

# Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2014 Data Summary

A Study by the Washington State Department of Agriculture

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# A Study by the Washington State Department of Agriculture

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# Summary:

In 2003, the Washington State Departments of Agriculture and Ecology began a multi-year monitoring program to characterize pesticide concentrations in selected salmon-bearing streams during the typical pesticide application season (March – September) in Washington.

Monitoring in 2014 was conducted in seven WRIA's<sup>1</sup>, five agricultural and two urban basins, for a total of 15 sample sites:

#### Agricultural basins:

- WRIA 1, Nooksack basin representing berry agriculture: Upper Bertrand Creek and Lower Bertrand Creek
- WRIA 3, Lower Skagit-Samish basin representing western Washington rotational agriculture: Indian Slough, Browns Slough, Upper Big Ditch, and Lower Big Ditch
- WRIA 37, Lower Yakima basin representing irrigated agriculture: Marion Drain, Sulphur Creek Wasteway, and Spring Creek
- WRIA 40, Alkali-Squilchuck representing tree fruit agriculture: Stemilt Creek
- WRIA 45, Wenatchee basin representing tree fruit agriculture: Peshastin Creek, Mission Creek, and Brender Creek.

#### Urban basins:

- WRIA 8, Cedar-Sammamish basin, representing urban land use: Thornton Creek
- WRIA 9, Green-Duwamish basin, representing urban land use: Longfellow Creek

This report summarizes data collected during the 2014 monitoring season. In 2014, surface water samples were analyzed for 181 pesticides and pesticide-related compounds including 76 insecticides, 61 herbicides, 31 pesticide degradates, 10 fungicides, 2 pesticide synergists, 1 wood preservative, as well as total suspended solids (TSS). Field measurements were also collected for streamflow, temperature, pH, dissolved oxygen, and conductivity at all site visits.

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<sup>&</sup>lt;sup>1</sup> Water Resource Inventory Area

# Introduction:

The Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) began a multi-year monitoring study to evaluate pesticide concentrations in surface waters in 2003. The study assesses pesticide-presence in salmon-bearing streams during the typical pesticide use season (March through September) in Washington State.

The data generated by the monitoring program is used by WSDA, the U.S. Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA) National Marine Fisheries Service, and the U.S. Fish and Wildlife Service (USFWS) to refine exposure assessments for pesticides 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 in 2014, document changes in the monitoring program during the year, and provide a basis for potential modifications to the program in upcoming years.

# Study Area:

This pesticide monitoring program has been ongoing since 2003. As the project has progressed, sampling sites have been added or removed based on pesticide detection history, site conditions, land use patterns, and fisheries populations. The 2014 season saw the removal of two monitoring sites, Wenatchee River in the Wenatchee Basin (WRIA 45), and Samish River in the Lower Skagit-Samish Basin (WRIA3). Samish River and Wenatchee River were removed due to high streamflow and a low number of detections.



Figure 1: Map of Washington State showing the five agricultural and two urban basins monitored during 2014

# Basins Monitored During 2014

The seven basins monitored in 2014 are presented in Figure 1: two urban and five agricultural. 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.

Information about monitoring locations including coordinates and duration of sampling, are described in Appendix A. Agricultural land use statistics, salmon fishery information, and climate information can be found in previous reports (Sargeant et al., 2011 and 2013).

# Nooksack basin (WRIA 1)

Two monitoring sites located on Bertrand Creek were selected to represent the Nooksack Basin (WRIA 1). These sites have been monitored since 2013. Approximately 61% of the land use in the Bertrand Creek subbasin is in agricultural production (the U.S. portion is approximately half of the entire watershed) including 20% currently producing blueberries, caneberries (raspberries, blackberries, and marionberries), and strawberries (WSDA, 2013).

- The <u>Upper Bertrand</u> monitoring site is located near the U.S. Canadian border.
- The <u>Lower Bertrand</u> monitoring site is located near the bottom of the watershed approximately 1 mile upstream where the tributary enters the Nooksack River.

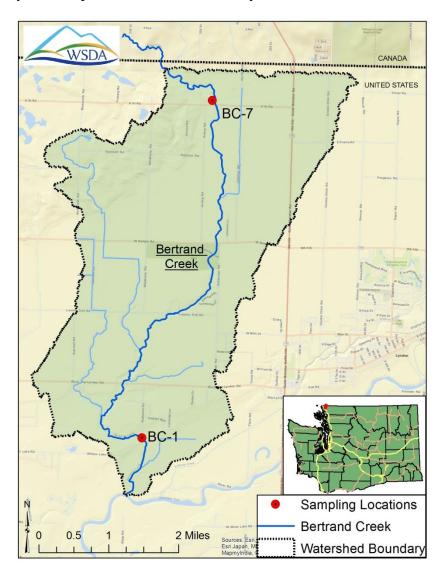


Figure 2: Map of Nooksack Basin Monitoring Locations

# Lower Skagit-Samish basin (WRIA 3)

Four monitoring sites in three subbasins of the lower Skagit-Samish basin (WRIA 3) were selected to represent western Washington agricultural land-use practices. These sites have been monitored since 2006.

- The <u>Upper Big Ditch</u> monitoring site is located on the upstream side of the bridge at Eleanor Lane.
- The <u>Lower Big Ditch</u> monitoring site is located on the upstream side of the bridge at Milltown Road.
- The <u>Browns Slough</u> monitoring site is located downstream of the tidegate on Fir Island Road.
- The <u>Indian Slough</u> monitoring site is located on the upstream side of the tidegate at Bayview-Edison Road.

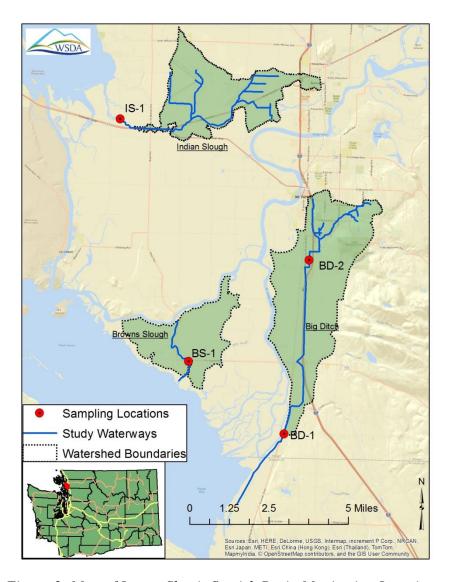


Figure 3: Map of Lower Skagit-Samish Basin Monitoring Locations

# Cedar-Sammamish basin (WRIA 8)

The Thornton Creek subbasin is located in the Cedar-Sammamish basin (WRIA 8) and is an example of urban land-use. One to four sites have been sampled yearly on this creek from 2003 to the present. The site at the mouth of Thornton Creek was sampled in 2013.

• The <u>Thornton Creek</u> monitoring site is located downstream of the pedestrian footbridge near Matthews Beach Park.



Figure 4: Map of Cedar-Sammamish Basin Monitoring Location

# *Green-Duwamish basin (WRIA 9)*

The Longfellow Creek subbasin is located in the Green-Duwamish basin (WRIA 9) and is another example of urban land-use. This monitoring site was added to the program in 2009 to investigate if pesticides could be contributing to storm water runoff that was causing pre-spawn mortality in salmon in the area.

• The <u>Longfellow Creek</u> monitoring site is located upstream of the culvert under the 12th fairway on the West Seattle Golf Course.



Figure 5: Map of Green-Duwamish Basin Monitoring Location

# Lower Yakima basin (WRIA 37)

Three subbasins of the Lower Yakima basin (WRIA 37) were selected to represent eastern Washington irrigated crop-land agricultural practices. Three waterbodies have been sampled from 2003 to the present.

- The <u>Marion Drain</u> monitoring site is located approximately 15 meters upstream of the bridge at Indian Church Road.
- The <u>Sulphur Creek Wasteway</u> monitoring site is located on the downstream side of the bridge at Holaday Road.
- The <u>Spring Creek</u> monitoring site is located on the downstream side of the culvert on McCreadie Road.



Figure 6: Map of Lower Yakima Basin Monitoring Locations

# Alkali-Squilchuck basin (WRIA 40)

One site in the Alkali-Squilchuck basin (WRIA 40) was added to represent central Washington agricultural tree fruit practices in addition to the monitoring sites in the Wenatchee basin. The monitoring site is located at the mouth of Stemilt Creek.

• The <u>Stemilt Creek</u> monitoring site is located just upstream of where Stemilt Creek enters into the Columbia River.

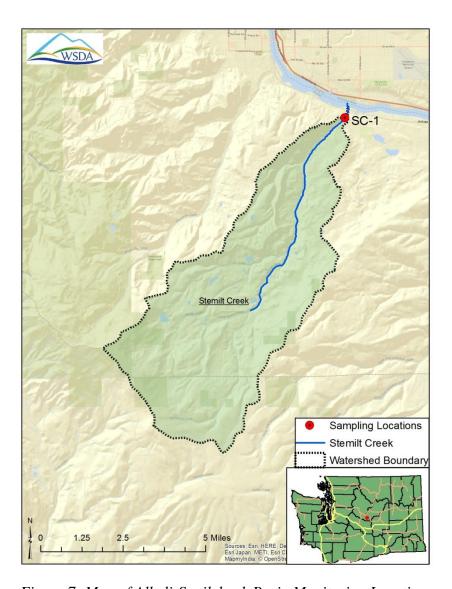


Figure 7: Map of Alkali-Squilchuck Basin Monitoring Location

# Wenatchee basin (WRIA 45)

Three subbasins of the Wenatchee basin (WRIA 45) were selected to represent central Washington agricultural tree fruit practices. Three sites have been sampled from 2007 to the present. Wenatchee River monitoring site was removed in 2014 due to high streamflows and low number of detections

- The <u>Peshastin Creek</u> monitoring site is located approximately 30 meters downstream of the bridge at Saunders Road.
- The <u>Mission Creek</u> monitoring site is located on Mission Creek Road off of Trip Canyon Road.
- The <u>Brender Creek</u> monitoring site is located on upstream side of the culvert at Evergreen Drive.

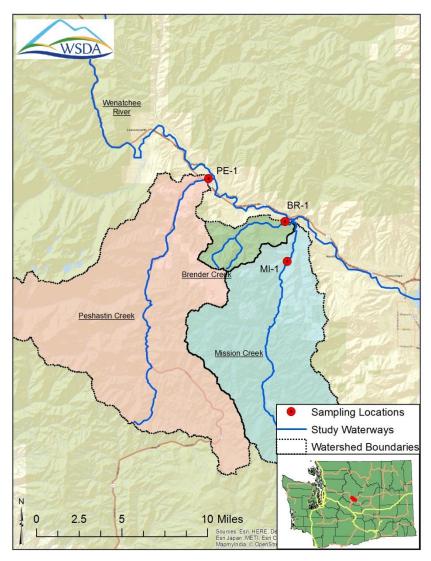


Figure 8: Map of Wenatchee Basin Monitoring Locations

# Methodology:

# Study Design and Methods

Sampling was designed to assess 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: pH, conductivity, continuous temperature data (collected at 30-minute intervals), dissolved oxygen, and streamflow. Samples were collected and sent to the lab for total suspended solids (TSS). 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; Sargeant, 2013), and the triennial reports (Burke et al., 2006; Sargeant et al., 2010; Sargeant et al., 2013).

During 2014, samples collected for analysis of 181 pesticides and pesticide-related compounds included: 76 insecticides, 61 herbicides, 31 pesticide degradates, 10 fungicides, 2 pesticide synergists, and 1 wood preservative. See Table B-3 in Appendix B for the 2014 chemical analyte list.

# Sampling Sites and Sampling Frequency

In 2014, sampling was conducted weekly at most monitoring locations for 27 consecutive weeks, beginning the second week in March and continuing through the second week in September.

# 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; Sargeant, 2013).

Field methods for grab sampling are a direct application or modification of United States Geological Survey (USGS) or EPA procedures. Surface water samples were collected by hand-compositing grab samples from quarter-point transects across each stream following Ecology's Standard Operating Procedure for Sampling of Pesticides in Surface Waters, SOP EAP003 (Anderson and Sargeant, 2011). 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. After collection, all samples were labeled and preserved according to the QA Project Plan (Johnson and Cowles, 2003).

Ecology's Manchester Environmental Laboratory (MEL) analyzed all pesticide samples, TSS samples, and conductivity QA samples. A list of target analytes for this study is presented in Table B-3 (Appendix B). Table 1 provides a summary of the extraction and analytical methods used by the MEL.

Table 1:	Summary	of i	laboratory	methods,	2014

	Met		
Analytes	Extraction Analytical		Instrumentation
	Reference	Reference	
Pesticides	3535A	8270D	GC/MS
Herbicide Analysis	3535A	8270D	GC/MS
Carbamates	n/a	8321B	LC/MS/MS
TSS	n/a	SM 2540D	Gravimetric
Conductivity	n/a SM 2510		Electrode

<sup>1</sup>All analytical methods refer to EPA SW 846, unless otherwise noted.

n/a: not applicable

TSS: total suspended solids

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

mass spectrometry

GC/MS: gas chromatography/mass spectrometry

Field meters were calibrated at the beginning of the sampling event 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 week using known standards. Dissolved oxygen meter measurements were compared to grab samples analyzed by Winkler Titration for dissolved oxygen following Ecology SOPs (Ward, 2007). Three to five Winkler grab samples were obtained during each sample week, one at the beginning and end of each day and one replicate Winkler. Continuous, 30-minute interval, temperature data were collected from the first week of March through the third week of September for eastern Washington monitoring sites. Continuous, 30-minute interval temperature data were collected from the last week in February, through the third week in September for western Washington monitoring sites with the exception of Upper Bertrand Creek where temperature loggers were installed the second week of March, through the third week of September. Due to an equipment malfunction, some temperature data was lost for western Washington monitoring sites and is discussed further after Table 27. Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Wagner et al., 2000). Data quality objectives for field meters are described in Anderson and Sargeant (2009). The 2014 field data quality results are summarized in Appendix B of this report. Measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler DO comparisons are described in Anderson and Sargeant (2009). Data that did not meet MQOs were qualified.

Discharge (streamflow) for sites other than Lower Bertrand Creek, Sulphur Creek Wasteway, Longfellow Creek, and Peshastin Creek were measured using a OTT MF pro flow meter and top-setting wading rod, as described in Ecology SOP EAP056 (Shedd, 2014). Discharge data for Lower Bertrand Creek were obtained from an Ecology gauging station located at Rathbone Road (Station ID: 01N060). Discharge data for Lonfellow Creek were obtained from a gauging station operated by King County in the West Seattle Golf Course (STA098A). Discharge data for Sulphur Creek Wasteway were obtained from an adjacent U.S. Bureau of Reclamation gauging station on Sulphur Creek at Holaday Road near Sunnyside. Discharge data for Peshastin Creek were obtained from an Ecology gauging station located at Green Bridge Road (StationID: 45F070). Fifteen-minute discharges were available during the sampling period. The recorded streamflow closest to the actual sampling time was used in lieu of field measurements.

# Laboratory and Field Data Quality

#### QA/QC Measures

Performance of sample 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, laboratory blanks, laboratory control samples (LCS), and laboratory control sample duplicates (LCSD) are analyzed as the laboratory component of QA/QC. Field blanks, field replicates, matrix spikes (MS), and matrix spike duplicates (MSD) integrate field and laboratory components. In 2014, 15.7% of the field samples collected in the field were QA samples. Highlights of laboratory and field data quality are presented below and a full analysis of the QA/QC results is contained in Appendix B.

#### Field and Laboratory Blank Samples

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

In 2014, there were two field blank detections for the pesticide analysis. 4,4'-DDE was detected at Brender Creek on June 13<sup>th</sup> of at a concentration of 0.024  $\mu$ g/L. The analyte was positively identified and the concentration was detected at the detection limit. The detection limit was 0.024  $\mu$ g/L. The reported concentration is an approximation. 4,4'-DDE was not detected in the grab sample associated with that site visit. Tebuthiuron was detected on August 27th at Indian Slough at a concentration of 0.096  $\mu$ g/L. The analyte was positively identified and the concentration was detected above the reporting limit. The reporting limit was 0.032  $\mu$ g/L. Tebuthiuron was also detected in the grab samples at Indian Slough and at Upper Big Ditch on the same day at a concentration of 0.1  $\mu$ g/L and 0.091  $\mu$ g/L respectively. Tebuthiuron results from this batch should be used with caution.

In 2014 there were also two field blank detections for TSS. TSS was detected in the field blank on April 7th at Longfellow Creek at a concentration of 2 mg/L. The analyte was positively

identified and the concentration was detected above the reporting limit. The reporting limit was 1 mg/L. TSS was also detected in the grab sample during that site visit at 6 mg/L. TSS was detected in the field blank on August 27th at Brender Creek at a concentration of 36 mg/L. The analyte was positively identified and the concentration was detected above the reporting limit. The reporting limit was 2 mg/L. TSS was also detected in the grab sample taken at that site as well as at the LCS and LCSD at 37 mg/L, 37 mg/L and 38 mg/L respectively. TSS results from this batch data from this should be used with caution.

For 2014, there were no detections in laboratory blanks reported by MEL.

#### Field Replicate Samples

During 2014, sampling frequency for the field replicate samples was 7.71% for pesticides and TSS samples. Precision between replicate pairs was calculated using the relative percent difference (RPD) statistic. 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. Precision, between detections consistently identified in both the grab sample and replicate sample are presented in Appendix B (Table B-4). *Consistent identification* refers to compounds identified in both the original sample and field replicate.

For pesticides the average RPD of the consistently detected replicates was 14.4% and 76.5% of the replicates pairs had an RPD of less than 20%. For TSS the average RPD of the consistently detected replicates was 21.3% and 72.4% of the replicates had an RPD of less than 20%. Of the 110 consistently identified replicate pairs, there were only six pairs that exceeded the 40% RPD criterion. Three of the six criteria exceedances were for total suspended solids, two were for the insecticide thiamethoxam, and one for the herbicide dacthal (DCPA). It is important to note that RPD statistic has limited effectiveness in assessing variability at low levels (Mathieu, 2006) because the RPD statistic can become large even though the actual difference between the pairs is low when the concentrations of analytes are very small. Four out of the six exceedances including the April 15th dacthal results, the April 15th TSS result, the May 13th TSS result and the July 21st TSS results are not considered of acceptable data quality and the results will be requalified as "J" to reflect that the numerical value is only an approximation of the concentration of the analyte in the sample. Those data results should be used with caution. The other two exceedances for thiamethoxam were already below the reporting limit and the reported concentrations are already qualified as an estimate. The remaining data for pesticide and TSS field replicates are of acceptable data quality.

In 2014 there were 17 inconsistently identified replicate pairs for pesticides and no inconsistently identified replicate pairs for TSS (see Table B-5). The majority of the inconsistently identified pairs were due to the detections being very close to the detection limit. There were 11 replicate pairs where a positive detection was paired with a "non-detect" value ("U" or "UJ"). The remaining six pairs included a detection paired with a tentative detection (Table B-5).

On average the RPD between detections in replicate samples was small. Table 2 shows the pooled average RPD where RPD values were averaged for pesticides and TSS. All pesticide and TSS data for replicates are of acceptable data quality.

Table 2: Pooled average RPD of consistent field replicate pairs data in 2014

Parameter	Pooled Average RPD	Number of Replicate Pairs	
Pesticides	20.3%	56	
TSS	21.3%	34	

#### Matrix Spike Samples

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. Statistics for analyte recoveries and RPD from MS/MSD samples that fell within the control limits are presented in Table B-7 in Appendix B. Statistics for analyte recoveries and RPD from MS/MSD samples that did not fall within the control limits are presented in Table B-8 in Appendix B. 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 (Table B-7).

#### **Surrogates Compounds**

Surrogates are used to evaluate recovery for a group of compounds. The majority of 2014 surrogate recoveries fell within the QC limits established by MEL for all compounds. The percentage of time a surrogate recovery did meet the QC limits is described in Table B-10 of Appendix B. Surrogate recoveries were within control limits for 96.8-100% of samples. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

#### **Laboratory Control Samples**

Laboratory control samples are composed of 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. The average percent recovery and average RPD for the LCS and the LCSD pairs is presented in Table B-11 in Appendix B. For most compounds, recovery and RPDs of LCS and LCSD showed acceptable performance and were within limits for the project. Table B-12 in Appendix B describes the number of detections for each analyte not meeting the target recovery range. Sample results were qualified as estimates if the LCS recoveries did not meet laboratory QC criteria.

#### Field Data Quality

On July 16, 2014 a side-by-side field audit was conducted to determine comparability of the field equipment. Results of the field audit are described in Appendix B. All meter results were acceptable based on the MQOs described in Table B-14.

# Reporting Methods and Data Analysis

Laboratory data were qualified as needed, and qualifiers are described in Table B-1 in Appendix B. Positive pesticide detections included "D" values and values qualified with a "J" or "E". Values qualified with "NJ", "U," or "UJ" were considered non-detects.

The 2014 field and laboratory data were compiled and organized using Excel<sup>®</sup> spreadsheet software and Access<sup>®</sup> database software (Microsoft Corporation, 2007).

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

# Comparison to Assessment Criteria and Water Quality Standards

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

# Replicate Values

Field and laboratory replicates were obtained to determine data quality. Field and laboratory replicate values were averaged for comparisons to pesticide assessment criteria and water quality standards. If the sample or the replicate sample was a non-detect value while the other was a positive detection, the positively detected value was used.

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

# Toxicity Unit Analysis

Pesticide registration toxicity data, risk assessment criteria, and regulatory standards apply to the effects of a single pesticide and its effects on aquatic life. However, organisms in the environment may experience many physical, biological, and chemical stressors simultaneously, changing the impact of exposure. Current criteria and standards do not take into account the effects of pesticide mixtures. Mixtures of two or more chemicals can be described as additive, where the effect of the co-exposure is anticipated to be the sum of their individual effects, synergistic (greater than additive toxicity), or antagonistic (less than additive toxicity). In addition to mixtures of pesticides, the effects of environmental stressors including high temperatures, low dissolved oxygen, or food source impacts are not taken into consideration in the criteria or standards.

How to address pesticide mixtures in the risk assessment process is a major source of uncertainty in the current risk assessment paradigm. The National Research Council (NRC) of the National Academy of Science convened a committee on Ecological Risk Assessment under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and the Endangered Species Act (ESA) to review the scientific and technical issues related to determining risks posed to listed species by pesticides. The NRC committee recently published their review of the risk assessment process entitled Assessing Risks to Endangered and Threatened Species from Pesticides<sup>2</sup>. The review provided recommendations to EPA and the Services (US Fish and Wildlife Service and National Marine Fisheries Service). The NRC was specifically asked to assess the scientific information available for estimating effects of mixtures and inert ingredients; and to consider the use of uncertainty factors to account for gaps in data.

A study by Broderius and Kahl (1985) found when a large number of chemicals are included in mixture experiments; an additive response is typically found (Lydy et al., 2004). One of the most common methods of assessing the additive effects of pesticide mixtures is by using toxicity units (TUs) (Lydy et al., 2004).

For this report toxicity units (TUs) were used to estimate the additive effects of pesticide mixtures, as described by Faust et al. in 1993 (Lydy et al., 2004). As an example, TUs can be calculated for a multi-component mixture using the formula below and the LC<sub>50</sub> (lethal concentration to cause mortality in 50% of test species) as an assessment endpoint:

$$\sum \left( \frac{x_1}{LC_{50}(x_1)} + \frac{x_2}{LC_{50}(x_2)} + \cdots \right) = TU$$

In the equation above, TU is equal to the sum of the individual risk quotients where  $x_1$  and  $x_2$  are the concentrations of the mixture components  $X_1$  and  $X_2$ ,  $LC_{50}(X_1)$  and  $LC_{50}(X_2)$  are the effect concentrations of the individual compounds producing the same effect.

In this example, a TU value  $\geq 1$  means 50% or more of the organisms tested may experience lethality based on the lethality measure used. Lethality measures used in this report include: acute and chronic fish and invertebrate exposure assessment concentrations described in Appendix C. A TU value  $\geq 1$  means a lethal or sublethal (for chronic criteria) effect may occur with an increasing likelihood depending on the degree to which TUs exceed 1.0. The effect concentrations in the denominator of the risk quotient can also be multiplied by the level of concern<sup>3</sup> (LOC) to conveniently assess if the level of concern has been exceeded by the pesticide mixture.

$$\sum \left(\frac{x_1}{LC_{50}(x_1) \times LOC} + \frac{x_2}{LC_{50}(x_2) \times LOC} + \cdots\right) = TU$$

<sup>&</sup>lt;sup>2</sup> http://www.nap.edu/catalog/18344/assessing-risks-to-endangered-and-threatened-species-from-pesticides

<sup>&</sup>lt;sup>3</sup> Seepage 32 in the Assessment Criteria and Washington State Water Quality Standards section of this report

# Assessment Criteria and Washington State Water Quality Standards:

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

- In this report, **Assessment Criteria** refer to:
  - Data from Studies that Determine Hazard to Non-target Organisms are used to fulfill the Data Requirements for Pesticide Registration (Code of Federal Regulations 40CFR Part 158: Subpart G 158.630 and 158.660). Toxicity data from these studies are commonly used to conduct screening-level risk assessments and will be referred to in this report as **pesticide registration toxicity data**. Toxicity data used in this report include:
    - Lowest tested EC<sub>50</sub> or LC<sub>50</sub> values for freshwater fish, freshwater invertebrates and estuarine/marine fish and invertebrates from acute toxicity tests.
    - Lowest NOAEC values for freshwater fish, freshwater invertebrates and estuarine/marine fish and invertebrates from early life-stage or full lifecycle tests.
  - EPA's <u>National Recommended Water Quality Criteria</u> (NRWQC) for the
    protection of aquatic life and human health in surface water for approximately
    150 pollutants. These criteria are published pursuant to Section 304(a) of the
    Clean Water Act (CWA) and provide guidance for states and tribes to use in
    adopting water quality standards.
- In this report, **State Water Quality Standards** refer to
  - Numeric values from the <u>Water Quality Standards For Surface Waters of The State of Washington (WAC 173-201A).</u>

Pesticide registration toxicity data (acute and chronic) for fish, invertebrates, and aquatic plants are presented in Appendix C. Numeric exceedances of the values in Appendix C do not necessarily indicate water quality criteria have been exceeded as there is typically a temporal duration of exposure criteria associated with the numeric criteria. Assessment criteria and water quality standards are developed by evaluating the effects of a single chemical on a specific species and do not take into account the effects of multiple chemicals or pesticide mixtures on an organism.

# Pesticide Registration Toxicity Data

Acute toxicity is calculated by standardized toxicity tests using lethality as the measured criteria. A properly conducted test will use a representative (sensitive) 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 Observable Adverse Effect Concentration** (NOAEC) is the highest concentration in the toxicity test not showing a statistically significant difference from the control.
- The **Lowest Observable Adverse Effect Concentration** (LOEC) is the lowest concentration in a toxicity test showing a statistically significant difference from the control. The NOAEC is by definition the next concentration below the LOEC in the concentration series.
- The LC<sub>50</sub> is the "lethal concentration" causing mortality in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and using that equation to calculate the concentration for any level of effect, in this case the 50% value.
- The EC<sub>50</sub> is the "effect concentration" causing an effect in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and using that equation to calculate the concentration for any level of effect, in this case the 50% value.

For fish, the acute lethality test is conducted over 96 hours and the acute test for invertebrates is normally conducted over 48 hours, with the criteria being mortality (LC<sub>50</sub>) or immobility (EC<sub>50</sub>). The acute toxicity test for aquatic plants is conducted over 96 hours, and the biological endpoint is reduction in growth (EC<sub>50</sub>).

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 acute tests (21 day for fish, 14 days for invertebrates, 4 to 60 days for plants) to simulate exposure resulting from a persistent chemical, or effect of repeated applications.

When comparing the monitoring data either to the aquatic life criteria or directly to the pesticide registration toxicity data, both the duration of exposure and the numeric toxicity value must be considered. It is not possible to determine if the toxicity values or criteria were exceeded based solely on an individual sample because the sampling frequency is usually weekly, not allowing for assessment of the temporal component of the criteria.

Pesticide concentrations in streams are constantly changing and may occur above aquatic life criteria for durations of time less than or greater than the test durations used to set the aquatic life criteria.

- If the stream concentration of a pesticide is above its aquatic life criterion for less time than the test duration, then comparison to the criterion may overestimate the risk.
- If the concentration for a pesticide is above its aquatic life criterion for a longer time than the test duration, then comparison to the criterion will likely underestimate the risk.

The EPA uses a deterministic approach to assess the potential risk of a pesticide to non-target organisms. In this approach risk quotients (RQ) are calculated by dividing a point estimate of environmental exposure by a point estimate of effect and are an expression of concentration over toxicity.

$$Risk\ Quotient = \frac{Pesticide\ Exposure}{Pesticide\ Toxicity}$$

The risk quotients are unit-less values that are compared to Levels of Concern (LOC). Levels of Concern provide an additional safety factor to increase the likelihood that non-target organisms exposed to a pesticide at a given concentration will not experience unreasonable adverse effects. The LOCs set by EPA are presented in Table 3.

Table 3: Risk Quotients and Levels of Concern

Risk Presumptions	Risk Quotient	LOC	Description of Risk for Salmonids
Acute High Risk	EEC/LC <sub>50</sub> or EC <sub>50</sub>	≥0.5	Potential for acute risk to non-target organisms which may warrant regulatory action in addition to restricted use classification
Acute Restricted Use	EEC/LC <sub>50</sub> or EC <sub>50</sub>	≥0.1	Potential for acute risk to non-target organisms, but may be mitigated through restricted use classification
Acute Endangered Species	EEC/LC <sub>50</sub> or EC <sub>50</sub>	≥0.05	Endangered species may be potentially affected at this level
Chronic Risk	EEC/NOAEC	≥1	Potential for chronic risk may warrant regulatory action, endangered species may potentially be affected through chronic exposure including growth, reproduction, and effects on progeny.
Aquatic Plants - Acute High Risk	EEC/EC <sub>25</sub>	≥1	May have indirect effects on aquatic vegetative cover for threatened and endangered fish.
Aquatic Plants - Acute Endangered Species	EEC/EC <sub>05</sub> or NOEC	≥1	May have indirect effects on aquatic vegetative cover for threatened and endangered fish.

EEC = Estimated environmental concentration

Table 3 is adapted from EPA's <u>Technical Overview of Ecological Risk Assessment</u>

The endangered species LOC ( $\geq$ 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 1/20th of the LC<sub>50</sub>. To assess the potential risk of a pesticide to salmonids, the LC<sub>50</sub> for rainbow trout is commonly used as a surrogate species. Thus the endangered species LOC presented in subsequent tables are 1/20th of the rainbow trout LC<sub>50</sub>. When available, the endangered species LOC for specific salmonids is also presented.

# 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 for 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.

# Numeric 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. The numeric criteria of the Washington State water quality standards are based on the aquatic life uses as shown in Table 4.

Table 4: Washington Aquatic Life Uses & Criteria for Conventional Water Quality Parameters

	Temperature	Dissolved	рН	Monitoring Locations		
Aquatic Life Uses	Highest 7- DADMax ( <sup>0</sup> C)	Oxygen (Lowest 1-day minimum) (Standard Units)		Western Washington	Eastern Washington	
Freshwater - Core Summer Salmonid Habitat	16.0 °C	9.5 mg/L	6.5-8.5 (with a human caused variation within the above range of <0.2 units)	Thornton Creek	NA	
Freshwater - Salmonid Spawning, Rearing, and Migration Habitat	17.5 °C	8.0 mg/L	6.5-8.5 (with a human caused variation within the above range of <0.5 units)	Upper and Lower Bertrand Creek, Upper and Lower Big Ditch, Indian Slough, Longfellow Creek	Marion Drain, Spring Creek, Sulphur Creek, Peshastin Creek, Brender Creek, Mission Creek, Stemilt Creek	
Freshwater - Supplemental Spawning and Incubation Temperature Criteria - October 1-May 15	13.0 °C	NA	NA	Thornton Creek	NA	
Marine waters - Aquatic Life Excellent use	16.0 °C	6.0 mg/L	7.0-8.5 (with a human caused variation within the above range of <0.5 units)	Browns Slough	NA	

7-DADmax: water temperature is measured by the 7-day average of the daily maximum temperature.

Freshwater - Core Summer Salmonid Habitat: The key identifying characteristics of this use are summer (June 15 - September 15) salmonid spawning or emergence, or adult holding; use as important summer rearing habitat by one or more salmonids; or foraging by adult and subadult native char. Other common characteristic aquatic life uses for waters in this category include spawning outside of the summer season, rearing, and migration by salmonids.

Freshwater - Salmonid Spawning, Rearing, and Migration Habitat: The key identifying characteristic of this use is salmon or trout spawning and emergence that only occurs outside of the summer season (September 16 - June 14). Other common characteristic aquatic life uses for waters in this category include rearing and migration by salmonids.

# **Results Summary:**

# Pesticide Detection Summary

A summary of the results from the 2014 monitoring season are described in this section. Data presented in this section of the report only include results where pesticides were positively identified ("D", "J", or "E"). Data where pesticides were tentatively identified ("NJ"), rejected ("REJ"), or not detected ("U", or "UJ") were not included in this summary section. Table 5 provides a statewide overview of the 61 positively identified pesticides detected in 2014 (organized by general use category). The minimum method detection limits and ESLOC values are provided for comparison.

Table 5: Summary of Pesticide Detections at All Monitoring Locations in 2014

Pesticides Detected in 2014 by Use Category	Total Number of Detections	Maximum Concentration (μg/L)	Average Concentration (µg/L)*	Standard Deviation (µg/L)*	Method Detection Limits (µg/L)	ESLOC for Freshwater Fish (µg/L)
HERBICIDES	698					
Dichlobenil	96	0.091	0.02	0.01	0.01	246.50
2,4-D	94	0.740	0.13	0.14	0.04	21.40
Diuron	60	7.510	0.16	0.97	0.01	97.50
Metolachlor	56	0.290	0.05	0.05	0.02	190.00
Imazapyr	50	1.460	0.08	0.22	0.02	5000.00
Triclopyr	46	0.640	0.14	0.15	0.02	95.00
Terbacil	41	0.270	0.09	0.06	0.01	2310.00
Simazine	35	1.400	0.16	0.24	0.03	2025.00
MCPA	26	0.290	0.09	0.08	0.03	38.00
Mecoprop (MCPP)	25	0.190	0.04	0.04	0.01	6240.00
Dicamba	20	0.063	0.03	0.01	0.02	1400.00
Bentazon	18	0.320	0.14	0.06	0.05	5000.00
Chlorpropham	17	99.000	8.74	24.02	0.01	285.00
Dacthal (DCPA)	17	0.620	0.24	0.23	0.02	330.00
Tebuthiuron	15	0.230	0.09	0.05	0.01	7150.00
Trifluralin	14	0.031	0.03	0.00	0.02	2.18
Picloram	12	0.180	0.10	0.04	0.05	275.00
Pendimethalin	11	0.140	0.06	0.03	0.02	6.90
Eptam	9	0.920	0.17	0.29	0.03	700.00
Bromacil	8	0.064	0.05	0.01	0.03	1800.00
Atrazine	6	0.075	0.03	0.02	0.02	265.00
Norflurazon	5	0.046	0.03	0.01	0.03	405.00
Bromoxynil	3	0.057	0.04	0.02	0.02	2.50
Diphenamid	3	0.027	0.03	0.00	0.02	4850.00
Hexazinone	3	0.091	0.07	0.02	0.05	9000.00
Metribuzin	3	0.048	0.04	0.01	0.03	2100.00
Prometon	2	0.030	0.03	0.00	0.03	600.00
Cycloate	1	0.110	0.11	n/a	0.11	225.00
Monuron	1	0.007	0.01	n/a	0.01	no criteria
Napropamide	1	0.053	0.05	n/a	0.05	320.00

Pesticides Detected in 2014 by Use Category	Total Number of Detections	Maximum Concentration (μg/L)	Average Concentration (µg/L)*	Standard Deviation (µg/L)*	Method Detection Limits (µg/L)	ESLOC for Freshwater Fish (µg/L)
INSECTICIDES	248					
Oxamyl	63	0.141	0.04	0.04	0.00	210.00
Dinotefuran	49	6.970	1.03	1.37	0.01	4955.00
Thiamethoxam	41	0.070	0.03	0.01	0.01	5000.00
Chlorpyrifos	29	2.100	0.11	0.38	0.01	0.15
Diazinon	19	0.100	0.04	0.02	0.01	4.50
Imidacloprid	19	0.180	0.08	0.06	0.02	4150.00
Carbaryl	6	0.087	0.04	0.03	0.01	60.00
Methomyl	6	0.013	0.01	0.00	0.00	43.00
Acetamiprid	3	0.029	0.02	0.01	0.02	5000.00
Bifenthrin	3	0.082	0.05	0.03	0.03	0.01
Etoxazole	3	0.310	0.15	0.14	0.05	18.50
Methoxyfenozide	3	0.006	0.01	0.00	0.01	210.00
4,4'-DDT	1	0.028	0.03	n/a	0.03	no criteria
Malathion	1	0.077	0.08	n/a	0.08	1.64
Methiocarb	1	0.046	0.05	n/a	0.05	21.80
Propargite	1	0.029	0.03	n/a	0.03	5.90
FUNGICIDES	96					
Metalaxyl	59	1.100	0.10	0.16	0.02	920.00
Boscalid	28	0.335	0.12	0.07	0.03	135.00
Cyprodinil	5	0.015	0.01	0.00	0.01	12.05
Chlorothalonil (Daconil)	2	0.700	0.37	0.47	0.03	2.12
Fenarimol	2	0.064	0.06	0.01	0.05	105.00
DEGRADATES	86					
Oxamyl oxime	29	0.111	0.05	0.02	0.01	no criteria
4,4'-DDE	25	0.100	0.03	0.02	0.01	no criteria
Tetrahydrophthalimide	10	0.340	0.20	0.10	0.03	no criteria
4-Nitrophenol	8	0.770	0.25	0.25	0.05	200.00
Malaoxon	8	0.026	0.01	0.01	0.00	1.64
4,4'-DDD	3	0.012	0.01	0.00	0.01	no criteria
3,5-Dichlorobenzoic Acid	2	0.012	0.01	0.00	0.01	no criteria
2,3,4,6-Tetrachlorophenol	1	0.040	0.04	n/a	0.04	no criteria
WOOD PRESERVATIVES	19					
Pentachlorophenol	19	2.100	0.16	0.47	0.02	0.75
SYNERGISTS	4					
Piperonyl Butoxide (PBO)	4	0.700	0.23	0.31	0.03	95.00

 $<sup>\</sup>ensuremath{\text{n/a}}$ : Unable to calculate a standard deviation from a single detection

<sup>\*</sup>Values have been rounded to two decimal places for readability in this column

During 2014, there were 1,151 individual detections of 61 pesticides (and pesticide-related compounds) at 15 sites sampled statewide (Table 5 and Figure 9).

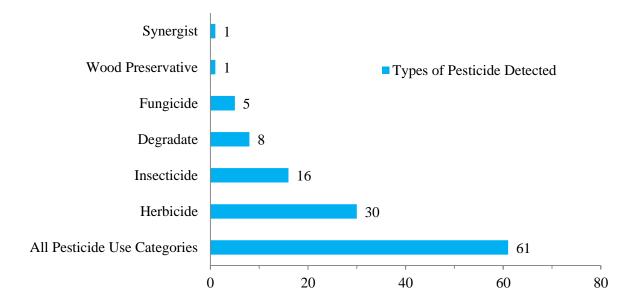


Figure 9: Types of Pesticides Detected in 2014

Herbicides were the most frequently detected class of pesticide, followed by insecticides, fungicides, pesticide degradates, wood preservatives, and then synergists (Figure 10). In 2013 (for comparison), there were 1,572 detections of 67 pesticides (and pesticide-related compounds) for the 17 sites sampled statewide.

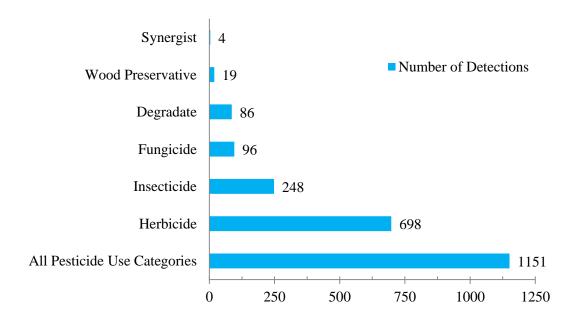


Figure 10: Pesticide Detections by Use Category in 2014

#### Herbicide Detections

Herbicides were the most frequently detected use group making up approximately 60.6% of the total detections. Out of the 61 herbicides included in the laboratory analysis, 30, or approximately half were positively identified in 2014. Dichlobenil, 2,4-D, and diuron were the most commonly detected herbicides with 96, 94, and 60 detections respectively. Diuron was the only herbicide to exceed the assessment criteria in 2014.

#### **Insecticide Detections**

Insecticides were the second most frequently detected pesticides making up approximately 21.5% of the total detections. Out of the 76 insecticides and isomers included in the laboratory analysis, 16, or slightly less than one quarter were positively identified in 2014. Oxamyl, dinotefuran, and thiamethoxam were the most commonly detected insecticides with 63, 49, and 41 detections respectively.

#### **Fungicide Detections**

Fungicides were the third most frequently detected pesticides making up 96 (8.3%) of the total detections. Out of 10 fungicides included in the laboratory analysis, 5, or exactly half were positively identified in 2014. Metalaxyl, boscalid, and cyprodinil were the most commonly detected fungicides with 59, 28, and 5 detections respectively.

## **Degradate Detections**

There were 86 detections of pesticide degradates found in 2014 accounting for approximately 7.5% of the total detections. Oxamyl oxime (degradate of the carbamate insecticide/acaricide/nematicide oxamyl) was the most frequently found degradate with 29 detections, followed by 4,4'-DDE (degradate of 4,4'-DDT) with 25 detections, and tetrahydrophthalimide (a degradate of the fungicide captan) with 10 positive detections.

## Comparison of Upper Bertrand Creek to Lower Bertrand Creek

During the 2014 sample season both the upstream (Upper) and downstream (Lower) Bertrand Creek monitoring sites were sampled weekly on the same day. Between March and September, 24 pesticides were detected between the two monitoring locations, including 7 pesticides detected only at the downstream site (Table 6).

Table 6: Comparison between Upper Bertrand Creek and Lower Bertrand Creek
Pesticide Detections

D41.11.	Number of	Detections
Pesticide	Upper Bertrand Creek	Lower Bertrand Creek
2,4-D	3	1
Atrazine*	-	1
Boscalid	6	5
Bromacil*		6
Cyprodinil*		4
Diazinon	1	8
Dicamba	2	1
Dichlobenil	11	11
Diuron*	-	3
Imidacloprid	3	2
Malaoxon*	-	3
MCPA	6	2
Mecoprop (MCPP)	4	3
Metalaxyl	5	25
Metolachlor	4	3
Napropamide*	-	1
Oxamyl	21	27
Oxamyl oxime	6	23
Pentachlorophenol*	-	2
Simazine	17	10
Terbacil	15	4
Tetrahydrophthalimide	2	8
Thiamethoxam	8	19
Triclopyr	3	1
Total Number of Detections	117	173

<sup>--</sup> Pesticide was not detected at this monitoring station.

## Comparison of Upper Big Ditch to Lower Big Ditch

During the 2014 sample season both the upstream (Upper) and downstream (Lower) Big Ditch sites were sampled weekly. Between March and September a total of 165 pesticides were

<sup>\*</sup>Pesticides detected only at Lower Bertrand Creek: atrazine, bromacil, cyprodinil, diuron, maloaxon, napropamide, and pentachlorophenol

detected at Upper Big Ditch and 118 pesticides were detected at Lower Big Ditch. Of the 30 pesticides that were detected between the two monitoring sites, 11 were detected only at the upstream site and five others were detected only at the downstream site (Table 7).

Table 7: Comparison between Upper Big Ditch and Lower Big Ditch Pesticide Detections

D. (1.11)	Number of	Detections
Pesticide	Upper Big Ditch	Lower Big Ditch
2,4-D	12	8
3,5-Dichlorobenzoic Acid*	2	
4-Nitrophenol*	1	
Atrazine**		1
Bifenthrin*	3	
Boscalid*	15	
Chlorothalonil (Daconil)*	1	
Chlorpropham**		11
Chlorpyrifos*	1	
Cyprodinil*	1	
Diazinon**		2
Dicamba*	1	
Dichlobenil	17	11
Dinotefuran	27	21
Diuron	6	4
Eptam**		1
Imazapyr	21	3
Imidacloprid	8	2
MCPA	1	4
Mecoprop (MCPP)	6	3
Metalaxyl	14	7
Methiocarb*	1	
Metolachlor	1	22
Metribuzin**		2
Pentachlorophenol	3	1
Picloram*	1	
Prometon	1	1
Tebuthiuron*	6	
Thiamethoxam	4	2
Triclopyr	11	12
Total Number of Detections	165	118

<sup>--</sup> Pesticide was not detected at this monitoring station.

<sup>\*</sup>Pesticides detected only at Upper Big Ditch: 3,5-dichlorobenzoic acid, 4-nitrophenol, bifenthrin, boscalid, chlorothanonil (daconil), chlorpyrifos, cyprodinil, dicamba, methiocarb, picloram, and tebuthiuron

<sup>\*\*</sup>Pesticides detected only at Lower Big Ditch: atrazine, chlorpropham, diazinon, eptam, and metribuzin

# Pesticides Exceedances Summary

In 2014 there were 1,151 total detections. 48 detections exceeded criteria. Nine compounds made up that total of 48. Those nine compounds were detected 144 times total (Table 8.) Thirty-three percent of the time those nine compounds were detected, the concentrations exceeded the criteria. The exceedances are summarized in Table 8.

Table 8: Summary of Pesticides in Exceedance of Assessment Criteria and State Water Quality Standards

Pesticide	Pesticide Use Category	Number of Detections in 2014	Number of Detections Above Criteria or Standards	Percentage of Detections Above Criteria or Standards	Monitoring Locations where Exceedances Occurred
Bifenthrin	Pyrethroid Insecticide	3	3	100.00%	Upper Big Ditch
Chlorpyrifos	Organophosphate Insecticide	29	12	41.38%	Brender Creek, Marion Drain, Mission Creek, Stemilt Creek, Spring Creek, Sulphur Creek Wasteway
Malathion	Organophosphate Insecticide	1	1	100.00%	Stemilt Creek
Etoxazole	Organoflourine Insecticide	3	1	33.33%	Mission Creek
Pentachlorophenol	Wood Preservative	19	1	5.26%	Stemilt Creek
Diuron	Phenylurea Herbicide	60	1	1.67%	Spring Creek
4,4'-DDT <sup>A</sup>	Organochlorine Insecticide	1	1	100.00%	Brender Creek
4,4'-DDE <sup>A</sup>	Degradate (Organochlorine)	25	25	100.00%	Brender Creek, Sulphur Creek Wasteway
4,4'-DDD <sup>A</sup>	Degradate (Organochlorine)	3	3	100.00%	Brender Creek
	Total	144	48	33.33%	

<sup>&</sup>lt;sup>A</sup> Detections of DDT and its degradates (4,4'-DDE and 4,4'-DDD) are a result of sediment runoff in areas where DDT was historically used and are not a result of current pesticide use patterns

Pesticide exceedances were found at 7 of the 15 monitoring locations; Upper Big Ditch, Stemilt Creek, Marion Drain, Spring Creek, Sulphur Creek Wasteway, Brender Creek, and Mission Creek. Of the 48 exceedances, 28 (58.3%) occurred at Brender Creek and 25 (89.3%) of the total exceedances at Brender Creek were DDT and its degradates DDE and DDD (Table 11). For comparison, there were 76 exceedances in 2013 for one herbicide, six current use insecticides, one legacy insecticide, and three different degradates of organochlorine insecticides (1 current use and 2 historical use).

At 8 of the 15 monitoring locations (Thornton Creek, Longfellow Creek, Upper and Lower Bertrand Creek, Browns Slough, Indian Slough, Peshastin Creek, and Lower Big Ditch), all pesticide detections were at concentrations below available pesticide assessment criteria and standards.

Of the 48 pesticide exceedances, 3 (6.3%) were at monitoring locations in western Washington and the other 45 (93.7%) occurred at monitoring locations in eastern Washington (Figure 11).

#### Exceedances by Legacy Insecticides

DDT and its degradates accounted for 60.4% of the exceedances detected in 2014, (Figure 11). Of the 29 DDT, DDD, and DDE detections, 100% exceeded the state water quality criteria. Because of its persistence in soils, DDT and its degradates (4,4'-DDE, and 4,4'-DDD) are detected because of either sediment entering surface water as a result of runoff in agricultural areas or stream sediment disturbance in areas where DDT was historically used. These detections are not a result of current pesticide use patterns.

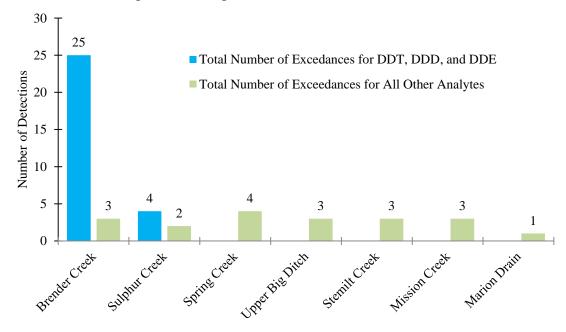


Figure 11: Monitoring Locations Where Pesticide Exceedances Occurred in 2014

#### Current use Insecticide Exceedances

Current use insecticides including two organophosphate insecticides (chlorpyrifos and malathion), one organoflourine insecticide (etoxazole), and one pyrethroid (bifenthrin), accounted for 35.4% of all exceedances.

#### Herbicide Exceedances

Although there were 698 total detections of herbicides, only one herbicide detection was above the assessment criteria accounting for 2.1% of the total exceedances in 2014. Diuron was the third most commonly detected herbicide (60 detections) in 2014 and the only herbicide to exceed the assessment criteria.

#### **Wood Preservative Exceedances**

There were 19 detections of the wood preservative pentachlorophenol in 2014. Only one detection was above the assessment criteria accounting for 2.1% of all exceedances in 2014.

# Pesticide Mixtures Analysis

For the purposes of this report, *pesticide mixtures* will refer to environmental mixtures containing two or more pesticides. This term is different than pesticide tank mixtures, a combination of one or more agricultural or non-agricultural chemicals intentionally mixed before pesticide application for a variety of reasons.

The data from the 2014 monitoring season shows pesticide mixtures were found at more than half of the 405 site visits. Two or more pesticides were detected 240 times (59.26%). There were 78 instances (19.26%) where only one pesticide was detected, and 87 site visits (21.48%) where no pesticides were detected (Figure 12).

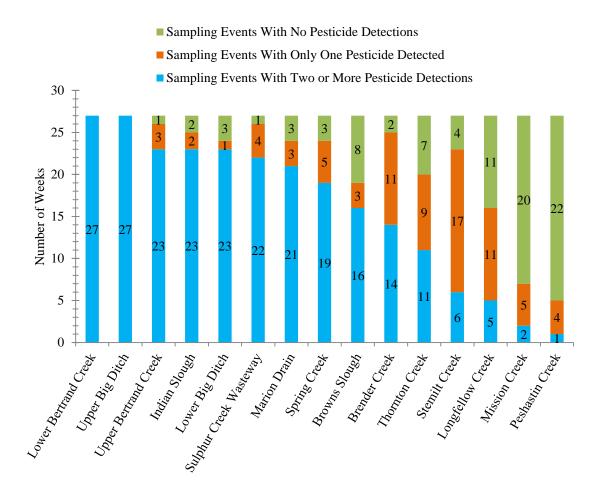


Figure 12: Number of Weeks Where Mixtures Were Detected at Site Visits in 2014

At least one pesticide mixture was detected at every monitoring location in 2014 and the frequency of mixtures detected varied greatly between locations. Of the 15 monitoring locations, pesticide mixtures were detected every week of the 27 week monitoring season for Lower Bertrand Creek in the Nooksack watershed (WRIA 1) and Upper Big Ditch in the Lower Skagit-Samish watershed (WRIA 3). In contrast, pesticide mixtures were detected in two or less weeks at two of the monitoring sites located in the Wenatchee watershed (WRIA 45).

The average number of pesticides detected at site visits over the whole season for all sites was 2.84 and by site ranged from 0.2 detections per site visit at the Peshastin Creek monitoring location to 6.4 detections per site visit at the at Lower Bertrand Creek monitoring location

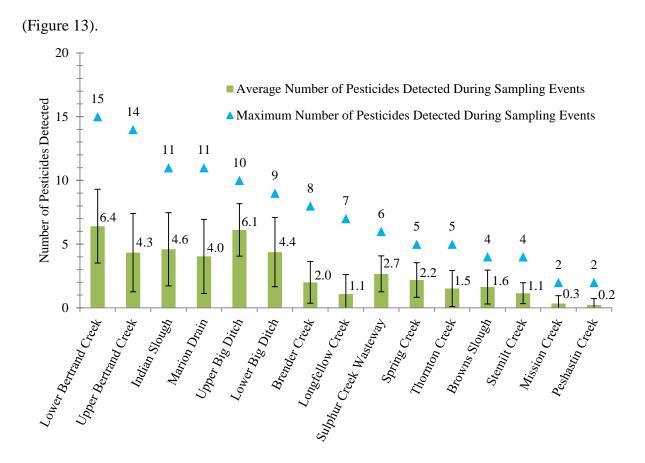


Figure 13: Average and Maximum Number of Pesticides in a Mixture Detected in 2014

The maximum number of pesticides detected at a single site visit over the whole season was 15 at Lower Bertrand Creek. The lowest number of pesticides detected during a single site visit was two at Peshastin and Mission Creeks.

# Toxicity Unit Analysis

Although, there is currently no formal guidance from EPA on assessing risk to aquatic life from exposure to environmental mixtures containing two or more unrelated chemicals, it is possible to estimate the potential risk to aquatic species by making some assumptions using the same assessment criteria used to evaluate risk from a single chemical exposure.

In order to estimate the potential risk to aquatic life from exposure to pesticide mixtures, a toxicity unit analysis was completed using the method discussed on pages 28-29 of this report. Table 9 provides a summary of the 13 site visits with pesticide mixtures having an overall estimated toxicity above one of the levels of concern ( $TU \ge 1.0$ ). Values in Table 9 exceeding the LOC are highlighted in bold.

The analysis used the same assessment criteria shown in Appendix C to evaluate risk from a single chemical exposure. Toxicity units were calculated for all 405 site visits. Of the 405 site visits, 13 were associated occurrences where the sum of the individual risk quotients (toxicity units) were greater than or equal to 1 ( $TU \ge 1.0$ ) as compared to 5 different LOCs for Endangered Species, Acute, and Chronic LOCs (discussed on pages 31-33 in the *Assessment Criteria and Washington State Water Quality Standards* section of this report).

Of the 13 site visits exceeding one or more of the five LOCs, six were primarily due to an elevated concentration of a single pesticide without the contribution of other pesticides in a mixture or were the only pesticide detected.

The most common pesticides representing significant contributions to the Overall TU Values ( $\geq$  0.01 TU) are chlorpyrifos and bifenthrin.

Table 9: Toxicity Unit Analysis for Endangered Species, Acute, and Chronic LOCs

	Site Visit		Level	of Concern (LO	OC) <sup>A,C</sup>		Number of	Pesticides Representing a
Monitoring Site	Date	Endangered Species	Fisheries Acute	Invertebrate Acute	Fisheries Chronic	Invertebrate Chronic	Pesticides in the Mixture	Significant Contribution to the Overall TU Values (≥ 0.01 TU)
Upper Big Ditch	5/6/2014	<u>4.14</u>	0.41	0.78	0.04	23.85	6	Bifenthrin <sup>B</sup>
Upper Big Ditch	6/2/2014	<u>4.54</u>	0.45	0.85	0.05	<u>26.15</u>	8	Bifenthrin <sup>B</sup>
Upper Big Ditch	8/19/2014	10.94	1.09	2.05	0.11	63.11	9	Bifenthrin <sup>B</sup> , Metolachlor
Brender Creek	4/1/2014	0.41	0.04	0.11	1.22	1.53	3	Chlorpyrifos <sup>B</sup>
Brender Creek	4/22/2014	0.31	0.03	0.12	0.98	<u>1.30</u>	3	Chlorpyrifos <sup>B</sup> , Diazinon
Marion Drain	5/28/2014	0.40	0.04	0.13	<u>1.11</u>	<u>1.40</u>	11	Chlorpyrifos <sup>B</sup> , Trifluralin
Mission Creek	4/1/2014	<u>14.01</u>	<u>1.40</u>	3.70	42.00	<u>52.52</u>	2	Chlorpyrifos <sup>B</sup> , Piperonyl Butoxide (PBO)
Stemilt Creek	6/24/2014	0.06	0.01	0.01	0.35	<u>1.72</u>	4	Malathion <sup>B</sup> , Malaoxon
Spring Creek	3/25/2014	0.98	0.10	0.51	<u>2.61</u>	3.29	5	Chlorpyrifos <sup>B</sup> , Diuron
Spring Creek	3/31/2014	0.65	0.06	0.27	<u>2.06</u>	2.77	4	Chlorpyrifos <sup>B</sup> , Diazinon
Spring Creek Wasteway	4/8/2014	0.34	0.03	0.09	1.02	<u>1.28</u>	2	Chlorpyrifos <sup>B</sup>
Sulfur Creek Wasteway	3/19/2014	0.56	0.06	0.15	<u>1.68</u>	2.10	5	Chlorpyrifos <sup>B</sup>
Sulfur Creek Wasteway	3/25/2014	<u>1.13</u>	0.11	0.30	3.40	4.25	3	Chlorpyrifos <sup>B</sup>

<sup>&</sup>lt;sup>A</sup> Toxicity units where  $TU \ge 1.0$ ) are indicated by **bold and underlined** values and signify the additive toxicity was above a level of concern.

<sup>&</sup>lt;sup>B</sup> Indicates the level of concern was exceeded primarily due to an elevated concentration of a single pesticide.

<sup>&</sup>lt;sup>C</sup> The toxicity unit values could be slightly underestimated in some cases due to the lack of criteria for some pesticides and their metabolites.

#### Pesticide Calendars

The calendars provide a chronological overview of the pesticides detected during the 2014 monitoring season. The calendars provide a visual comparison to the assessment criteria (pesticide registration toxicity data and NRWQC) and to the state water quality standards (numeric Washington State Water Quality Standards). For specific values and information on assessment criteria development refer to Appendix C: Assessment Criteria and Water Quality Standards.

Table 10 presents the color codes used in Tables 11 through 25 to compare detected pesticide concentrations to assessment criteria and state water quality standards. In the calendars, the number below the months indicate the week of the year the site visit occurred and each column indicates the data associated with that event.

Table 10: Color codes for comparison to assessment criteria in the pesticide calendars

Calendar Color	Exceedance Description
	Magnitude of detection above the acute freshwater assessment criterion
	Magnitude of detection above the Endangered Species Level of Concern for fish (ESLOC)
	Magnitude of detection above the acute invertebrate assessment criterion
	Magnitude of detection above the acute freshwater criteria of the state water quality standard (WACA)
	Magnitude of detection above the chronic freshwater criteria of the state water quality standard (WAC <sup>A</sup> )
	Magnitude of detection above the NRWQC <sup>B</sup> CMC <sup>C</sup> criterion
	Magnitude of detection above the NRWQC <sup>B</sup> CCC <sup>D</sup> criterion
	Magnitude of detection above the chronic freshwater fisheries assessment criterion
	Magnitude of detection above the chronic freshwater invertebrate assessment criterion
	Magnitude of detection above the acute freshwater plant assessment criterion
	Magnitude of detection above the chronic freshwater plant assessment criterion
	Detection did not exceed criteria
	No published criteria available (no comparison made)
	Non-detect (no comparison made)

<sup>&</sup>lt;sup>A</sup> WAC: Washington Administrative Code

<sup>&</sup>lt;sup>B</sup> NRWQC: National Recommended Water Quality Criteria

<sup>&</sup>lt;sup>C</sup> CMC: Criterion Maximum Concentration <sup>D</sup> CCC: Criterion Continuous Concentration

Detection of a pesticide concentration above the assessment criteria does not necessarily indicate an exceedance has occurred because the temporal component of the criteria must also be exceeded. The 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. Please contact the <u>Pesticide Management Division</u> for more information on regulatory issues, technical assistance, and compliance questions. Please contact the <u>Natural Resources Assessment Section</u> for more information on mitigation and how to protect surface water, sensitive areas, and endangered species from pesticides applications.

# Nooksack basin (WRIA 1) Pesticide Calendars

## Upper Bertrand Creek 2014 Pesticide Calendar

In 2014, there was a total of 117 pesticide detections at Upper Bertrand Creek for 17 pesticides or pesticide related compounds (Table 11). All pesticides detected in Upper Bertrand Creek were below the pesticide assessment criteria and water quality standards.

Table 11: Upper Bertrand Creek, 2014 Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

11																			0 /									
Month			M	lar			A	pr			M	ay			J	un				Jul				Aı	ug		S	ep
Day of the Month	Use	10	17	25	31	8	14	23	28	7	12	21	27	3	9	17	23	1	7	15	21	29	4	11	18	25	2	8
2,4-D	Н									0.05			0.074					0.089										
Boscalid	F	0.23	0.12		0.076	0.14							0.12		0.031													
Diazinon	I-OP												0.033															
Dicamba	Н									0.042			0.032															
Dichlobenil	Н		0.006	0.009	0.033	0.034		0.022	0.013	0.015	0.011	0.009	0.022	0.008														
Imidacloprid	I-N										0.036		0.027			0.021												
MCPA	Н									0.089	0.084		0.17			0.044						0.041						0.046
Mecoprop (MCPP)	Н									0.034			0.073			0.022		0.014										
Metalaxyl	F					0.036				0.064			0.051					0.052										0.15
Metolachlor	Н							0.026		0.022						0.023	0.02											
Oxamyl	I-C	0.073	0.101	0.038	0.06	0.024	0.022	0.021	0.027	0.029	0.017	0.012	0.011	0.011	0.01	0.012	0.006	0.007	0.003			0.005			0.005			0.003
Oxamyl oxime	D-C			0.023			0.026		0.02					0.016				0.027	0.016									
Simazine	Н								0.091	0.13			0.35	0.099	0.07	0.072	0.057	1.4	0.22	0.16	0.099	0.088	0.093	0.08	0.091	0.05		0.062
Terbacil	Н	0.074	0.012	0.025	0.012	0.072		0.07	0.069	0.12	0.082	0.08	0.12	0.079	0.064		0.044	0.046										
Tetrahydrophthalimide	D-F									0.1			0.29															
Thiamethoxam	I-N													0.024	0.027			0.017	0.024	0.015	0.009	0.018						0.019
Triclopyr	Н												0.033					0.055	0.021									
Total Suspended Solids	NA	9	19	2	6	2	2	2	2	4	2	2	3	2	2	2	2	2	1	4	2.5	1	1	5	1		1	

C: Carbamate, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, NA: Not applicable

### Lower Bertrand Creek 2014 Pesticide Calendar

In 2014, there was a total of 172 pesticide detections at Lower Bertrand Creek for 24 pesticides or pesticide related compounds (Table 12). All pesticides detected in Lower Bertrand Creek were below the pesticide assessment criteria and water quality standards.

Table 12: Lower Bertrand Creek 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month				lar			A				M					un				Jul					1g			ер
Day of the Month	Use	10	17	25	31	8	14	23	28	7	12	21	27	3	9	17	23	1	7	15	21	29	4	11	18	25	2	8
2,4-D	Н												0.062															
Atrazine	Н																	0.037										
Boscalid	F	0.19	0.096		0.064					0.051												0.07					1	
Bromacil	Н											0.031								0.049	0.044		0.049		0.039		0.047	
Cyprodinil	F																	0.014	0.012	0.01	0.015							
Diazinon	I-OP							0.031		0.049	0.033	0.027	0.039	0.021								0.04	0.014					
Dicamba	Н									0.032																		
Dichlobenil	Н		0.01	0.01	0.026	0.024		0.021	0.016	0.014	0.01		0.013	0.007	0.006													
Diuron	Н																	0.013	0.015	0.017							1	
Imidacloprid	I-N									0.035		0.046																
MCPA	Н									0.071			0.075														l	
Malaoxon	D-OP																		0.003	0.004	0.008						<u> </u>	
Mecoprop (MCPP)	Н									0.024	0.017		0.038														L	
Metalaxyl	F	0.065			0.019		0.062	0.07	0.06	0.088	0.065	0.073	0.071	0.065	0.071	0.05	0.056	0.065	0.068	0.072	0.069	0.074	0.077	0.066	0.067	0.066	0.074	0.083
Metolachlor	Н							0.029		0.02						0.018											L	
Napropamide	Н				0.053																						<u> </u>	
Oxamyl	I-C	0.102	0.122	0.112	0.095	0.101	0.092	0.072	0.092	0.052	0.081	0.061	0.075	0.046	0.053	0.048	0.141	0.055	0.05	0.07	0.065	0.063	0.078	0.1	0.083	0.07	0.064	0.084
Oxamyl oxime	D-C			0.059		0.063	0.07	0.046	0.056	0.03	0.045	0.071	0.086	0.111		0.053	0.007	0.05	0.039	0.039	0.046	0.039	0.027	0.039	0.042	0.069	0.059	0.096
Pentachlorophenol	WP	0.022			0.067																						<u> </u>	
Simazine	Н							0.087	0.16	0.14			0.18	0.058				0.06	0.087	0.058		0.053			0.036		<u> </u>	
Terbacil	Н	0.059								0.11			0.085	0.04													L	
Tetrahydrophthalimide	D-F				0.029					0.21			0.15				0.25	0.255	0.25	0.085	0.34						<u> </u>	
Thiamethoxam	I-N						0.03	0.024		0.022	0.01		0.025	0.07	0.01		0.006	0.034	0.028	0.044	0.04	0.037	0.04	0.043	0.026	0.029	0.039	0.046
Triclopyr	Н																		0.035									
Total Suspended Solids	NA	16	32	7	12	4	2	5	6	12	6	3.5	6	3	6	2	2	4		2	5	1	2	2	1			

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

# Lower Skagit-Samish Basin (WRIA 3) Pesticide Calendars

## Upper Big Ditch 2014 Pesticide Calendar

In 2014, there was a total of 165 pesticide detections at Upper Big Ditch for 25 pesticides or pesticide related compounds (Table 13). There were three detections of bifenthrin above the ESLOC ( $0.0075 \mu g/L$ ) on May  $6^{th}$ , June  $2^{nd}$ , and August  $19^{th}$ . Bifenthrin detected on August  $19^{th}$  also exceeded the acute freshwater fisheries assessment criterion ( $0.075 \mu g/L$ ). All other pesticides detected in Upper Big Ditch were below the pesticide assessment criteria and water quality standards.

*Table 13: Upper Big Ditch 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)* 

Month			Mar				Apr				M	av				Jun		_		Jì	nl			Αι	1σ		Se	en
Day of the Month	Use	11	18	24	1	7	14	22	29	6	12	20	27	2	9	16	24	30	7	14	22	28	4	12	19	26	2	8 8
2,4-D	H	11	0.1	24	1	0.43	14	0.52	0.058	0.11	0.088		0.081		9	0.35	24	0.077	/	14	22	0.081	0.05	12	19	20	0.12	0
3,5-Dichlorobenzoic Acid	D-M		0.1			0.43		0.32	0.038	0.11	0.088		0.081			0.55		0.077				0.081	0.03			0.012	0.12	$\vdash$
4-Nitrophenol	D-M							0.13															0.011			0.012		
Bifenthrin	I-PY							0.13		0.031				0.034											0.082			
Boscalid	1-P1				0.063					0.031	0.040	0.14	0.066					0.14		0.335	0.12	0.11	0.17	0.13	0.082	0.18		0.12
Chlorothalonil (Daconil)	F				0.063					0.080	0.049	0.14	0.000	0.099				0.14		0.333	0.12	0.11	0.17	0.13	0.29	0.18		0.12
` ,	I-OP											0.055														0.022		
Chlorpyrifos	F																			0.007						0.022		
Cyprodinil Dicamba								0.038												0.007								$\vdash$
Dichlobenil	H	0.009	0.029	0.011	0.010	0.016		0.058	0.025	0.001	0.061	0.015	0.015	0.011	0.008	0.012									0.006		0.008	0.000
	H							0.052									0.624	1.20	0.206	2.07	1.7	1 40	2.24					
Dinotefuran	I-N	0.65	0.716	0.865	0.89	0.82	1.09	0.872	0.872	0.597	0.919	6.97	4.48 0.016	2.61	0.974	0.716	0.624	0.024	0.286	3.97	1./	1.48	3.34	0.934	4.01		0.205	0.200
Diuron	H	0.025	0.025	0.025	0.026	0.022	0.026	0.021	0.023					0.022	0.036		0.020		0.008	0.023	0.022	0.027	0.024	0.026	0.024	0.015	0.009	
Imazapyr		0.025	0.025	0.025	0.036	0.023	0.026	0.021	0.023				0.043			0.052	0.029		0.025		0.022	0.027	0.024		0.024		0.022	$\vdash$
Imidac loprid	I-N							0.10				0.155		0.18	0.039			0.059	0.035	0.175					0.137	0.038		
MCPA	H		0.044			0.000		0.13			0.000											0.046	0.056					
Mecoprop (MCPP)	Н		0.041			0.033		0.19			0.032	0.05	0.070	0.11					0.05		0.4		0.056	0.070	0.40	0.10	0.050	0.10
Metalaxyl	F										0.064	0.07	0.073	0.11					0.06	1.1	0.1	0.63	0.36	0.072	0.18	0.12	0.073	0.12
Methiocarb	I-C																	0.045										
Metolachlor	Н																								0.036			
Pentachlorophenol	WP		0.029				0.028	0.04																				
Picloram	Н																				0.11							
Prometon	Н																										0.029	
Tebuthiuron	Н											0.078					0.066							0.091		0.13	0.12	0.099
Thiamethoxam	I-N												0.027					0.011		0.023					0.012			$\vdash$
Triclopyr	Н						0.094	0.27	0.069		0.088		0.078	0.04		0.15		0.086									0.1	
Total Suspended Solids	NA	9	11	9	5	4	5	10	5	7	10	6	6.5	9	27	21	15	7	33	32	12	8	10	8	17	9	6	10

C: Carbamate, D: Degradate, M: Multiple, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, PY: Pyrethroid, OP: Organophosphate, WP: Wood preservative, NA: Not applicable

## Lower Big Ditch 2014 Pesticide Calendar

In 2014, there was a total of 118 pesticide detections at Lower Big Ditch for 19 pesticides or pesticide related compounds (Table 14). All pesticides detected in Lower Big Ditch were below the pesticide assessment criteria and water quality standards.

Table 14: Lower Big Ditch 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr				M	ay				Jun		., 0		Jı	ul			Aı	1g		S	ер
Day of the Month	Use	11	18	24	1	7	15	22	29	6	13	20	28	2	10	16	24	30	8	14	22	28	5	12	19	26	3	9
2,4-D	Н					0.34		0.063		0.41	0.091					0.66						0.073			0.16			0.12
Atrazine	Н																						0.024					
Chlorpropham	Н	0.23	2.2	0.62	3.1	0.7	99	17	20	4.8	0.17	0.083																
Diazinon	I-OP									0.062	0.037																	
Dichlobenil	Н		0.015		0.012	0.007		0.013	0.017	0.065	0.03	0.011	0.01	0.008														0.011
Dinotefuran	I-N		0.239		0.265	0.204	0.284	0.238	1.09	0.234	0.34	0.182	0.24	0.64	0.496	0.408	0.088	0.02				0.096	0.144		0.223	0.149	0.352	0.126
Diuron	Н					0.009							0.016	0.025														0.009
Eptam	Н													0.046														
Imazapyr	Н				0.015								0.025												0.019			
Imidacloprid	I-N						0.083							0.093														
MCPA	Н					0.053		0.061		0.072			0.069															
Mecoprop (MCPP)	Н									0.057						0.023						0.014						
Metalaxyl	F								0.21		0.064			0.13									0.054		0.067		0.032	0.079
Metolachlor	Н	0.043	0.039	0.015	0.035	0.041	0.026	0.094	0.076	0.18	0.098	0.12	0.29	0.15	0.028	0.049	0.11	0.025	0.022				0.02			0.02	0.022	0.031
Metribuzin	Н															0.048	0.04											
Pentachlorophenol	WP		0.029																									
Prometon	Н																											0.03
Thiamethoxam	I-N		0.01												0.053													
Triclopyr	Н	0.065	0.067			0.29		0.05		0.29	0.11		0.047	0.036		0.16						0.041			0.095			0.13
Total Suspended Solids	NA	20	24	33	24	26	12	70	24	21	19.5	28	12	18	10	12	10	8	10	8	7	5	4	5	6	9	11	8

F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, WP: Wood preservative, NA: Not applicable

## Indian Slough 2014 Pesticide Calendar

In 2014, there was a total of 124 pesticide detections at Indian Slough for 24 pesticides or pesticide related compounds (Table 15). All pesticides detected in Indian Slough were below the available pesticide assessment criteria and water quality standards.

Table 15: Indian Slough 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr				M					Jun					ul				ug			ер
Day of the Month	Use	14	18	24	1	7	15	22	29	6	13	20	28	2	10	16	24	30	8	14	22	28	5	12	19	26	3	9
2,4-D	Н							0.078	0.058	0.24			0.39		0.13	0.38	0.22					0.5	0.051		0.74			0.23
4-Nitrophenol	D-M						0.057																					
Chlorothalonil (Daconil)	F							0.7																				
Chlorpropham	Н	0.3			0.012	0.055	0.085					0.048	0.14															
Cycloate	Н									0.11																		
Diazinon	I-OP									0.1																		
Dicamba	Н												0.033			0.037												
Dichlobenil	Н	0.01	0.015		0.009	0.007		0.011	0.017	0.015	0.014	0.01	0.015		0.011	0.006						0.06			0.011			0.037
Diphenamid	Н					0.023																				0.027	0.025	
Diuron	Н	0.024						0.009		0.035			0.009									0.056				0.008		0.038
Eptam	Н												0.039															
Hexazinone	Н									0.091													0.064					
Imazapyr	Н		0.026		0.037	0.025		0.026	0.028				0.037			0.07	0.13	0.022				0.598	0.054	0.022	0.476	0.055	0.031	1.46
MCPA	Н														0.29	0.074	0.17		0.038			0.28	0.045					0.25
Mecoprop (MCPP)	Н															0.031												
Metalaxyl	F																											0.043
Methomyl	I-C									0.012																		
Metolachlor	Н		0.026					0.025	0.028	0.027	0.046		0.027	0.017		0.069	0.026	0.025				0.027						0.047
Monuron	Н																									0.007		
Pentachlorophenol	WP	0.023							0.022																			
Simazine	Н									0.53	0.21																	0.051
Tebuthiuron	Н			0.017	0.01	0.044	0.078										0.097							0.1		0.089	0.089	
Thiamethoxam	I-N		0.033			0.013				0.036	0.03		0.019	0.043														
Triclopyr	Н							0.082	0.066	0.18	0.057		0.43	0.051	0.103	0.39	0.13	0.04				0.58	0.054		0.64	0.036		0.32
Total Suspended Solids	NA	9	11	9	7	7	13.5	6	3	4	150.5	8	8	10	8	4	5	9	6	6	12	4	3	3	4	3	3	2

C: Carbamate, D: Degradate, M: Multiple, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, WP: Wood preservative, NA: Not applicable

# Browns Slough 2014 Pesticide Calendar

In 2014, there was a total of 44 pesticide detections at Browns Slough for 10 pesticides or pesticide related compounds (Table 16). All pesticides detected in Browns Slough were below the available pesticide assessment criteria and water quality standards.

Table 16: Browns Slough 2014, Comparison to Freshwater and Marine Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr				M	ay				Jun				J	ul			Aı	ıg		S	ер
Day of the Month	Use	14	18	24	1	7	15	22	29	6	13	20	28	2	10	16	24	30	8	14	22	28	5	12	19	26	3	9
2,4-D	Н						0.085																					
4-Nitrophenol	D-M															0.049												
Dacthal (DCPA)	Н	0.62	0.55	0.11	0.23	0.1	0.128	0.49	0.59	0.079	0.19	0.57	0.022	0.29		0.054	0.036	0.061										0.021
Diazinon	I-OP																								0.019			
Dichlobenil	Н								0.018																			
Eptam	Н												0.23	0.92		0.046												
Imazapyr	Н												0.023															
Metolachlor	Н		0.017				0.061	0.044	0.028	0.036	0.039	0.17	0.058	0.028	0.037	0.028	0.036	0.026										0.019
Oxamyl	I-C					0.009																						
Simazine	Н	0.052	0.37		0.064				0.027																			
Total Suspended Solids	NA	12	24	14	15	35	13	9.5	18	11	9	6	6	10	6	11	7	5	40	23	14	5	8	6	14	6	11	11

C: Carbamate, D: Degradate, M: Multiple, H: Herbicide, I: Insecticide, OP: Organophosphate, NA: Not applicable

# Cedar-Sammamish Basin (WRIA 8) Pesticide Calendar

### Thornton Creek 2014 Pesticide Calendar

In 2014, there was a total of 41 pesticide detections at Thornton Creek for 10 pesticides or pesticide related compounds (Table 17). All pesticides detected in Thornton Creek were below the available pesticide assessment criteria and water quality standards.

*Table 17: Thornton Creek 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)* 

Month			M	ar			A	pr			M	ay				Jun				J	ul			A	ug		S	ер
Day of the Month	Use	10	17	24	31	7	14	22	28	6	12	20	27	2	9	16	23	30	7	15	21	29	4	11	18	25	2	8
2,4-D	Н							0.45								0.102					0.047	0.04	0.046				0.079	
4-Nitrophenol	D-M	0.14						0.28																				
Carbaryl	I-C																										0.064	0.023
Dicamba	Н							0.063																				
Dichlobenil	Н	0.025	0.017		0.022	0.008		0.039	0.017	0.017	0.013	0.011	0.01	0.01		0.052											0.012	0.008
Diuron	Н	0.025											0.009														0.014	0.012
Imazapyr	Н			0.022		0.016							0.028										0.015		0.015			
Mecoprop (MCPP)	Н							0.16		0.019						0.035					0.019						0.023	
Pentachlorophenol	WP																		0.17									
Tebuthiuron	Н								0.23																			
Total Suspended Solids	NA	11	9	5	6	3	2	20	4	6	7	13	5	10	8	9	5	5	4	4	4	4	4	4	5	3	3	5

C: Carbamate, D: Degradate, M: Multiple, H: Herbicide, I: Insecticide, WP: Wood preservative, NA: Not applicable

# Green-Duwamish Basin (WRIA 9) Pesticide Calendar

## Longfellow Creek 2014 Pesticide Calendar

In 2014, there was a total of 87 pesticide detections at Longfellow Creek for 11 pesticides or pesticide related compounds (Table 18). All pesticides detected in Longfellow Creek were below the available pesticide assessment criteria and water quality standards.

Table 18: Longfellow Creek 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			N.	Iar			A	pr			M	ay			J	un				Jul				Aı	1g		S	ер
Day of the Month	Use	10	18	25	31	7	14	22	28	6	12	20	27	2	9	17	23	1	7	15	21	29	4	11	18	25	2	8
2,4-D	Н							0.24								0.065					0.068							
4-Nitrophenol	D-M							0.49																				
Boscalid	F																						0.12					
Dichlobenil	Н	0.032	0.018	0.009	0.025	0.013		0.049		0.031	0.015	0.012	0.012	0.009													0.009	0.006
Dinotefuran	I-N												0.009															
Diuron	Н							0.066					0.019														0.019	
Imazapyr	Н							0.085					0.021															
Mecoprop (MCPP)	Н							0.086		0.015						0.019												
Triclopyr	Н							0.064		0.038																		
Total Suspended Solids	NA	13	12	16	5	6	15	20	13	8.5	7	7	9	35	8	7	8	10	8	9	18	12	8	15	7	6	20	20

D: Degradate, M: Multiple, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, NA: Not applicable

# Lower Yakima Basin (WRIA 37) Pesticide Calendars

#### Marion Drain 2014 Pesticide Calendar

In 2014, there was a total of 109 pesticide detections at Marion Drain for 18 pesticides or pesticide related compounds (Table 19). There was one detection of chlorpyrifos on May  $28^{th}$  above the acute freshwater invertebrate assessment criterion (0.05  $\mu$ g/L). All other pesticides detected in Marion Drain were below the available pesticide assessment criteria and water quality standards.

Table 19: Marion Drain 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			N.	Iar			A	pr			M	ay				Jun				Jı	ul			A	ug		S	ер
Day of the Month	Use	11	18	25	31	8	14	21	28	6	12	19	28	2	10	16	23	30	7	15	21	29	5	12	19	26	2	9
2,4-D	Н									0.2			0.06	0.054	0.059	0.044	0.056	0.054	0.053	0.042		0.049	0.1	0.048		0.089	0.036	
Atrazine	Н									0.026																		
Bentazon	Н									0.078		0.051	0.13	0.093	0.14	0.088	0.13	0.14	0.12	0.16	0.14	0.32	0.23	0.15	0.14	0.09	0.12	0.11
Bromoxynil	Н							0.036		0.057			0.021															
Chlorpyrifos	I-OP			0.007		0.025							0.055	0.031														
Dicamba	Н												0.029	0.019	0.022					0.032								
Diuron	Н		0.043					0.019	0.02	0.032		0.02	0.015						0.021									
Eptam	Н									0.089	0.046	0.045	0.029															
MCPA	Н												0.033															
Methomyl	I-C																		0.013	0.005	0.004			0.005	0.004		<b> </b>	
Metribuzin	Н																		0.03									
Oxamyl	I-C														0.005	0.004	0.005	0.009	0.003	0.005	0.005	0.004						
Pendimethalin	Н							0.063	0.048	0.14	0.071	0.076	0.083	0.075	0.049	0.036	0.023										<u> </u>	
Propargite	I-SE																					0.029						
Simazine	Н									0.036																	<u> </u>	
Terbacil	Н							0.17	0.081	0.27	0.095	0.1	0.083	0.12	0.081	0.056	0.065		0.1	0.19	0.091	0.15	0.084	0.05		0.024	0.19	0.24
Thiamethoxam	I-N																			0.012								
Trifluralin	Н									0.031	0.03	0.029	0.029	0.027	0.025	0.022												
Total Suspended Solids	NA	34	59	28	34	46	23	17	20	26	32	35	22	58	3	12	4	4	4	6	3	10.5	3	6	11	6	2	10

C: Carbamate, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, SE: Sulfite ester, NA: Not applicable

## Spring Creek 2014 Pesticide Calendar

In 2014, there was a total of 59 pesticide detections at Spring Creek for 15 pesticides or pesticide related compounds (Table 20). There were three detections of chlorpyrifos on March  $25^{th}$ , March  $31^{st}$ , and April  $8^{nd}$  above the acute freshwater invertebrate assessment criterion (0.05 µg/L). Detections of chlorpyrifos on March  $25^{th}$  and March  $31^{st}$  were also above the acute freshwater criteria of the state water quality standard (0.083 µg/L, a 1-hour average concentration not to be exceeded more than once every three years on the average). The concentration of chlorpyrifos on March 25th was near, but did not exceed the ESLOC (0.015 µg/L). There was one detection of diuron on March  $25^{th}$  above the acute freshwater plant assessment criterion (2.4 µg/L). All other pesticides detected in Spring Creek were below the available pesticide assessment criteria and water quality standards.

*Table 20: Spring Creek 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)* 

Month			M	lar			A	pr			M	ay				Jun				Jı	ul			Aı	ıg		S	ер
Day of the Month	Use	11	18	25	31	8	14	21	28	6	12	19	28	2	10	16	23	30	7	15	21	29	5	12	19	26	2	9
2,4-D	Н							0.044	0.053	0.06	0.072		0.042	0.043	0.039	0.04	0.042	0.046		0.04			0.05					0.047
Atrazine	Н																					0.017						
Chlorpyrifos	I-OP		0.018	0.13	0.094	0.051	0.018																					
Diazinon	I-OP				0.071		0.011														0.015							
Dicamba	Н								0.026		0.024																	
Dichlobenil	Н			0.01	0.01																							
Diuron	Н		0.056	7.51	0.389	0.089	0.062	0.019	0.009	0.099	0.103	0.068	0.013				0.016		0.017							0.028		
Imidacloprid	I-N														0.035													
MCPA	Н							0.047	0.057		0.028				0.045													
Metalaxyl	F													0.05		0.039	0.038		0.036	0.033	0.025	0.022						
Methoxyfenozide	I																			0.006				0.006		0.005		
Norflurazon	Н			0.031																								
Oxamyl	I-C																					0.005						
Pentachlorophenol	WP			0.025																								
Triclopyr	Н										0.021																	
Total Suspended Solids	NA	2	12	142	42	28	30	18	18	28	38	50	38	33.5	18	16	12	8	20	1	3		15	1		3	14	12

C: Carbamate, F: Fungicide, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, WP: Wood preservative, NA: Not applicable

## Sulphur Creek Wasteway 2014 Pesticide Calendar

In 2014, there was a total of 72 pesticide detections at Sulphur Creek Wasteway for 20 pesticides or pesticide related compounds (Table 21). Chlorpyrifos was detected once above the ESLOC (0.015  $\mu$ g/L) on March 31<sup>th</sup>, and once above the acute freshwater invertebrate assessment criterion on March 19th. There were also three detections of 4,4'-DDE (a degradate of DDT) above the chronic freshwater criteria of the state water quality standard (0.001  $\mu$ g/L, a 4-day average concentration not to be exceeded more than once every three years on the average). All other pesticides detected in Sulphur Creek Wasteway were below the available pesticide assessment criteria and water quality standards.

Table 21: Sulphur Creek Wasteway 2014, Comparison to Freshwater Criteria for pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			N.	Iar			A	pr			M	ay				Jun				Jı	ul			Aı	1g		S	ер
Day of the Month	Use	11	19	25	31	8	14	21	28	6	12	19	28	2	10	16	23	30	7	15	21	29	5	12	19	26	2	9
2,4-D	Н		0.048					0.053	0.051	0.088	0.059	0.056	0.085	0.17	0.185	0.085	0.078	0.18	0.08	0.086	0.085	0.087	0.11		0.055	0.089	0.25	0.19
4,4'-DDE	D-OC		0.015										0.025	0.017		0.007												
Atrazine	Н												0.074										0.016					
Boscalid	F		0.081																									
Bromacil	Н	0.064				0.039																						
Carbaryl	I-C									0.087																		
Chlorpyrifos	I-OP		0.084	0.17	0.03	0.032																						
Diazinon	I-OP																	0.023										
Dicamba	Н								0.032	0.037	0.033			0.02		0.022				0.019								0.022
Dichlobenil	Н									0.009																		
Diuron	Н	0.051	0.109	0.038		0.017	0.019				0.073	0.017							0.007	0.022						0.009		0.006
Imazapyr	Н												0.022														L	
MCPA	Н												0.036															
Malaoxon	D-OP																			0.003							L	
Norflurazon	Н			0.028																								
Oxamyl	I-C																0.003										L	
Pendimethalin	Н						0.025																					
Terbacil	Н																			0.069		0.038						0.083
Triclopyr	Н							0.028																				
Trifluralin	Н										0.025	0.025			0.024	0.022			0.025	0.023			0.021					
Total Suspended Solids	NA	13	248	172	90	51	39	55	37	37	34	49	85	55	23	87.5	17	14	22	20	23	16	18	23	15	17	26	21

C: Carbamate, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, OP: Organophosphate, NA: Not applicable

# Alkali-Squilchuck basin (WRIA 40) Pesticide Calendar

#### Stemilt Creek 2014 Pesticide Calendar

In 2014, there was a total of 31 pesticide detections at Stemilt Creek for 9 pesticides or pesticide related compounds (Table 22). On March 24th, chlorpyrifos was detected above the acute freshwater invertebrate assessment criterion (0.05  $\mu$ g/L), as well as the chronic freshwater criteria of the state water quality standard (0.041  $\mu$ g/L, a 4-day average concentration not to be exceeded more than once every three years on the average). On May 20<sup>th</sup>, pentachlorophenol was detected above the ESLOC (0.75  $\mu$ g/L). A single detection of malathion was above the chronic freshwater invertebrate assessment criterion (NOAEC<sup>4</sup> = 0.06  $\mu$ g/L) on June 24<sup>th</sup>. All other pesticides detected in Stemilt Creek were below the available pesticide assessment criteria and water quality standards.

Table 22: Stemilt Creek 2014, Comparison to Freshwater Criteria for Pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr				M	ay			Jı	un				Jul				Αι	ıg		S	ер
Day of the Month	Use	10	17	24	1	7	15	22	29	5	13	20	27	3	9	17	24	1	8	16	23	30	4	13	18	27	3	10
2,3,4,6-Tetrachlorophenol	D											0.04																
Chlorpyrifos	I-OP			0.056	0.016	0.03	0.018																					
Hexazinone	Н																						0.049					
Imidacloprid	I-N	0.087																										
Malaoxon	D-OP																0.026		0.002	0.004								
Malathion	I-OP																0.077											
Oxamyl	I-C																0.002											
Pentachlorophenol	WP								0.065	0.13	0.06	2.1	0.1	0.033	0.037	0.022												
Picloram	Н								0.076	•							0.074	0.085	0.054	0.078	0.18		0.078	0.088	0.1	0.096	•	0.16
Total Suspended Solids	NA	84	24	9	9	78	8	6	2	14	12	56	28	24	12	39	3	5	4	2	2	6	2	2	3	2	1	2

C: Carbamate, D: Degradate, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, WP: Wood preservative, NA: Not applicable

<sup>&</sup>lt;sup>4</sup> No Observable Adverse Effect Concentration derived from a chronic toxicity test.

# Wenatchee and Entiat Basins (WRIA 45) Pesticide Calendars

### Peshastin Creek 2014 Pesticide Calendar

In 2014, there was a total of 6 pesticide detections at Peshastin Creek for 4 pesticides or pesticide related compounds (Table 23). All pesticides detected in Peshastin Creek were below the available pesticide assessment criteria and water quality standards.

Table 23: Peshastin Creek 2014, Comparison to Freshwater Criteria for Pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr				M	ay			Jı	ın				Jul				Αι	ıg		Se	ер
Day of the Month	Use	10	17	24	1	7	15	22	29	5	13	20	27	3	9	17	24	1	8	16	23	30	4	13	18	27	3	10
Chlorpyrifos	I-OP				0.007	0.032																						
Fenarimol	F														0.051		0.064											
Oxamyl	I-C																							0.004				
Piperonyl butoxide (PBO)	SY				0.11																							
Total Suspended Solids	NA	96	13	4	3	7	7	6	4	29	12	19	11.5	18	7	4	6	3	3	2.5	4	2	2	28000	12	5	5	2

C: Carbamate, F: Fungicide, I: Insecticide, OP: Organophosphate, SY: Synergist, NA: Not applicable

#### Mission Creek 2014 Pesticide Calendar

In 2014, there was a total of 9 pesticide detections at Mission Creek for 7 pesticides or pesticide related compounds (Table 24). Chlorpyrifos was detected above the acute freshwater fisheries assessment criterion (0.9  $\mu$ g/L) on April 1<sup>st</sup>, and above the acute freshwater invertebrate assessment criterion (0.05  $\mu$ g/L) on April 7<sup>th</sup>. A single detection of Etoxazole on July 8<sup>th</sup> was above the chronic freshwater invertebrate assessment criterion (0.13  $\mu$ g/L). All other pesticides detected in Mission Creek were below the available pesticide assessment criteria and water quality standards.

Table 24: Mission Creek 2014, Comparison to Freshwater Criteria for Pesticides (µg/L) and Total Suspended Solids (mg/L)

																		O	/							١ ٥		
Month			Mar				Apr				M	ay			Jı	un				Jul				Aı	ıg		Se	ер
Day of the Month	Use	10	17	24	1	7	15	22	29	5	13	20	27	3	9	17	24	1	8	16	23	30	4	13	18	27	3	10
4-Nitrophenol	D-M																							0.77				
Acetamiprid	I-N																				0.016							
Chlorpyrifos	I-OP				2.1	0.051	0.012																					
Etoxazole	I																		0.31									
Imidacloprid	I-N																								0.162			
Malaoxon	D-OP																							0.008				
Piperonyl butoxide (PBO)	SY				0.7																							
Total Suspended Solids	NA	893	153	19	23	24	16	12	6	47	18	54	15.5	9	5	4	5	4	5	2	4	2	5	2440	34	6	2	2

D: Degradate, M: Multiple, I: Insecticide, N: Neonicotinoid, SY: Synergist OP: Organophosphate, NA: Not applicable

#### Brender Creek 2014 Pesticide Calendar

In 2014, there was a total of 54 pesticide detections at Brender Creek for 18 pesticides or pesticide related compounds (Table 25). 4,4'-DDT was detected once on April 15<sup>th</sup> while its degradates, 4,4'-DDD and 4,4'-DDE were detected more often throughout the monitoring season. There were 21 detections of 4,4'-DDE (Average = 0.032  $\mu$ g/L, Maximum = 0.052  $\mu$ g/L), and 3 detections of 4,4'-DDD (Average = 0.010  $\mu$ g/L, Maximum = 0.012  $\mu$ g/L). All detections exceeded the chronic freshwater criteria of the state water quality standard (0.001  $\mu$ g/L, 4-day average concentration not to be exceeded more than once every three years on the average). Detections of chlorpyrifos on April 1<sup>st</sup>, April 7<sup>th</sup>, and April 22<sup>nd</sup> exceeded the chronic freshwater criteria of the state water quality standard (0.041  $\mu$ g/L, a 4-day average concentration not to be exceeded more than once every three years on the average) and the detections on April 1<sup>st</sup> and April 7<sup>th</sup> also exceeded the acute freshwater invertebrate assessment criterion (0.05  $\mu$ g/L). All other pesticides detected in Mission Creek were below the available pesticide assessment criteria and water quality standards.

Table 25: Brender Creek 2014, Comparison to Freshwater Criteria for Pesticides (µg/L) and Total Suspended Solids (mg/L)

Month			Mar				Apr					ay				un	· · · · · ·			Jul					ıg	`		ер
												_																
Day of the Month	Use	10	17	24	1	7	15	22	29	5	13	20	27	3	9	17	24	1	8	16	23	30	4	13	18	27	3	10
2,4-D	Н												0.049															
4,4'-DDD	D-OC								0.012			0.011												0.008				
4,4'-DDE	D-OC	0.029	0.018		0.016		0.026	0.036	0.034	0.035	0.03	0.025	0.026			0.029	0.025	0.028		0.022	0.036		0.034	0.1	0.052	0.014	0.014	0.042
4,4'-DDT	I-OC						0.028																					
4-Nitrophenol	D-M																							0.12				
Acetamiprid	I-N						0.015																	0.029				
Carbaryl	I-C										0.048	0.009	0.005															
Chlorpyrifos	I-OP				0.061	0.062	0.023	0.045	0.027	0.024																		
Diazinon	I-OP							0.03													0.028							
Diuron	Н								0.037																			
Etoxazole	I											0.047						0.094										
Imazapyr	Н																							0.018				
Imidacloprid	I-N																							0.049				
Norflurazon	Н														0.025		0.043		0.046									
Oxamyl	I-C																						0.006	0.046				
Pentachlorophenol	WP	0.025																										
Piperonyl butoxide (PBO)	SY			0.093	0.027																							
Thiamethoxam	I-N																							0.014				
Total Suspended Solids	NA	13	7	6	6	5	14	67	47	39	41	36	30	19	25	63	57	37	11	25	72	48	53	184	82	13	30	76

C: Carbamate, D: Degradate, H: Herbicide, I: Insecticide, N: Neonicotinoid, OP: Organophosphate, OC: Organochlorine, WP: Wood preservative, SY: Synergist, NA: Not applicable

# Conventional Water Quality Parameters Summary

Table 26 provides a statewide overview of the conventional water quality parameters not including temperature. Measurements for streamflow, pH, dissolved oxygen, and conductivity were collected in the field during all site visits. Total Suspended Solids (mg/L) was collected in the field and analyzed by the Manchester Environmental Lab.

Table 26: Summary of Conventional Water Quality Parameters for 2014 Site Visits

Watershed		Total Suspended Solids (mg/L)	Stream Discharge (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)
			Upper Bertra	and Creek		
	Weeks Sampled	27	24	27	27	27
	Mean	3.1	18.03	7.4	189.6	9.91
WRIA 1:	Minimum	1	0.97	7.0	125.8	6.49
Nooksack Basin	Maximum	19	90.97	8.4	220.3	12.88
(Agricultural			Lower Bertra	and Creek		
Watershed)	Weeks Sampled	27	25	27	27	26
,	Mean	6	39.83	7.1	251.9	9.63
	Minimum	1	7.70	6.5	147.0	7.81
	Maximum	32	164.00	7.3	288.3	11.31
			Indian S	lough		
	Weeks Sampled	27	21	24	25	25
	Mean	12	31.06	6.86	1493.1	6.85
	Minimum	2	11.47	6.4	258.9	3.50
	Maximum	151	54	7.7	9284.0	10.46
			Browns S	Slough		
	Weeks Sampled	27	24	24	24	21
	Mean	13	9.75	7.6	8846.3	9.03
WRIA 3:	Minimum	5	0.00	6.7	4239.0	4.13
Lower Skagit- Samish Basin	Maximum	40	23.70	8.7	25728.0	14.68
(Agricultural			Upper Big	g Ditch		
Watershed)	Weeks Sampled	27	25	27	27	27
ŕ	Mean	11	3.01	6.7	339.2	6.37
	Minimum	4	0.00	6.5	194.1	2.19
	Maximum	33	10.25	6.9	420.6	10.19
			Lower Bi	g Ditch		
	Weeks Sampled	27	22	27	27	27
	Mean	17	17.75	6.9	385.6	7.69
	Minimum	4	8.44	6.6	44.7	2.67
	Maximum	70	28.62	7.5	855.5	14.40
WRIA 8:			Thornton	Creek		
Cedar-	Weeks Sampled	27	27	26	26	26
Sammamish	Mean	6	9.24	7.6	219.4	9.96
(Urban	Minimum	2	2.48	7.1	110.2	8.70
Watershed)	Maximum	20	54.68	7.9	253.7	11.59

		Total				
Watershed		Suspended Solids	Stream Discharge (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)
		(mg/L)	Longfellov	v Crook		
WRIA 9:	Washa Campled	27	27	26	26	25
Green- Duwamish	Weeks Sampled Mean	12	2.09	7.6	293.2	10.06
(Urban	Minimum	5		7.0	121.1	
Watershed)		35	0.68 9.87		+	8.61
	Maximum	33	9.87 Peshastin	8.4	352.6	11.76
	Washa Campled	27	27	27	27	27
	Weeks Sampled Mean	1048	260.66	8.0	112.1	11.31
	Minimum	2	14.70	7.2	54.4	9.08
				8.2		
	Maximum	28000	822.00 Brender		183.4	13.16
WRIA 45:	Washa Campled	27	27	27	27	27
Wenatchee	Weeks Sampled Mean	41	3.38	8.1	225.8	10.37
(Agricultural	Minimum	5	0.26	7.4	136.3	
Watershed)	Maximum		8.79			8.94
	Maximum	184	8.79 Mission	8.5	403.6	11.82
	Washa Campled	27	26	27	27	27
	Weeks Sampled Mean	141	22.18	8.4	225.5	11.31
	Minimum	2	1.24	7.4	+	9.00
	Maximum	2440	86.25	8.9	171.1 277.7	12.96
WRIA 40:	Iviaxiiiiuiii	2440	Stemilt (		211.1	12.90
Alkali-	Weeks Sampled	27	23	27	27	27
Squilchuck	Mean	16	3.03	8.3	320.5	10.16
Basin	Minimum	10	0.03	7.8	129.1	8.48
(Agricultural						
Watershed)	Maximum	84	10.42 <b>Marion</b>	8.7	626.7	13.37
	Washa Campled	27		ı	27	27
	Weeks Sampled Mean	27 19	26 123.74	26 8.3	27 240.5	27 12.53
	Minimum	2			182.7	
	Maximum	59	18.16 336.8	7.4 9.3		10.10 15.68
	Iviaxiiiiuiii	39	Sulphur Creek		351.8	13.08
WRIA 37:	Weeks Sampled	27	27	27	27	27
Lower Yakima		48			+	
(Agricultural	Mean Minimum	13	249.89	8.4 7.3	287.3	10.54
Watershed)		248	259.90 407.30	8.9	197.9	9.11 12.13
	Maximum	248	Spring (		776.6	12.13
	Weeks Sampled	27	27	27	27	27
	•	22	31.34	8.9	239.1	9.97
	Mean Minimum		1.86	8.9	112.8	
		1 142				8.63
	Maximum	142	61.92	9.8	568.3	13.07

## Conventional Water Quality Parameters Exceedances

The aquatic life criteria of the Washington State Water Quality Standards are location dependent based on aquatic life uses. Aquatic life uses are based on the presence of salmonid species, or the intent to provide protection for all indigenous fish and non-fish aquatic species.

#### Temperature Exceedances above the Aquatic Life Criteria

Water temperature was monitored continuously during the sampling season from March, 7 – October 23, 2014 at eastern Washington monitoring locations and from February 28 – September 23, 2014 at western Washington monitoring locations, with the exception of Longfellow Creek which was monitored from February 28 – September 7. Table 27 provides a list of the time periods where the aquatic life temperature criteria were exceeded. Criteria are based on the designated aquatic life uses at each monitoring location. Water temperature criteria are listed in the standard as the highest 7-day average of the daily maximum temperatures (7-DADMax) allowable.

Table 27: Water Temperatures Not Meeting the Washington State Aquatic Life Criteria

	Wasnington State Aquatic Life Criteria for Temperature
ľ	Freshwater water quality standard for Core Summer Salmonid Habitat - Highest 7-DADMax = $16.0^{\circ}$ C
	Freshwater water quality standard for Salmonid Spawning, Rearing, and Migration Habitat - Highest 7-DADMax = 17.5°C
	Freshwater Supplemental Spawning and Incubation criteria - October 1-May 15 - Highest 7-DADMax =13.0°C
	Marine water quality standard for Aquatic Life Excellent use - Highest 7-DADMax = $16^{\circ}$ C

Wat	er Temperature Exceedanc	ces During 2014	
Aquatic Life Uses	Period of Temperature Exceedance (Start - End)	Maximum Temperature During Period	7-DADMax Range During Period (Minimum - Maximum)
		<b>Upper Bertrand Creek</b>	
	June 5 - 9	18.60	17.56 - 17.74
	June 16 - July 3	No Data	No Data
	July 4	18.70	17.85
	July 7 - 8	17.37	17.66 - 17.83
	July 9 - 31	No Data	No Data
	August 1 - 30	20.86	17.84 - 20.50
Fort des Colons 11 Constitution		<b>Lower Bertrand Creek</b>	
Freshwater - Salmonid Spawning, Rearing, and Migration Habitat -	July 9 - 17	18.60	17.64 - 18.31
(>17.5°C)	July 29 - August 5	18.30	17.56 - 17.96
(* 17.10 ° 5)		Upper Big Ditch	
	May 31 - July 2	No Data	No Data
	July 7 - 30	No Data	No Data
	July 31 - August 27	18.84	17.56 - 18.48
		Lower Big Ditch	
	May 13 - June 12	27.75	17.66 - 20.51
	June 19 - 29	21.03	17.69 - 19.87
	July 3 - September 19	24.63	17.88 - 23.45

	Pariod of Tomparatura	Maximum Temperature	7-DADMax Range	
Aquatic Life Uses	Period of Temperature Exceedance (Start - End)	During Period	During Period	
	Exceedance (Start - End)	During 1 criou	(Minimum - Maximum)	
	Longfellow Creek			
	February 28 - May 29	No Exceedances	No Exceedances	
	May 30 - August 13	No Data	No Data	
	August 14 - September 4	No Exceedances	No Exceedances	
Freshwater - Salmonid Spawning,	Indian Slough			
Rearing, and Migration Habitat -	May 15 - 21	18.67	17.63 - 17.84	
$(>17.5^{\circ}C)$	May 30	18.08	17.68	
	May 31 - July 2	No Data	No Data	
	July 3 - 5	21.03	20.35 - 21.40	
	July 6 - 30	No Data	No Data	
	July 31 - September 19	24.32	17.54 - 23.76	
		Browns Slough		
	April 10 - 16	19.70	16.24 - 16.89	
	April 26 - May 30	29.07	16.37 - 25.46	
Marine Water - (>16 <sup>0</sup> C)	May 31 - July 2	No Data	No Data	
, ,	July 3 - 5	23.26	22.24 - 23.74	
	July 6 - 30	No Data	No Data	
	July 31 - September 19	27.46	18.56 - 26.17	
	Thornton Creek			
	June 5	16.2	16.49	
Freshwater - Core Summer Salmonid	June 8 - 10	17.30	16.59 - 16.69	
Habitat - (>16 <sup>0</sup> C)	June 21 - September 10	20.32	16.53 - 19.60	
	September 17 - 20	17.25	16.58 - 16.80	
Freshwater Supplemental Spawning and	Thornton Creek			
Incubation - [Oct. 1-May 15] - (>13.0°C)	April 28 - May 15	16.84	13.32 - 15.62	
<del>-</del>	•	Marion Drain	•	
	May 19 - 24	19.20	13.54 - 17.81	
	May 30 - September 11	24.19	17.66 - 22.71	
	September 16 - 24	18.94	17.55 - 18.44	
	1	Spring Creek	l	
	May 2 - 4	18.65	17.57 - 17.78	
	May 12 - September 9	29.69	17.55 - 28.25	
	Sulphur Creek Wasteway			
	May 11 - September 30	25.11	17.58 - 23.94	
Freshwater - Salmonid Spawning,	September 7 - 8	18.41	17.60 - 17.62	
Rearing, and Migration Habitat -		Peshastin Creek		
(>17.5 <sup>o</sup> C)	July 7 - September 1	23.81	17.55 - 22.20	
	September 3	17.65	17.65	
	Brender Creek			
	July 9 - 19	19.36	17.63 - 18.54	
	July 28 - August 8	19.27	17.68 - 18.63	
	August 15 - 21	19.17	17.74 - 18.49	
	Mission Creek			
	July 5 - 20	20.63	17.54 - 19.63	
	July 26 - August 21	21.29	17.76 - 20.55	
	Jan 20 11agast 21	21.27	17.70 - 20.33	

Aquatic Life Uses	Period of Temperature Exceedance (Start - End)	Maximum Temperature During Period	7-DADMax Range During Period (Minimum - Maximum)
Freshwater - Salmonid Spawning,	Stemilt Creek		
Rearing, and Migration Habitat -	June 21 - 26	19.15	17.60 - 17.87
(>17.5°C)	June 30 - August 31	23.11	17.67 - 22.07

<sup>7-</sup>DADmax: Water temperature measured by the 7-day average of the daily maximum temperature in degrees centigrade.
7-DADMax Range: Lists the minimum 7-DADMax and the maximum 7-DADMax values that occurred during the period of temperature exceedance

There were 21 time periods where the water temperature exceeded the aquatic life temperature criteria at western Washington monitoring locations. It should be noted there is no data available for the following western Washington monitoring locations and dates, due to equipment malfunction:

- Upper Bertrand Creek, June 16 July 3 and July 9 July 31
- Upper Big Ditch, May 31 July 2 and July 7 July 30
- Longfellow Creek, May 30 August 13
- Indian Slough, May 31 July 2 and July 6 July 30
- Browns Slough, May 31 July 2 and July 6 July 30

There were 16 time periods where the water temperature exceeded the aquatic life temperature criteria at eastern Washington monitoring locations. All eastern Washington monitoring locations had a temperature exceedance in 2014.

For the following locations and dates, temperature data was obtained from other agencies with continuous temperature loggers on-site, to be used in lieu of missing, or anomalous data.

- Lower Bertrand Creek, February 28 September 24 (Washington State Department of Ecology)
- Upper Bertrand Creek, June 3 June 15 (Washington State Department of Ecology)
- Thornton Creek, June 2 June 30 and July 11 July 29 (King County Hydrologic Information Center)
- Peshastin Creek, March 7 July 9 (Washington State Department of Ecology)

#### Dissolved Oxygen Measurements Below the Acceptable Aquatic Life Criteria

Dissolved oxygen was measured at all monitoring locations in 2014. Table 28 provides a list of occurrences where dissolved oxygen was measured at levels below the aquatic life dissolved oxygen criteria. Dissolved oxygen criteria are listed in the standard as the lowest 1-day minimum. Dissolved oxygen measurements are point estimates (not continuous) taken at the time of sampling.

Table 28: Dissolved Oxygen Levels Not Meeting the Washington State Aquatic Life Criteria

Table 28: Dissolved Oxygen Le	veis ivoi meeting the washing	ion siate Aquatic Life Criteria	
Washington Sta	te Aquatic Life Criteria for Dissol	lved Oxygen	
Freshwater water quality standard for C Freshwater water quality standard for S	almonid Spawning, Rearing, and Mi minimum: 8.0 mg/L	gration Habitat - Dissolved Oxygen	
Marine water quality standard for A	Aquatic Life Excellent use - Dissolv	ed Oxygen minimum: 6.0 mg/L	
Monitoring Locations T	That Meet The Dissolved Oxygen C	Criteria During 2014	
Western Washington	Eastern Washington		
Longfellow Creek	Brender Creek		
	Marion Drain		
	Mission Creek Peshastin Creek Stemilt Creek Spring Creek		
Sulphur Creek Wasteway		ek Wasteway	
<b>Monitoring Locations</b>	With DO Measurements Below Co	riteria During 2014	
Aquatic Life Criteria	Dates of DO Measurements	DO Measurements	
	Upper Ber	trand Creek	
	July 15, 29	6.5, 7.2	
	Lower Bertrand Creek		
	July 15 7.8		
		Big Ditch	
	May 20, 27	6.8, 6.9	
	June 2, 9, 16, 24, 30	5.3, 5.6, 6.7, 5.2, 5.1	
	July 7, 14, 22, 28	5.6, 5.8, 5.6, 3.7	
	August 4, 12, 19, 26	4.9, 2.5, 2.2, 3.3	
	September 2, 9	4.0, 2.4	
	March 18, 24	<b>Big Ditch</b> 6.4, 6.3	
Freshwater - Salmonid Spawning,	April 1, 29	7.2, 6.9	
Rearing, and Migration Habitat -	May 6, 13, 20	7.7, 5.3, 7.2	
(<8.0  mg/L)	June 10	7.3	
	July 22	7.9	
	August 5, 12, 19, 26	3.3, 5.8, 2.7, 7.1	
	September 3, 9	3.3, 5.1	
	Indian Slough		
	March 14, 18, 24	6.8, 7.2, 6.8	
	April 1, 7, 15, 22, 29	5.8, 5.9, 6.8, 7.8, 4.8	
	May 6, 13, 20, 28	7.3, 3.5, 4.4, 4.8	
	June 2, 16, 24	7.4, 5.6, 7.3	
	July 8, 14	5.9, 7.5	
	August 19	7.8	
	September 9	5.5	
Marine Water - (<6.0 mg/L)	Browns Slough		
	July 8, 22	4.1, 5.5	

August 12, 26

5.0, 4.2

Aquatic Life Criteria	Dates of DO Measurements	DO Measurements	
Freshwater - Core Summer Salmonid Habitat - (<9.5 mg/L)	Thornton Creek		
	May 20	9.3	
	June 9, 23	9.2, 9.3	
	July 7, 15, 21, 29	9.1, 8.7, 9.1, 8.7	
	August 4, 11	8.9, 8.9	
	September 2, 8	9.2, 9.2	

DO: Dissolved Oxygen

There were 69 individual occurrences where the dissolved oxygen level was measured below the aquatic life criteria at western Washington monitoring locations. Longfellow Creek was the only western Washington monitoring location that met the dissolved oxygen criteria for the entire 2014 monitoring season.

All seven of the eastern Washington monitoring locations had dissolved oxygen measurements above the aquatic life criteria throughout the 2014 monitoring season.

#### pH Measurements Outside The Acceptable Aquatic Life Criteria

Measurements were collected for pH at all monitoring locations in 2014. Table 29 (page 72) provides a list of occurrences where pH was measured at levels below or above the aquatic life criteria for pH. The pH criteria are listed in the standard as ranges (between a minimum and maximum) of acceptable pH values for each aquatic life use category.

There were five occurrences where the pH measurement was outside of the range listed in the aquatic life pH criteria at two western Washington locations (Indian Slough and Browns Slough) and 56 occurrences were outside of the range listed at five eastern Washington locations (Mission Creek, Spring Creek, Sulphur Creek Wasteway, and Stemilt Creek). On June 16<sup>th</sup>, a pH of 55.9 was recorded at Indian Slough. This pH value is a data entry error and was omitted from summary calculations.

The other five western Washington monitoring locations and two eastern Washington monitoring locations had pH measurements within the acceptable range listed for the aquatic life pH criteria during the 2014 monitoring season.

Table 29: pH Levels Not Meeting the Washington State Aquatic Life Criteria

### Washington State Aquatic Life Criteria for pH

Freshwater water quality standard for Core Summer Salmonid Habitat - pH:6.5-8.5 (allowable human-caused variation within listed range of <0.2 units)

Freshwater water quality standard for Salmonid Spawning, Rearing, and Migration Habitat - pH: 6.5-8.5 (allowable human-caused variation within listed range of <0.5 units)

· ·	-caused variation within listed range	•	
Marine water quality standard for Aqua		allowable human-caused variation	
	within listed range of <0.5 units)		
	ations That Meet The pH Criteria		
Western Washington	Eastern Washington		
Thornton Creek	Brender Creek		
Upper Bertrand Creek	Peshastin Creek		
Lower Bertrand Creek			
Longfellow Creek			
Upper Big Ditch			
Monitoring Locations With	n pH Measurements Outside Crite	ria Range During 2014	
Aquatic Life Uses	Dates of pH Measurements	pH Measurements	
	Browns	Slough	
	June 30	8.7	
Marine Water - pH 7.0-8.5	July 8	6.7	
	August 12	6.9	
	September 9	8.6	
	Indian	Slough	
	March 14	6.4	
	Mission	n Creek	
	June 9, 17, 24	8.8, 8.6, 8.8	
	July 1, 16, 23, 30	8.6, 8.6, 8.6, 8.7	
	August 4, 18, 27	8.8, 8.6, 8.8	
	September 3, 10	8.9, 8.8	
	Spring	Creek	
	March 11, 18	8.9, 9.2	
	April 8, 14, 21, 28	9.0, 9.2, 9.3, 9.4	
	May 6, 12	8.7, 8.6	
	June 2, 10, 16, 23, 30	8.6, 9.0, 8.6, 9.1, 9.0	
Freshwater - Salmonid Spawning,	July 7, 15, 21, 29	8.9, 9.3, 9.8, 9.1	
Rearing, and Migration - pH: 6.5-8.5	August 5, 12, 19, 26	8.8, 9.1, 8.6, 8.8	
	September 2, 9	8.7, 8.8	
	Sulphur Creek Wasteway		
	April 8, 14	8.7, 8.7	
	May 12, 19	8.8, 8.6	
	June 2, 10, 23, 30	8.6, 8.7, 8.6, 8.9	
	July 7, 15, 21, 29	8.7, 8.7, 8.8, 8.6	
	Marion Drain		
	June 10, 30	9.1, 9.3	
	July 7, 15, 21, 29	9.0, 9.2, 9.0, 8.7	
	August 12	8.8	
	Stemilt Creek		
	April 22	8.7	

# Summary Conclusions and Program Changes for 2014:

### Summary Conclusions

Compared to findings the 2013 monitoring season, there was an overall 27% decrease in the total number of detections (1572 to 1151) from 2013 to 2014. There was also an overall 37% reduction in the total number of exceedances of a threshold value (76 to 48) from 2013 to 2014. It should be noted that sites were dropped between the 2013 and 2014 sampling seasons, and this may partially account for the decrease in detections and decrease in exceedances.

The data generated by this program helps to keep the agricultural community and the general public informed of the occurrence of pesticides in surface water through report publication and through numerous public presentations. The data generated by the monitoring program is used by WSDA, the U.S. Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA) National Marine Fisheries Service, and the U.S. Fish and Wildlife Service (USFWS) to refine exposure assessments for pesticides 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 ambient monitoring program is an invaluable tool for identifying state specific pesticide issues and addressing them according to WSDA's EPA approved Pesticide Management Strategy. The ambient monitoring program can also be used in conjunction with the adaptive management strategy as a mechanism for investigating and addressing concerns regarding pesticide use patterns leading to surface water or ground water contamination problems. NRAS is currently working with the Pesticide Management Division on two separate projects under the adaptive management strategy; dacthal contamination of groundwater in specific areas of Washington<sup>5</sup> and surface water contamination of chlorpyrifos and diazinon in Grays Harbor and Pacific counties<sup>6</sup>.

The state-wide surface water monitoring program also forms the groundwork for designing additional studies focusing on particular scientific questions of interest regarding pesticide fate and transport. This can include runoff, drift and deposition from various application methods, and sediment toxicity investigations. These targeted studies along with technical assistance efforts can help to further reduce the frequency and potential risk for off target pesticide movement.

<sup>6</sup> Cranberry Report 2013

<sup>&</sup>lt;sup>5</sup> Dacthal Report 2014

### Program Changes for 2015

#### Changes in Sites

Sampling will continue at all long-term monitoring sites with the exception of Longfellow Creek. Monitoring at Longfellow Creek will be discontinued in 2015. Monitoring will continue at the three sites added in 2013, two on Bertrand Creek and the Stemilt Creek site.

#### Changes in Parameters

Twenty five new pesticides will be added to the pesticide analyses for 2015 including 12 fungicides, 9 new herbicides, and 6 new insecticides.

In addition to routine monitoring, a five week glyphosate sampling project will take place during the 2015 field season where glyphosate samples will be collected weekly at every monitoring location from mid April through mid May to coincide with the peak application period. Data regarding the pilot glyphosate sampling project will be incorporated in the 2015 annual report.

A sediment sampling pilot project will also be completed during the 2015 sampling season. Sediment samples will be collected during three sampling events at five monitoring sites (three in western Washington and two in eastern Washington). Data generated from the sediment sampling pilot project will be summarized and reported separately.

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[2014 DATA SUMMARY, PESTICIDES IN SALMONID-BEARING STREAMS]	<b>December 31, 2015</b>
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# Appendix A: Monitoring Location Data

### Monitoring Locations in 2014

Table A-1: 2014 Monitoring Location Details

Site Name	Site ID	Duration	Latitude	Longitude	Location Description
nish basin (V	VRIA 8):				
Thornton Creek	TC-3	March- September	47.695	-122.276	Downstream of pedestrian footbridge near Matthews Beach Park.
sh basin (Wl	RIA 9):				
Longfellow Creek	LC-1	March- September	47.5623	-122.367	Upstream of the culvert under the 12 <sup>th</sup> fairway on West Seattle Golf Course
amish basin	(WRIA 3):				
Lower Big Ditch	BD-1	March- September	48.3085	-122.347	Upstream side of bridge at Milltown Road.
Upper Big Ditch	BD-2	March- September	48.3882	-122.333	Upstream side of bridge at Eleanor Lane.
Browns Slough	BS-1	March- September	48.3407	-122.414	Downstream of tidegate on Fir Island Road.
Indian Slough	IS-1	March- September	48.4506	-122.465	Inside upstream side of tidegate at Bayview- Edison Road.
(WRIA 1):					
Lower Bertrand	BC-1	March- September	48.9241	-122.53	Upstream side of the bridge over the creek on Rathbone Road. Parallel to staff gauge.
Upper Bertrand	BC-7	March- September	48.9935	-122.509	Upstream side of the bridge over the creek on H Street Road.
basin (WRIA	<b>A</b> 37):				
Marion Drain	MA-2	March- September	46.3307	-120.2	Approximately 50 meters upstream of bridge at Indian Church Road.
Spring Creek	SP-2	March- September	46.2571	-119.711	Downstream side of culvert on McCreadie Road.
Sulphur Creek Wasteway	SU-1	March- September	46.251	-120.02	Downstream side of bridge at Holaday Road.
in (WRIA 45	):				
Mission Creek	MI-1	March- September	47.4874	-120.484	Mission Creek Road off of Trip Canyon Road.
Peshastin Creek	PE-1	March- September	47.5573	-120.582	Approximately 30 meters downstream of bridge at Saunders Road.
Brender Creek	BR-1	March- September	47.521	-120.487	Upstream side of culvert at Evergreen Drive and the footbridge.
ck basin (W	RIA 40):				
Stemilt Creek	SC-1	March- September	47.3748	-120.25	About 7 meters upstream of the bridge over the creek on Old West Malaga Road.
	mish basin (V Thornton Creek sh basin (WI Longfellow Creek amish basin Lower Big Ditch Upper Big Ditch Browns Slough Indian Slough Indian Slough Upper Bertrand Upper Bertrand Upper Bertrand Upper Bertrand Varion Drain Spring Creek Sulphur Creek Wasteway n (WRIA 45 Mission Creek Peshastin Creek Brender Creek Stemilt	mish basin (WRIA 8):  Thornton Creek  sh basin (WRIA 9):  Longfellow Creek  amish basin (WRIA 3):  Lower Big Ditch  Upper Big Ditch  Browns Slough  Indian Slough  Indian Slough  Image: Bertrand Bertrand  Upper Bertrand Bertrand  Upper Bertrand Bertrand  Upper Bertrand Bertrand  Spring Creek Sulphur Creek Sulphur Creek Sulphur Creek Wasteway  n (WRIA 45):  Mission MI-1  Peshastin Creek Brender Creek Brender Creek Stemilt SC-1	mish basin (WRIA 8):  Thornton Creek  Sh basin (WRIA 9):  Longfellow Creek  I LC-1  I March-September  I Mar	Thornton Creek TC-3 March-September 47.5623  Sh basin (WRIA 9):  Longfellow Creek LC-1 March-September 47.5623  Amish basin (WRIA 3):  Lower Big Ditch BD-1 March-September 48.3085  Upper Big Ditch BS-1 September 48.3407  Browns Slough BS-1 March-September 48.3407  Indian Slough IS-1 March-September 48.4506  (WRIA 1):  Lower Bertrand BC-1 March-September 48.9241  Upper Bertrand BC-7 March-September 48.9935  basin (WRIA 37):  Marion Drain MA-2 March-September 46.2571  Spring Creek SU-1 March-September 46.2571  Sulphur Creek SU-1 March-September 46.251  Mission (WRIA 45):  Mission Creek BR-1 March-September 47.521  Peshastin Creek BR-1 September 47.521  Stemilt SC 1 March-September 47.3748	Thornton Creek   TC-3

HUC= Hydrologic Unit Code (<u>USGS</u>)

Datum in north American Datum (NAD) 83

# Appendix B: 2014 Quality Assurance Summary

### 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). Detections quantified below reporting limits are qualified as estimates according to Table B-1. Definitions of data qualifiers are presented in Table B-1.

Table B-1: Data Qualification Definitions

Qualifier	Definition
D	The analyte was positively identified and was detected at the reported concentration.
Е	Reported result is an estimate because it falls outside of 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.

MEL, 2000, 2008; EPA, 2008

Performance measures are used by the laboratory and field staff to determine when data should be qualified. Relative percent difference (RPD) is used as a performance measure to represent the precision of the analysis by comparing the difference between replicate pairs for matrix spikes, laboratory control samples and field replicates. Percent recovery is also used as a performance measure to represent the bias of the analysis by comparing the difference between replicate pairs for matrix spikes, laboratory control samples, and surrogate recovery. RPD and % Recovery are also used by the analyst to qualify the results of the grab samples when quality assurance (QA) and quality control (QC) samples fall below the lower control limits or fall above the upper control limits. Control limits can be either be analyte specific control limits as determined by the analysts or default limits specified by the EPA method. Upper and lower analyte specific control limits are calculated from the mean of the most recent one hundred pairs,

 $\pm$  three standard deviations. Performance measures for QA and QC samples are presented in Table B-2.

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

Analysis Method <sup>1</sup>	Parameter Type	Parameter Name	RPD Upper Control Limit (%)	Lower Control Limit <sup>2</sup>	Upper Control Limit <sup>2</sup>
		1-Naphthol	≥40	40	130
		2,4'-DDD	≥40	29	125
		2,4'-DDE	≥40	37	116
		2,4'-DDT	≥40	25	118
		4,4'-DDD	≥40	49	143
		4,4'-DDE	≥40	40	130
		4,4'-DDT	≥40	42	120
		4,4'-Dichlorobenzophenone	≥40	30	130
		Acetochlor	≥40	30	130
		Alachlor	≥40	16	181
		Aldrin	≥40	30	141
		Alpha-BHC	≥40	83	162
		Atrazine	≥40	13	172
		Azinphos-methyl	≥40	10	503
		Benfluralin	≥40	50	151
		Beta-BHC	≥40	83	172
		Bifenazate	≥40	50	150
GCMS	Pesticides	Bifenthrin	≥40	30	130
		Boscalid	≥40	50	150
		Bromacil	≥40	55	181
		Butachlor	≥40	30	130
		Butylate	≥40	41	147
		Captan	≥40	10	219
		Chlorothalonil (Daconil)	≥40	57	227
		Chlorpropham	≥40	53	181
		Chlorpyrifos	≥40	52	152
		Chlorpyrifos O.A.	≥40	30	130
		Chlorpyrifos-methyl	≥40	50	144
		cis-Chlordane	≥40	45	161
		Cis-Nonachlor	≥40	25	105
		cis-Permethrin	≥40	17	201
		Coumaphos	≥40	10	487
		Cyanazine	≥40	14	268
		Cycloate	≥40	49	151
		Cypermethrin	≥40	30	130

Analysis Method <sup>1</sup>	Parameter Type	Parameter Name	RPD Upper Control Limit (%)	Lower Control Limit <sup>2</sup>	Upper Control Limit <sup>2</sup>
		Delta-BHC	≥40	81	173
		Deltamethrin	≥40	30	130
		Di-allate (Avadex)	≥40	30	130
		Diazinon	≥40	59	168
		Diazoxon	≥40	30	130
		Dichlobenil	≥40	34	153
		Dichlorvos (DDVP)	≥40	27	169
		Dicofol	≥40	10	265
		Dieldrin	≥40	69	143
		Dimethoate	≥40	65	217
		Diphenamid	≥40	52	170
		Disulfoton Sulfoxide	≥40	30	130
		Endosulfan I	≥40	58	195
		Endosulfan II	≥40	72	146
		Endosulfan Sulfate	≥40	77	140
		Endrin	≥40	62	145
		Endrin Aldehyde	≥40	32	134
	D. d. t.	Endrin Ketone	≥40	34	119
GCMS		EPN	≥40	43	185
GCMS	Pesticides	Eptam	≥40	41	159
		Ethalfluralin (Sonalan)	≥40	6	243
		Ethion	≥40	41	132
		Ethoprop	≥40	10	263
		Etoxazole	≥40	50	150
		Fenamiphos	≥40	10	375
		Fenamiphos Sulfone	≥40	30	130
		Fenarimol	≥40	30	130
		Fenvalerate	≥40	30	130
		Fipronil	≥40	30	130
		Fipronil Disulfinyl	≥40	30	130
		Fipronil Sulfide	≥40	30	130
		Fipronil Sulfone	≥40	30	130
		Fluridone	≥40	10	375
		Fonofos	≥40	30	130
		Heptachlor	≥40	43	157
		Heptachlor Epoxide	≥40	73	167
		Hexachlorobenzene	≥40	33	120
		Hexazinone	≥40	41	183

Analysis Method <sup>1</sup>	Parameter Type	Parameter Name	RPD Upper Control Limit (%)	Lower Control Limit <sup>2</sup>	Upper Control Limit <sup>2</sup>
		Lindane	≥40	78	177
		Malathion	≥40	50	147
		Metalaxyl	≥40	56	149
		Methidathion	≥40	52	186
		Methoxychlor	≥40	15	181
		Methyl Paraoxon	≥40	37	269
		Methyl Parathion	≥40	35	170
		Metolachlor	≥40	55	180
		Metribuzin	≥40	30	130
		Mevinphos	≥40	10	448
		MGK264	≥40	49	193
		Mirex	≥40	16	97
		Monocrotophos	≥40	10	196
		Naled	≥40	10	220
		Napropamide	≥40	70	180
		Norflurazon	≥40	70	168
		Oryzalin	≥40	10	230
		Oxychlordane	≥40	41	111
GCMS	Pesticides	Oxyfluorfen	≥40	51	153
GCMS	Pesticides	Parathion	≥40	29	204
		Pebulate	≥40	45	162
		Pendimethalin	≥40	39	163
		Phenothrin	≥40	22	130
		Phorate	≥40	12	130
		Phosmet	≥40	32	203
		Piperonyl Butoxide (PBO)	≥40	30	130
		Prometon	≥40	55	164
		Prometryn	≥40	62	165
		Pronamide (Kerb)	≥40	63	169
		Propachlor (Ramrod)	≥40	13	189
		Propargite	≥40	30	130
		Propazine	≥40	56	161
		Resmethrin	≥40	10	65
		Simazine	≥40	72	192
		Simetryn	≥40	61	171
		Sulfotepp	≥40	57	139
		Tebuthiuron	≥40	10	235
		Terbacil	≥40	27	237

Analysis Method <sup>1</sup>	Parameter Type	Parameter Name	RPD Upper Control Limit (%)	Lower Control Limit <sup>2</sup>	Upper Control Limit <sup>2</sup>
		Tetrachlorvinphos (Gardona)	≥40	70	196
		Tetrahydrophthalimide	≥40	50	150
		Thiobencarb	≥40	54	144
	Pesticides	Tokuthion	≥40	28	141
		trans-Chlordane	≥40	42	148
GCMS		Trans-Nonachlor	≥40	35	178
		Triadimefon	≥40	61	178
		Triallate	≥40	52	128
		Trichloronate	≥40	34	131
		Tricyclazole	≥40	30	130
		Trifluralin	≥40	58	174
LCMS/MS	Pesticides	-	≥40	40*	130*
GCMS-H	Herbicides	-	≥40	40*	130*
TSS	TSS	TSS	≥20	40*	130*

<sup>&</sup>lt;sup>1</sup> 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.

#### **Lower Practical Quantitation Limits**

Lower practical quantitation limits (LPQLs) are the lowest concentrations at which laboratories may report data without classifying the concentration as an estimate below the lowest calibration standard. The LPQL is determined by calculating the average of the method detection limit (MDL) per analyte for all batches over the study period. The MDL is defined by the Federal code of Regulation 40 Appendix B to Part 136 as, "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." In addition to the MDL, the lab also reports the method reporting limit (MRL) which is the lowest concentration standard in the calibration range of each parameter. The concentration of the result reported by the laboratory that fall above the MDL but below the MRL are estimates because they fall outside of the calibration range. LPQL data for 2014 are presented in Table B-3.

<sup>&</sup>lt;sup>2</sup> Control limits can be either be analyte specific control limits, or (\*) default limits specified by the EPA method.

Table B-3: Mean performance lower practical quantitation limits (LPQL) in µg/L, 2014

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
90-15-3	1-Naphthol	Carbaryl	Degradate / Carbamate	GCMS	NA	NA
4901-51-3	2,3,4,5- Tetrachlorophenol	Pentachlorophenol	Degradate	GCMS-H	0.0040	4.3E-10
58-90-2	2,3,4,6- Tetrachlorophenol	Pentachlorophenol	Degradate	GCMS-H	0.0070	5.9E-05
93-76-5	2,4,5-T		Herbicide	GCMS-H	0.0090	7.9E-10
95-95-4	2,4,5-Trichlorophenol		Fungicide	GCMS-H	0.0080	1.1E-04
88-06-2	2,4,6-Trichlorophenol		Degradate / Multiple	GCMS-H	0.0110	7.3E-10
94-75-7	2,4-D		Herbicide	GCMS-H	0.0120	2.0E-04
94-82-6	2,4-DB		Herbicide	GCMS-H	0.0080	1.1E-04
53-19-0	2,4'-DDD	DDT	Degradate / Organochlorine	GCMS	0.0301	3.9E-03
3424-82-6	2,4'-DDE	DDT	Degradate / Organochlorine	GCMS	0.0253	3.1E-03
789-02-6	2,4'-DDT	DDT	Insecticide / Organochlorine	GCMS	0.0061	8.7E-04
51-36-5	3,5-Dichlorobenzoic Acid		Degradate / Herbicide	GCMS-H	0.0070	3.1E-10
16655-82-6	3-Hydroxycarbofuran	Carbofuran	Degradate / Carbamate	LCMS/MS	0.0030	5.2E-10
72-54-8	4,4'-DDD	DDT	Degradate / Organochlorine	GCMS	0.0314	4.0E-03
72-55-9	4,4'-DDE	DDT	Degradate / Organochlorine	GCMS	0.0240	3.1E-03
50-29-3	4,4'-DDT		Insecticide / Organochlorine	GCMS	0.0283	3.7E-03
90-98-2	4,4'- Dichlorobenzophenone		Degradate	GCMS	0.0501	6.3E-03
100-02-7	4-Nitrophenol		Degradate / Herbicide	GCMS-H	0.0211	3.5E-04
135410-20-7	Acetamiprid		Insecticide / Neonicotinoid	LCMS/MS	0.0119	2.1E-03
34256-82-1	Acetochlor		Herbicide	GCMS	0.0501	6.3E-03
62476-59-9	Acifluorfen, sodium salt		Herbicide	GCMS-H	0.0534	5.9E-04
15972-60-8	Alachlor		Herbicide	GCMS	0.0040	5.6E-04
116-06-3	Aldicarb		Insecticide / Carbamate	LCMS/MS	0.0020	2.1E-10
1646-88-4	Aldicarb Sulfone	Aldicarb	Degradate / Carbamate	LCMS/MS	0.0030	5.2E-10
1646-87-3	Aldicarb Sulfoxide	Aldicarb	Degradate / Carbamate	LCMS/MS	0.0040	4.3E-10
309-00-2	Aldrin		Insecticide / Organochlorine	GCMS	0.0122	1.5E-03

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
319-84-6	Alpha-BHC		Insecticide / Organochlorine	GCMS	0.0101	1.2E-03
1912-24-9	Atrazine		Herbicide	GCMS	0.0131	1.6E-03
2642-71-9	Azinphos-ethyl		Insecticide / Organophosphate	GCMS	0.0182	2.4E-03
86-50-0	Azinphos-methyl		Insecticide / Organophosphate	GCMS	0.0225	2.9E-03
1861-40-1	Benfluralin		Herbicide	GCMS	0.0278	3.4E-03
25057-89-0	Bentazon		Herbicide	GCMS-H	0.0065	5.0E-04
319-85-7	Beta-BHC		Insecticide / Organochlorine	GCMS	0.0101	1.2E-03
149877-41-8	Bifenazate		Insecticide	GCMS	0.0202	2.4E-03
82657-04-3	Bifenthrin		Insecticide / Pyrethroid	GCMS	0.0502	6.6E-03
188425-85-6	Boscalid		Fungicide	GCMS	0.0346	4.4E-03
314-40-9	Bromacil		Herbicide	GCMS	0.0129	1.6E-03
1689-84-5	Bromoxynil		Herbicide	GCMS-H	0.0060	1.0E-09
23184-66-9	Butachlor		Herbicide	GCMS	0.1000	1.2E-02
2008-41-5	Butylate		Herbicide	GCMS	0.0114	1.5E-03
133-06-2	Captan		Fungicide	GCMS	0.0162	2.0E-03
63-25-2	Carbaryl		Insecticide / Carbamate	LCMS/MS	0.0030	5.2E-10
1563-66-2	Carbofuran		Insecticide / Carbamate	LCMS/MS	0.0030	5.2E-10
1897-45-6	Chlorothalonil (Daconil)		Fungicide	GCMS	0.0091	1.1E-03
101-21-3	Chlorpropham		Herbicide	GCMS	0.0191	8.2E-02
2921-88-2	Chlorpyrifos		Insecticide / Organophosphate	GCMS	0.0146	3.2E-03
5598-15-2	Chlorpyrifos O.A.		Degradate / Organophosphate	GCMS	0.0501	6.3E-03
5598-13-0	Chlorpyrifos-methyl		Insecticide / Organophosphate	GCMS	0.0081	1.0E-03
5103-71-9	cis-Chlordane		Insecticide / Organochlorine	GCMS	0.0216	2.7E-03
5103-73-1	Cis-Nonachlor		Insecticide / Organochlorine	GCMS	0.0445	5.7E-03
54774-45-7	cis-Permethrin		Insecticide / Pyrethroid	GCMS	0.0250	3.2E-03
1702-17-6	Clopyralid		Herbicide	GCMS-H	0.0081	3.0E-04
210880-92-5	Clothianidin		Insecticide / Neonicotinoid	LCMS/MS	0.0500	9.0E-09

# [2014 DATA SUMMARY, PESTICIDES IN SALMONID-BEARING STREAMS]

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
56-72-4	Coumaphos		Insecticide / Organophosphate	GCMS	0.0360	4.9E-03
21725-46-2	Cyanazine		Herbicide	GCMS	0.0091	1.0E-03
1134-23-2	Cycloate		Herbicide	GCMS	0.0091	1.1E-03
52315-07-8	Cypermethrin		Insecticide / Pyrethroid	GCMS	0.0502	6.6E-03
121552-61-2	Cyprodinil		Fungicide	LCMS/MS	0.0030	5.2E-10
1861-32-1	Dacthal (DCPA)		Herbicide	GCMS-H	0.0050	1.1E-04
319-86-8	Delta-BHC		Insecticide / Organochlorine	GCMS	0.0070	8.0E-04
52918-63-5	Deltamethrin		Insecticide / Pyrethroid	GCMS	0.0101	1.3E-03
2303-16-4	Di-allate (Avadex)		Herbicide	GCMS	0.0097	1.3E-03
333-41-5	Diazinon		Insecticide / Organophosphate	GCMS	0.0139	1.7E-03
962-58-3	Diazoxon	Diazinon	Degradate / Organophosphate	GCMS	0.0182	2.3E-03
1918-00-9	Dicamba		Herbicide	GCMS-H	0.0070	3.1E-10
1194-65-6	Dichlobenil		Herbicide	GCMS	0.0091	1.0E-03
120-36-5	Dichlorprop		Herbicide	GCMS-H	0.0081	3.5E-04
62-73-7	Dichlorvos (DDVP)		Insecticide / Organophosphate	GCMS	0.0111	1.4E-03
51338-27-3	Diclofop-Methyl		Herbicide	GCMS-H	0.0169	3.5E-04
115-32-2	Dicofol		Insecticide / Organochlorine	GCMS	0.0273	3.5E-03
60-57-1	Dieldrin		Insecticide / Organochlorine	GCMS	0.0172	2.1E-03
60-51-5	Dimethoate		Insecticide / Organophosphate	GCMS	0.0303	3.7E-03
88-85-7	Dinoseb		Herbicide	GCMS-H	0.0405	5.8E-04
165252-70-0	Dinotefuran		Insecticide / Neonicotinoid	LCMS/MS	0.0100	6.6E-03
957-51-7	Diphenamid		Herbicide	GCMS	0.0101	1.2E-03
2497-06-5	Disulfoton Sulfone		Insecticide / Organophosphate	GCMS	0.0501	6.5E-03
2497-07-6	Disulfoton Sulfoxide		Degradate / Organophosphate	GCMS	0.0501	6.3E-03
330-54-1	Diuron		Herbicide	LCMS/MS	0.0062	5.1E-03
959-98-8	Endosulfan I		Insecticide / Organochlorine	GCMS	0.0117	1.5E-03
33213-65-9	Endosulfan II		Insecticide / Organochlorine	GCMS	0.0101	1.3E-03

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
1031-07-8	Endosulfan Sulfate	Endosulfan	Degradate / Organochlorine	GCMS	0.0114	1.6E-03
72-20-8	Endrin		Insecticide / Organochlorine	GCMS	0.0152	2.0E-03
7421-93-4	Endrin Aldehyde	Endrin	Degradate / Organochlorine	GCMS	0.0327	4.3E-03
53494-70-5	Endrin Ketone	Endrin	Degradate / Organochlorine	GCMS	0.0131	1.7E-03
2104-64-5	EPN		Insecticide / Organophosphate	GCMS	0.0202	2.6E-03
759-94-4	Eptam		Herbicide	GCMS	0.0081	1.1E-03
55283-68-6	Ethalfluralin (Sonalan)		Herbicide	GCMS	0.0172	2.1E-03
563-12-2	Ethion		Insecticide / Organophosphate	GCMS	0.0142	1.9E-03
13194-48-4	Ethoprop		Insecticide / Organophosphate	GCMS	0.0141	1.7E-03
153233-91-1	Etoxazole		Insecticide	GCMS	0.0206	2.7E-03
22224-92-6	Fenamiphos		Insecticide / Organophosphate	GCMS	0.0131	1.7E-03
31972-44-8	Fenamiphos Sulfone		Degradate / Organophosphate	GCMS	0.0502	6.6E-03
60168-88-9	Fenarimol		Fungicide	GCMS	0.0212	2.7E-03
51630-58-1	Fenvalerate		Insecticide / Pyrethroid	GCMS	0.0210	2.7E-03
120068-37-3	Fipronil		Insecticide / Pyrazole	GCMS	0.0502	6.6E-03
205650-65-3	Fipronil Disulfinyl		Degradate / Insecticide	GCMS	0.0501	6.3E-03
120067-83-6	Fipronil Sulfide		Degradate / Insecticide	GCMS	0.0502	6.6E-03
120068-36-2	Fipronil Sulfone		Degradate / Insecticide	GCMS	0.0502	6.6E-03
59756-60-4	Fluridone		Herbicide	GCMS	0.0344	4.4E-03
944-22-9	Fonofos		Insecticide / Organophosphate	GCMS	0.0091	1.1E-03
76-44-8	Heptachlor		Insecticide / Organochlorine	GCMS	0.0121	1.5E-03
1024-57-3	Heptachlor Epoxide	Heptachlor	Degradate / Organochlorine	GCMS	0.0091	1.1E-03
118-74-1	Hexachlorobenzene		Fungicide	GCMS	0.0071	8.6E-04
51235-04-2	Hexazinone		Herbicide	GCMS	0.0125	1.7E-03
104098-48-8	Imazapic		Herbicide	LCMS/MS	0.0180	1.5E-09
81334-34-1	Imazapyr		Herbicide	LCMS/MS	0.0140	6.0E-10
138261-41-3	Imidacloprid		Insecticide / Neonicotinoid	LCMS/MS	0.0020	2.1E-10

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
1689-83-4	Ioxynil		Herbicide	GCMS-H	0.0160	5.9E-05
58-89-9	Lindane		Insecticide / Organochlorine	GCMS	0.0114	1.5E-03
330-55-2	Linuron		Herbicide	LCMS/MS	0.0040	4.3E-10
1634-78-2	Malaoxon	Malathion	Degradate / Organophosphate	LCMS/MS	0.0010	1.1E-10
121-75-5	Malathion		Insecticide / Organophosphate	GCMS	0.0071	9.5E-04
94-74-6	MCPA		Herbicide	GCMS-H	0.0080	5.9E-05
93-65-2	Mecoprop (MCPP)		Herbicide	GCMS-H	0.0080	8.6E-10
57837-19-1	Metalaxyl		Fungicide	GCMS	0.0254	4.3E-03
950-37-8	Methidathion		Insecticide / Organophosphate	GCMS	0.0111	1.4E-03
2032-65-7	Methiocarb		Insecticide / Carbamate	LCMS/MS	0.0020	2.1E-10
16752-77-5	Methomyl		Insecticide / Carbamate	LCMS/MS	0.0030	5.2E-10
13749-94-5	Methomyl oxime	Thiodicarb	Degradate / Carbamate	LCMS/MS	0.0030	5.2E-10
72-43-5	Methoxychlor		Insecticide / Organochlorine	GCMS	0.0358	4.9E-03
161050-58-4	Methoxyfenozide		Insecticide	LCMS/MS	0.0045	8.4E-04
950-35-6	Methyl Paraoxon	Methyl parathion	Degradate / Organophosphate	GCMS	0.0095	1.3E-03
298-00-0	Methyl Parathion		Insecticide / Organophosphate	GCMS	0.0095	1.3E-03
51218-45-2	Metolachlor		Herbicide	GCMS	0.0071	9.6E-04
21087-64-9	Metribuzin		Herbicide	GCMS	0.0154	1.9E-03
7786-34-7	Mevinphos		Insecticide / Organophosphate	GCMS	0.0216	2.7E-03
113-48-4	MGK264		Synergist / Insecticide	GCMS	0.0171	2.1E-03
2385-85-5	Mirex		Insecticide / Organochlorine	GCMS	0.0131	1.7E-03
6923-22-4	Monocrotophos		Insecticide / Organophosphate	GCMS	0.0172	2.1E-03
150-68-5	Monuron		Herbicide	LCMS/MS	0.0060	1.0E-09
300-76-5	Naled		Insecticide / Organophosphate	GCMS	0.0222	2.7E-03
15299-99-7	Napropamide		Herbicide	GCMS	0.0141	1.7E-03
555-37-3	Neburon		Herbicide	LCMS/MS	0.0110	7.3E-10
27314-13-2	Norflurazon		Herbicide	GCMS	0.0121	1.6E-03

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
19044-88-3	Oryzalin		Herbicide	GCMS	0.0261	3.3E-03
23135-22-0	Oxamyl		Insecticide / Carbamate	LCMS/MS	0.0020	2.1E-10
30558-43-1	Oxamyl oxime	Oxamyl	Degradate / Carbamate	LCMS/MS	0.0020	2.1E-10
27304-13-8	Oxychlordane	Chlordane	Degradate / Organochlorine	GCMS	0.0181	2.2E-03
42874-03-3	Oxyfluorfen		Herbicide	GCMS	0.0583	7.5E-03
56-38-2	Parathion		Insecticide / Organophosphate	GCMS	0.0081	1.0E-03
1114-71-2	Pebulate		Herbicide	GCMS	0.0081	1.0E-03
40487-42-1	Pendimethalin		Herbicide	GCMS	0.0285	3.5E-03
87-86-5	Pentachlorophenol		Wood Preservative	GCMS-H	0.0070	1.1E-03
26002-80-2	Phenothrin		Insecticide / Pyrethroid	GCMS	0.0206	2.7E-03
298-02-2	Phorate		Insecticide / Organophosphate	GCMS	0.0101	1.1E-03
2600-69-3	Phorate O.A.		Insecticide / Organophosphate	GCMS	0.0501	6.5E-03
732-11-6	Phosmet		Insecticide / Organophosphate	GCMS	0.0111	1.4E-03
1918-02-1	Picloram		Herbicide	GCMS-H	0.0177	4.5E-04
51-03-6	Piperonyl Butoxide (PBO)		Synergist	GCMS	0.0502	6.6E-03
2631-37-0	Promecarb		Insecticide / Carbamate	LCMS/MS	0.0040	4.3E-10
1610-18-0	Prometon		Herbicide	GCMS	0.0141	1.7E-03
7287-19-6	Prometryn		Herbicide	GCMS	0.0092	1.2E-03
23950-58-5	Pronamide (Kerb)		Herbicide	GCMS	0.0091	1.2E-03
1918-16-7	Propachlor (Ramrod)		Herbicide	GCMS	0.0111	1.3E-03
2312-35-8	Propargite		Insecticide / Sulfite Ester	GCMS	0.0491	6.4E-03
139-40-2	Propazine		Herbicide	GCMS	0.0131	1.7E-03
114-26-1	Propoxur		Insecticide / Carbamate	LCMS/MS	0.0040	4.3E-10
10453-86-8	Resmethrin		Insecticide / Pyrethroid	GCMS	0.0141	1.8E-03
93-72-1	Silvex		Herbicide	GCMS-H	0.0100	1.9E-09
122-34-9	Simazine		Herbicide	GCMS	0.0121	1.9E-03
1014-70-6	Simetryn		Herbicide	GCMS	0.0101	1.3E-03

CAS Number	Parameter	Parent Chemical	Use / Type	Analysis Method <sup>1</sup>	LPQL	Standard Deviation
3689-24-5	Sulfotepp		Insecticide / Organophosphate	GCMS	0.0111	1.4E-03
946578-00-3	Sulfoxaflor		Insecticide / Neonicotinoid- like	LCMS/MS	0.0070	3.1E-10
34014-18-1	Tebuthiuron		Herbicide	GCMS	0.0162	2.0E-03
5902-51-2	Terbacil		Herbicide	GCMS	0.0147	1.9E-03
961-11-5	Tetrachlorvinphos (Gardona)		Insecticide / Organophosphate	GCMS	0.0091	1.2E-03
27813-21-4	Tetrahydrophthalimide	Captan	Degradate / Fungicide	GCMS	0.0301	3.7E-03
111988-49-9	Thiacloprid		Insecticide / Neonicotinoid	LCMS/MS	0.0100	1.9E-09
153719-23-4	Thiamethoxam		Insecticide / Neonicotinoid	LCMS/MS	0.0060	1.0E-09
28249-77-6	Thiobencarb		Herbicide / Carbamate	GCMS	0.0500	6.1E-03
34643-46-4	Tokuthion		Insecticide / Organophosphate	GCMS	0.0613	7.8E-03
66841-25-6	Tralomethrin		Insecticide / Pyrethroid	GCMS	0.0102	1.4E-03
5103-74-2	trans-Chlordane		Insecticide / Organophosphate	GCMS	0.0292	3.6E-03
39765-80-5	trans-Nonachlor		Insecticide / Organochlorine	GCMS	0.0369	4.6E-03
61949-77-7	trans-Permethrin		Insecticide / Pyrethroid	GCMS	0.0251	3.4E-03
43121-43-3	Triadimefon		Fungicide	GCMS	0.0081	9.3E-04
2303-17-5	Triallate		Herbicide	GCMS	0.0141	1.7E-03
327-98-0	Trichloronate		Insecticide / Organophosphate	GCMS	0.0171	2.1E-03
55335-06-3	Triclopyr		Herbicide	GCMS-H	0.0070	3.1E-10
41814-78-2	Tricyclazole		Fungicide	GCMS	0.0609	7.9E-03
1582-09-8	Trifluralin		Herbicide	GCMS	0.0202	2.5E-03

<sup>&</sup>lt;sup>1</sup> 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.

### Quality Assurance and Quality Control Samples

Quality assurance (QA) samples are collected alongside grab samples in the field and analyzed. Quality control (QC) samples are generated by the laboratory for every batch of field samples

submitted. QA and QC samples assure consistency and accuracy throughout sample collection, sample analysis, and the data reporting process.

For this project, QA samples include: field replicates, field blanks, and matrix spike and matrix spike duplicates (MS/MSD). Laboratory control samples (LCS), LCS duplicates (LCSD), surrogate spikes, and method blanks are included as QC samples in each batch of samples analyzed for pesticides as are method blanks and split sample duplicates each batch of TSS and conductivity samples.

#### **Quality Assurance Samples**

In 2014, 15.7% of the field samples collected in the field were QA samples. There were 90 field replicates collected in total divided evenly among each for carbamate, herbicide, and pesticide gas chromatography/mass spectroscopy (GCMS) analysis; and 30 field replicates for total suspended solids (TSS). QA samples included 60 field blanks for each of the following: carbamate, herbicide, pesticide GCMS, and TSS analysis. There were also 90 MS/MSD samples each for carbamates, herbicides, and pesticide GCMS analysis.

#### Field Quality Assurance Sample Results

#### Field Replicates Results

During 2014, sampling frequency the field replicate samples was 7.71% for pesticides and TSS samples. Precision between replicate pairs was calculated using the relative percent difference (RPD) statistic. 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.

In 2014 there were 81 consistently identified pairs for pesticide analysis and 29 consistently identified pairs for TSS analysis (see Table B-4). *Consistent identification* refers to compounds identified in both the original sample and field replicate. Conversely, inconsistently identified replicate pairs refer to when an analyte was positively identified in either the replicate sample or the grab sample but not in both.

Table B-4 presents the data, data qualification, and relative percent difference (RPD) for analytes consistently identified in both the grab sample and replicate sample.

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
2,4-D	4/15/2014	BS-1	0.063	0.085	μg/L	0.08 μg/L "J" 0.09 μg/L "J"	11.8
2,4-D	4/22/2014	BD-1	0.062	0.063	μg/L	0.061 μg/L "J" 0.065 μg/L "D"	6.3

Table B-4: Consistently detected pairs within field replicate results, 2014

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
2,4-D	5/6/2014	BD-1	0.061	0.41	μg/L	0.47 μg/L "D" 0.35 μg/L "D"	29.3
2,4-D	5/12/2014	BD-2	0.062	0.088	μg/L	0.092 μg/L "D" 0.084 μg/L "D"	9.1
2,4-D	6/10/2014	SU-1	0.062	0.185	μg/L	0.18 μg/L "D" 0.19 μg/L "D"	5.4
2,4-D	6/10/2014	IS-1	0.061	0.13	μg/L	0.14 μg/L "D" 0.12 μg/L "D"	15.4
2,4-D	6/16/2014	MA-2	0.062	0.0445	μg/L	0.041 μg/L "J" 0.048 μg/L "J"	15.7
2,4-D	6/16/2014	TC-3	0.061	0.102	μg/L	0.084 μg/L "J" 0.12 μg/L "J"	35.3
2,4-D	7/15/2014	SU-1	0.061	0.0865	μg/L	0.093 μg/L "D" 0.08 μg/L "D"	15.0
4,4'-DDE	6/24/2014	BR-1	0.033	0.025	μg/L	0.024 μg/L "J" 0.026 μg/L "J"	8.0
Atrazine	5/28/2014	SU-1	0.033	0.0745	μg/L	0.075 μg/L "D" 0.074 μg/L "D"	1.3
Atrazine	7/1/2014	BC-1	0.033	0.037	μg/L	0.039 μg/L "D" 0.035 μg/L "D"	10.8
Bentazon	6/16/2014	MA-2	0.062	0.0885	μg/L	0.098 μg/L "D" 0.079 μg/L "D"	21.5
Boscalid	7/14/2014	BD-2	0.098	0.335	μg/L	0.34 μg/L "D" 0.33 μg/L "D"	3.0
Chlorpyrifos	4/7/2014	MI-1	0.033	0.0505	μg/L	0.051 μg/L "D" 0.05 μg/L "D"	2.0
Chlorpyrifos	4/14/2014	SP-3	0.033	0.0185	μg/L	0.017 μg/L "J" 0.02 μg/L "J"	16.2
Chlorpyrifos	5/28/2014	MA-2	0.033	0.055	μg/L	0.053 μg/L "D" 0.057 μg/L "D"	7.3
Cyprodinil	7/15/2014	BC-1	0.01	0.01	μg/L	0.01 μg/L "J" 0.01 μg/L "J"	0.0
Dacthal (DCPA)	4/15/2014	BS-1	0.063	0.1275	μg/L	0.2 μg/L "J" 0.055 μg/L "J"	113.7
Dacthal (DCPA)	6/24/2014	BS-1	0.062	0.036	μg/L	0.037 μg/L "J" 0.035 μg/L "J"	5.6
Diazinon	4/14/2014	SP-3	0.033	0.011	μg/L	0.012 μg/L "J" 0.01 μg/L "J"	18.2
Diazinon	5/12/2014	BC-1	0.032	0.0325	μg/L	0.032 μg/L "J" 0.033 μg/L "D"	3.1
Dichlobenil	4/7/2014	TC-3	0.032	0.008	μg/L	0.008 μg/L "J" 0.008 μg/L "J"	0.0
Dichlobenil	4/22/2014	LC-1	0.033	0.0485	μg/L	0.049 μg/L "D" 0.048 μg/L "D"	2.1
Dichlobenil	5/12/2014	TC-3	0.032	0.013	μg/L	0.013 μg/L "J" 0.013 μg/L "J"	0.0
Dichlobenil	5/12/2014	BC-1	0.032	0.01	μg/L	0.01 μg/L "J" 0.01 μg/L "J"	0.0
Dichlobenil	5/20/2014	LC-1	0.033	0.012	μg/L	0.011 μg/L "J" 0.013 μg/L "J"	16.7

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
Dinotefuran	4/7/2014	BD-1	0.01	0.204	μg/L	0.213 μg/L "D" 0.195 μg/L "D"	8.8
Dinotefuran	4/22/2014	BD-2	0.01	0.8715	μg/L	0.841 μg/L "D" 0.902 μg/L "D"	7.0
Dinotefuran	5/28/2014	BD-1	0.01	0.2405	μg/L	0.239 μg/L "D" 0.242 μg/L "D"	1.2
Dinotefuran	6/30/2014	BD-2	0.06	1.29	μg/L	1.06 μg/L "D" 1.52 μg/L "D"	35.7
Diuron	4/7/2014	BD-1	0.01	0.009	μg/L	0.01 μg/L "D" 0.008 μg/L "J"	22.2
Diuron	4/21/2014	SP-3	0.01	0.019	μg/L	0.016 μg/L "D" 0.022 μg/L "D"	31.6
Diuron	5/19/2014	SP-3	0.01	0.068	μg/L	0.068 μg/L "D" 0.068 μg/L "D"	0.0
Diuron	5/28/2014	MA-2	0.02	0.0145	μg/L	0.012 μg/L "J" 0.017 μg/L "J"	34.5
Diuron	5/28/2014	BD-1	0.02	0.016	μg/L	0.015 μg/L "J" 0.017 μg/L "J"	12.5
Diuron	6/30/2014	BD-2	0.01	0.024	μg/L	0.022 μg/L "D" 0.026 μg/L "D"	16.7
Eptam	5/28/2014	MA-2	0.033	0.0285	μg/L	0.029 μg/L "J" 0.028 μg/L "J"	3.5
Imazapyr	4/22/2014	IS-1	0.1	0.0265	μg/L	0.031 μg/L "J" 0.022 μg/L "J"	34.0
Imazapyr	4/22/2014	BD-2	0.1	0.021	μg/L	0.017 μg/L "J" 0.025 μg/L "J"	38.1
Imazapyr	5/28/2014	BD-1	0.1	0.0255	μg/L	0.025 μg/L "J" 0.026 μg/L "J"	3.9
Imazapyr	6/30/2014	BD-2	0.1	0.0245	μg/L	0.02 μg/L "J" 0.029 μg/L "J"	36.7
Imidacloprid	6/30/2014	BD-2	0.02	0.059	μg/L	0.062 μg/L "D" 0.056 μg/L "D"	10.2
Malaoxon	7/15/2014	BC-1	0.01	0.004	μg/L	0.004 μg/L "J" 0.004 μg/L "J"	0.0
Malaoxon	7/16/2014	SC-1	0.01	0.0035	μg/L	0.004 μg/L "J" 0.003 μg/L "J"	28.6
MCPA	5/6/2014	BD-1	0.061	0.072	μg/L	0.075 μg/L "D" 0.069 μg/L "D"	8.3
MCPA	6/10/2014	IS-1	0.061	0.29	μg/L	0.3 μg/L "D" 0.28 μg/L "D"	6.9
Mecoprop (MCPP)	5/6/2014	BD-1	0.061	0.057	μg/L	0.058 μg/L "J" 0.056 μg/L "J"	3.5
Mecoprop (MCPP)	5/12/2014	BD-2	0.062	0.0315	μg/L	0.034 μg/L "J" 0.029 μg/L "J"	15.9
Mecoprop (MCPP)	6/16/2014	TC-3	0.061	0.0345	μg/L	0.031 μg/L "J" 0.038 μg/L "J"	20.3
Metalaxyl	5/12/2014	BC-1	0.032	0.0645	μg/L	0.07 μg/L "D" 0.059 μg/L "D"	17.1
Metalaxyl	7/1/2014	BC-1	0.033	0.0645	μg/L	0.066 μg/L "D" 0.063 μg/L "D"	4.7

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
Metalaxyl	7/14/2014	BD-2	0.097	1.1	μg/L	1.1 μg/L "D" 1.1 μg/L "D"	0.0
Methiocarb	6/30/2014	BD-2	0.05	0.0455	μg/L	0.051 μg/L "D" 0.04 μg/L "J"	24.2
Metolachlor	6/10/2014	BS-1	0.033	0.0375	μg/L	0.037 μg/L "D" 0.038 μg/L "D"	2.7
Metolachlor	7/8/2014	BD-1	0.033	0.022	μg/L	0.023 μg/L "J" 0.021 μg/L "J"	9.1
Norflurazon	6/24/2014	BR-1	0.033	0.0435	μg/L	0.043 μg/L "D" 0.044 μg/L "D"	2.3
Oxamyl	4/28/2014	BC-1	0.02	0.0925	μg/L	0.098 μg/L "D" 0.087 μg/L "D"	11.9
Oxamyl	5/12/2014	BC-7	0.02	0.017	μg/L	0.016 μg/L "J" 0.018 μg/L "J"	11.8
Oxamyl	6/23/2014	MA-2	0.01	0.005	μg/L	0.005 μg/L "J" 0.005 μg/L "J"	0.0
Oxamyl	7/1/2014	BC-7	0.01	0.007	μg/L	0.006 μg/L "J" 0.008 μg/L "J"	28.6
Oxamyl	7/15/2014	BC-1	0.01	0.0705	μg/L	0.073 μg/L "D" 0.068 μg/L "D"	7.1
Oxamyl oxime	4/28/2014	BC-1	0.01	0.0555	μg/L	0.06 μg/L "D" 0.051 μg/L "D"	16.2
Oxamyl oxime	7/1/2014	BC-7	0.01	0.0265	μg/L	0.022 μg/L "D" 0.031 μg/L "D"	34.0
Oxamyl oxime	7/15/2014	BC-1	0.02	0.039	μg/L	0.036 μg/L "D" 0.042 μg/L "D"	15.4
Pendimethalin	5/28/2014	MA-2	0.033	0.083	μg/L	0.084 μg/L "D" 0.082 μg/L "D"	2.4
Pentachlorophenol	5/5/2014	SC-1	0.062	0.13	μg/L	0.12 μg/L "D" 0.14 μg/L "D"	15.4
Picloram	7/8/2014	SC-1	0.062	0.0545	μg/L	0.051 μg/L "J" 0.058 μg/L "J"	12.8
Simazine	7/1/2014	BC-1	0.033	0.0605	μg/L	0.059 μg/L "D" 0.062 μg/L "D"	5.0
Simazine	7/7/2014	BC-7	0.033	0.22	μg/L	0.2 μg/L "D" 0.24 μg/L "D"	18.2
Simazine	8/11/2014	BC-7	0.032	0.0795	μg/L	0.088 μg/L "D" 0.071 μg/L "D"	21.4
Terbacil	5/28/2014	MA-2	0.033	0.083	μg/L	0.084 μg/L "D" 0.082 μg/L "D"	2.4
Tetrahydrophthalimide	7/1/2014	BC-1	0.099	0.255	μg/L	0.25 μg/L "D" 0.26 μg/L "D"	3.9
Thiamethoxam	6/30/2014	BD-2	0.02	0.0115	μg/L	0.009 μg/L "J" 0.014 μg/L "J"	43.5
Thiamethoxam	7/1/2014	BC-7	0.02	0.0165	μg/L	0.012 μg/L "J" 0.021 μg/L "J"	54.5
Thiamethoxam	7/15/2014	BC-1	0.01	0.044	μg/L	0.046 μg/L "D" 0.042 μg/L "D"	9.1
Total Suspended Solids	3/10/2014	BC-7	2	9	mg/L	8 mg/L "D" 10 mg/L "D"	22.2

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
Total Suspended Solids	3/24/2014	SC-1	2	9	mg/L	9 mg/L "J" 9 mg/L "J"	0.0
Total Suspended Solids	3/31/2014	SP-3	3	42	mg/L	42 mg/L "D" 42 mg/L "D"	0.0
Total Suspended Solids	4/1/2014	BD-1	3	24	mg/L	25 mg/L "D" 23 mg/L "D"	8.3
Total Suspended Solids	4/7/2014	SC-1	5	78	mg/L	78 mg/L "J" 78 mg/L "J"	0.0
Total Suspended Solids	4/15/2014	IS-1	3	13.5	mg/L	9 mg/L "J" 18 mg/L "J"	66.7
Total Suspended Solids	4/21/2014	SU-1	2	55	mg/L	57 mg/L "J" 53 mg/L "J"	7.3
Total Suspended Solids	4/22/2014	TC-3	3	20	mg/L	21 mg/L "D" 19 mg/L "D"	10.0
Total Suspended Solids	4/22/2014	BS-1	2	9.5	mg/L	9 mg/L "D" 10 mg/L "D"	10.5
Total Suspended Solids	4/29/2014	MI-1	1	6	mg/L	6 mg/L "D" 6 mg/L "D"	0.0
Total Suspended Solids	4/29/2014	BD-2	2	5	mg/L	5 mg/L "D" 5 mg/L "D"	0.0
Total Suspended Solids	5/6/2014	LC-1	2	8.5	mg/L	9 mg/L "D" 8 mg/L "D"	11.8
Total Suspended Solids	5/13/2014	BR-1	2	41	mg/L	42 mg/L "D" 40 mg/L "J"	4.9
Total Suspended Solids	5/13/2014	IS-1	3	150.5	mg/L	4 mg/L "D" 297 mg/L "D"	194.7
Total Suspended Solids	5/13/2014	BD-1	3	19.5	mg/L	19 mg/L "D" 20 mg/L "D"	5.1
Total Suspended Solids	5/20/2014	BS-1	2	6	mg/L	6 mg/L "D" 6 mg/L "D"	0.0
Total Suspended Solids	5/21/2014	BC-1	2	3.5	mg/L	3 mg/L "D" 4 mg/L "D"	28.6
Total Suspended Solids	5/27/2014	PE-1	1	11.5	mg/L	13 mg/L "D" 10 mg/L "D"	26.1
Total Suspended Solids	5/27/2014	MI-1	2	15.5	mg/L	16 mg/L "D" 15 mg/L "D"	6.5
Total Suspended Solids	5/27/2014	BD-2	2	6.5	mg/L	7 mg/L "D" 6 mg/L "D"	15.4
Total Suspended Solids	6/2/2014	SP-3	3	33.5	mg/L	33 mg/L "D" 34 mg/L "D"	3.0
Total Suspended Solids	6/2/2014	LC-1	2	35	mg/L	35 mg/L "D" 35 mg/L "D"	0.0
Total Suspended Solids	6/16/2014	SU-1	5	87.5	mg/L	100 mg/L "J" 75 mg/L "J"	28.6
Total Suspended Solids	6/16/2014	TC-3	2	9	mg/L	9 mg/L "D" 9 mg/L "D"	0.0
Total Suspended Solids	6/17/2014	BC-1	1	2	mg/L	2 mg/L "D" 2 mg/L "D"	0.0
Total Suspended Solids	6/23/2014	MA-2	1	4	mg/L	4 mg/L "D" 4 mg/L "D"	0.0

Parameter	Sample Date	Site-ID	Reporting Limit	Averaged Result	Unit of Measurement	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
Total Suspended Solids	7/16/2014	PE-1	1	2.5	mg/L	3 mg/L "D" 2 mg/L "D"	40.0
Total Suspended Solids	7/21/2014	BC-7	1	2.5	mg/L	1 mg/L "D" 4 mg/L "D"	120.0
Total Suspended Solids	7/29/2014	MA-2	2	10.5	mg/L	10 mg/L "D" 11 mg/L "D"	9.5
Triclopyr	4/22/2014	BD-1	0.062	0.0495	μg/L	0.05 μg/L "J" 0.049 μg/L "J"	2.0
Triclopyr	5/6/2014	BD-1	0.061	0.29	μg/L	0.3 μg/L "D" 0.28 μg/L "D"	6.9
Triclopyr	5/12/2014	BD-2	0.062	0.088	μg/L	0.096 μg/L "D" 0.08 μg/L "D"	18.2
Triclopyr	6/10/2014	IS-1	0.061	0.1035	μg/L	0.097 μg/L "D" 0.11 μg/L "D"	12.6
Trifluralin	5/28/2014	MA-2	0.033	0.0295	μg/L	0.03 μg/L "J" 0.029 μg/L "J"	3.4

For pesticides, the average RPD of the consistently detected replicates was 14.4% and 76.5% of the replicate pairs that had a RPD of less than 20%. For TSS, the average RPD of the consistently detected replicates was 21.3% and 72.4% of the replicate pairs that had an RPD of less than 20%.

Of the 110 consistently identified replicate pairs, there were only six pairs that exceeded the 40% RPD criterion. Three of the six criteria exceedances were for total suspended solids, two were for the insecticide thiamethoxam, and one for the herbicide dacthal (DCPA). It is important to note that the RPD statistic has limited effectiveness in assessing variability at low levels (Mathieu, 2006) because the RPD statistic can become large even though the actual difference between the pairs is low when the concentrations of analytes are very small. Four out of the six exceedances are not considered of acceptable data quality and the results will be requalified as "J" to reflect that the numerical value is only an approximation of the concentration of the analyte in the sample. The qualified data include the April 15<sup>th</sup> dacthal, April 15<sup>th</sup> TSS, May 13<sup>th</sup> TSS, and the July 21<sup>st</sup> TSS results. Those data results should be used with caution. The other two exceedances for thiamethoxam were already below the reporting limit and the reported concentrations are already qualified as an estimate. The remaining data for pesticide and TSS field replicates are of acceptable data quality.

In 2014 there were 17 inconsistently identified replicate pairs for pesticides and no inconsistently identified replicate pairs for TSS (see Table B-5). The majority of the inconsistently identified pairs were due to the detections being very close to the detection limit. There were 11 replicate pairs where a positive detection was paired with a "non-detect" value ("U" or "UJ"). The remaining six pairs included a detection paired with a tentative detection or (Table B-5).

Table B-5: Inconsistent field replicate detections (µg/L), 2014

Parameter	Sample Date	Site-ID	Sample Type	Reporting Limit (µg/L)	Averaged Result (µg/L)	Sample and Replicate Sample Details (Results and Corresponding Qualifiers)	RPD (%)
4,4'-DDE	5/28/2014	SU-1	Sample	0.033	0.025	0.017 μg/L "J" 0.033 μg/L "U"	64.0
4-Nitrophenol	6/16/2014	TC-5	Replicate	0.061	0.1355	0.21 μg/L "D" 0.061 μg/L "U"	110.0
Dicamba	7/15/2014	SU-1	Sample	0.061	0.0195	0.02 μg/L "J" 0.019 μg/L "NJ"	5.1
Diuron	4/22/2014	IS-1	Sample	0.01	0.0095	0.01 μg/L "U" 0.009 μg/L "J"	10.5
Diuron	7/15/2014	BC-1	Sample	0.02	0.0165	0.02 μg/L "U" 0.013 μg/L "J"	42.4
Fenarimol	6/9/2014	PE-1	Sample	0.033	0.051	0.033 μg/L "U" 0.069 μg/L "D"	70.6
Imazapyr	4/7/2014	BD-3	Replicate	0.1	0.057	0.1 μg/L "U" 0.014 μg/L "J"	150.9
Imazapyr	6/16/2014	SU-2	Replicate	0.1	0.0585	0.017 μg/L "J" 0.1 μg/L "U"	141.9
Imidacloprid	5/12/2014	BC-7	Sample	0.03	0.036	0.042 μg/L "D" 0.03 μg/L "U"	33.3
MCPA	4/22/2014	BD-1	Sample	0.062	0.0615	0.059 μg/L "NJ" 0.064 μg/L "D"	8.1
MCPA	5/12/2014	BD-4	Replicate	0.062	0.0505	0.062 μg/L "U" 0.039 μg/L "J"	45.5
MCPA	7/8/2014	IS-1	Sample	0.061	0.038	0.037 μg/L "NJ" 0.039 μg/L "J"	5.3
Metolachlor	7/28/2014	BD-3	Replicate	0.032	0.0245	0.017 μg/L "J" 0.032 μg/L "U"	61.2
Pentachlorophenol	3/31/2014	BC-1	Sample	0.062	0.067	0.062 μg/L "U" 0.072 μg/L "D"	14.9
Pentachlorophenol	5/12/2014	BD-4	Replicate	0.062	0.0225	0.022 μg/L "J" 0.023 μg/L "NJ"	4.4
Picloram	7/22/2014	BD-2	Sample	0.061	0.11	0.12 μg/L "D" 0.1 μg/L "NJ"	18.2
Simazine	5/12/2014	BC-3	Replicate	0.032	0.0465	0.039 μg/L "NJ" 0.054 μg/L "D"	32.3

#### Field Blank Results

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 2014, there were two field blank detections for the pesticide analysis.

- 4,4'-DDE was detected on June 13<sup>th</sup> at Brender Creek at a concentration of 0.024 μg/L.
  The analyte was positively identified and the concentration was detected at the detection
  limit. The detection limit was 0.024 μg/L. The reported concentration is an
  approximation. 4,4'-DDE was not detected in the grab sample associated with that site
  visit.
- Tebuthiuron was detected on August 27<sup>th</sup> at Indian Slough at a concentration of 0.096 μg/L. The analyte was positively identified and the concentration was detected above the reporting limit. The reporting limit was 0.032 μg/L. Tebuthiuron was also detected in the grab samples at Indian Slough and at Upper Big Ditch on the same day at a concentration of 0.1 μg/L and 0.091 μg/L respectively. Tebuthiuron results from this batch should be used with caution.

There were also two field blank detection for TSS

- TSS was detected in the field blank on April 7<sup>th</sup> at Longfellow Creek at a concentration of 2 mg/L. The analyte was positively identified and the concentration was detected above the reporting limit. The reporting limit was 1 mg/L. TSS was also detected in the grab sample during that site visit at 6 mg/L.
- TSS was detected in the field blank on August 27<sup>th</sup> at Brender Creek at a concentration of 36 mg/L. The analyte was positively identified and the concentration was detected above the reporting limit. The reporting limit was 2 mg/L. TSS was also detected in the grab sample taken at that site as well at the LCS and LCSD at 37 mg/L, 37 mg/L and 38 mg/L respectively. TSS results from this batch data from this should be used with caution.

#### Matrix Spike/Matrix Spike Duplicate (MS/MSD) Results

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 in the sampling process.

Table B-7 presents the mean, minimum, and maximum percent recovery for the MS/MSD for the three types of analysis as well as the RPD for the MS and MSDs for 2014.

Analytical Method and Parameter Name	Number of Results	Average Recovery (%)	Maximum Recovery (%)	Minimum Recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Carbamates (LC/MS/MS)	870	96	214	28	11	107	0
3-Hydroxycarbofuran	30	94	121	71	9	16	0

Table B-7: Summary Statistics for MS/MSD Recoveries and RPD, 2014

Analytical Method and Parameter Name	Number of Results	Average Recovery (%)	Maximum Recovery (%)	Minimum Recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Acetamiprid	30	96	127	72	11	23	0
Aldicarb	30	85	106	65	11	29	0
Aldicarb Sulfone	30	132	214	83	14	30	2
Aldicarb Sulfoxide	30	115	155	92	7	25	0
Carbaryl	30	101	133	71	11	24	1
Carbofuran	30	102	131	84	8	20	0
Clothianidin	30	103	153	51	34	68	8
Cyprodinil	30	47	87	28	9	22	0
Dinotefuran	30	121	165	90	9	23	1
Diuron	30	96	132	65	8	22	0
Imazapic	30	91	136	52	9	19	1
Imazapyr	30	105	139	82	5	19	0
Imidacloprid	30	94	126	72	12	31	1
Linuron	30	92	155	36	25	107	0
Malaoxon	30	92	119	76	7	25	0
Methiocarb	30	91	116	60	11	34	0
Methomyl	30	91	116	78	8	18	1
Methomyl oxime	30	95	135	73	19	41	3
Methoxyfenozide	30	92	142	65	9	27	1
Monuron	30	96	127	80	8	23	1
Neburon	30	77	114	56	8	19	0
Oxamyl	30	104	134	87	8	20	1
Oxamyl oxime	30	98	133	75	6	26	0
Promecarb	30	98	136	78	11	31	1
Propoxur	30	96	113	81	9	21	1
Sulfoxaflor	30	86	121	65	12	29	1
Thiacloprid	30	96	121	76	10	29	0
Thiamethoxam	30	97	121	71	12	25	1
HERBS (GC/MS)	750	83	159	18	10	86	0
2,3,4,5-Tetrachlorophenol	30	81	92	70	6	19	1
2,3,4,6-Tetrachlorophenol	30	72	80	59	6	17	1
2,4,5-T	30	80	92	61	9	25	0
2,4,5-Trichlorophenol	30	73	88	57	9	29	1
2,4,6-Trichlorophenol	30	71	88	51	14	38	1
2,4-D	30	74	93	51	12	36	0
2,4-DB	30	108	139	93	6	14	0
3,5-Dichlorobenzoic Acid	30	82	96	68	5	12	0
4-Nitrophenol	30	83	125	31	27	84	2
Acifluorfen, sodium salt	30	134	159	108	9	24	1

Analytical Method and Parameter Name	Number of Results	Average Recovery (%)	Maximum Recovery (%)	Minimum Recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Bentazon	30	82	94	65	8	26	0
Bromoxynil	30	80	91	69	6	15	0
Clopyralid	30	51	76	27	24	58	2
Dacthal (DCPA)	30	90	103	80	7	20	0
Dicamba	30	72	83	62	5	18	0
Dichlorprop	30	90	108	62	6	41	0
Diclofop-Methyl	30	111	122	103	4	8	0
Dinoseb	30	89	113	40	14	38	0
Ioxynil	30	81	90	72	7	14	0
MCPA	30	77	93	61	8	21	0
Mecoprop (MCPP)	30	91	105	81	5	12	1
Pentachlorophenol	30	78	86	70	5	11	0
Picloram	30	44	83	18	38	86	2
Silvex	30	90	101	82	3	12	0
Triclopyr	30	90	101	76	6	16	1
PESTMS (GC/MS)	1984	98	340	0	8	146	0
1-Naphthol	10	103	123	61	13	33	2
2,4'-DDD	19	96	143	73	6	32	0
2,4'-DDE	19	81	98	63	7	11	1
2,4'-DDT	19	77	110	55	7	20	0
4,4'-DDD	19	102	155	71	7	39	0
4,4'-DDE	19	85	131	59	9	29	2
4,4'-DDT	19	82	115	70	7	32	1
4,4'-Dichlorobenzophenone	10	99	117	93	6	19	1
Acetochlor	10	106	120	93	7	21	0
Alachlor	10	102	106	96	4	9	1
Aldrin	19	77	82	66	4	9	1
Alpha-BHC	19	97	122	80	5	12	1
Atrazine	10	102	112	93	3	6	1
Azinphos-methyl	19	150	261	64	16	84	1
Benfluralin	19	93	116	77	3	7	0
Beta-BHC	19	102	123	87	5	13	0
Bifenazate	29	130	340	42	13	44	1
Bifenthrin	10	82	94	71	4	7	3
Boscalid	10	61	136	25	10	21	0
Bromacil	10	110	122	94	6	10	3
Butachlor	10	115	121	105	6	11	2
Butylate	10	89	115	69	5	13	1
Captan	19	53	97	11	32	119	8

# [2014 DATA SUMMARY, PESTICIDES IN SALMONID-BEARING STREAMS]

Analytical Method and Parameter Name	Number of Results	Average Recovery (%)	Maximum Recovery (%)	Minimum Recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Chlorothalonil (Daconil)	19	79	98	46	10	25	0
Chlorpropham	10	97	112	75	10	18	0
Chlorpyrifos	19	101	118	89	5	10	2
Chlorpyrifos O.A.	10	115	130	98	6	11	0
Chlorpyrifos-methyl	19	109	128	92	2	7	1
cis-Chlordane	19	82	97	71	5	12	1
Cis-Nonachlor	19	83	109	67	9	25	1
cis-Permethrin	19	97	145	46	10	52	1
Coumaphos	19	113	184	42	17	87	2
Cyanazine	29	120	165	17	15	146	0
Cycloate	10	92	101	82	5	7	0
Cypermethrin	10	75	126	40	10	16	0
Delta-BHC	19	102	118	89	6	12	1
Deltamethrin	29	59	198	8	18	89	1
Di-allate (Avadex)	19	104	131	91	6	15	0
Diazinon	19	115	158	95	5	15	2
Diazoxon	25	46	139	0	6	22	0
Dichlobenil	19	89	108	71	4	8	1
Dichlorvos (DDVP)	19	112	129	94	3	10	0
Dicofol	10	89	153	57	6	12	0
Dieldrin	19	106	150	80	8	24	2
Dimethoate	10	129	145	116	13	22	8
Diphenamid	10	101	109	90	5	13	0
Disulfoton Sulfoxide	10	91	173	34	18	58	2
Endosulfan I	19	109	181	64	9	30	1
Endosulfan II	19	102	139	72	7	23	0
Endosulfan Sulfate	19	104	140	90	7	27	2
Endrin	19	119	179	85	8	39	0
Endrin Aldehyde	19	90	131	57	9	21	0
Endrin Ketone	19	98	127	72	10	23	3
EPN	10	106	122	88	3	6	1
Eptam	10	91	125	65	5	13	0
Ethalfluralin (Sonalan)	19	98	115	79	6	12	1
Ethion (Somman)	19	122	172	99	5	25	0
Ethoprop	19	119	174	92	5	13	2
Etoxazole	29	133	220	100	8	24	1
Fenamiphos	29	148	220	99	8	36	1
Fenamiphos Sulfone	10	82	238	26	18	31	4
Fenarimol Fenarimol	10	88	127	57	3	12	0
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# [2014 DATA SUMMARY, PESTICIDES IN SALMONID-BEARING STREAMS]

Fenvalerate         19         92           Fipronil         10         136           Figranil Disulfand         10         110	214 150 121 102	32 123	23	۱	
	121	123		86	1
Einsonil Disulfinyl 10 110			6	11	2
Fipronil Disulfinyl 10 110	102	104	3	10	0
Fipronil Sulfide 10 93		79	6	8	4
Fipronil Sulfone 10 93	110	55	7	20	1
Fluridone 10 39	169	0	15	24	1
Fonofos 19 103	111	91	7	12	1
Heptachlor 19 97	114	78	6	14	1
Heptachlor Epoxide 19 95	108	80	7	15	2
Hexachlorobenzene 19 75	92	65	5	12	2
Hexazinone 10 82	119	61	9	16	0
Lindane 19 96	124	81	6	12	0
Malathion 10 128	136	119	5	9	2
Metalaxyl 19 125	146	103	6	15	0
Methidathion 19 133	179	97	8	31	2
Methoxychlor 19 71	96	0	9	24	0
Methyl Paraoxon 10 108	118	94	2	4	0
Methyl Parathion 19 119	135	100	7	23	0
Metolachlor 10 101	106	95	4	11	1
Metribuzin 29 86	106	58	8	21	1
Mevinphos 19 100	138	44	11	72	0
MGK264 10 100	113	90	4	11	0
Mirex 19 77	105	61	5	21	1
Monocrotophos 29 116	191	16	8	27	0
Naled 19 70	98	45	17	35	4
Napropamide 10 117	129	107	6	13	1
Norflurazon 10 72	118	39	6	14	1
Oryzalin 29 45	238	0	42	122	5
Oxychlordane 19 86	108	64	10	20	5
Oxyfluorfen 19 112	158	78	8	31	2
Parathion 10 110	119	93	4	7	2
Pebulate 10 89	105	73	4	12	0
Pendimethalin 19 104	121	90	5	7	1
Phenothrin 19 101	153	54	7	23	0
Phorate 29 88	125	70	8	17	1
Phosmet 19 110	190	36	16	76	1
Piperonyl Butoxide (PBO) 10 123	168	98	4	7	1
Prometon 10 112	120	103	6	15	1
Prometryn 10 111	116	104	3	8	0

Analytical Method and Parameter Name	Number of Results	Average Recovery (%)	Maximum Recovery (%)	Minimum Recovery (%)	Mean RPD	Maximum RPD	Minimum RPD
Pronamide (Kerb)	10	102	110	96	4	13	1
Propachlor (Ramrod)	29	104	153	83	3	8	0
Propargite	19	104	192	81	11	40	1
Propazine	10	97	101	91	5	6	4
Resmethrin	19	13	31	0	26	76	0
Simazine	10	93	99	86	9	14	4
Simetryn	10	117	135	100	3	8	1
Sulfotepp	10	117	130	109	6	12	2
Tebuthiuron	10	123	238	70	6	15	0
Terbacil	10	127	136	116	4	7	0
Tetrachlorvinphos (Gardona)	19	111	139	90	6	16	0
Tetrahydrophthalimide	10	109	130	91	8	16	0
Thiobencarb	29	106	150	79	8	21	1
Tokuthion	19	102	125	82	5	13	0
trans-Chlordane	19	82	94	62	7	14	1
Trans-Nonachlor	19	86	119	64	8	28	0
Triadimefon	10	118	130	109	8	17	2
Triallate	19	96	110	87	3	9	1
Trichloronate	19	99	109	89	5	13	0
Tricyclazole	10	69	128	31	13	29	6
Trifluralin	10	80	87	72	4	8	2
Grand Total	3604	94	340	0	9	146	0

The percentage of MS\MSD samples with percent recoveries that fell within the target range were:

- LCMS\MS analysis: 92% fell within the control limits.
- GCMS-Herbicide analysis: 95% fell within the control limits.
- GCMS-Pesticide analysis: 92% fell within the control limits.

Analytes not meeting the target recovery range and the percentage of occurrences are described in Table B-8. Table B-8 also describes the number of detections for each analyte not meeting the target recovery range. Detections of analytes not meeting MS/MSD target recoveries and/or analyte results were qualified as estimates (qualified with a 'J').

Table B-8: MS/MSD Parameters outside of control limits in 2014

Analysis Method	Parameter Name	Percentage of Recoveries Outside Control Limits (%)	Fell below or Exceeded Control Limits	Lower Control Limit (%)	Upper Control Limit (%)	Number of Detections in 2014
	Aldicarb Sulfone	47	Exceeded	40	130	0
	Aldicarb Sulfoxide	20	Exceeded	40	130	0
	Carbaryl	7	Exceeded	40	130	6
	Carbofuran	3	Exceeded	40	130	0
	Clothianidin	20	Exceeded	40	130	0
	Cyprodinil	40	Fell Below	40	130	5
	Dinotefuran	37	Exceeded	40	130	49
Carbamates	Diuron	3	Exceeded	40	130	60
(LC/MS/MS)	Imazapic	7	Exceeded	40	130	0
	Imazapyr	7	Exceeded	40	130	50
	Linuron	27	Both	40	130	0
	Methomyl oxime	3	Exceeded	40	130	0
	Methoxyfenozide	3	Exceeded	40	130	3
	Oxamyl	7	Exceeded	40	130	63
	Oxamyl oxime	3	Exceeded	40	130	29
	Promecarb	7	Exceeded	40	130	0
	2,4-DB	7	Exceeded	40	130	94
	4-Nitrophenol	3	Fell Below	40	130	8
HERBS	Acifluorfen, sodium salt	60	Exceeded	40	130	0
(GC/MS)	Clopyralid	17	Fell Below	40	130	0
	Dinoseb	3	Fell Below	40	130	0
	Picloram	47	Fell Below	40	130	12
	2,4'-DDD	21	Exceeded	29	125	0
	4,4'-DDD	16	Exceeded	49	143	3
	4,4'-DDE	5	Exceeded	40	130	25
	Alpha-BHC	11	Fell Below	83	162	0
	Bifenazate	24	Both	50	150	0
	Boscalid	60	Fell Below	50	150	28
	Chlorothalonil (Daconil)	11	Fell Below	57	227	2
PESTMS (GC/MS)	Chlorpyrifos O.A.	10	Exceeded	30	130	29
(GC/MB)	Cis-Nonachlor	5	Exceeded	25	105	0
	Deltamethrin	59	Both	30	130	0
	Di-allate (Avadex)	11	Exceeded	30	130	0
	Diazoxon	64	Exceeded	30	130	0
	Dieldrin	11	Exceeded	69	143	0
	Disulfoton Sulfoxide	40	Exceeded	30	130	0
	Endosulfan II	5	Fell Below	72	146	0

Analysis Method	Parameter Name	Percentage of Recoveries Outside Control Limits (%)	Fell below or Exceeded Control Limits	Lower Control Limit (%)	Upper Control Limit (%)	Number of Detections in 2014
	Endosulfan Sulfate	5	Exceeded	77	140	0
	Endrin	26	Exceeded	62	145	0
	Endrin Ketone	11	Exceeded	34	119	0
	Ethion	26	Exceeded	41	132	0
	Etoxazole	17	Exceeded	50	150	3
	Fenamiphos Sulfone	40	Both	30	130	0
	Fenvalerate	21	Exceeded	30	130	0
	Fipronil	70	Exceeded	30	130	0
	Fluridone	60	Fell Below	10	375	0
PESTMS	Methoxychlor	11	Fell Below	15	181	0
(GC/MS)	Mirex	16	Exceeded	16	97	0
	Norflurazon	60	Fell Below	70	168	5
	Oryzalin	69	Fell Below	10	230	0
	Oxyfluorfen	16	Exceeded	51	153	0
	Phenothrin	21	Exceeded	22	130	0
	Piperonyl Butoxide (PBO)	20	Exceeded	30	130	4
	Propargite	5	Exceeded	30	130	1
	Resmethrin	42	Fell Below	10	65	0
	Tebuthiuron	10	Exceeded	10	235	15
	Thiobencarb	10	Exceeded	54	144	0

# **Quality Control Samples**

Quality control (QC) samples are collected and analyzed each year to assure consistency and accuracy of sample analysis.

For this project, QA samples include: field replicates, field blanks, and matrix spike and matrix spike duplicates (MS/MSD). Laboratory control samples (LCS), LCS duplicates (LCSD), surrogate spikes, and method blanks are included as QC samples in each batch of samples analyzed for pesticides as are method blanks and split sample duplicates each batch of TSS and conductivity samples.

### **Laboratory Duplicates**

MEL uses laboratory split sample duplicates to ensure consistency of TSS and conductivity analyses. In 2014, there were 100 laboratory replicate pairs for TSS and 21 replicate pairs for conductivity.

For TSS the pooled average RPD was 4.0%; the maximum RPD was 20%. Only one of the 100 replicate pairs met, or exceeded the 20% RPD criterion. For this replicate, results were low, and the RPD statistic has limited effectiveness in assessing variability at low levels (Mathieu, 2006).

For conductivity the pooled average RPD was 1.43%; the maximum RPD was 14%. All of the conductivity pairs are below the RPD exceedance criterion.

### 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. In 2014, 3-hydroxycarbofuran was positively detected in a laboratory blank for samples taken during the week of May 19th. No samples from the week of May 19th had detections for 3-hydroxycarbofuran, therefore values from this week are accepted. No other laboratory blanks were reported during 2014.

#### Surrogates

Surrogates are compounds spiked into field samples at the laboratory. Surrogates are used to assess recovery for a group of structurally related compounds. For instance, triphenyl phosphate is a surrogate for organophosphorus insecticides. Structurally related compounds, summary statistics, and control limits for surrogate recoveries are presented in Table B-9.

Structurally Average Minimum Maximum Lower Analytical Upper Control Control Parameter Name Related Recovery Recovery Recovery Method Limit (%) Compounds Limit (%) (%) (%)(%) Carbamates Carbamate Carbaryl C13 95 130 40 130 63 by pesticides (LC/MS/MS) 105 130 2,4,6-Tribromophenol 75 3 40 Herbicides Acid-derivitizable 2,4-Dichlorophenylacetic by (GC/MS) herbicides 73 4 105 40 130 acid 1,3-Dimethyl-2-Nitrogen 95 247 41 135 43 nitrobenzene containing Trifluralin-D14 79 20 117 pesticides 24 121 Chlorinated and nitrogen Atrazine-D5 105 134 167 48 45 Pesticides by containing (GC/MS) pesticides 178 4,4'-DDE-13C12 103 29 127 30 Chlorinated Decachlorobiphenyl (DCB) pesticides 65 4 106 13 98 Chlorpyrifos-D10 88 29 141 26 180 Organophosphorus Triphenyl Phosphate pesticides 101 46 153 45 137

Table B-9: Pesticide surrogates

The majority of 2014 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 B-10. High and low pesticide surrogate recovery requires all related data to be qualified as estimates (qualified with a 'J').

Analytical Method	Parameter Name	Structurally Related Compounds	Lower Control Limit (%)	Upper Control Limit (%)	Recoveries Within Control Limits (%)
Carbamates by (LC/MS/MS)	Carbaryl C13	Carbamate pesticides	40	130	96.8
	2,4,6-Tribromophenol		40	130	98.4
Herbicides by (GC/MS)	2,4- Dichlorophenylacetic acid	Acid-derivitizable herbicides	40	130	98.9
	1,3-Dimethyl-2- nitrobenzene	Nitrogen containing	41	135	99.6
	Trifluralin-D14	pesticides	26	180	100.0
Pesticides by	Atrazine-D5	Chlorinated and nitrogen containing pesticides	45	167	100.0
(GC/MS)	4,4'-DDE-13C12		20	117	100.0
	Decachlorobiphenyl (DCB)	Chlorinated pesticides	13	98	98.4
	Chlorpyrifos-D10	Organophosphorus	30	178	99.8
	Triphenyl Phosphate	pesticides	45	137	98.6

Table B-10: Surrogate Compound Recovery Results for 2014

#### **Laboratory Control Samples:**

Laboratory control samples (LCS) are analyte compounds spiked into deionized water at known concentrations and subjected to extraction and analysis conditions. 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 LCSD.

Table B-11 presents the mean, minimum, and maximum percent recovery for the LCS and LCSD for the three types of analysis, as well as the RPD between the LCS and the paired LCSD for 2014.

Analytical Method and Analyte	Number of Results	Average % Recovery	Maximum % Recovery	Minimum % Recovery	Mean RPD	Maximum RPD	Minimum RPD
Carbamates (LC/MS/MS)	1566	97	392	27	10	80	0
3-Hydroxycarbofuran	54	100	123	77	6	24	0
Acetamiprid	54	100	141	77	8	39	0
Aldicarb	54	85	106	70	7	29	0

Table B-11: Summary Statistics for LCS and LCSD Recovery and RPD, 2014

Analytical Method and Analyte	Number of Results	Average % Recovery	Maximum % Recovery	Minimum % Recovery	Mean RPD	Maximum RPD	Minimum RPD
Aldicarb Sulfone	54	120	226	47	13	34	1
Aldicarb Sulfoxide	54	109	164	87	6	26	1
Carbaryl	54	98	121	75	8	26	0
Carbofuran	54	99	117	75	7	22	0
Clothianidin	54	105	179	59	25	61	1
Cyprodinil	54	56	95	34	8	32	0
Dinotefuran	54	110	169	76	8	25	0
Diuron	54	94	122	66	10	29	0
Imazapic	54	109	314	69	9	44	2
Imazapyr	54	124	392	83	10	45	1
Imidacloprid	54	101	169	60	13	38	1
Linuron	54	97	193	27	28	80	1
Malaoxon	54	88	112	72	6	29	0
Methiocarb	54	92	133	66	10	28	1
Methomyl	54	98	137	74	7	29	1
Methomyl oxime	54	91	165	30	26	69	1
Methoxyfenozide	54	87	111	63	6	31	1
Monuron	54	95	107	65	7	25	1
Neburon	54	77	102	52	8	40	0
Oxamyl	54	102	136	80	6	26	0
Oxamyl oxime	54	96	125	75	7	20	0
Promecarb	54	97	130	73	9	27	1
Propoxur	54	97	118	76	8	32	1
Sulfoxaflor	54	90	115	64	9	38	1
Thiacloprid	54	99	144	73	9	36	0
Thiamethoxam	54	102	147	71	11	34	1
HERBS (GC/MS)	1400	78	150	0	13	122	0
2,3,4,5-Tetrachlorophenol	56	77	95	30	11	92	1
2,3,4,6-Tetrachlorophenol	56	68	91	23	12	108	0
2,4,5-T	56	74	102	37	15	78	1
2,4,5-Trichlorophenol	56	72	97	24	11	105	0
2,4,6-Trichlorophenol	56	67	86	22	15	116	1
2,4-D	56	69	104	32	19	81	0
2,4-DB	56	102	135	76	8	32	0
3,5-Dichlorobenzoic Acid	56	80	101	39	8	70	0
4-Nitrophenol	56	98	126	52	13	68	0
Acifluorfen, sodium salt	56	99	150	16	30	122	3
Bentazon	56	84	109	61	9	33	0
Bromoxynil	56	77	100	38	10	69	0
Clopyralid	56	57	81	21	13	68	1

Analytical Method and Analyte	Number of Results	Average % Recovery	Maximum % Recovery	Minimum % Recovery	Mean RPD	Maximum RPD	Minimum RPD
Dacthal (DCPA)	56	86	105	67	6	28	1
Dicamba	56	72	95	40	8	51	1
Dichlorprop	56	85	106	51	9	48	0
Diclofop-Methyl	56	99	137	68	9	37	1
Dinoseb	56	64	106	0	28	113	0
Ioxynil	56	77	96	57	9	27	0
MCPA	56	74	102	40	9	55	0
Mecoprop (MCPP)	56	85	108	52	7	51	0
Pentachlorophenol	56	72	89	39	9	65	0
Picloram	56	48	88	8	35	121	1
Silvex	56	85	108	56	8	35	0
Triclopyr	56	86	119	54	10	38	1
PESTMS (GC/MS)	3635	96	300	0	6	79	0
1-Naphthol	28	86	111	67	6	12	1
2,4'-DDD	27	82	109	59	7	21	1
2,4'-DDE	27	80	101	60	7	15	2
2,4'-DDT	27	81	104	62	7	16	0
4,4'-DDD	27	84	109 65		5	14	0
4,4'-DDE	27 77		111 53		10	21	1
4,4'-DDT	27	82	116	59	7	21	1
4,4'-Dichlorobenzophenone	28	94	112	78	7	15	2
Acetochlor	28	105	120	93	7	17	0
Alachlor	28	94	104	81	5	13	1
Aldrin	27	72	90	59	5	13	1
Alpha-BHC	27	89	114	78	4	14	0
Atrazine	28	95	111	81	5	12	1
Azinphos-methyl	27	137	183	94	4	12	1
Benfluralin	27	88	143	72	7	35	0
Beta-BHC	27	94	108	82	6	9	1
Bifenazate	50	72	123	42	9	25	1
Bifenthrin	28	91	108	68	5	17	0
Boscalid	28	124	147	102	4	13	0
Bromacil	28	101	117	81	4	12	0
Butachlor	28	105	116	85	4	8	0
Butylate	28	86	117	53	8	44	0
Captan	27	84	120	18	9	21	1
Chlorothalonil (Daconil)	27	85	104	60	6	25	0
Chlorpropham	28	91	106	75	7	15	0
Chlorpyrifos	27	92	110	79	7	19	0
Chlorpyrifos O.A.	28	108	128	88	4	12	0

Analytical Method and Analyte	Number of Results	Average % Recovery	Maximum % Recovery	Minimum % Recovery	Mean RPD	Maximum RPD	Minimum RPD
Chlorpyrifos-methyl	27	96	111	82	4	9	0
cis-Chlordane	27	82	107	67	6	14	0
Cis-Nonachlor	27	79	96	58	7	21	1
cis-Permethrin	27	97	122	72	5	14	1
Coumaphos	27	138	151	111	4	11	0
Cyanazine	55	105	136	76	5	14	0
Cycloate	28	89	100	60	9	43	1
Cypermethrin	28	119	137	99	4	11	1
Delta-BHC	27	93	107	80	7	14	2
Deltamethrin	50	105	160	48	9	24	0
Di-allate (Avadex)	27	97	113	83	5	12	1
Diazinon	27	100	115	82	6	12	1
Diazoxon	40	54	205	0	7	15	1
Dichlobenil	27	91	146	73	7	27	0
Dichlorvos (DDVP)	27	103	118	84	7	19	2
Dicofol	28	102	132	84	8	26	1
Dieldrin	27	90	110	74	7	22	0
Dimethoate	28	101	117	85	7	13	1
Diphenamid	28	96	112 77		5	13	0
Disulfoton Sulfoxide	26	87	200	42	16	38	1
Endosulfan I	27	105	150	78	8	26	0
Endosulfan II	27	88	111	73	7	23	0
Endosulfan Sulfate	27	95	110	83	5	11	1
Endrin	27	95	108	69	8	26	1
Endrin Aldehyde	27	82	105	66	7	19	0
Endrin Ketone	27	94	112	81	6	17	1
EPN	28	113	139	88	4	11	0
Eptam	28	87	124	51	10	39	1
Ethalfluralin (Sonalan)	27	90	141	72	8	31	1
Ethion	27	100	118	86	5	15	1
Ethoprop	27	99	133	74	8	27	0
Etoxazole	50	112	141	92	5	19	0
Fenamiphos	54	123	157	92	4	30	1
Fenamiphos Sulfone	28	136	200	97	4	12	0
Fenarimol	28	101	130	84	8	26	1
Fenvalerate	27	124	205	74	8	24	0
Fipronil	28	113	150	95	5	12	0
Fipronil Disulfinyl	28	105	121	79	5	16	0
Fipronil Sulfide	28	95	105	82	3	7	0
Fipronil Sulfone	28	106	118	101	4	14	1

Analytical Method and Analyte	Number of Results	Average % Recovery	Maximum % Recovery	Minimum % Recovery	Mean RPD	Maximum RPD	Minimum RPD
Fluridone	28	179	300	51	12	79	0
Fonofos	27	96	108	83	5	16	1
Heptachlor	27	87	106	76	6	14	1
Heptachlor Epoxide	27	92	111	79	7	18	0
Hexachlorobenzene	27	73	98	45	8	21	0
Hexazinone	28	99	118	85	6	14	0
Lindane	27	89	107	77	4	11	0
Malathion	28	110	132	90	5	18	1
Metalaxyl	27	109	129	92	6	14	1
Methidathion	27	110	138	88	7	15	1
Methoxychlor	27	82	104	0	5	12	1
Methyl Paraoxon	28	107	121	85	7	14	0
Methyl Parathion	27	103	124	85	8	17	2
Metolachlor	28	95	109	80	4	10	0
Metribuzin	54	75	97	53	5	16	0
Mevinphos	27	104	127	82	4	9	1
MGK264	28	93	106	73	7	18	1
Mirex	27 73		92	52	7	21	2
Monocrotophos	54 106 1		156	82	5	18	0
Naled	27	92	115	73	6	11	1
Napropamide	28	104	121	79	5	12	0
Norflurazon	28	108	136	85	3	8	0
Oryzalin	50	84	170	34	16	58	1
Oxychlordane	27	87	110	74	7	12	0
Oxyfluorfen	27	97	117	79	6	17	1
Parathion	28	105	125	84	5	11	1
Pebulate	28	83	102	54	7	37	0
Pendimethalin	27	96	114	80	6	13	1
Phenothrin	27	87	112	58	5	15	1
Phorate	51	77	112	63	6	19	1
Phosmet	27	101	132	35	7	32	2
Piperonyl Butoxide (PBO)	28	118	155	106	4	8	1
Prometon	28	102	116	85	4	13	0
Prometryn	28	101	116	92	6	14	0
Pronamide (Kerb)	28	97	105	85	4	12	1
Propachlor (Ramrod)	55	94	129	69	6	25	0
Propargite	27	92	170	52	7 16		0
Propazine	28	90	102			17	2
Resmethrin	27	77	99	52	7	24	0
Simazine	28	91	109	82	5	22	1

Analytical Method and Analyte	Number of Results	5		Mean RPD	Maximum RPD	Minimum RPD	
Simetryn	28	103	118	89	4	8	0
Sulfotepp	28	98	120	75	7	26	1
Tebuthiuron	28	86	156	53	17	73	2
Terbacil	28	104	132	85	5	11	0
Tetrachlorvinphos (Gardona)	27	105	123	86	6	11	0
Tetrahydrophthalimide	28	68	104	52	8	36	1
Thiobencarb	54	96	129	129 72		10	1
Tokuthion	27	93	113	75	7	15	0
trans-Chlordane	27	83	96	65	8	16	0
Trans-Nonachlor	27	86	107	70	7	19	1
Triadimefon	28	101	118	81	5	15	0
Triallate	27	91	103	83	5	16	1
Trichloronate	27	88	102	77	6	17	2
Tricyclazole	28	95	118	47	10	54	0
Trifluralin	28	82	96	60	7	23	0
Grand Total	6601	92	392	0	9	122	0

The percentage of LCS and LCSD samples having recoveries that fell within the target limits were:

- LCMS\MS analysis: 94% fell within the control limits.
- GCMS-Herbicide analysis: 95% fell within the control limits.
- GCMS-Pesticide analysis: 96% fell within the control limits.
- For TSS and conductivity, all recoveries were within the control limits.

Analytes for LCS and LCSD samples not within the control limits and the percentage of those occurrences are described in Table B-12. Table B-12 also describes the number of detections for each analyte not meeting the target recovery range. When analytes did not meet LCS and LCSD target recoveries field sample results were qualified as estimates for that site visit.

Table B-12: LCS/LCSD Parameters outside of control limits in 2014

Analysis Method	Parameter Name	Percentage of Recoveries Outside Control Limits (%)	Fell below or Exceeded Control Limits	Lower Control Limit (%)	Upper Control Limit (%)	Number of Detections in 2014
	Acetamiprid	2	Fell Below	40	130	3
	Aldicarb Sulfone	30	Fell Below	40	130	0
Carbamates	Aldicarb Sulfoxide	9	Fell Below	40	130	0
(LC/MS/MS)	Clothianidin	15	Fell Below	40	130	0
	Cyprodinil	11	Exceeded	40	130	5
	Dinotefuran	13	Fell Below	40	130	49

Analysis Method	Parameter Name	Percentage of Recoveries Outside Control Limits (%)	Fell below or Exceeded Control Limits	Lower Control Limit (%)	Upper Control Limit (%)	Number of Detections in 2014
	Imazapic	9	Fell Below	40	130	0
	Imazapyr	22	Fell Below	40	130	50
	Imidacloprid	7	Fell Below	40	130	19
	Linuron	19	Both	40	130	0
	Methiocarb	2	Fell Below	40	130	1
Carbamates (LC/MS/MS)	Methomyl	22	Fell Below	40	130	6
(LC/MS/MS)	Methomyl oxime	9	Both	40	130	0
	Oxamyl	6	Fell Below	40	130	63
	Promecarb	2	Fell Below	40	130	0
	Thiacloprid	2	Fell Below	40	130	0
	Thiamethoxam	2	Fell Below	40	130	41
	2,3,4,5-Tetrachlorophenol	2	Exceeded	40	130	0
	2,3,4,6-Tetrachlorophenol	2	Exceeded	40	130	1
	2,4,5-T	2	Exceeded	40	130	0
	2,4,5-Trichlorophenol	2	Exceeded	40	130	0
	2,4,6-Trichlorophenol	5	Exceeded	40	130	0
	2,4-D	5	Exceeded	40	130	94
	2,4-DB	4	Fell Below	40	130	0
HERBS	3,5-Dichlorobenzoic Acid	2	Exceeded	40	130	2
(GC/MS)	Acifluorfen, sodium salt	14	Both	40	130	0
	Bromoxynil	2	Exceeded	40	130	3
	Clopyralid	5	Exceeded	40	130	0
	Diclofop-Methyl	2	Fell Below	40	130	0
	Dinoseb	18	Exceeded	40	130	0
	MCPA	2	Exceeded	40	130	26
	Pentachlorophenol	2	Exceeded	40	130	19
	Picloram	9	Exceeded	40	130	12
	Benfluralin	4	Exceeded	44	143	0
	Bifenazate	8	Fell Below	50	150	0
	Captan	7	Fell Below	36	168	0
	Chlorothalonil (Daconil)	44	Fell Below	86	221	2
PESTMS	Cypermethrin	21	Exceeded	30	130	0
(GC/MS)	Deltamethrin	14	Exceeded	30	130	0
	Diazoxon	63	Exceeded	30	130	0
	Dichlobenil	4	Exceeded	44	139	96
	Disulfoton Sulfoxide	12	Exceeded	30	130	0
	Endrin Ketone	11	Exceeded	50	108	0

Analysis Method	Parameter Name	Percentage of Recoveries Outside Control Limits (%)	Fell below or Exceeded Control Limits	Lower Control Limit (%)	Upper Control Limit (%)	Number of Detections in 2014
	Fenamiphos Sulfone	64	Exceeded	30	130	0
	Fenarimol	4	Exceeded	30	130	2
	Fenvalerate	37	Exceeded	30	130	0
	Fipronil	7	Exceeded	30	130	0
	Fluridone	46	Exceeded	60	178	0
	Heptachlor Epoxide	4	Fell Below	79	165	0
	Methoxychlor	7	Fell Below	64	175	0
PESTMS	Napropamide	7	Fell Below	82	176	1
(GC/MS)	Norflurazon	4	Fell Below	85	143	5
	Phenothrin	30	Exceeded	20	95	0
	Phosmet	4	Fell Below	44	190	0
	Piperonyl Butoxide (PBO)	7	Exceeded	30	130	4
	Propargite	7	Exceeded	30	130	1
	Resmethrin	74	Exceeded	10	65	0
	Tebuthiuron	21	Exceeded	10	94	15

## Field Meter Data Quality

## **Quality Control Procedures**

Field meters were calibrated at the beginning of the field day according to manufacturer specifications, using Ecology SOP EAP033 *Standard Operating Procedure for Hydrolab DataSonde*® *and MiniSonde*® *Multiprobes* (Swanson, 2010). Field meters were post-checked, using known standards, at the end of the sampling week.

Dissolved oxygen (DO) meter results were compared to results from grab samples analyzed using the Winkler laboratory titration method. DO grab samples for Winkler titrations were collected and analyzed according to the SOP (Ward, 2007). Winkler grab samples are collected separately for eastern Washington and western Washington locations. Winkler grab samples are collected at one site at the beginning of the day and at one site the end of the day. Additionally one replicate Winkler grab sample is collected per week at either the beginning or the end of one of the sampling days.

To check conductivity meter results, grab water samples were obtained and sent to MEL for conductivity analysis. Approximately 4% of the conductivity meter readings were checked with MEL conductivity results.

Measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler DO comparisons are described in Anderson and Sargeant (2009).

## 2014 Field Data Quality Results

The Hydrolab field meter met MQOs for laboratory conductivity comparisons for all monitoring locations, and DO Winkler comparisons for eastern Washington locations (Table B-13). Hydrolab field meter post-check values for conductivity fell outside of the acceptable MQO range described in Anderson, 2009, for nine weeks from March 7<sup>th</sup> through June 9<sup>th</sup> in western Washington. Meter and laboratory conductivity comparisons for this time period meet MQO's. Based on lack of instrument drift between calibration and post-check values and meter and laboratory agreeance, conductivity values for these dates are accepted. For the week of 7/29/2015, the eastern Washington Hydrolab field meter exceeded the pH post-check MQO for buffer 4.0. Measured field values for this week are never lower than 7.0. Post-check values for pH buffer 7.0 and 9.0 meet the MQOs, therefore measured values for this week will be accepted.

Table B-13: Quality control results for field meter and Winkler replicates, 2014

Replicate Meter Parameter	MOO	Western Wa	shington Sites	Eastern Washington Sites		
Replicate Meter Farameter	MQO	Average	Maximum	Average	Maximum	
Winkler and meter DO	10% RSD	3% RSD	21% RSD	2% RSD	8% RSD	
Replicate Winkler's for DO	±0.2 mg/L	0.1 mg/L	0.7 mg/L	0.1 mg/L	0.5 mg/L	
Conductivity meter/laboratory comparisons	10% RSD	2% RSD	5% RSD	2% RSD	4% RSD	
Streamflow (Discharge Volume)	10% RSD	7% RSD	53% RSD	6% RSD	47% RSD	

DO: dissolved oxygen

MQO: measurement quality objective

Acceptance of Hydrolab field meter results were based on the Measurement Quality Objectives (MQO) described in Anderson and Sargeant (2009). The MQOs for conventional field parameters are shown in Table B-14.

Table B-14: Measurement Quality Objectives for Conventional Parameters Measured by Field Meters or Determined by a Standard Method

Parameter	Method/Equipment	Field Replicate MQO	Reporting Limits
Discharge Volume	OTT MF pro flow meter	10% RSD	0.1 ft/s
Water Temperature	Hydrolab MiniSonde®	±0.2° C	0.1° C
Conductivity	Hydrolab MiniSonde®	10% RSD	0.1 μS/cm
pН	Hydrolab MiniSonde®	10% RSD	0.1 s.u.
Dissolved Oxygen	Hydrolab MiniSonde®	10% RSD	0.1 mg/L
Dissolved Oxygen	SM4500OC	±0.2 mg/L	0.1 mg/L

MQO: measurement quality objective RSD: relative standard deviation

s.u.: standard units

Hydrolab field meter results exceeded MQOs for DO Winkler comparisons five times in western Washington for the following locations and dates:

- Lower Bertrand Creek, 21% RSD, March 10, 2014 (14.6 and 10.8 mg/L).
- Lower Big Ditch, 13% RSD, April 1, 2014 (5.95 and 7.15 mg/L).
- Browns Slough, 20 % RSD, June 16, 2014 (7.69 and 10.22 mg/L).
- Indian Slough, 21% RSD, July 8, 2014 (7.92 and 5.87).
- Upper Big Ditch, 12% RSD, September 2, 2014 (3.34 and 3.98 mg/L).

Winkler and DO exceedances for Upper Big Ditch occurred during low dissolved oxygen conditions when the percent RSD statistic produces higher variability (Mathieu, 2006). Winkler results for these days are acceptable.

Winkler and DO results for Lower Bertrand Creek, Lower Big Ditch, Browns Slough, and Indian Slough will be reported and qualified as estimates.

2014 Winkler replicate values for both eastern and western Washington locations met the MQOs with the exceptions of the following sites and dates:

- Longfellow Creek, difference 0.5, March 11, 2014 (12.5 and 12.0 mg/L).
- Indian Slough, difference of 0.6, July 22, 2014 (8.88 and 8.28 mg/L).
- Upper Big Ditch, difference of 0.7, August 4, 2014 (5.26 and 5.92 mg/L)
- Lower Bertrand Creek, difference of 0.35, July 1, 2014 (8.65 and 9.00 mg/L)
- Stemilt Creek, difference of 0.25, April 7, 2014 (10.8 and 11.05 mg/L)
- Peshastin Creek, difference of 0.26, May 5, 2014 (11.5 and 11.76 mg/L)
- Peshastin Creek, difference of 0.6, July 30, 2014 (9.25 and 9.55 mg/L)
- Marion Drain, difference of 0.25, June 16, 2014 (12 and 11.75 mg/L)
- Marion Drain, difference of 0.47, August 5, 2014 (13.53 and 13.06 mg/L)

The 2014 streamflow replicate results for both the eastern and western Washington sites met MQOs (Table 13) except for the following sites and dates:

- Mission Creek, 16% RSD, July 16, 2014 (6.28 and 7.84 cfs).
- Stemilt Creek, 16% RSD, March 24, 2014 (4.66 and 5.89 cfs).
- Brender Creek, 9% RSD, April 1, 2014 (0.26 and 1.31 cfs).
- Spring Creek, 47% RSD, March 18, 2014 (8.44, 4.2, 1.85 cfs).
- Upper Big Ditch, 26% RSD, September 2, 2014 (0.29 and 0.42 cfs).
- Indian Slough, 12 % RSD, June 2, 2014 (25.49 and 21.64 cfs).
- Longfellow Creek, 16% RSD, March 18, 214 (2.79 and 3.51 cfs).
- Upper Bertrand Creek, 53% RSD, August 18, 2014 (3.03 and 1.37 cfs).

Streamflow replicates not meeting the MQOs for Stemilt Creek, Upper Big Ditch, Longfellow Creek, and Upper Bertrand Creek all occurred during low-flow conditions when the percent RSD statistic produces higher variability (Mathieu, 2006). Streamflow results for these days are acceptable. Streamflow replicates for Brender Creek occurred during low-flow conditions when

the percent RSD statistic produces higher variability (Mathieu, 2006). Streamflow results for this day will be averaged and reported as an estimate based on higher statistical variability coupled with difficulty measuring consistent streamflow during periods of low-flow. This replicate pair was not included in Table B-13 as it skewed the average.

Field notes for the March 18, 2014 streamflow replicate at Spring Creek indicate that the water level in Spring Creek appeared to be fluctuating during sampling. The three streamflows obtained for this day will be averaged, and the averaged streamflow will be reported and qualified as an estimate.

Staff gauge readings at Indian Slough show a change of 0.4 ft during the streamflow measurement. The streamflow replicate values will be averaged, and the averaged streamflow will be reported and qualified as an estimate.

The July 16, 2014 Mission Creek streamflow replicate has a 16% RSD. This streamflow will be reported and qualified as an estimate.

#### 2014 Field Audit

The purpose of the field audit was to ensure sampling methodologies were consistent. For field audits, both the western and eastern Washington field teams met at a surface water location. The teams measured Hydrolab field parameters and streamflow and obtained samples for measuring Winkler DO. Results and methods were compared to ensure field teams were using consistent sampling methodologies resulting in comparable data.

On July 16, 2014, a field audit was conducted at Mission Creek in Chelan County. The Westside team calibrated their Hach Hydrolab Multi-Meter at the Natural Resource Building (NRB), located in Olympia, on July 11, 2014, and conducted a post-check for accuracy on July 15, 2014 prior to the audit. The Eastside team calibrated their Hach Hydrolab Multi-Meter on July 15, 2014 at the WSDA building, located in Yakima. Both teams met at the Mission Creek sample site to perform the field audit simultaneously. Table 15 shows the results.

Table B-15: July 16, 2014 Hydrolab meter readings, streamflow measurements, and Winkler results for dissolved oxygen from Mission Creek.

Meter or Method	Temp (°C)	pH (s.u.)	Conductivity (µS/cm)	DO (mg/L)	DO (% sat)
Westside Hydrolab Meter	19.90	8.3	255.0	8.74	95.0
Eastside Hydrolab Meter	19.84	8.6	253.9	9.40	106.4
Winkler Dissolved Oxygen (Westside)	-	-	-	8.97	-
Winkler Dissolved Oxygen (Eastside)	-	-	-	9.10	-
Streamflow Results	Dischar	ge (cfs)			
Streamnow Results	Westside	Eastside			
OTT MF pro	3.53	3.68	-	-	-

cfs: cubic feet per second

All meter results were acceptable based on the Measurement Quality Objectives (MQO) described in Anderson and Sargeant (2009). Table B-14 shows the MQOs for conventional field parameters.

## Quality Assurance Summary References

Anderson, P. and D. Sargeant, 2009. Addendum 3 to Quality Assurance Project Plan: Washington State Surface Water Monitoring Program for Pesticides in Salmonid Habitat for Two Index Watersheds. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-104ADD3.

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

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Swanson, T., 2010. Standard Operating Procedure (SOP) for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html

Ward, W., 2007. Standard Operating Procedures (SOP) for the Collection and Analysis of Dissolved Oxygen (Winkler Method). Washington State Department of Ecology, Olympia, WA. SOP Number EAP023. <a href="https://www.ecy.wa.gov/programs/eap/quality.html">www.ecy.wa.gov/programs/eap/quality.html</a>

# Appendix C: Assessment Criteria and Water Quality Standards for Pesticides

## EPA Toxicity Criteria

In this Report, *Assessment Criteria* include data taken from studies determining hazard to non-target organisms and refer to acute and chronic hazard levels for fish, invertebrates, and aquatic plants. Various Environmental Fate and Effects Division (EFED) risk assessments (including: Pesticide Effects Determinations, Reregistration Eligibility Decisions (RED), and ecological risk assessments) were reviewed to determine the most comparable and up-to-date toxicity guidelines for freshwater (Table C-1) and marine species (Table C-2).

Rainbow trout (*Oncorhynchus mykiss*) are a surrogate for freshwater endangered and threatened species. *Daphnia magna* (invertebrate) and *Pseudokirchneria subcapitata* (green algae formerly called *Selenastrum capriocornutum*) 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 eligibility decision. 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 the Water Quality Standards For Surface Waters of The State of Washington (<u>WAC 173-201A</u>) and EPA National Recommended Water Quality Criteria (<u>NRWQC</u>) 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).

Table C-1: Freshwater toxicity and regulatory guideline values (All values reported in  $\mu$ g/L)

				P	esticide F	Registrat	ion Toxici	ty Data for Fr	esh Wate	er <sup>1</sup>				NRW	QC for	_	State Water	Maximum (	Conc. Limit
Chemical Name			Fisheri	ies		Invertebrate			Aquatic Plant				Fresh Water <sup>3</sup>			Water <sup>2</sup>	Biologica (NM	al Opinion IFS)	
	ESLOC	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	CMC	CCC	Acute	Chronic	Acute	Ref.
1-Naphthol	70	700	100	RT-A; FM-C	10	350		DM	10	1100		SC	10						
2,4'-DDD														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		ĺ
2,4'-DDE														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		
2,4'-DDT														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		
2,4-D <sup>m</sup>	21.4	214	14200	RT; FM; BS	1	2485	200	DM	1	3880	1440	ND	1					100	91
3-Hydroxycarbofuran	4.4	44	5.7	RT; BS	54, 60	1.115	0.75	CD; DM	54										
4,4'-DDD														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		
4,4'-DDE														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		
4,4'-DDT														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>		ĺ
4-Nitrophenol	200	2000		RT	69	2500		DM	69				1	1					
Acetamiprid	5000	5000	19200	RT/FM	101	10.5	2.1	CR	101								1		
Acetochlor	19	190	130	RT	70	4100	22.1	DM	70	1.43		SC	70				1		
Alachlor	90	900	187	RT	2	3850	110	DM	2	1.64	0.35	SC	2						
Aldicarb	2.6	26	0.46	BS	3	10	3	CT	3	5000		MD	3						
Aldicarb Sulfone	2100	21000		RT	3	140	3	DM	3										
Aldicarb Sulfoxide	357	3570		RT	3	21.5	3	DM	3										
Atrazine	265	2650	65	RT-A; BT-C	4	1750	140	DM	4	49		SC	4						
Azinphos-Ethyl	1	10		RT	71	2		DM	71										
Azinphos-methyl	0.145	1.45	0.44	RT	5	0.565	0.25	DM	5						0.01				90
Bentazon	5000	50000		RT	6	50000		DM	6	4500		SC	6						
Bifenazate	29	290		BS	103	250	150	DM	103	890			103						
Bifenthrin	0.0075	0.075	0.04	RT-A; FM-C	72	0.8	0.0013	DM	72										ĺ
Boscalid	135	1350	116		94	533	790		94	1340			94						ĺ
Bromacil	1800	18000	3000	RT	7	60500	8200	DM	7	6.8	1100	SC	7						ĺ
Bromoxynil	2.5	25	9	RT-A; FM-C	8	5.5	2.5	DM	8	80		SC	83						
Captan	1.31	13.1	16.5	BrT-A; FM-C	73	4200	560	DM	73	1770		SC	73						91
Carbaryl	60	600	210	RT-A; FM-C	9, 10	2.8	1.5	DM	10	1100	370	SC	10						89
Carbofuran	4.4	44	5.7	RT; BS	54,60	1.115	9.8	CD; DM	54, 60										89
Carboxin	115	1150		RT	74	42200		DM	74	370	110	SC	74						<u> </u>
Chlorothalonil (Daconil)	2.115	21.15	3	RT; FM	46	34	39	DM	46	190		SC	46					1.05	91
Chlorpropham	285	2850		RT	47	1850	770	DM	47										
Chlorpyrifos	0.15	0.9	0.57	RT; FM	11; 12	0.05	0.04	DM	11					0.083 <sup>d</sup>	0.041 <sup>e</sup>	0.083	0.041	1.122	88
Clopyralid	98400	984000		BS	64	56500		DM	64	6900	13	SC	64						
Clothianidin	5075	50750	9700	RT/FM	104	11	11	CR	104										
Cycloate	225	2250		RT	87	12000		DM	87										
Cypermethrin	0.0195	0.195	0.14		95	0.21	0.39		95										
Cyprodinil	12.05	120.5	230		96	160	8.2		96	2250			96						1

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

Dechal (DCPA)	Maximum Conc. Lim for Salmon from Biological Opinion	r N	State Water		Ctor	NRWC					er <sup>1</sup>	esh Wate	ty Data for Fre	on Toxici	Registrati	esticide F	Pe				Chemical Name
Dathal (DCPA)   330	(NMFS)		Water <sup>2</sup>	Fresh	vater	rresnv		Aquatic Plant					Invertebrate				es	Fisheri			Chemical Name
Dazinon	Acute Ref.		Chronic	Acute	CCC	СМС	.	Ref.	Spp.	Chronic	Acute	Ref.	Spp.	Chronic	Acute	Ref.	Spp.	Chronic	Acute	ESLOC	
Diazinon			0.001	1.1	0.001	1.1															DDT-Total
Disamba								56	SC		12380	56	DM		13500	56	RT		3300	330	Dacthal (DCPA)
Dichlobenii   246.5   246.5   246.5   330   RT   16;17   3100   560   DM   17   1500   160   SC   17	1.122 88				0.17	0.17		13	SC		3700	13	DM	0.17	0.4	13; 14	RT; BT	8.0	45	4.5	Diazinon
Dichloprop   10700   10700   14700   RT   76   27900   74900   DM   76   77   13   NP   76								15	SC	3700	3700	15	DM	16400	17300	15	RT		14000	1400	Dicamba
Dichloros (DDVP)								17	SC	160	1500	17	DM	560	3100	16; 17	RT	330	2465	246.5	Dichlobenil
Dicotol								76	NP	13	77	76	DM	74900	279000	76	RT	14700	107000	10700	Dichlorprop
Dimethoate   310   310   430   RT   29   1660   40   DM   29   36000   SC   29								75	ND		14000	75	DM	0.0058	0.035	75	LT-A; RT-C	5.2	91.5	9.15	Dichlorvos (DDVP)
Dinotefuran											5000	98		19	70	97,98		2.75	26.5	2.65	Dicofol
Dipenamid	60 90							29	SC		36000	29	DM	40	1660	29	RT	430	3100	310	Dimethoate
Disulfoton (Di-Syston)   92.5   925   220   RT   19   6.5   0.037   DM   19								106	SC		976000	106	DM	95300	484150	105	Carp		49550	4955	Dinotefuran
Disulfoton Suffoxide   3000   30000   RT   19   32   1.53   DM   19		1										59	DM		29000	59	RT		48500	4850	Diphenamid
Disulfoton Sulfoxide   3000   30000   RT   19   32   1.53   DM   19	90											19	DM	0.037	6.5	19	RT	220	925	92.5	Disulfoton (Di-Syston)
Diuron   97.5   975   26.4   RT-A; FMC   21, 22   700   200   DM   21, 22   2.4   SC   21, 22         5   5   5   5   5   5   5												19	DM	1.53	32	19	RT		30000	3000	Disulfoton Sulfoxide
EPN   7.15   71.5   RT   84   84   84   84   84   84   84   8		1										19	DM	0.14	17.5	19	RT		4600	460	Disulfoton sulfone
Endosulfan	5 91	1					2	21, 22	SC		2.4	21, 22	DM	200	700	21, 22	RT-A; FM-C	26.4	975	97.5	Diuron
Endosulfan II		1														84	RT		71.5	7.15	EPN
Endosulfan Sulfate		1	0.056 <sup>i</sup>	0.22 <sup>i</sup>	0.056 <sup>c,f</sup>	).22 <sup>b,f</sup>	(					23	DM	2	83	23	RT	0.1	0.4	0.04	Endosulfan I
Endosulfan Sulfate		1	0.056 <sup>i</sup>	0.22 <sup>i</sup>	0.056 <sup>c,f</sup>	).22 <sup>b,f</sup>	(					23	DM	2	83	23	RT	0.1	0.4	0.04	Endosulfan II
Endosulfan-Total   0.04   0.4   0.1   83   2		+										23	DM		290	82	RT		0.7	0.07	
Eptam   700   7000   BS   24   3250   810   DM   24   1400   900   SC   24		+	0.056	0.22	0.056	0.22								2	83			0.1	0.4	0.04	
Ethoprop         51         510         180         RT; FM         25         22         0.8         DM         25           20           Etoxazole         18.5         185         15         RT         107         3.65         0.13         DM         107         51.9         NP         107  .		1						24	SC	900	1400	24	DM	810	3250	24	BS		7000	700	
Etoxazole	20 90	1										25	DM	0.8	22	25	RT; FM	180	510	51	-
Fenarimol   105   1050   870   RT   67   3400   113   DM   67   100   SC   67		1						107	NP		51.9	107	DM	0.13	3.65	107	RT	15	185	18.5	
Fipronil         12.3         123         6.6         RT         78         95         9.8         DM         78         140         140         SC         78           Fipronil Sulfide         4.15         41.5         6.6         ND         78         50         0.11         DM-A; ND-C         78         140         140         ND         ND           Fipronil Sulfone         1.95         19.5         0.67         RT-A; ND-C         78         14.5         0.037         DM-A; ND-C         78         140         ND         ND           Hexachlorobenzene         1.5         15         3.68         RT         26         15         16         DM         26         30         SC         26           Hexazinone         9000         90000         17000         RT; FM         27; 28         75800         20000         DM         27         7         4         SC         27           Imazapic         5000         50000         96000         RT/FM         108         50000         97100         DM         109         18         LM         109	90	1										77	DM	0.12	0.65	77	RT	3.8	34	3.4	Fenamiphos
Fiproni		1						67	SC	100		67	DM	113	3400	67	RT	870	1050	105	Fenarimol
Fipronii Sulfone   1.95   19.5   0.67   RT-A; ND-C   78   14.5   0.037   DM-A; ND-C   78   140   140   ND		1						78	SC	140	140	78	DM	9.8	95	78	RT	6.6	123	12.3	
Fipronil Sulfone   1.95   19.5   0.67   RT-A; ND-C   78   14.5   0.037   DM-A; ND-C   78   140   140   ND		1							ND	140	140	78	DM-A; ND-C	0.11	50	78	ND	6.6	41.5	4.15	Fipronil Sulfide
Hexachlorobenzene         1.5         15         3.68         RT         26         15         16         DM         26         30         SC         26         1           Hexazinone         9000         9000         17000         RT; FM         27; 28         75800         20000         DM         27         7         4         SC         27           Imazapic         5000         50000         96000         RT/FM         108         50000         96000         DM         108         44.1         6.22         LM         108           Imazapyr         5000         50000         118000         RT/FM         109         50000         97100         DM         109         18         LM         109		1							ND	140	140	78	DM-A; ND-C	0.037	14.5	78	RT-A; ND-C	0.67	19.5	1.95	
Hexazinone         9000         9000         17000         RT; FM         27; 28         75800         20000         DM         27         7         4         SC         27           Imazapic         5000         50000         96000         RT/FM         108         50000         96000         DM         108         44.1         6.22         LM         108           Imazapyr         5000         50000         118000         RT/FM         109         50000         97100         DM         109         18         LM         109         LM		1					1	26	SC		30	26	DM				RT				
Imazapic         5000         5000         96000         RT/FM         108         5000         96000         DM         108         44.1         6.22         LM         108           Imazapyr         5000         50000         118000         RT/FM         109         50000         97100         DM         109         18         LM         109		1					1	27	SC	4	7	27	DM	20000	75800	27; 28	RT; FM	17000	90000	9000	
Imazapyr 5000 50000 118000 RT/FM 109 50000 97100 DM 109 18 LM 109		$\top$						108	LM	6.22	44.1	108	DM	96000	50000	108	RT/FM	96000	50000	5000	
		$\top$	<del>                                     </del>					109	LM		18	109	DM			109	RT/FM			5000	· ·
Imidacloprid   4150   41500   1200   RT   61   34.5   1300   CT-A; DM-CT 61   10000     ND   61		1					1	61	ND		10000	61	CT-A; DM-C	1300	34.5	61	RT	1200	41500	4150	Imidacloprid
Linuron 150 1500 5.58 RT 48 60 0.09 DM 48 67 SC 49	91	$\top$	<del>                                     </del>				1					_	, ,								
MCPA 38 380 12000 100 90 11000 100 20 SC 32		+														-					

*Table C-1 (continued): Freshwater toxicity and regulatory guideline values (All values reported in μg/L)* 

Chemical Name				Pe	esticide	Registrati	on Toxici	ty Data for Fi	resh Wate	er <sup>1</sup>				NRW(	QC for	Quality St	State Water andards for	for Salm	Conc. Limit non from al Opinion
Chemical Name			Fisheri	es			Invertebrate				Aqua	atic Plant		пезн	water	Fresh	Water <sup>2</sup>		MFS)
	ESLOC	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	CMC	CCC	Acute	Chronic	Acute	Ref.
Malaoxon	1.64	16.4	8.6	RT	31	0.295	0.06	DM	31	2400			99						
Malathion	1.64	16.4	8.6	RT	31	0.295	0.06	DM	31	2400			99		0.1			1.122	88
Mecoprop (MCPP)	6240	62400		RT	65	50000	50800	DM	65; 93	14	9	SC	93						
Metalaxyl	920	9200	9100	RT-A; FM-C	51	6000	1270	DM	51	100000		SC	51						
Methiocarb	21.8	218	50	ND	30	3.5	0.1	ND	30										
Methomyl	43	430	57	RT-A; FM-C	57	2.5	0.7	DM	57										89
Methoxyfenozide	210	2100	530	FM	110	25	6.3	CR	110	3400		SC	110						
Metolachlor	190	1900	2500	RT	33	550	1	DM	33	8	1.5	SC	33						
Metribuzin	2100	21000	3000	RT	52	2100	1290	DM	52	11.9	8.9	NP	52						
Napropamide	320	3200	1100	RT	80	7150	1100	DM	80	3400	71	SC-A; LM-C	80						
Norflurazon	405	4050	770	RT	34	7500	1000	DM	34	9.7	3.2	SC	34						
Oryzalin	163	1630	460	RT	85	750	358	DM	85	52	13.8	SC	85					10	92
Oxamyl	210	2100	770	RT	62	210	27	DM	62	120	30000	SC	62						
Oxvfluorfen	12.5	125	38	RT-A; FM-C	35	40	13	DM	35	0.29	0.1	SC	35						
Pendimethalin	6.9	69	6.3	RT-A; FM-C	37	140	14.5	DM	37	5.4	3	SC	37					1	92
Pentachlorophenol	0.75	7.5	11	RT	38	225	240	DM	38	50		SC	38	7.9 <sup>d,g</sup>	6.1 <sup>e,h</sup>	8.2 <sup>j</sup>	5.2 <sup>k</sup>		-
Phosmet	11.5	115	3	RT	79	3	0.8	DM	79	150		SC	79			_	-		
Picloram	275	2750		RT	53	17200		DM	53										
Piperonyl butoxide (PBO)	95	950	40	RT	81	255	30	DM	81										
Prometon	600	6000	9500	RT-A: FM-C	68	12850	3500	DM	68	98	32	SC	68						
Pronamide (Kerb)	3600	36000	7700	RT	66	2800	600	DM	66	4000	390	AF	66						
Propargite	5.9	59	16	RT-A; FM-C	40	37	9	DM	40	66.2	5	SC	40						
Propazine			720	FM-C	20	2660	47	DM	20	29	12	SC	20						
Propoxur	185	1850		RT	63	5.5		DM	63										
Simazine	2025	20250	2500	RT	36, 41	500		DM	41	36	5.4	SC	36						
Sulfoxaflor	19350	193500	660	RT/FM	111	200000	50500	DM	111	81200		NP	111						
Tebuthiuron	7150	71500	26000	RT	42	148500	21800	DM	42	50	13	SC	42						
Terbacil	2310	23110	1200	RT	43	32500	640	DM	43	11	7	NP	43				<b>†</b>		
Thiacloprid	1260	12600	918	BS/RT	112	18.9	0.97	HA	112	45000		SC	112				İ		
Thiamethoxam	5000	50000	20000	BS/RT	113	17.5	50000	CT	113	9000		LM	113				<b>†</b>		
Triadimefon	205	2050	41	RT	55	800	52	DM	55	1710	100	SC	55				<b>†</b>		
Triclopyr	95	950	19	RT	44	6700	25000	DM	44	2300	2	SC-A: NP-C	44			1	İ		91
Trifluralin	2.18	21.8	2.18	RT	45	125.5	2.4	DM	45	7.52	5.37	SC	45				İ	1	92
cis-Permethrin <sup>n</sup>	0.0395	0.395	0.3	BS-A: FM-C	58	0.52	0.039	DM	58	1		1				1	1		
trans-Permethrin	0.145	1.45	0.3	20.,110	30	0.05	0.039	2111	1 30	0.039						1	<b>†</b>		
uans-i eimeullii	0.170		<u> </u>			0.00	0.000			0.500		L		L					<u> </u>

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

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-Browns 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),

<sup>2</sup>WAC: Promulgated standards according to Chapter 173-201A WAC.

<sup>3</sup>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 ( $\Sigma$ DDT).

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

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

(continued on next page)

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.

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

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

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

 $k \le e[1.005(pH)-5.134]$ , 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 cispermethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for permethrin.

Table C-2: Marine toxicity and regulatory guideline values for the Browns Slough site (All values reported in  $\mu$ g/L)

1-Naphthol 2,4'-DDD 2,4'-DDE 2,4'-DDT 2,4-D"	ESLOC 60	Acute 1200	Fisheries Chronic				14/-	or Marine iter <sup>3</sup>	Washington State Wa Quality Standards for								
1-Naphthol 2,4'-DDD 2,4'-DDE 2,4'-DDT 2,4-D <sup>m</sup>			Chronic				Inver	tebrate			Aquat	ic Plant		wa	ter	Marine	Water <sup>2</sup>
2,4'-DDD 2,4'-DDE 2,4'-DDT 2,4-D <sup>m</sup>	60	1200		Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	CMC	CCC	Acute	Chronic
2,4'-DDE 2,4'-DDT 2,4-D <sup>m</sup>				SM	10	200		MS	10								
2,4'-DDT 2,4-D <sup>m</sup>														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
2,4-D <sup>m</sup>														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
,														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
3-Hvdroxycarbofuran	4000	80000		TS	1	57000		EO	1								
	1.65	33	2.6			4.6	0.4										
4,4'-DDD														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
4,4'-DDE														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
4,4'-DDT														1.1 <sup>a,b</sup>	0.001 <sup>a,c</sup>	1.1 <sup>a</sup>	0.001 <sup>a</sup>
4-Nitrophenol															0.001		0.001
Acetamiprid						66	2.5	MS	102								
Acetochlor																	
Alachlor																	
Aldicarb																	
Aldicarb Sulfone																	
Aldicarb Sulfoxide																	
Atrazine	100	2000	1100	SM	4	94	100	AT-A; PO-C	4	22		IG	4				
Azinphos-Ethyl	.00	2000		S		٠.		7.1.7,1.0.0	•								
Azinphos-methyl															0.01		
Bentazon	6.8	136		SM	6	109		PS; EO	6								
Bifenazate	20.8	416		SM	103	58		MS	103								
Bifenthrin	20.0			S													
	190.5	3860			94	1020			94								
Bromacil	8.1	162			0.	130			· ·								
Bromoxynil	8.5	170		SM	8	65		MS	8	140		SkC	83				
Captan																	
Carbaryl	12.5	250		AS	9, 10	5.7		MS	10								
Carbofuran	1.65	33	2.6	AS-A; SM-C	54	4.6	0.4	PS-A; MS-C	54								
Carboxin				,		14000	***	,									
Chlorothalonil (Daconil)	1.6	32				3.6	1.2										
Chlorpropham																	
Chlorpyrifos	13.5	270	0.28	SM-A; AS-C	11	0.035	0.0046	MS	11					0.011 <sup>d</sup>	0.0056 <sup>e</sup>	0.011	0.0056
Clopyralid	. 0.0	2.0	0.20	S, , , , , , ,		0.000	0.0010		•					0.011	0.0030	0.011	0.0000
	4570	91400		SM	104	53	5.1	MS	104								
Cycloate	.0.0	01.100		S			0										
	0.00475	0.95	0.34		95	0.00475	0.000781		95								
Cyprodinil	62.5	1250	130		96	8.14	1.9		96				1	<b>†</b>			
DDT-Total	32.0					- · · · ·	10						<del>                                     </del>	1.1	0.001	1.1	0.001
Dacthal (DCPA)	50	1000		SM	56	620		EO	56	11000		SkC	56	<del> </del>	0.00.	1.1	0.001
Diazinon	7.5	150	0.47	SM	14	25	0.23	MS	14			CAO	1 30	0.82	0.82		
	9000	180000	V.71	SM	15		5.20			1			+	5.02	5.02		
Dichlobenil	700	14000		SM	16	1000		PS; EO	16				1	<b>†</b>			
Dichlorprop				5.01		.500		. 5, 25		1			+	<b>+</b>			
Dichlorvos (DDVP)																	
Dicofol	18.5	370		SM	97	15.1		EO	97				1	<b>†</b>			
	5550	111000		SM	18	15000	1	MS	18	1			+	<b>-</b>			
	5450	10900		SM	106	790	<del>                                     </del>	MS	106	<b>-</b>	<del>                                     </del>		<del>                                     </del>	<del>                                     </del>			
Diphenamid	3430	10300		Oivi	100	730		IVIO	100				<del>                                     </del>	<del> </del>	1	1	

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

Chemical Name					Pesticide Registration Toxicity Data for Marine Water <sup>1</sup>											Washington State Water Quality Standards for		
Chemical Name			Fisheries					rtebrate			Aquat	ic Plant			ater <sup>3</sup>	Marine	e Water <sup>2</sup>	
	ESLOC	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	CMC	CCC	Acute	Chronic	
Disulfoton (Di-Syston)																		
Disulfoton Sulfoxide																		
Disulfoton sulfone																		
Diuron	335	6700	440	SM	21	4900	270	EO-A; MS-C	21									
EPN																		
Endosulfan I														0.22 <sup>b,f</sup>	0.056 <sup>c,f</sup>	0.22 <sup>i</sup>	0.056 <sup>i</sup>	
Endosulfan II														0.22 <sup>b,f</sup>	0.056 <sup>c,f</sup>	0.22 <sup>i</sup>	0.056 <sup>i</sup>	
Endosulfan Sulfate	0.155	3.1		SM	82		0.38	MS	82									
Endosulfan-Total														0.22	0.056	0.22	0.056	
Eptam																	1	
Ethoprop																		
Etoxazole	8	160		SM	107	1.1	0.32	MS/EO	107									
Fenamiphos						6.2											1	
Fenarimol																		
Fipronil																	1	
Fipronil Sulfide																		
Fipronil Sulfone																	1	
Hexachlorobenzene																		
Hexazinone																	1	
Imazapic	4935	98700		SM	108	97700		MS	108								1	
lmazapyr	9200	184000		SvM	109	132000		EO	109								1	
Imidacloprid	8150	163000		SM	61	37	0.6	MS	61								1	
Linuron	44.5	890				890											1	
MCPA	135	2700		AS	32	130		EO	32	15		SkC	32				1	
Malaoxon	1.35	27	17.3		31,99	2.2	0.13		31									
Malathion	1.35	27	17.3		31,99	2.2	0.13		31						0.1			
Mecoprop (MCPP)																		
Metalaxyl						4400		EO	51									
Methiocarb																	1	
Methomyl	58	1160	260	SM	50	230	29	MS	50								1	
Methoxyfenozide	140	2800		SM	110	1200	25	MS/EO	110									
Metolachlor	490	9800	3600	SM	33	1600	700	EO	33	61	1.7	SkC	33					
Metribuzin	4250	85000		SM	52	42000		EO	52	8.7	5.8	SkC	52					
Napropamide	700	14000				1400											1	
Norflurazon																	1	
Oryzalin																	1	
Oxamyl	130	2600		SM	62	400		EO	62								1	
Oxyfluorfen																		

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

Chemical Name					Pesticide	Registration	on Toxicity	Data for Marin	e Water <sup>1</sup>						or Marine	Washington State Wate Quality Standards for		
Chemical Name			Fisheries				Inve	rtebrate			Aquati	c Plant		vva	iter	Marine	e Water <sup>2</sup>	
	ESLOC	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	CMC	CCC	Acute	Chronic	
Pendimethalin																		
Pentachlorophenol	12	240	64	SM	38	48		PO	38	27		SkC	38	13.0°	7.9 <sup>d</sup>	13.0 <sup>j</sup>	7.9 <sup>k</sup>	
Phosmet																		
Picloram																		
Piperonyl butoxide (PBO)																		
Prometon	2365	47300				18000												
Pronamide (Kerb)																		
Propargite																		
Propazine																		
Propoxur																		
Simazine	215	4300		SM	41	3700		PS; EO	41	600	250	SkC	36					
Sulfoxaflor	13300	266000	1200	SM	111	640	110	MS	111									
Tebuthiuron						62000		PS	42	31	50	SkC	42					
Terbacil	5425	108500	2800	SM	43	4900		EO	43									
Thiacloprid	985	19700	598	SM	112	31.3	1.1	MS	112									
Thiamethoxam	5550	111000		SM	113	6900		MS	113									
Triadimefon																		
Triclopyr	6500	130000		TS	86	58000		EO	86	6700	400	SkC	86					
Trifluralin	12	240	1.3	SM	45	136	138	MS-A; GS-C	45	28	4.6	SkC	45					
cis-Permethrin <sup>n</sup>	0.11	2.2	0.83			0.019	0.011											
trans-Permethrin	0.11	2.2	0.83			0.019	0.011											

<sup>&</sup>lt;sup>1</sup>Criteria identified in EPA reregistration and review documents or peer reviewed literature. References listed separately.

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

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 ( $\Sigma$ 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.

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

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

<sup>&</sup>lt;sup>2</sup> WAC: Promulgated standards according to Chapter 173-201A WAC.

<sup>&</sup>lt;sup>3</sup> EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

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

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

(continued on next page)

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

 $k \le e[1.005(pH)-5.134]$ , 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 cispermethrin isomer, the more toxic of the two; and cis-permethrin concentrations are compared to the assessment criteria for Permethrin.

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# Appendix D: Glossary, Acronyms, and Abbreviations

## Glossary

**Analyte:** Chemical being measured by a laboratory method.

**Assessment criteria:** Assessment criteria in this report are non-regulatory values used to assess risk to aquatic species and include a combination of toxicity data acquired from EPA pesticide registration documents and numeric criteria acquired from NRWQC (see Appendix C).

**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 acetylcholinesterase 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.

EC50: The "effect concentration" causing an effect in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and using that equation to calculate the concentration for any level of effect, in this case the 50% value.

**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.

LC<sub>50</sub>: The "lethal concentration" causing mortality in 50% of test species. This value is calculated by plotting the dose response curve and fitting a mathematical equation to the data and

using that equation to calculate the concentration for any level of effect, in this case the 50% value.

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

**Loading:** The input of pollutants into a waterbody.

**Lowest Observable Adverse Effect Concentration (LOEC):** The lowest concentration in a toxicity test showing a statistically significant difference from the control. The NOAEC is by definition the next concentration below the LOEC in the concentration series.

Marine water (seawater): Salt water.

No Observable Adverse Effect Concentration (NOAEC): The highest concentration in the toxicity test not showing a statistically significant difference from the control.

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

**Parameter:** Water quality constituent being measured. 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 registration toxicity data**: Includes toxicity data from laboratory studies generated to fulfill the <u>Data Requirements for Pesticide Registration</u> (Code of Federal Regulations - 40CFR Part 158: Subpart G 158.630 and 158.660). Toxicity data used in this study are acquired from pesticide registration documents including EPA risk assessment documents and are not acquired directly from the toxicity studies (see Appendix C).

**Pesticide Synergist** (**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.

**Risk Quotient (RQ):** A risk quotient (RQ) is calculated by dividing a point estimate of environmental exposure by a point estimate of effect. Risk quotients are an expression of concentration over toxicity and are used by EPA and others to assess risk given just two pieces of information for screening level risk assessments.

**Site visit:** A single event where samples and field measurements were collected from a single monitoring location on a single day and may refer to all of the sample data and field data from that event.

**Salmonid:** Fish that belong to the family *Salmonidae*. Any species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

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

**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

DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
DO	Dissolved oxygen
Ecology	Washington State Department of Ecology
EPA	United States Environmental Protection Agency
ESA	Endangered Species Act
ESLOC	Endangered species level of concern (EPA)
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
GCMS	Gas chromatograph coupled with mass spectrometer
LC50	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

7-day Average of the Daily Maximum Temperatures

LOC Level of concern

LPQL Lower practical quantitation limit
MEL Manchester Environmental Laboratory

MQO Measurement quality objective

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

TSS (See Glossary above)

TU Toxicity 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

μg/L Micrograms per liter (parts per billion)