine, bentazon, bromoxynil, carbofuran, chlorpropham, cycloate, diazinon, eptam, ethoprop, metribuzin, monuron, oxamyl, propazine, and simazine.

Month			Μ	lar			A	pr			Μ	lay				Jun					Jul				A	ug		Sep
Calendar Week	Use	10	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
2,4-D	Н					0.028		0.110	0.048	0.320	0.056		0.780	0.093	0.590		0.084	0.053				0.078						
Carbaryl	I-C							0.017																				
Chlorothalonil	F			0.035																								
Dicamba I	Н									0.017			0.041		0.035													
Dichlobenil	Н		0.059	0.020	0.018	0.025	0.016	0.220	0.045	0.062	0.026		0.044	0.040	0.045	0.039	0.032	0.042	0.017	0.012	0.012	0.017	0.010	0.011	0.010	0.011	0.010	0.010
Diuron	Η				0.007			0.007	0.008					0.010	0.008	0.007					0.007			0.006	0.008	0.006		
Imidacloprid	I-N									0.013		0.023		0.066		0.102				0.113	0.017				0.017	0.015		0.038
MCPA	Η							0.028		0.029																		
Mecoprop (MCPP)	Н					0.016		0.041	0.025	0.100	0.032		0.069	0.023	0.105		0.042	0.034										
Metalaxyl	F					0.055						0.074											0.055	0.610	0.120			
Metolachlor	Η													0.056	0.099	0.051												
Pentachlorophenol	WP		0.020					0.008	0.014	0.099	0.011	0.026	0.290	0.076	0.110	0.026	0.034	0.044	0.030	0.028	0.027	0.039		0.019		0.026		
Picloram	Η											0.038																
Prometon	Η									0.041																		
Tebuthiuron	Η																										0.072	0.075
Triclopyr	Н							0.110	0.069	0.062			0.420	0.075	0.275		0.042	0.057	0.024			0.037						
Total Suspended Solids	NA	5.0	18.0	6.0	6.0	5.0	5.0	7.0	4.0	45.0	7.0	6.0	27.0	8.0	21.0	8.0	7.0	10.0	11.0	8.0	7.5	5.0	5.0	5.0	7.0	7.0	6.0	7.0
C: Carbamate, F: Fungici	de, H: H	Ierbici	de, I: I	Insectio	cide, N	Neon	icotino	id, NA	: Not a	applica	ble, W	P: Wo	od Pre	servati	ive													

Table D-4. Upstream Big Ditch, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Month			Μ	ar			A	pr			Μ	ay				Jun					Jul					Sep		
Calendar Week	Use	10	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
2,4-D	Η					0.019		0.460	0.064	0.081	0.022		1.500	0.085	0.032		0.140	0.240	0.067			0.290						
Alachlor	Н																	0.035										
Atrazine	Н		0.081														0.062	0.046	3.100	0.098	0.046	0.066						
Bentazon	Н											0.053			0.050													
Bromoxynil	Н							0.059										0.029										
Carbaryl	I-C																0.011	0.020										
Carbofuran	I-C												0.006					0.008										
Chlorpropham	Н	0.110	0.120	0.130	0.100	0.150	0.470	0.895	0.094	0.440	0.880	13.00	0.610	0.110	0.076													
Cycloate	Н											0.081	0.140	0.040														
Diazinon	I-OP											0.150	0.130	0.056	0.130		0.120	0.044										
Dicamba I	Н								0.015							0.039	0.053					0.059						
Dichlobenil	Н	0.025	0.046	0.013	0.010	0.013	0.009	0.125	0.011	0.014	0.017		0.006	0.016	0.014		0.034	0.034	0.016			0.009						
Diuron	Н	0.055	1.110	0.053	0.044	0.054	0.033	0.277	0.046	1.350	0.043	0.034		0.029	0.029	0.008	0.034	0.033	0.029	0.010	0.012	0.013						
Eptam	Н					0.053	0.045		0.051		0.083			0.099	0.073	0.140												
Ethoprop	I-OP																0.200											
Imidacloprid	I-N		0.036							0.031								0.173										
MCPA	Н							0.400	0.110	0.073	0.016					0.030	0.050	0.057	0.021									
Mecoprop (MCPP)	Н							0.053		0.020				0.019			0.033	0.043										
Metalaxyl	F																	0.055							0.044			
Metolachlor	Н	0.062	0.095	0.047	0.040	0.053	0.054	0.370	0.045	0.094	0.051	0.044	0.200	0.110	0.330	0.078	1.60	0.880	0.130	0.043	0.027	0.025	0.014					
Metribuzin	Н																0.190	0.320										
Monuron	Н										0.009								0.007									
Oxamyl	I-C																	0.003										
Pentachlorophenol	WP	0.012	0.018	0.009	0.009	0.009		0.030	0.011	0.022	0.008	0.023	0.032	0.030	0.027		0.046	0.042			0.020							
Propazine	Н																		0.050									
Simazine	Н		0.180					0.210																				
Triclopyr	Н								0.024				1.000	0.020	0.019		0.089	0.180	0.040			0.060						
Total Suspended Solids	NA	29.0	131.0	24.0	21.0	23.0	19.0	21.0	22.0	67.0	23.0	12.0	13.0	12.0	10.0	14.0	9.0	12.0	4.0	7.0	4.0	4.0	7.0	6.0	4.0	4.0	2.0	2.0
C: Carbamate, F: Fungici	de, H: I	Ierbici	de, I: I	nsectio	cide, N	Neon	icotino	id, NA	: Not a	applica	ble, Ol	P: Orga	anopho	sphate	e, WP:	Wood	1 Prese	rvative	•									

Table D-5. Downstream Big Ditch, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Indian Slough

A total of 20 pesticide compounds were detected in Indian Slough in 2012 (Table D-6). In 2012, pesticide detections at the Indian Slough site met available pesticide assessment criteria and water quality standards.

Month			Μ	lar			A	pr			М	ay				Jun	· · · · · · · · · · · · · · · · · · ·			· · · · ·	Jul			Aug				Sep
Calendar Week	Use	10	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
2,4-D	Н							1.300		0.580				0.160	0.088		0.620	0.170	0.077		0.086	0.060	0.055	0.030		0.034		
Atrazine	Н							0.078																				
Bentazon	Н															0.046				0.047	0.054						0.056	
Bromacil	Н						0.042	0.630		0.053						0.083			0.075		0.055	0.120	0.062	0.044				
Chlorothalonil	F	0.073	1.400		0.043			0.130		0.036																		
Chlorpropham	Н													0.250		0.110	0.410											
Dicamba I	Н							0.032									0.031		0.031			0.032						
Dichlobenil	Н	0.012		0.011		0.013	0.008	0.100	0.007	0.026	0.016		0.007	0.018	0.013		0.062	0.036	0.017	0.031	0.010	0.014	0.009	0.008				
Diphenamid	Н						0.030															0.023		0.023				
Diuron	Н	0.020	0.213	0.033	0.018	0.031	0.014	0.392	0.021	0.080	0.019		0.012	0.018	0.010		0.060	0.035	0.007		0.013		0.019	0.008		0.006		
Eptam	Н														0.100			0.065										
Imidacloprid	I-N		0.026																									
MCPA	Н																	0.090	0.041									
Mecoprop (MCPP)	Н							0.061									0.032											
Metalaxyl	F		0.064																									
Methomyl	I-C																									0.004		
Metolachlor	Н	0.032	0.140	0.031	0.025	0.028		0.066	0.025	0.110	0.030		0.026	0.030	0.026		0.051	0.068	0.021	0.028	0.019				0.038			
Pentachlorophenol	WP		0.008				0.004					0.018	0.022	0.019				0.025										
Tebuthiuron	Н																						0.095		0.110	0.110	0.098	0.110
Triclopyr	Н		0.027					1.300	0.046	0.063				0.140	0.170	0.024	0.715	0.260	0.060		0.100	0.100	0.055	0.035	0.027	0.016		
Total Suspended Solids	NA	13.0	30.0	10.0	12.0	13.0	10.0	16.0	8.0	13.5	8.0	9.0	13.0	11.0	11.0	10.0	9.0	8.5	8.0	7.0	9.0	8.0	7.0	6.0	7.0	10.0	5.0	8.0
C: Carbamate, F: Fungic	ide, H:	Herbici	de, I: I	Insecti	cide, N	Neor	icotino	oid, NA	A: Not	applic	able, V	VP: W	ood pr	eserva	tive													

Table D-6. Indian Slough, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Browns Slough

A total of 21 pesticide compounds were detected in Browns Slough in 2012 (Table D-7). In 2012, two pesticide detections did not meet pesticide assessment criteria or water quality standards.

On May 4, 2012, a metolachlor detection of 2.3 ug/L did not meet the chronic assessment criteria for freshwater invertebrates and marine plants. On May 21, 2012, a diazinon detection was above the chronic freshwater invertebrate criterion.

Month			Μ	lar			A			Μ	ay				Jun					Jul					Sep			
Calendar Week	Use	10	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
2,4-D	Н					0.056											0.071		0.049	0.026	0.031	0.022						
4-Nitrophenol	D-M		0.037																									
Atrazine	Н																		0.071		0.020							
Bentazon	Н											0.045			0.070		0.036	0.066	0.051			0.049						
Carbaryl	I-C												0.017															
Cycloate	Н												0.160	0.037			0.025											
DCPA	Н	0.150	0.028	0.042	0.066	0.043	0.029	0.150	0.140	0.042	0.032		0.100	0.028	0.031	0.023	0.044	0.026	0.031		0.029		0.026					
Diazinon	I-OP												0.230	0.031	0.045		0.049	0.032										
Dicamba I	Н																		0.036		0.024							
Dichlobenil	Н					0.023				0.016	0.013							0.009									0.017	0.010
Diuron	Н	0.248	0.600	0.322	0.115	0.272	0.086	0.046	0.208	0.416	0.140	0.078	0.054	0.036	0.020	0.020	0.017	0.015	0.016	0.009	0.008		0.009	0.009	0.008			
Eptam	Н											0.140	0.190	0.150			0.140											
Imidacloprid	I-N		0.060							0.033																		
Linuron	Н										0.006																	
MCPA	Н							0.440	0.031																			
Metolachlor	Н	0.059	0.200	0.052	0.030	0.053	0.032	0.075		2.30	0.072	0.030	0.063	0.150	0.053	0.053	0.080	0.295	0.029			0.014	0.023					
Metribuzin	Н		0.110														0.055											
Oxamyl	I-C																	0.002										
Simazine	Н	0.096	0.880	0.190		0.180			0.069	0.110																		
Triclopyr	Н																0.046	0.022										
Trifluralin	Н		0.032																									
Total Suspended Solids	NA	13.0	112.0	11.0	8.0	6.0	10.0	5.5	16.0	22.0	11.0	9.0	7.0	7.0	6.0	6.0	8.0	5.0	6.0	6.0	5.0	4.0	7.0	5.0	5.0	7.0	4.0	7.0
C: Carbamate, D: Degrad	date of p	oesticio	le, H: 1	Herbici	ide, I: I	nsectio	ide, N:	Neon	icotinc	id, NA	A: Not	applic	able, C	P: Org	anoph	ospha	te, WF	P: Woo	d pres	ervativ	'e							

Table D-7. Browns Slough, 2012 – Freshwater and Marine Criteria (pesticides in ug/L, TSS in mg/L).
Samish River

A total of seven pesticides were detected in Samish River in 2012 (Table D-8). In 2012, pesticide detections in Samish River met available pesticide assessment criteria and water quality standards.

Month			Μ	lar			A	pr			Μ	ay				Jun					Jul				A	ug		Sep
Calendar Week	Use	10	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
2,4-D	Н							0.018		0.015				0.035			0.041	0.020				0.029						
Dicamba I	Н													0.033			0.037											
Dichlobenil	Н		0.007																									
MCPA	Н							0.014																				
Pentachlorophenol	WP																					0.022						
Prometon	Н							0.045																				
Triclopyr	Н									0.016							0.012	0.015				0.032	0.019					
Total Suspended Solids	NA	26.0	31.0	20.0	17.0	22.0	16.0	43.0	24.0	29.0	19.0	12.0	16.0	10.0	8.0	6.0	21.0	15.0	9.0	10.0	6.0	8.0	4.0	5.0	3.0	5.0	2.0	6.0
H: Herbicide, NA: Not a	pplicabl	e, WP:	Woo	d pres	ervativ	e																						

Lower Yakima Basin

Marion Drain

A total of 28 pesticide and pesticide degradate compounds were detected in Marion Drain in 2012 (Table D-9). During 2012, three pesticide detections did not meet a pesticide assessment criteria or water quality standard.

On May 2, 2012, a detection of bifenthrin, a pyrethroid insecticide, exceeded the ESLOC for fish, and was above the chronic assessment criteria for fish and invertebrates. Malathion concentrations were above the chronic invertebrate assessment criterion on May 29 and above both the chronic NRWQC and the chronic invertebrate assessment criterion on June 12, 2012.



Table D-9. Marion Drain, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Spring Creek

A total of 13 pesticides were detected in Spring Creek in (Table D-10). For four consecutive weekly sampling events, March 28 through April 18, 2012, chlorpyrifos concentrations exceeded the chronic invertebrate assessment criterion. In addition, for the first three weeks the chronic Water Quality Standard and the NRWQC were exceeded.

On June 25, 2012, a malathion detection exceeded the ESLOC for fish, the chronic NRWQC, and the chronic invertebrate assessment criterion.

On September 4, 2012, a very high concentration of the herbicide 2,4-D (42 ug/L) exceeded the ESLOC for fish.

Month			Μ	ar	-		A	pr				May	-			Jı	un				Jul				A	ug		Sep
Calendar Week	Use	10	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
2,4-D	Н					0.020		0.023		0.015	0.051	0.018	0.038	0.024	0.037	0.018	0.034	0.035		0.032	0.048					0.028		42
Acetochlor	Н														0.040													
Atrazine	Н	0.035	0.034									0.022																
Carbaryl	I-C									0.026	0.031	0.019	0.022							0.017								
Chlorpyrifos	I-OP				0.100	0.080	0.081	0.040	0.024																			
Diazinon	I-OP																		0.022			0.022						
Dicamba I	Н														0.021			0.024		0.022								
Dichlobenil	Н					0.008																						
Diuron	Н	0.025	0.015	0.013	0.015	0.020	0.008																0.034					
Malathion	I-OP																	0.580										
MCPA	Н									0.012																		
Simazine	Н																						0.092					
Triclopyr	Н												0.088		0.013													
Total Suspended Solids	NA	1.0	1.0	1.0	107.0	40.0	5.0	8.0	13.0	37.0	22.0	16.0	88.0	52.0	54.0	24.0	19.0	25.0	20.0	25.0	46.0	6.0	5.0	11.0	19.5	7.0	2.0	3.0
C: Carbamate, H: Herbici	de, I: In	secticio	le, NA	: Not	applica	ble, Ol	P: Orga	anopho	osphate	e, WP:	Wood	l prese	ervative	e														

Table D-10. Downstream Spring Creek, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Sulphur Creek Wasteway

A total of 19 pesticide and pesticide degradate compounds were detected in Sulphur Creek Wasteway in 2012 (Table D-11).

A number of chlorpyrifos detections exceeded a pesticide assessment criteria or water quality standard. For three consecutive weekly sample events, March 28 through April 10, 2012, chlorpyrifos concentrations exceeded the chronic water quality standard, the chronic NRWQC as well as the chronic invertebrate assessment criterion. For two consecutive weekly sample events, July 18 and 24, 2012, chlorpyrifos concentrations again exceeded the chronic water quality standard and the chronic NRWQC as well as the chronic invertebrate assessment criterion.

On July 5, 2012, a single malathion detection that was above the chronic NRWQC, and the chronic invertebrate assessment criterion.

On March 20, 2012, a single detection of 4,4'-DDE, a degradate of the legacy insecticide DDT, was above the chronic water quality standard for DDT (and metabolites).

					-																							
Month			Μ	ar			A	pr				May				Jı	un				Jul				A	ıg		Sep
Calendar Week	Use	10	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
2,4-D	Н	0.016	0.016	0.015		0.016		0.017	0.022	0.017	0.088	0.044	0.056	0.034	0.076	0.019	0.096	0.051	0.050	0.180	0.600	0.045	0.069	1.300	0.068	0.099	0.092	0.076
4,4'-DDE	D-OC			0.016																								
Acetochlor	Н										0.031																	
Atrazine	Н	0.026																										
Bromacil	Н								0.034																			
Carbaryl	I-C									0.077	0.029	0.051	0.032	0.025			0.010	0.010	0.014	0.014			0.012	0.012	0.009			
Chlorpyrifos	I-OP				0.100	0.053	0.078	0.033													0.056	0.057	0.016					
Diazinon	I-OP																					0.023						
Dicamba I	Н														0.032		0.024	0.033		0.026	0.032	0.027	0.025					
Diuron	Н	0.023	0.025	0.109	0.041	0.044	0.031	0.043	0.021		0.010	0.027	0.028	0.018	0.032	0.008	0.008						0.008	0.006				
Imidacloprid	I-N																						0.008					
Malathion	I-OP																	0.042	0.110									
MCPA	Н								0.013	0.012					0.016													
Pendimethalin	Н						0.032																					
Pentachlorophenol	WP																					0.016				0.019		
Prometon	Н																								0.017			
Terbacil	Н								0.025												0.031	0.061			0.027			
Triclopyr	Н														0.020													
Trifluralin	Н											0.014		0.026														
Total Suspended Solids	NA	12.0	9.0	286.0	56.0	51.0	22.0	37.0	13.0	39.5	16.0	25.0	65.5	64.0	58.0	31.0	39.0	44.0	17.0	20.0	27.0	37.0	7.0	16.0	20.0	17.0	19.0	10.0
C: Carbamate, D: Degrad	late of a	pestic	ide, H:	Herbi	cide, I:	Insect	icide, N	I: Neo	nicotin	oid, N	A: Not	t applic	cable, (DC: Or	ganocl	hlorine	, OP: 0	Organo	phosp	hate, V	VP: W	ood pi	eserva	tive				

Table D-11.	Sulphur Creek Wasteway	v, 2012 – Freshwater Criteria ((pesticides in ug/L, TSS in mg/L).
14010 0 111	Sulphur Creek wasteway		

Wenatchee and Entiat Basins

Peshastin Creek

A total of two pesticides and a pesticide synergist were detected in Peshastin Creek in 2012 (Table D-12).

The April 4, 2012, endosulfan levels exceeded the ESLOC for fish, and the acute and chronic water quality standard and acute and chronic NRWQC for endosulfan.

Month			Μ	lar			A	pr				May				Jı	ın			J	ul				Aug			Sep
Calendar Week	Use	10	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
Endosulfan I	I-OC						0.230							\succ														
Endosulfan II	I-OC						0.091							\succ														
Piperonyl butoxide	Sy						0.094							\times														
Total Suspended Solids	NA	2.0	1.0	1.0	2.0	4.0	2.0	5.0	54.0	7.0	3.0	20.0	5.0	3.0	14.0	3.0	3.0	3.0	4.0	4.5	12.0	2.0	2.0	2.0	< 1	< 1	< 1	< 1
I: Insecticide, NA: Not a	oplicable	e, OC:	Organ	ochlori	ine, Sy	Pesti	cide sy	nergis	t																			

Mission Creek

A total of three pesticides and a pesticide synergist were detected in Mission Creek in 2012 (Table D-13). All 2012 Mission Creek pesticide detections met available pesticide assessment criteria and water quality standards.

Month			Μ	lar			A	pr				May				Jı	ın			J	ul				Aug			Sep
Calendar Week	Use	10	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
Chlorpyrifos	I-OP							0.031																				
Imidacloprid	I-N																										0.013	
Oryzalin	Н										0.590																	
Piperonyl butoxide	Sy				0.190																							
Total Suspended Solids	NA	14.0	6.0	3.0	11.0	19.0	8.0	42.0	199.0	43.0	16.0	24.0	10.0	5.0	16.0	8.0	4.0	5.0	4.0	10.0	5.0	3.0	2.0	3.0	1.0	2.0	< 1	1.0
H: Herbicide, I: Insecticio	le, N: N	leonico	tinoid,	, NA: 1	Not app	olicable	e, OP:	Organı	ohosph	nate, Sy	: Pest	icide s	ynergi	st														

Table D-13. Mission Creek, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Wenatchee River

A total of two pesticides and a pesticide synergist were detected in the Wenatchee River in 2012 (Table D-14). All 2012 Wenatchee River pesticide detections met (did not exceed) available pesticide assessment criteria and water quality standards.

Month			Μ	ar			A	pr				May				Jı	ın			J	ul				Aug			Sep
Calendar Week	Use	10	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
Carbaryl	I-C																							0.008				
Chlorpyrifos	I-OP						0.039																					
Piperonyl butoxide	Sy						0.110																					
Total Suspended Solids	NA	4.0	2.0	2.0	2.0	4.0	5.0	8.0	51.0	9.0	8.0	45.0	17.0	10.0	16.0	4.0	11.0	5.0	7.0	20.0	11.0	6.0	4.0	3.0	2.0	2.0	2.0	1.0
C: Carbamate, I: Insectici	ide, NA:	Not a	pplicat	le, OP	: Orga	nopho	sphate	, Sy: F	Pesticid	e syne	rgist																	

Brender Creek

A total of 15 pesticides and a pesticide synergist were detected in Brender Creek in 2012 (Table D-15).

Detections of the legacy pesticide DDT and DDT degradates occurred consistently during 2012. All detections exceeded the total DDT chronic NRWQC and the chronic water quality standard. The chronic water quality standard is based on a 24-hour average concentration.

In April 2012, a single detection of chlorpyrifos was above the chronic invertebrate assessment criterion, the chronic water quality standard, and the chronic NRWQC.

Total endosulfan concentrations exceeded the ESLOC for fish during four sample events: three consecutive events, March 27, April 4, and April 9; and again on April 25, 2012. In addition, during all of these sample events, endosulfan exceeded the chronic water quality standard and the chronic NRWQC.

Month			Μ	lar			A	pr				May				Jı	m			J	ul				Aug			Sep
Calendar Week	Use	10	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
2,4-D	Н											0.025									0.023							
4,4'-DDD	D-OC										0.019		0.022	0.016	0.021	0.083		0.020	0.019	0.021	0.021	0.019	0.018	0.019	0.019	0.022	0.021	0.020
4,4'-DDE	D-OC				0.022	0.045	0.033	0.039	0.064	0.039	0.044	0.038	0.032	0.029	0.053	0.080	0.013	0.035	0.028	0.039	0.040	0.025	0.026	0.024	0.024	0.027	0.037	0.034
4,4'-DDT	I-OC	0.043	0.025	0.024	0.025	0.034	0.030	0.036	0.037	0.023	0.030	0.017	0.026	0.024	0.039	0.091		0.024	0.022	0.026	0.026	0.021	0.020	0.021	0.020	0.024	0.029	0.022
Carbaryl	I-C					0.031						0.051									0.017							
Chlorpyrifos	I-OP						0.033	0.072	0.021																			
Diazinon	I-OP							0.110	0.020														0.059					
Diuron	Н	0.011										0.091																
Endosulfan I	I-OC				0.069	0.096	0.077		0.082																			
Endosulfan II	I-OC								0.077																			
Endosulfan Sulfate	D-OC	0.052	0.035		0.048	0.043	0.055	0.048	0.100	0.039	0.034	0.038	0.033	0.031	0.030			0.030	0.033	0.033	0.038	0.030						
Imidacloprid	I-N																								0.010	0.011		
Norflurazon	Н																											0.028
Oryzalin	Н											0.320																
Pendimethalin	Н	0.049																										
Piperonyl butoxide	Sy					1.200	0.160							0.043														
Total Suspended Solids	NA	20.0	8.0	9.0	6.0	30.0	16.0	44.0	216.0	118.0	70.0	37.0	29.0	32.0	110.0	70.0	15.0	43.0	30.0	49.0	63.0	27.0	24.0	24.0	16.0	39.0	43.0	35.0
C: Carbamate, D: Degrad	late of a	pestic	ide, H:	Herbi	cide. I:	Insect	icide. N	I: Neo	nicotin	oid. N	A: No	t applic	cable. (DC: Or	ganocl	lorine	. OP: 0	Drgano	phosp	hate. S	v: Svr	nergist.	WP: Y	Wood	preserv	vative		

Table D-15. Brender Creek, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Entiat River

A total of two pesticides and a pesticide synergist were detected in the Entiat River in 2012 (Table D-16). All 2012 Entiat River pesticide detections met available pesticide assessment criteria and water quality standards.

Month			Μ	ar			A	pr				May				Jı	ın			J	ul				Aug			Sep
Calendar Week	Use	10	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
Carbaryl	I-C																								0.012			
Pentachlorophenol	WP																								0.018			
Piperonyl butoxide	Sy			0.120		0.074																						
Total Suspended Solids	NA	3.0	3.0	2.0	3.0	4.0	2.0	4.0	36.0	8.0	4.0	37.0	9.0	5.0	20.0	6.0	7.0	6.0	7.0	15.0	6.0	4.0	3.0	3.0	3.0	3.0	2.0	2.0
C: Carbamate, I: Insectici	ide, NA:	Not a	pplicat	ble, Sy	Pesti	cide sy	nergist	, WP:	Wood	preser	vative																	

Table D-16. Entiat River, 2012 – Freshwater Criteria (pesticides in ug/L, TSS in mg/L).

Appendix E. 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 Federal Insecticide Fungicide and Rodenticide Act (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.

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: A pesticide that is no longer registered for use, but persists in the environment.

Loading: The input of pollutants into a waterbody.

Marine water (seawater): Salt water.

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

Pesticide Synergist: A natural or synthetic chemical which increases the lethality and effectiveness of currently available pesticides.

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: Fish that belong to the family *Salmonidae*. 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 effects: An effect which 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

7-DADMax	7-day Average of the Daily Maximum Temperatures
DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
DO	Dissolved oxygen
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
LCMS/MS	Liquid chromatograph coupled with tandem 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
NAD	North American Datum
n	Number
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
RPD	Relative percent difference
RQ	Risk quotient
RSD	Relative standard deviation
SOP	Standard operation procedures
TMDL	(See Glossary above)
TSS	(See Glossary above)

TSU	Toxics Studies Unit
TU	Toxic units
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

Units of Measurement

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