

Washington State Department of Agriculture

# Ambient Monitoring for Pesticides in Washington State Surface Water

**2019 Technical Report** 

July 2021

Washington State Department of Agriculture Natural Resources Assessment Section

Derek I. Sandison, Director

Visit the Department of Agriculture's website at <u>agr.wa.gov/AgScience</u> to view or download this report.

#### **Contact Information**

Eastern Washington Program Lead	Matthew Bischof 509-895-9368 Natural Resources Assessment Section Washington State Department of Agriculture Yakima, WA <u>MBischof@agr.wa.gov</u>
Western Washington Program Lead	Katie Noland 360-819-3690 Natural Resources Assessment Section Washington State Department of Agriculture Olympia, WA <u>KNoland@agr.wa.gov</u>
Communications Director	Hector Castro 360-902-1815 Washington State Department of Agriculture Olympia, WA <u>HCastro@agr.wa.gov</u>

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



Publication No. 102-629 (R/7/21)

Do you need this publication in an alternate format? Please call the WSDA Receptionist at 360-902-1976 or TTY 800-833-6388.

# Ambient Monitoring for Pesticides in Washington State Surface Water

## **2019 Technical Report**

July 2021

Washington State Department of Agriculture Natural Resources Assessment Section

Co-authors: Katie Noland, Abbey Nickelson, Jadey Ryan, and Margaret Drennan

## Acknowledgments

The authors of this report would like to thank the following people and organizations for their important contributions to this study:

- The Washington State Department of Ecology Manchester Environmental Laboratory staff for their care and attention to detail in every step of the process: method development, sample transport, logging, extraction, analysis, quality assurance and quality control, and data reporting. Without their work, this project would not be possible.
- WSDA Natural Resources Assessment Section staff for their sampling assistance.
- Yakama Nation: Elizabeth Sanchey, Environmental Management Program Manager
- WSDA Pesticide Compliance: Gail Amos, Chris Sutherland, and David Bryson
- Roza-Sunnyside Board of Joint Control: Elaine Brouillard and Forrest Chapin
- Chelan County Natural Resource Department: Mike Kaputa and Pete Cruickshank
- The many private landowners who allow us to access our monitoring sites through their property.

## **Table of Contents**

Acknowledgments	ii
Table of Contents	iii
List of Figures	v
List of Tables	
Executive Summary	
Introduction	
Study Area	
Study Methodology	
Study Design	
Field Procedures	
Laboratory Analyses	
Data Quality, Quality Assurance, and Quality Control Measures	
Field Replicates	
Blanks	
Surrogates, Matrix Spikes, and Laboratory Control Samples	
Assessment Criteria	
Pesticide Registration Toxicity Data	
National Recommended Water Quality Criteria	
Washington State Water Quality Standards for Pesticides	
Relationship between WSDA Assessment Criteria and Sources Pesticide of Concern Decision Matrix	
Numeric Water Quality Standards for Temperature, pH, and Dissolved Oxygen	
Monitoring Site Results	
Bertrand Creek	
Upper Big Ditch	
Lower Big Ditch	
Burnt Bridge Creek	
Indian Slough	
Woodland Creek	
Brender Creek	
Lower Crab Creek	
Marion Drain	
Mission Creek	
Naneum Creek	61
Snipes Creek	65
Stemilt Creek	70
Sulphur Creek Wasteway	73
Touchet River	77
Statewide Results	81
Pesticide Detection Summary	82
Herbicide Detections	
Fungicide Detections	
Insecticide Detections	
Glyphosate, AMPA and Glufosinate-ammonium Detections Degradate and Other Pesticide Product Detections	
Legacy Pesticide Detections	
Toxic Unit Analysis	
Conclusions	
Program Changes	
r rogram onanges	30

References	
Appendix A: Assessment Criteria for Pesticides	
Assessment Criteria References	104
Appendix B: 2019 Quality Assurance Summary	113
Data Qualification	
Analytical Quality Assurance and Quality Control Sample Summaries	120
Field Replicate Results	
Laboratory Duplicates	125
Field Blank Results	125
Matrix Spike/Matrix Spike Duplicate Results	
Laboratory Blanks	133
Surrogates	
Laboratory Control Samples	136
Field Data Quality Control Measures	143
Field Data Collection Performance	
Field Audit	144
Quality Assurance Summary References	145

## **List of Figures**

Figure 1 – Subbasins monitored in Washington State in 2019       6         Figure 2 – Map of Bertrand Creek and its drainage area with associated sampling locations and crop groups identified       17         Figure 3 – Upper Bertrand Creek site upstream view       17         Figure 4 – Lower Bertrand Creek site upstream view       18         Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria       10
22 Figure 6 – Lower Bertrand Creek water quality measurements and exceedances of assessment criteria 23
Figure 7 – Map of Upper Big Ditch and its drainage area with associated sampling location and crop groups identified
groups identified
Figure 13 – Lower Big Ditch pH measurements and exceedances of assessment criteria
36 Figure 17 – Map of Indian Slough and its drainage area with associated sampling location and crop groups identified
43 Figure 23 – Map of Brender Creek and its drainage area with associated sampling location and crop groups identified
51 Figure 29 – Map of Marion Drain and its drainage area with associated sampling location and crop groups identified

Figure 36 – Map of Naneum Creek and its drainage area with associated sampling location and groups identified	61
, Figure 37 – Naneum Creek downstream view	61
Figure 38 – Naneum Creek water quality measurements and exceedances of assessment criter	ia.63
Figure 39 - Map of Snipes Creek and its drainage area with associated sampling location and	
groups identified	65
Figure 40 – Snipes Creek upstream view with average streamflow	
Figure 41 – Snipes Creek water quality measurements and exceedances of assessment criteria	
Figure 42 – Snipes Creek pH measurements and exceedances of assessment criteria	
Figure 43 – Map of Stemilt Creek and its drainage area with associated sampling location and groups identified	
groups identified Figure 44 – Stemilt Creek upstream view	70
Figure 45 – Stemilt Creek dissolved oxygen measurements and exceedances of assessment c	
Figure 46 – Map of Sulphur Creek Wasteway and its drainage area with associated sampling loc and crop groups identified	
Figure 47 – Sulphur Creek Wasteway downstream view	
Figure 48 – Sulphur Creek Wasteway water quality measurements and exceedances of assess criteria	
Figure 49 – Map of Touchet River and its drainage area with associated sampling location and groups identified	
Figure 50 - Touchet River downstream view	77
Figure 51 – Touchet River water quality measurements and exceedances of assessment criteria Figure 52 – Touchet River pH measurements and exceedances of assessment criteria	

## **List of Tables**

Table 1 – Summary of laboratory methods	8
Table 2 - Summary of WSDA assessment criteria derived safety factors from toxicity stu	ıdies,
NRWQC, and WAC	
Table 3 - WSDA watershed POC and POI decision matrix	
Table 4 – Water quality standards for Washington State by aquatic life use	14
Table 5 – Upper Bertrand pesticide calendar, µg/L,	
Table 6 – Lower Bertrand pesticide calendar, µg/L,	21
Table 7 – Upper Big Ditch pesticide calendar, µg/L ,	
Table 8 – Lower Big Ditch pesticide calendar, µg/L ,	
Table 9 – Burnt Bridge Creek pesticide calendar, µg/L	35
Table 10 – Indian Slough pesticide calendar, µg/L,	39
Table 11 – Woodland Creek pesticide calendar, µg/L ,	
Table 12 – Brender Creek pesticide calendar, µg/L ,	
Table 13 – Lower Crab Creek pesticide calendar, µg/L	50
Table 14 – Marion Drain pesticide calendar, µg/L,	54
Table 15 – Mission Creek pesticide calendar, µg/L ,	58
Table 16 – Naneum Creek pesticide calendar, µg/L ,	62
Table 17 – Snipes Creek pesticide calendar, µg/L,	
Table 18 – Stemilt Creek pesticide calendar, µg/L ,	
Table 19 – Sulphur Creek Wasteway pesticide calendar, µg/L ,	75
Table 20 – Touchet River pesticide calendar, µg/L	78
Table 21 – Statewide pesticide detections summarized by general use category	81
Table 22 – Statewide summary of herbicides with one or more detections in 2019	
Table 23 – Statewide summary of fungicides with one or more detections in 2019	84
Table 24 – Statewide summary of insecticides with one or more detections in 2019	85
Table 25 – Statewide summary of glyphosate, AMPA and glufosinate-ammonium in 2019	88
Table 26 – Statewide summary of degradates and other pesticide products in 2019	88
Table 27 – Statewide summary of legacy pesticides and their degradate detections in 2019	90
Table 28 – Summary of WSDA assessment criteria exceedances from current-use pesticides	93
Table 29 – Additional analytes tested for in 2020	95
Table 30a – WSDA Freshwater assessment criteria (WSDA safety factors applied, µg/L)	99
Table 31b – Mean performance of method reporting limits (LLOQ) in ng/L	114
Table 32b – Data qualification definitions	118
Table 33b – Variability of pesticide detections in field replicates and mean RPDs	120
Table 34b – Laboratory duplicate results	125
Table 35b – Analyte detections in field blanks	126
Table 36b – Summary statistics for MS/MSD recoveries and RPD	127
Table 37b – Analyte detections in laboratory blanks	133
Table 38b – Pesticide surrogates	135
Table 39b – Summary statistics for LCS/LCSD recoveries and RPD	137
Table 40b – Quality control results for conventional water qualiter parameter replicates	143
Table 41b – Data quality objectives for YSI ProDSS or other field meter post-checks	
Table 42b – Conventional water quality parameter and flow data from field audit	144

### **Executive Summary**

Washington State Department of Agriculture (WSDA) has been generating surface water monitoring data for pesticides since 2003 in an ongoing effort to assess the frequency and concentration of pesticide presence in surface water across a diverse cross section of landuse patterns in Washington State. State and federal agencies use this data to evaluate water quality and make exposure assessments for pesticides registered for use in Washington State.

In 2019, WSDA's Natural Resources Assessment Section (NRAS) collected surface water samples weekly or biweekly from March through November at 16 monitoring sites. Staff selected sites with high proportions of agriculture specifically dominated by a few crops, mixed agriculture and urban, or urban to identify trends that may be associated with those land uses. Sites were located in Benton, Chelan, Clark, Grant, Kittitas, Skagit, Thurston, Walla Walla, Whatcom, and Yakima counties with watershed areas ranging from 2,000 acres to over 200,000 acres. Land use within each watershed varied from commercial, residential, and urban to agricultural uses like tree fruit, berry, wheat, corn, grass hay, and potato production. The Manchester Environmental Laboratory (MEL) in Port Orchard, Washington provided the sample analysis.

The United States Endangered Species Act lists several species of endangered salmonids found in Washington State's waterways including some in the waterways WSDA monitors (ESA, 1973). Salmonids are valuable in the Pacific Northwest due to their cultural significance, contribution to the economy, and function in the ecosystem. All of the watersheds sampled in 2019 either have historically supported salmonid populations, contain habitat, or flow into habitat conducive to salmonid use. To assess potential biological effects and to be protective of endangered and non-endangered species, WSDA compares detected pesticide concentrations from surface water samples to WSDA assessment criteria. WSDA assessment criteria are adapted from toxicity study criteria and state and national water quality standards. Exceedances of WSDA assessment criteria indicate pesticide concentrations approaching levels with possible adverse effects to aquatic life such as fish, invertebrates, and aquatic plants. WSDA maintains and updates a list of current-use pesticides that gualify as either statewide or watershed Pesticides of Concern (POC) by evaluating the most recent three years of pesticide detection data using a POC decision matrix. Statewide POCs were chlorpyrifos, imidacloprid, and malathion. Additional pesticides identified as watershed POCs were bifenthrin, clothianidin, diazinon, diuron, fipronil, metolachlor, pyriproxyfen, sulfometuron-methyl, tefluthrin, pyridaben, thiamethoxam, and fluvalinate.

This report summarizes activities and data from the 16 separate sites selected for the 2019 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 292 surface water sampling events between March 25 and November 5.
- Out of 159 pesticide active ingredients and breakdown products tested for, there were 122 unique pesticides detected.

- There were 5,606 positively identified pesticide detections.
- At 288 of the 292 sampling events, mixtures of two or more pesticides were detected.
- Boscalid was the most frequently detected fungicide (189 times), thiamethoxam was the most frequently detected insecticide (170 times), and bromacil was the most frequently detected herbicide (183 times) of the pesticides WSDA tested for.
- In a special 2019 project, WSDA tested for glyphosate, AMPA (a glyphosate breakdown product), and glufosinate-ammonium at 14 of the 16 monitoring sites every other week. Glyphosate and AMPA were the most frequently detected chemicals. We detected both in over 90% of samples tested. All detections were below a level of concern.
- A breakdown product of dichlobenil (2,6-dichlorobenzamide) had the most total detections with 245, followed by boscalid, with 189 detections. Detections of these analytes occurred in over 65% of sampling events.
- There were 308 unique pesticide detections with concentrations exceeding WSDA assessment criteria (5.5% of total detections), approaching levels that could adversely affect aquatic life.
  - The legacy insecticide DDT and its breakdown products accounted for 154 of the exceedances (50% of exceedances).
  - Current-use pesticides and one degradate accounted for 154 of the exceedances (50% of exceedances). The chemicals include:
    - bifenthrin (9 exceedances),
    - chlorpyrifos (13 exceedances),
    - clothianidin (12 exceedances),
    - diazinon (1 exceedance),
    - diuron (1 exceedance),
    - fipronil (4 exceedances),
    - total fluvalinate (8 exceedances),
    - imidacloprid (83 exceedances),
- malaoxon (1 exceedance),
  malathion (9 exceedances),
  - pyridaben (2 exceedances),
  - tefluthrin (6 exceedances),
  - tetramethrin (1 exceedance),
  - permethrin (2 exceedances),
- and pyriproxyfen (2 exceedances).

Of the 308 detections that exceeded WSDA assessment criteria, many (78% or 240 detections) also exceeded state, national, or toxicity study criteria. Current-use pesticides accounted for 38% (91 detections) of these exceedances without the WSDA safety factor. Each detection of bifenthrin (9) exceeded both the WSDA assessment criteria and its chronic invertebrate toxicity study criterion. Chlorpyrifos (11 exceedances) and/or malathion (2 exceedances) were detected above toxicity study criteria, state standards, or national water standards. Imidacloprid, found at 11 of the 16 monitoring sites, exceeded the chronic invertebrate toxicity study criterion 65 times out of a total 104 detections. Two reasons imidacloprid is detected so often exceeding criterion. Other pesticides detected less often that still exceeded state, national, or toxicity study criteria included clothianidin, pyriproxyfen, fluvalinate, and permethrin. Legacy pesticide DDT and its associated degradates accounted for the remaining 61% (150 detections) of the total detected exceedances of state or national standards.

WSDA collected samples for total suspended solids analysis and measured dissolved oxygen, pH, conductivity, water temperature, and streamflow in the field at sampling events.

WSDA also collected continuous air and water temperature measurements during the entire monitoring season in situ. Dissolved oxygen, pH, and water temperature measurements were compared to Water Quality Standards for Surface Waters of the State of Washington (WAC, 2019). At least one conventional water quality parameter did not meet state water quality standards at 14 of the 16 monitoring sites. When these exceedances coincide with exceedances of WSDA pesticide assessment criteria, it could compound stress on aquatic life.

Maintaining the highest level of data quality is an essential component of the monitoring program. WSDA staff closely adhere to detailed field procedures while MEL staff reliably produce high quality testing results to achieve the highest quality assurance standards recommended by the Environmental Protection Agency (EPA) (EPA, 2017). Appendix B: 2019 Quality Assurance Summary provides a summary of quality assurance and quality control sample results with a detailed analysis of how the field and laboratory methods performed over the season.

The NRAS ambient monitoring program is a tool for identifying state-specific pesticide issues that can be addressed according to WSDA's EPA-approved Pesticide Management Strategy (Cook and Cowles, 2009). Maintaining an adaptive monitoring approach helps identify pesticide use patterns that can lead to water contamination. The statewide ambient surface water monitoring program also forms the groundwork for additional studies focusing on particular scientific questions of interest regarding pesticide fate and transport. WSDA shares the data generated by this program with the agricultural community, regulatory and scientific community, and the public through WSDA's website, reports, watershed-specific fact sheets, and numerous public presentations.

## Introduction

Washington State Department of Agriculture (WSDA) has authority as a state lead agency to regulate the sale and use of pesticides in Washington State under federal regulation according to the amended Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, 1947), and state regulation according to Washington Pesticide Control Act (WPCA, 1971) and Washington Pesticide Application Act (WPAA, 1971).

Since 2003, WSDA has received funding from the Washington State Legislature and the U.S. Environmental Protection Agency to administer a comprehensive program to assess the frequency and biological significance of pesticides detected in Washington State surface waters. To make that evaluation, WSDA's Natural Resources Assessment Section (NRAS) collects three kinds of information:

- Pesticide usage data: types of pesticides used on different crops, application rate, timing, and frequency.
- Agricultural land-use data: crop types grown and their locations in the state.
- Ambient monitoring data: pesticide concentrations in surface water.

NRAS's ambient surface water monitoring program provides information about the fate, transport, and potential effects of pesticides in the environment, allowing regulators to refine exposure assessments for pesticides registered for use in Washington State and providing feedback to pesticide users. It is of critical importance to minimize the potential effects of pesticides on aquatic systems while also minimizing the economic impacts to agricultural systems that are responsible for providing a sustainable food supply.

The technical report:

- Summarizes results, data quality, and monitoring activities conducted in 2019.
- Provides data for the pesticides that are listed for agency Endangered Species Act consultations.
- Determines if any pesticides in surface waters may be present at concentrations that could adversely affect aquatic life.
- Provides a basis for potential modifications to the program in upcoming years.
- Provides data to support implementation decisions under the agency's Pesticide Management Strategy (Cook and Cowles, 2009).

WSDA conducted ambient surface water monitoring for pesticides in 2019 from March to November throughout the state. During the first year of monitoring (2003), WSDA sampled at nine monitoring sites in agricultural and urban areas. By 2019, the program had expanded to 16 monitoring sites, including two of the nine original sites. WSDA has monitored surface water in 20 unique watersheds since the start of the program. No site changes occurred between 2018 and 2019.

WSDA sent water samples to the Manchester Environmental Lab for analysis of pesticide and pesticide-related chemicals such as insecticides, herbicides, fungicides, degradates, an antimicrobial, a wood preservative, an insect repellent, and synergists. A substantial increase in pesticide detections since 2017 is largely due to new equipment at the lab and does not necessarily reflect an increase in pesticide usage. In 2019, WSDA tested for 159 chemicals, with 122 confirmed chemicals detected in surface water samples. Between the 2018 and 2019 monitoring seasons, 15 chemicals were added to the testing list. The list of chemicals analyzed for every year may change because of new use restrictions, changes in pesticide registration, analytical cost, or lack of detections in surface water.

WSDA compares the surface water data to internal assessment criteria that are derived by applying a safety factor to state and national water quality standards and toxicity study criteria in order to be protective of aquatic life. Persistent contamination of surface waters with pesticides or pesticide-related chemicals can trigger the implementation of adaptive management techniques described in WSDA's EPA-approved Pesticide Management Strategy (Cook and Cowles, 2009). These techniques can include voluntary best management practices, voluntary use prohibition, technical assistance, stakeholder outreach, and intensive monitoring. In addition, WSDA identifies Pesticides of Concern (POCs) each year based on detection frequency and which WSDA assessment criteria were exceeded.

NRAS's ambient surface water monitoring program provides a non-regulatory framework for addressing off-target pesticide movement into streams and rivers. WSDA uses the ambient surface water monitoring program results to identify targets for technical assistance and outreach efforts from other private and public organizations to address local and regional water quality issues. WSDA keeps the agricultural community, regulatory community, and the public informed about pesticide detection trends that occurred in surface water with numerous public presentations and annual reports. In addition to this report, site-specific fact sheets are published yearly to share data and improve awareness of simple practices that can protect surface water.

## **Study Area**

Since the ambient surface water monitoring program began in 2003, sampling sites and subbasins have been both added and removed based on pesticide detection history, changing pesticide usage practices, site conditions, land-use patterns, and the presence of federally-listed threatened or endangered species. Water Resource Inventory Areas (WRIA) are typically used to study and manage water resources within Washington. State agencies also use these subbasin boundaries for implementing surface water quality standards (WAC, 2019). Figure 1 shows the boundaries of the 10 subbasins that WSDA sampled in 2019, identified by their WRIA codes and corresponding subbasin names.

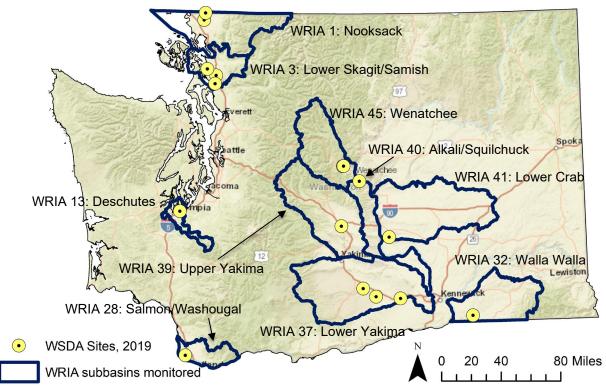


Figure 1 – Subbasins monitored in Washington State in 2019

All 10 subbasins are in the greater Pacific Northwest Region. Two of the subbasins represent mixed urban and residential landscapes and were selected due to land-use characteristics, history of pesticide detections, and the habitat provided for aquatic threatened and endangered species. The other eight subbasins represent a variety of agricultural landscapes and commodities in close proximity to streams. The proportion of watershed area in agricultural production varies widely, and all affect or provide habitat for endangered Pacific salmonids.

## **Study Methodology**

### **Study Design**

The objective of this sampling program was to assess pesticide presence and concentration in salmonid-bearing streams during a typical pesticide-use period of March through November. Staff collected surface water samples at 16 monitoring sites across the state, which Manchester Environmental Laboratory (MEL) analyzed for 159 pesticide active ingredients and pesticide breakdown products. The sampling schedule and analytes tested for was determined individually for each site by focusing sampling efforts during the duration of peak pesticide application as well as around the weeks with pesticide detections in previous years.

Conventional water quality parameters such as total suspended solids, pH, conductivity, continuous air and water temperature data (collected at 30-minute intervals), dissolved oxygen, and streamflow were monitored at all sampling events to assess overall stream health in relation to Washington State water quality standards.

Detailed information on study design and quality assurance/quality control methods are described in the *Quality Assurance Project Plan* (Bahr, 2019).

### **Field Procedures**

Surface water samples were collected using a 1-liter glass jar by hand grab or pole grab as described in the *NRAS Standard Operating Procedure (SOP): Water Quality and Pesticides Monitoring* (Bischof, 2019). Before delivery to MEL, staff labeled and preserved all samples according to the *NRAS Quality Assurance Project Plan* (Bahr, 2019).

Field staff used YSI ProDSS field meters to record water temperature, pH, dissolved oxygen, and specific conductivity at each sampling event. Field meters were calibrated and post-checked at the beginning and end of every sampling week based on the manufacturers' specifications, using the YSI ProDSS User Manual (YSI, 2018). WSDA followed Ecology's Standard Operating Procedure for Continuous Temperature Monitoring of Fresh Water Rivers and Streams for continuous, 30-minute-interval temperature data collection at 13 monitoring sites (Ward, 2018). Mission Creek, Lower Bertrand Creek, and Touchet River temperature data was obtained from Ecology gauging stations present at those monitoring sites. The 2019 field data quality results are summarized in Appendix B of this report.

Streamflow data in cubic feet per second was measured at 11 of the monitoring sites using an OTT MF Pro flow meter and top-setting wading rod, as described in Ecology *SOP EAP056* (Mathieu, 2019). WSDA obtained streamflow data for the remaining five sites from gauging stations managed by other agencies. Details of those gauging stations are listed below.

- Lower Bertrand Creek Ecology gauging station located at Rathbone Road (Station ID: 01N060)
- Lower Crab Creek United States Geological Survey (USGS) gauging station located near Beverly, Washington (Station ID: 12472600)
- Mission Creek Ecology gauging station located near north Cashmere (Station ID: 45E070)
- Sulphur Creek Wasteway US Bureau of Reclamation gauging station at Holaday Road near Sunnyside (Station ID: SUCW)
- Touchet River Ecology gauging station located at Cummins Road (Station ID: 32B075)

The gauging stations provided 15-minute streamflow measurements throughout the sampling season. WSDA used the recorded streamflow closest to the actual sampling start time.

### Laboratory Analyses

MEL analyzed the surface water grab samples for pesticides, TSS, and conductivity. Table 1 provides a summary of the extraction and analytical methods used by MEL.

Analytical method	Extraction method reference <sup>1</sup>	Analytical method reference <sup>1</sup>	Instrument
GCMS-Pesticides	3535A	8270E	GC/MS/MS
GCMS-Herbicides (Derivitizable acid herbicides)	3535A	8270E	GC/MS
LCMS-Glyphos	3535A	8321B	LC/MS/MS
LCMS-Pesticides	n/a	8321B	LC/MS/MS
TSS	n/a	SM 2540D	Gravimetric
Conductivity	n/a	SM 2510B	Electrode

Table 1 – Summary of laboratory methods

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

GC/MS: gas chromatography/mass spectrometry

GC/MS/MS: gas chromatography/triple quadrupole mass spectrometry

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

### Data Quality, Quality Assurance, and Quality Control Measures

The quality assurance (QA) and quality control (QC) protocol for this program employs blanks, replicates, and surrogate recoveries. As a laboratory component of QA/QC, MEL analyzed surrogate recoveries, laboratory blanks, laboratory control samples, and laboratory control sample duplicates. Field blanks, field replicates, matrix spikes, and matrix

spike duplicates integrate field and laboratory components. In 2019, 11% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2019 Quality Assurance Summary.

Laboratory data were qualified as needed. Positive pesticide detections included values not needing qualification and qualified as an approximate concentration (J) or estimated concentration outside of a calibration range (E). Data that was tentatively identified (NJ or N), rejected (REJ), or not detected (U or UJ) were not used for comparison to pesticide assessment criteria or water quality standards. Appendix B describes all qualifiers.

#### **Field Replicates**

WSDA collected field replicate samples to determine total sampling and analytical method variance. Identified replicate pairs can be considered consistently or inconsistently detected. Consistently identified replicate pairs are those where the pesticide or TSS was positively detected in both the sample and field replicate. Conversely, inconsistently identified replicate pairs are those where the pesticide or TSS was detected in only one of the two samples collected. Replicate pairs where no identified detections were found in both sample and field replicate were not used in the WSDA analysis. The highest concentration of the positively detected sample or field replicate was selected for comparison to WSDA assessment criteria, regardless if the replicate pair was consistently or inconsistently identified. This procedure ensures a conservative approach to assessment criteria comparison.

Precision between identified replicate pairs was evaluated using relative percent difference (RPD). Only 15 of the 280 consistently identified replicate pairs detected for pesticide and TSS analysis exceeded an RPD criterion (40% RPD for pesticides, 20% RPD for TSS). The results were not qualified for the 15 pairs because RPD has limited effectiveness in assessing variability at low levels (Mathieu, 2006). In most cases, the detections were at or below the method reporting limit but above the method detection limit.

To determine the uncertainty in replicate variability, WSDA completed an evaluation of the percentage of inconsistently identified replicate pairs and the upper 90% confidence bound associated with the pairs. It was found that only 2,6-dichlorobenzamide, sulfentrazone, metolachlor, glyphosate, AMPA, and TSS had low replicate variability among the 88 analytes detected in replicate pairs. There was not a high reproducibility of detections between replicate pairs for analytes detected in 2019. The analytes, in part, had high variability because of the small number of replicate pairs with at least one identified detection. Even so, all pesticide and TSS data for replicates were of acceptable data quality. There were no sample or field replicate detections qualified due to inconsistently identified replicate pair results.

Replicate streamflow measurements and conductivity samples were collected for precision analysis. A streamflow measurement was replicated once a week for each OTT MF Pro flow meter used. A conductivity sample was collected once at each monitoring site for comparison to a YSI ProDSS meter. In 2019, all relative standard deviations between the

measurements and replicate measurements/samples were below the measurement quality objective of 10%.

#### Blanks

Field and laboratory blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were 11 detections in field blanks and 254 detections in laboratory blanks. Detections in field blanks included analytes such as acetochlor, DEET, and triclosan, while detections in lab blanks included analytes such as 2-hydroxyatrazine, carbendazim, fenbutatin oxide, and DEET. The origin of these detections was unknown. Regular field sample detections corresponding to the field or lab blank samples in the same batch were qualified as non-detects if the regular sample concentration was less than five times the blank concentration.

#### Surrogates, Matrix Spikes, and Laboratory Control Samples

MEL spikes surrogates into all samples to evaluate recoveries for structurally similar groups of organic compounds. The majority (97%) of surrogate recoveries fell within the control limits established by MEL in 2019. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

Matrix spikes (MS) and matrix spike duplicates (MSD) provide an indication of bias due to interferences from components of the sample matrix. WSDA can use the duplicate spikes to estimate analytical precision at the concentration of the spiked samples and ensure the analytical method is efficient. For most compounds, percent recovery and relative percent differences (RPDs) of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Analyte recoveries from MS and MSD samples fell between both the upper and lower control limits 82% of the time and the RPDs of the paired recoveries fell below the 40% RPD upper control limit 99% of the time. If a MS/MSD sample exceeded MEL QC criteria, sample results were not qualified unless other QC criteria for that analyte was exceeded in the laboratory batch.

Laboratory control samples (LCS) are deionized water spiked with analytes at known concentrations and subjected to analysis. LCS help to evaluate precision and bias of pesticide residue recovery for a specific analyte. For most compounds, percent recovery and RPDs of LCS and LCS duplicates (LCSD) showed acceptable performance and were within limits for the project. Analyte recoveries from LCS and LCSD samples fell between both the upper and lower control limits 91% of the time and the RPDs of the paired recoveries fell below the 40% RPD upper control limit 99% of the time. Sample results were qualified as estimates if the LCS/LCSD recoveries did not meet MEL QC criteria.

Two detections of tralomethrin, a legacy insecticide, were qualified by WSDA to non-detects due to poor MS/MSD and LCS/LCSD recoveries.

### **Assessment Criteria**

To evaluate potential effects of pesticide exposure to aquatic life and endangered species, WSDA compared pesticide concentrations detected in surface water to reference values with known effects. The reference values for assessment criteria come from several sources: data from studies used to fulfill the requirements for pesticide registration under federal law (CFR, 2007), EPA's National Recommended Water Quality Criteria (EPA, 2019b), and Washington State regulations (WAC, 2019). WSDA applies a 0.5x safety factor to all of these reference values before comparison to detected pesticide concentrations to ensure that the criteria are protective of aquatic life and to detect potential water quality issues early on.

Several factors limit WSDA's ability to make comparisons between detection data and 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. Mixtures are frequently present and the effects of several pesticides in combination may be either more or less toxic than their individual effects. In addition, toxicity values such as those used for pesticide registration are determined from continuous exposure over time. WSDA collects weekly or biweekly discrete grab samples that cannot be used to determine the exposure duration that would be needed to determine whether the time threshold has been exceeded. However, this comparison is consistent with Ecology practices; for Clean Water Act section 303(d) listing purposes instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards and assessment criteria for acute and chronic criteria (Ecology, 2018). Appendix A: Assessment Criteria for Pesticides lists the WSDA assessment criteria for fish, invertebrates, and aquatic plants.

#### **Pesticide Registration Toxicity Data**

Toxicity data from studies generated following EPA-provided test guidelines are commonly used to conduct screening-level risk assessments of pesticides and pesticide degradates. EPA uses these values to develop aquatic life criteria (published as the Office of Pesticide Programs' Aquatic Life Benchmarks) for pesticide active ingredients by applying their own safety factors (EPA, 2019a).

Researchers calculate acute toxicity by exposing a sensitive (representative) species at a susceptible life stage to a range of pesticide concentrations to determine potential negative effects. The  $LC_{50}$  (concentration causing death to 50% of the organisms, in the case of fish) or  $EC_{50}$  (concentration causing immobility or growth reduction to 50% of the organisms, in the case of invertebrates or plants) is calculated. The test duration is 96 hours for fish and aquatic plants and 48 hours for invertebrates.

Chronic toxicity tests normally use either reproductive effects or effects to offspring as the measured effect. Researchers use chronic toxicity study values to derive a pesticide's No Observable Adverse Effects Concentration (NOAEC). The concentration signifies the highest concentration in the toxicity test not showing a statistically significant difference from

the control. The chronic toxicity test is longer than the 96-hour acute test (28 days for fish, 21 days for invertebrates) to simulate the type of exposure that would result from a persistent chemical or the effect of repeated applications.

WSDA uses an increased safety factor to provide an additional level of protection for endangered species. Researchers commonly use rainbow trout as a surrogate fish species to assess the potential risk of a pesticide to salmonids. As a result, the WSDA assessment criteria for endangered species (in this case, typically salmonids) is  $1/20^{th}$  of the most sensitive LC<sub>50</sub> for fish.

#### National Recommended Water Quality Criteria

EPA's National Recommended Water Quality Criteria (NRWQC) include a list of approximately 150 pollutants with criteria to protect aquatic life and human health (EPA, 2019b). Acute and chronic toxicity data from pesticide registration toxicity studies provide the pesticide criteria in the NRWQC. WSDA used the 2019 NRWQC to develop some of the WSDA assessment criteria in this report, presented in Appendix A: Assessment Criteria for Pesticides.

#### Washington State Water Quality Standards for Pesticides

Washington State maintains its own list of priority pollutants under the authority of Washington Administrative Code (WAC) 173-201A: Water Quality Standards for Surface Waters of The State of Washington (WAC, 2019). Washington State water quality standards include numeric criteria for current-use and legacy pesticides. For the purposes of this report, these values are referred to as "state water quality standards."

Washington State adopted some NRWQC data into the WAC. These 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 like DDT are to protect fish-eating wildlife from adverse effects due to bioaccumulation.

The exposure periods assigned to the acute criteria are: (1) an instantaneous concentration not to be exceeded at any time, or (2) a one-hour average concentration not to be exceeded more than once every three years on average. The exposure periods for the chronic criteria are either: (1) a 24-hour average not to be exceeded at any time, or (2) a four-day average concentration not to be exceeded more than once every three years on average.

Acute and chronic numeric criteria for fish, invertebrates, and aquatic plants from the WAC with the WSDA 0.5x safety factor, presented in Appendix A: Assessment Criteria for Pesticides.

#### **Relationship between WSDA Assessment Criteria and Sources**

WSDA uses a combination of pesticide registration toxicity study data and national and state standards to derive WSDA assessment criteria. Table 2 provides a summary of how WSDA uses different sources to develop WSDA assessment criteria referred to in this report.

Criteria type	Toxicity test	EPA safety factor	WSDA safety factor	Final multiplier for WSDA assessment criteria	Relationship to acute/chronic criteria & water quality standards
Fish or Invertebrate Acute*	$LC_{50}$ or $EC_{50}$	0.5	0.5	0.25	$\geq$ 25% of the most protective LC <sub>50</sub> for fish or invertebrates
Endangered Species Acute	LC <sub>50</sub>	0.05	0.5	0.025	$\geq$ 2.5% of the most protective LC <sub>50</sub> for fish
Fish or Invertebrate Chronic*	NOAEC	1	0.5	0.5	≥ 50% of the most protective NOAEC for fish or invertebrates
Aquatic Plant Acute*	EC <sub>50</sub>	1	0.5	0.5	≥ 50% of the most protective EC <sub>50</sub> for aquatic plants
NRWQC	N/A	N/A	0.5	0.5	≥ 50% of the NRWQC
WAC	N/A	N/A	0.5	0.5	≥ 50% of the WAC acute or chronic criteria

Table 2 – Summary of WSDA assessment criteria derived safety factors from toxicity studies, NRWQC, and
--

\* Criteria types used in the Pesticide of Concern decision matrix, found directly below this section.

#### **Pesticide of Concern Decision Matrix**

Annually, WSDA identifies Pesticides of Concern and Pesticides of Interest (POIs) using the most recent surface water data. Washington and the other EPA Region 10 states (Oregon, Idaho, and Alaska) adopted the same method to identify statewide and watershed-specific POCs in 2019. For current-use pesticides detected in 2019, WSDA used the past three years of data for each pesticide to sort each pesticide into a decision matrix by detection frequency and number of detections exceeding WSDA assessment criteria (Table 3).

Although there are two watersheds that contain multiple sites, staff chose to analyze Upper and Lower Big Ditch separately because of their extreme difference in watershed land-use characteristics. Upper and Lower Bertrand were also analyzed separately because the land use of the upper watershed, located in Canada, is unknown to WSDA.

Statewide POCs/POIs are current-use pesticides that were POCs/POIs in more than 30% of monitored watersheds. In 2019, three watershed POCs were found in five or more of the 16 monitored watersheds, making them statewide POCs.

For comparison, the statewide POC list in 2017 went from 21 pesticides to only three pesticides due to the new POC decision matrix. Having a smaller number of identified POCs enables WSDA to educate and outreach to pesticide applicators with focus on the highest

priority pesticides. It also allows WSDA to maintain a POC list per watershed that may be used in the future for special projects such as BMP effectiveness monitoring or pesticide stewardship programs.

Frequency of detection in % last 3 years	≥ 1 detection at or above acute WSDA assessment criteria	≥ 3 detections at or above chronic WSDA assessment criteria	1 or 2 detections at or above chronic WSDA assessment criteria	No detections over WSDA assessment criteria
100 to 65.1	Watershed POC	Watershed POC	Watershed POC	Watershed POI
65 to 35.1	Watershed POC	Watershed POC	Watershed POI	Watershed POI
35 to 0	Watershed POC	Watershed POC	Watershed POI	Low Level of Concern

Table 3 - WSDA watershed POC and POI decision matrix

Only current-use pesticides apply.

# Numeric Water Quality Standards for Temperature, pH, and Dissolved Oxygen

According to the Water Quality Standards for Surface Waters of the State of Washington (WAC, 2019), waterbodies are required to meet numeric water quality standards based on the beneficial uses of the waterbody. Table 4 shows the beneficial aquatic life uses for each of the segments of stream that include the monitoring sites. Every site staff monitored in 2019 was fresh water and was only compared to WAC fresh water criteria.

WSDA measured and compared conventional parameters including water temperature, dissolved oxygen (DO), and pH to the numeric criteria of the Washington State water quality standards according to the aquatic life uses. Table 4 lists the aquatic life use designations of the Water Quality Standards for Washington State.

WAC aquatic life uses	7-DADMax (°C), highest allowable	DO (mg/L), lowest one- day minimum	рН
Char Spawning and Rearing	12.0	9.5	6.5-8.5
Core Summer Salmonid Habitat	16.0	9.5	6.5-8.5
Salmonid Spawning, Rearing, & Migration	17.5	8.0	6.5-8.5
Salmonid Rearing and Migration Only	17.5	6.5	6.5-8.5

Table 4 – Water quality standards for Washington State by aquatic life use

Surface water temperature criteria are listed in the WAC as the highest allowable 7-day average of the daily maximum temperatures (7-DADMax). Additional temperature water quality standards are listed in "Waters Requiring Supplemental Spawning and Incubation Protection for Salmonid Species" to be used in conjunction with WAC standards (Payne, 2011). Only one WSDA monitoring site in 2019 has an additional temperature standard: the

Upper Bertrand Creek site. The minimum temperature standard in this part of the stream is a 7-DADMax of less than 13°C between February 15 and June 15.

Although the Water Quality Standards for Washington State lists dissolved oxygen criteria as the lowest one-day minimum, dissolved oxygen measurements are considered point estimates (not continuous) taken at the time of sampling. The point measurements may or may not be the lowest dissolved oxygen concentration of that day at an individual monitoring site.

### **Monitoring Site Results**

In 2019, WSDA monitored 16 sites located at private and public access points. The urban subbasins were chosen due to land-use characteristics, history of pesticide detections, and habitat use by salmonids. The agricultural subbasins were chosen because they support several salmonid populations, produce a variety of agricultural commodities, and have a high percentage of cultivated areas with historical pesticide usage. The number of pesticides detected at a given site can vary greatly from year to year due to several factors including the local and regional meteorology, pest pressure, sampling schedule, and other influences.

The summaries below describe monitoring site information and data in detail, including pesticide calendars, maps, agricultural land-use statistics, and water quality. Pesticide calendars provide a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria. For specific values and information on the assessment criteria development, please refer to Appendix A: Assessment Criteria for Pesticides.

In the calendars, the number below the months indicates the day of the month the sampling event occurred and each column below the sampling event date indicates the data associated with that event. The blank cells in the calendars often indicate no chemical detection, but can also mean a chemical was detected below reportable sample quantitation limits. Concentrations are presented in  $\mu$ g/L, rounded to the thousandths place. The addition of a "<" identifies concentrations less than 0.001  $\mu$ g/L.

Detection of a pesticide concentration above the WSDA assessment criteria does not necessarily indicate an exceedance has occurred because the temporal component of the criteria must also be exceeded. For WSDA assessment criteria, measurements of instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards and acute and chronic assessment criteria.

It is possible for a single pesticide detection to exceed more than one WSDA assessment criteria; however, this scenario cannot be shown in the pesticide calendars. If multiple criteria exceedances of one pesticide occur, it is described in the summary text above or below the calendar.

Monitoring site summaries are sorted below in this section of the report by Western and Eastern regions and then sub-sorted alphabetically.

### **Bertrand Creek**

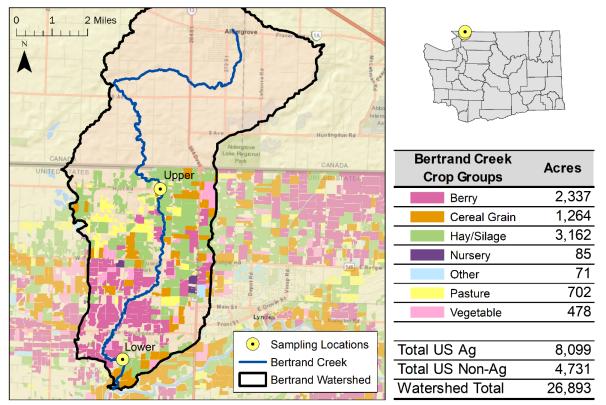


Figure 2 – Map of Bertrand Creek and its drainage area with associated sampling locations and crop groups identified

In 2013, WSDA started sampling the Bertrand watershed in Whatcom County. Monitoring takes place at two locations along this stream to provide an opportunity to compare potential pesticide inputs from Canada to pesticide detections downstream in the United States. The headwaters of Bertrand Creek are located in Canada and it flows approximately 11 miles before crossing the border. Currently, the Upper Bertrand Creek site is located approximately a quarter mile south of the Canadian border at the upstream side of H Street Road (latitude: 48.9935°, longitude: - 122.5094°) (Figure 2, Figure 3). The Lower Bertrand



Figure 3 – Upper Bertrand Creek site upstream view

Creek site is located about 7.8 miles downstream from the upper monitoring site and just upstream of the bridge crossing on Rathbone Road (latitude: 48.9241°, longitude: - 122.5300°) (Figure 2, Figure 4). From the Lower Bertrand Creek site, the creek flows approximately one more mile south to where it enters the Nooksack River.

Bertrand Creek water drains into the Nooksack River subbasin, known for its endangered salmon runs. Precipitation events and irrigation influence streamflow in Bertrand Creek. Washington Department of Fish and Wildlife (WDFW) has documented steelhead and Chinook, coho, chum, and sockeye salmon within the reaches of the creek that encompass both Bertrand sites (WDFW, 2019). WDFW identified a steelhead redd 30 feet downstream of the Upper Bertrand monitoring site in 2019. Staff have frequently observed juvenile fish of unknown species and freshwater lamprey at the Upper Bertrand Creek monitoring site (Figure 3).



Figure 4 – Lower Bertrand Creek site upstream view

The Bertrand Creek watershed has flat, low-lying terrain. Within the U.S. side of the Bertrand watershed, the agricultural land use is predominately grass hay, caneberries, field corn, blueberries, pasture, and potatoes. Roughly 30% of the agricultural acreage within the Bertrand watershed south of the border produces berries such as blueberries, raspberries, and strawberries. The 'Other' crop group category consists mostly of fallow fields (Figure 2). About 14,000 acres of the watershed is in Canada where the main crops and management practices are outside the scope of WSDA's Agricultural Land Use Mapping Program. The headwaters of Bertrand Creek are located in Aldergrove, British Columbia and the creek flows through areas with agricultural land uses similar to those in the U.S.

Below is a brief overview of the pesticide findings in Bertrand Creek in 2019.

- WSDA tested for 159 unique pesticides in Upper and Lower Bertrand Creek.
- Pesticides were detected at all 25 sampling events at each monitoring site.
- Up to 34 pesticides were detected at the same time in Upper Bertrand Creek and up to 39 in Lower Bertrand Creek.
- There were 51 pesticides that were detected at least once in both the Upper and Lower Bertrand Creek sites throughout the sampling season. Conversely, there were seven pesticides that were found only at the upper site and 13 pesticides that were found only at the lower site.
- There were 486 total pesticide detections in Upper Bertrand Creek from seven different use categories: 24 types of herbicides, 13 insecticides, 10 fungicides, 8 degradates, 1 antimicrobial, 1 synergist, and 1 insect repellent.
- Of the total pesticide detections in Upper Bertrand Creek, 26 were above WSDA's assessment criteria (Table 5).
  - $_{\odot}$  The single fluvalinate detection exceeded the WSDA Endangered Species Level of Concern (0.009  $\mu g/L).$
- There were 697 total pesticide detections in Lower Bertrand Creek from six different use categories: 25 types of herbicides, 15 insecticides, 11 fungicides, 10 degradates, 1 insect repellent, and 1 antimicrobial.
- Of the total pesticide detections in Lower Bertrand Creek, 27 were above WSDA's assessment criteria (Table 6).
  - $\circ~$  Only one of the 13 diazinon detections approached the invertebrate NOAEC (0.17  $\mu g/L)$  and invertebrate EC\_{50} (0.21  $\mu g/L).$

 $\circ$  The total permethrin concentration on April 8 is the summation of the detected cispermethrin and trans-permethrin concentrations. The total permethrin concentration exceeded the invertebrate NOAEC (0.0014 µg/L).

The Upper Bertrand Creek watershed POCs were diazinon, imidacloprid, and malathion. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- All 25 detections of imidacloprid approached or exceeded the invertebrate NOAEC (0.01  $\mu$ g/L). The detection on June 11 also approached the invertebrate EC<sub>50</sub> (0.77  $\mu$ g/L).
- The six detections of diazinon and six detections of malathion did not exceed any assessment criteria in 2019, but these pesticides were still classified as watershed POCs because of 2017 and 2018 detections that did exceed criteria.

The Lower Bertrand Creek watershed POCs were bifenthrin, imidacloprid, malathion, and thiamethoxam. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- All 19 detections of imidacloprid approached the invertebrate NOAEC (0.01  $\mu$ g/L). The detection July 9 also approached the invertebrate EC<sub>50</sub> (0.77  $\mu$ g/L).
- Out of 18 malathion detections, five approached the invertebrate EC<sub>50</sub> (0.098 µg/L).
  - Malaoxon has the same assessment criteria as malathion, its parent compound. Out of 16 malaoxon detections, only one approached the invertebrate  $EC_{50}$ .
- The 25 detections of thiamethoxam in 2019 did not exceed any assessment criteria, but the pesticide was still classified as a watershed POC because of a 2017 detection that did exceed criteria. Similarly, bifenthrin was not detected in 2019, but was considered a watershed POC because of 2018 detections that exceeded criteria.

The Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 5, Table 6). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

	Οp	per	DCI	uun		300		Juic	nuu	, μ	<i>y</i> –															
Month		Mar		Apr			Мау					Jun				Jul						Aug				
Day of the Month	Use*	26	1	8	16	23	30	7	14	21	28	4	11	17	25	1	9	16	23	29	6	13	19	26	4	9
2,4-D	Н	0.054		0.059		0.071				0.086	0.194					0.059										$\square$
2,6-Dichlorobenzamide	D	0.072	0.074	0.134	0.128	0.121	0.127	0.127	0.138	0.136	0.120	0.155	0.124	0.180	0.098	0.120	0.149	0.132	0.141	0.205	0.158	0.067	0.061	0.049	0.058	0.027
Acephate	I			0.023			0.004	0.150	0.091	0.325	0.041	0.171	0.011	0.005	0.017	0.126	0.009			0.016	0.026					
Acetamiprid	1															0.004										
Aminomethylphosphonic acid (AMPA)	Н	0.098		0.171		0.111		0.090		0.283		0.174		0.098		0.131		0.093		0.099		0.103		0.947		1.660
Atrazine	Н									0.005																
Azoxystrobin	F			0.002																						
Boscalid	F	0.053				0.134	0.084			0.136	0.142	0.057	0.063	0.071	0.117	0.069	0.081	0.072	0.074	0.095	0.078	0.093	0.036	0.031	0.029	0.029
Bromacil	Н	0.005						0.005																		
Carbendazim	F	0.007	0.005	0.003	0.004	0.005	0.005	0.004			0.005	0.004	0.007	0.004					0.003	0.004			0.002			
Chlorothalonil	F	0.003							0.006																	
Clothianidin	I									0.004						0.003				0.003						
Diazinon	1	0.004			0.009	0.006			0.011		0.005															
Dicamba acid	Н			0.015		0.037					0.043					0.032										
Dichlobenil	Н	0.017	0.089	0.096	0.051	0.064	0.036	0.034	0.027	0.043	0.062	0.038	0.040	0.019	0.008	0.024	0.014	0.006			0.007		0.004	0.004	0.003	L
Dimethoate	1	_																	0.019	0.022						L
Diuron	Н		0.001	0.003	0.007	0.005	0.005	0.00-	0.007	0.00-	0.001	<u> </u>		0.001	0.005	0.004						<u> </u>				
Fludioxonil	F		0.004	0.00-	0.006	0.005	0.005	0.005	0.006	0.005	0.004			0.004	0.005	0.004		L				<b> </b>				<b> </b>
Flumioxazin	Н			0.005		0.007																				L
Glufosinate-ammonium	H	0.440		0.007		0.070		0.000		0.404		0.040		0.007		0.004		0.006		0.004		0.000		0.000		0.040
Glyphosate	Н	0.116		0.148		0.073		0.030		0.181		0.049		0.037		0.034		0.036		0.024		0.026		0.099		0.912
Hexazinone	Н	-	0.003	0.000	0.005		0.004	0.005		0.004		0.005			0.005			0.005			0.004					<u> </u>
Imazapyr	Н	0.007	0.007	0.003	0.004	0.000	0.004	0.000	0.445	0.003		0.000	0.040	0.000	0.045	0.447	0.405	0.055	0.004	0.007	0.005	0.045	0.044	0.044	0.005	0.005
Imidacloprid	Н	0.027	0.027	0.023	0.034		0.034	0.068	0.115	0.140				0.090	0.045	0.117	0.125	0.055	0.061	0.067	0.035	0.015	0.014	0.014	0.005	0.005
MCPA		-				0.089					0.290	0.131	0.160		10.004	0.035				-0.004						H
Malaoxon	D	-														< 0.001	0.004	0.040	0.013	<0.001	0.005					<u> </u>
Malathion	H	-	-	0.086		0.102				0.070	0.132				0.004	0.004	0.004	0.012	0.013		0.005	-				<u> </u>
Mecoprop (MCPP) Metalaxyl	F	-	-	0.086			0.000	0.000	0.010		0.132					0.095						-				
Methamidophos	г D	0.001	0.001								0.013	0.021	0.002	0.002	0.007	0.024	0.004	0.002	0.002	0.005	0 000	0.002	0.002	0.002	0.004	0.002
Methomyl	1	0.001	0.001	0.002		0.001	0.002	0.031	0.019	0.041	0.011	0.031	0.003	0.003	0.007	0.024	0.004	0.002	0.002	0.005	0.008	0.002	0.002	0.002	0.004	0.003
Metolachlor	Н	0.007	0.007	0.003	0.066	0.068	0.017	0.010	0.010	0.010	0.024	0.008		0 000	0.004	0.006		0.006	0.006	0.008	0.006					$\vdash$
Metribuzin	н	0.007	0.007	0.095	0.000	0.000	0.017	0.010	0.010	0.010	0.024	0.000	0.010	0.009	0.004	0.000		0.000	0.000	0.000	0.000					
Myclobutanil	F		-	0.004	0.004		0.004	0.006	0.007	0.006		0.005	0.007									-				
N,N-Diethyl-m-toluamide (DEET)	lr			0.004			0.004	0.000	0.007	0.000		0.005	0.007													
Napropamide	н	0.005			0.040	0.029	0 000	0.006	0.007	0.008	0.006															
Oxadiazon	н	0.008									0.010	0.008	0.011	0.006		0.005		0.005	0.004		0.005					
Oxamyl	1	0.000	0.000	< 0.001							< 0.001	0.000	0.011	0.000		0.000		0.000	0.004		0.000					
Oxamyl oxime	D	0.007	0.007	\$0.001	0.009	-0.001						0.013	0.015	0.021	0.012	0.008	0.008	0.011	0.011	0.021	0.008					
Paclobutrazol	F	0.001	0.001		0.000		0.000	0.017	0.010	0.010	0.000	0.010	0.002	0.021	0.012	0.000	0.000	0.011	0.011	0.021	0.000					
Pendimethalin	H			0.006	0 005								0.002													
Phosmet	1			0.000	0.000									0.010												
Piperonyl butoxide (PBO)	Sy														0.006											
Propiconazole	F			0.059	0.035	0.019	0.009	0.010	0.008	0.009																
Pyrimethanil	F															0.005										
Pyriproxyfen	1	0.004																								
Simazine	Н	0.029							0.066	0.679	0.151	0.081	0.062	0.060	0.185	0.764	0.275	0.123	0.089	0.081	0.065	0.035	0.033	0.024	0.022	0.013
Sulfentrazone	Н			0.006		0.006					0.007					0.005									0.029	0.021
Sulfometuron-methyl	Н	0.129																	0.002							
Tebuthiuron	Н			0.012										0.006	0.003											
Terbacil	Н	0.032	0.025	0.035	0.040	0.040	0.048	0.047	0.051	0.042	0.025	0.022	0.020	0.026	0.019	0.077	0.037	0.023	0.020	0.037	0.017	0.006	0.004	0.005	0.004	
Tetrahydrophthalimide (THPI)	D	0.016				0.011					0.005															
Thiamethoxam	1			0.007	0.005	0.005	0.017	0.045	0.053	0.089	0.019	0.015	0.017	0.016	0.012	0.029	0.018	0.009	0.009	0.014	0.009	0.003	0.003	0.002	0.002	
Total Fluvalinate	1														0.012											
Triazine DEA degradate	D												0.003			0.002										
Triazine DIA degradate	D	0.005	0.005			0.018				0.071	0.037	0.017	0.017	0.020	0.012		0.045	0.029	0.027	0.027	0.019	0.011	0.008	0.006	0.006	0.005
Triazine HA degradate	D	0.003		0.006		0.006	0.004	0.004		0.004	0.005					0.006			0.004							0.004
Triclosan	А				0.008									0.022												
Total suspended solids (mg/L)		3	5	4	4	5	2	3	2	3	4	1	7	3	2	2	2	2	2	1	3	2	1	1		
Streamflow (cubic ft/sec)		18.8	10.8	44.2	42.1	61.6	16.1	10.0	6.8	16.4	8.5	4.4	4.1	2.9	2.0	2.5	2.5	2.0	1.6	2.5	1.3	1.2	0.9	1.1	0.9	1.6
Precipitation (total in/week)†		0.15	0.49	0.85	1.40	1.28	0.05	0	0	0.75	0.53	0.21	0.25	0.06	0.13	0.66	0.57	0.20	0.15	0.21	1.45	0.06	0.94	0.39	1.10	1.53
TI		4																								

#### Table 5 – Upper Bertrand pesticide calendar, μg/L

The "--" signifies a sample that was not collected.

Current-use exceedance

Detection

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist)

<sup>&</sup>lt;sup>†</sup> Washington State University AgWeatherNet station: Lynden, (latitude: 48.94°, longitude: -122.51°)

Tabi					-		5031				uur,	<u>µg/</u>						Ind	_							
Month		Mar			Apr			_		ay			Ju	-	0.5			Jul			-	Au	<u> </u>			ер
Day of the Month	Use*	26	1	8	16	23	30	7	14	21	28	4	11	17	25	1	9	16	23	29	6	13	19	26	4	9
1-(3,4-Dichlorophenyl)-3-methylurea	D													0.009	0.008		0.003									
2,4-D	Н	0.000	0.074		0.059			0.400	0.400		0.158	0.445	0.026	0.174	0.000	0.108	0.404	0.400	0.457	0.474	0.470	0.440	0.404	0.400	0.440	0.070
2,6-Dichlorobenzamide	D	0.080	0.074											0.171	0.066			0.163	0.157	0.174	0.173	0.110	0.121	0.120	0.110	0.073
Acephate	1			0.029	0.006	0.005	0.004	0.036	0.053	0.044	0.043	0.031	0.014				0.005	0.002	0.000		0.013					
Acetamiprid	D		0.010					0.000	0.011					0.000			0.003	0.003	0.002					0.010	0.059	
Acetochlor ESA	Н	0.049	0.016	0.117		0.088		0.033		0.067				0.022		0.012		0.038	0.018	0.043		0.051		0.010	0.059	0.580
Aminomethylphosphonic acid (AMPA) Azoxystrobin		0.049			0.005					0.007				0.000		0.003		0.000		0.043		0.051		0.417		0.560
Boscalid	F	0.037	0.026	0.002					0.051	0.087	0 100	0.042				0.065	0.060			0.080	0.081	0 100	0.030	0.047	0.041	0.050
Bromacil	Н	0.037														0.003										0.030
Carbendazim	F	0.003	0.013		0.007				0.040		0.003	0.007	0.003	0.000	0.020	0.043	0.000	0.000	0.000	0.000	0.007	0.000	0.044	0.042	0.043	0.044
Chlorothalonil	F	0.003		0.000	0.007	0.000	0.000	0.000	0.006	0.002	0.000		0.000													
Chlorpyrifos-methyl	1	0.000					0.005		0.000																	
Clopyralid	H						0.000						0.035													
Clothianidin	1			0.003	0.003	0.003	0.005	0.005	0.006	0.006	0.004	0.005		0.006	0.006	0.005	0.005	0 004	0.005	0.004	0.003			0 004	0.003	0.004
Cyprodinil	F			0.000	0.005	0.006	0.000	0.000	0.000	0.000	0.004	0.005	0.013			0.007					0.002	0.004		0.004	0.005	0.004
Diazinon	1				0.025		0 006	0 004	0 009	0 133	0.013	0.005			0.000		0.003		0.000		0.002	0.004				
Dicamba acid	н			0.015		0.013	0.000	0.004	0.003	0.100	0.025	0.000	0.017	0.000		0.003	0.005	0.004								
Dichlobenil	н	0.010	0.015			0.025	0.014	0.015	0.012	0.020		0.014	0.049	0.015	0.004	0.024	0.010	0.007	0.005	0.005	0.003					
Dinotefuran	1										0.004				0.004	0.020	0.010	0.007	0.000	0.000	0.000					
Diuron	H	0.023	0.013	0.004		0.004	0.001	0.013	0.006						0.051	0.021	0.013	0.010	0 000	0.006	0.007	0.004	0.003	0.005		
Fipronil	1			0.004	0.005				0.000	0.010	0.003	0.020	0.145	0.034	0.001	0.021	0.013	0.010	0.009	0.000	0.007	0.004	0.003	0.005		
Fludioxonil	F		0.004				0.008	0.007	0.008	0.005	0.005	0.004	0.011	0.000	0.008	0.011	0.016	0.018	0.020	0.020	0.016	0.012	0.006	0.007	0.006	0.007
Flumioxazin	Н		0.004		0.006		0.000	0.007	0.000	0.005	0.005	0.004	0.011	0.009	0.000	0.011	0.010	0.010	0.020	0.020	0.010	0.012	0.000	0.007	0.000	0.007
Glufosinate-ammonium	H			0.000																						
Glyphosate	H	0.022		0.103		0.066		0.018		0.038				0.027		0.025		0.010		0.009		0.005		0.010		0.032
	H	0.022		0.006		0.000		0.018		0.005		0.006		0.027		0.025		0.010		0.009	0.006					0.005
Hexazinone		0.025		0.000		0.020	0.006	0.007	0.031	0.005	0.049	0.006	0.005			0.043					0.006	0.006	0.006	0.005	0.006	0.005
Imidacloprid	Н	0.025	0.010	0.020	0.035	0.030	0.022	0.020	0.031	0.064	0.289		0.065	0.033	0.017	0.043	0.290	0.055	0.029		0.010			0.007		
MCPA Malaoxon	D	0.023		0.022	0.019	0.001	0.015	0.007	0.010			0.005	0.000			< 0.001		0.002	0.001	0.002	<0.001	-0.001				< 0.001
				0.033								0.005			0.002		0.021				0.001	0.001				<0.001
Malathion	Н	0.020	0.004		0.010	0.006	0.009	0.007	0.010		0.106	0.004	0.022		0.003	0.030	0.021	0.036	0.027	0.020	0.006	0.006				
Mecoprop (MCPP)	F	0.054	0.050	0.089		0.110	0.000	0.050	0.005	0.054	0.040		0.022			0.090										
Metalaxyl Methamidophos	г D	0.054	0.050	0.003							0.040	0.000	0.002			0.000	0.002				0.004				0.000	0.001
				0.003		0.001	0.001	0.007	0.010	0.009	0.011	0.008		0.000	0.000	< 0.023	0.002				0.004				0.002	0.001
Methomyl	Н	0.007	0.007	0 107	0.040	0.027	0.014	0.000	0.011	0.000	0.010	0.000				0.007		0.007	0.007	0.007	0.007	0.000	0.004		0.004	0.004
Metolachlor	F	0.007	0.007	0.127	0.049	0.037	0.014	0.009	0.005	0.008	0.010	0.006		0.008		0.007		0.007	0.007	0.007	0.007	0.006	0.004		0.004	0.004
Myclobutanil	lr			0.006		-			0.005				0.046	0.042	0.040											
N,N-Diethyl-m-toluamide (DEET)	Н	0.004				0.014	0.007	0.000	0.006	0.000	0.006								0.010							
Napropamide Norflurazon	Н	0.004		0.007	0.026	0.014	0.007	0.006	0.006	0.006	0.006			0.007	0.009	0.010	0.011		0.010	0.007	0.012	0.000	0.005	0.006	0.006	0.006
	Н				0.006				0.000					0.007	0.008	0.010	0.011	0.000	0.008	0.007	0.013	0.009	0.005	0.000	0.000	0.000
Oryzalin Oxadiazon	Н		0.004	0.009			0.007	0.005		0.007	0.007	0.004	0.005	0.004		0.003		-								
		0.020							0.050						0.005		0.007	0.004	0.001	0.050	0.060	0.058	0.004	0.000	0.000	0.000
Oxamyl Overnul evine	D															0.060										0.066
Oxamyl oxime	F	0.040	0.060	0.034			0.060	0.067	0.100	0.060	0.079	0.106	0.109	0.110	0.132	0.107	0.096	0.112	0.103	0.100	0.106	0.064	0.076	0.000	0.060	0.001
Paclobutrazol	Н			0.000	0.002															-						
Pendimethalin	н			0.006	0.005		0.000							0.040												
Phosmet	Н				0.089	0.027	0.006			0.000				0.010												
Prometon	н							0.004		0.003																
Propargite Propiconazole	F			0.020	0.004	0.042	0.000	0.006																		
	F			0.039	0.024	0.013	0.008				0.000				0.002			0.010		0.005		0.000				0.002
Pyrimethanil									0.000	0.000	0.006	0.040	0.070	0 4 2 2	0.003	0.042	0.400	0.010	0.052	0.005		0.003	0.010	0.015	0.011	0.003
Simazine	Н	0.000	0.001	0.010	0.040	0.017	0.005	0.022								0.643					0.050			0.015		0.011
Sulfentrazone	Н	0.026	0.021	0.018	0.018	0.017	0.025	0.032	0.049	0.035	0.033	0.020	0.032	0.034	0.044	0.042	0.061	0.063		0.071	0.050	0.050	0.037	0.036	0.037	0.045
Sulfometuron-methyl	Н			0.045						0.004			0.045	0.000	0.004	0.006		0.007	0.051	0.040	0.000	0.007	0.000	0.007	0.000	
Tebuthiuron	Н	0.045	0.044	0.015	0.005	0.005	0.004	0.004	0.040	0.004		0.000				0.008	0.040	0.007	0.007		0.008			0.007	0.006	
Terbacil	H										0.013					0.068						0.005		0.044	0.000	0.040
Tetrahydrophthalimide (THPI)	D	0.010																			0.009					
Thiamethoxam		0.021	0.024	0.017	0.019	0.025	0.032	0.043	0.052	0.072	0.043														0.031	0.028
Triazine DEA degradate	D	0.001	0.007	0.045	0.001	0.000	0.01	0.000	0.000	0.00	0.000										0.002	0.001		0.001	0.000	0.002
Triazine DIA degradate	D											0.008			0.016	0.045	0.019	0.013	0.009	0.007	0.006			0.002	0.003	
Triazine HA degradate	D	0.004	0.004	0.006			0.006	0.005	0.005	0.004	0.004		0.004													
Triclosan	A	L	<u> </u>		0.008		ļ	ļ	ļ											L			<u> </u>			
Total permethrin			L	0.016						L	L		L									ļ		ļ	L	
Total suspended solids (mg/L)		2	3	6	5	7	3	2	2	2	2							1								
Streamflow (cubic ft/sec)		40.4		75.9		110.0			18.3		21.9					10.5	9.3	7.2	5.9		4.3	4.3	5.1	6.4	5.3	6.3
Precipitation (total in/week)†			0.49	0.85	1.40	1.28	0.05	0	0	0.75	0.53	0.21	0.25	0.06	0.13	0.66	0.57	0.20	0.15	0.21	1.45	0.06	0.94	0.39	1.10	1.53
The "" signifies a sample that was not co	ollected	d.																								

#### Table 6 – Lower Bertrand pesticide calendar, µg/L

Current-use exceedance

Detection

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent)

<sup>&</sup>lt;sup>+</sup> Washington State University AgWeatherNet station: Lynden, (latitude: 48.94°, longitude: -122.51°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet state standards many times at Upper and Lower Bertrand sites. Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in Figure 6 are shown below.

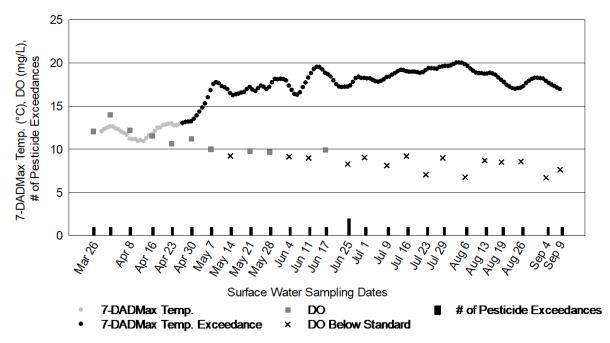
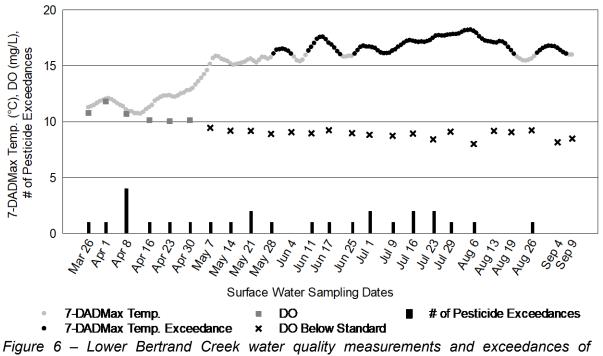


Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria

Pesticide exceedances in Upper Bertrand Creek coincided with water quality measurements that did not meet state standards at 21 of the 25 site visits (84%). All but one pH measurement met the state standard, ranging from 7.39 to 8.68 with an average of 7.63. On April 1, pH was 8.68, exceeding the state standard. DO measurements ranged from 6.70 mg/L to 13.97 mg/L with an average of 9.43 mg/L. More than half (60%) of these measurements did not meet the state standard in that 15 measurements were less than 9.5 mg/L. All pH and DO measurements that did not meet standards coincided with at least one pesticide exceedance and all DO measurements that did not meet the standard coincided with exceeding 7-DADMax temperatures.

Upper Bertrand Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different times of the sampling season. From February 15 through June 15, the 7-DADMax temperature should remain below 13 °C, while June 16 through the end of the sampling season should remain below 16 °C (WAC, 2019). From April 27 through the end of the sampling season, the 7-DADMax temperature exceeded the standard for 136 days. There was at least one pesticide exceedance at every site visit with a 7-DADMax temperature exceedance.



assessment criteria

Pesticide exceedances in Lower Bertrand Creek coincided with water quality measurements that did not meet state standards at 14 of the 25 site visits (56%). All pH measurements met the state standard, ranging from 7.28 to 7.67 with an average of 7.43. DO measurements ranged from 8.01 mg/L to 11.80 mg/L with an average of 9.31 mg/L. More than half (76%) of the measurements did not meet the standard in that 19 measurements were less than 9.5 mg/L. Fourteen of the DO measurements that did not meet the standard coincided with at least one pesticide exceedance. The 7-DADMax temperature exceeded the standard of 16°C for 86 days of the sampling season, primarily from May 29 through September 7. Pesticide exceedances overlapped with both 7-DADMax temperature exceedances and DO measurements that did not meet the standard at eight site visits.

Bertrand Creek has been designated as a freshwater body that provides core summer habitat for salmonids by the WAC (WAC, 2019). For several seasons, there has been a steelhead spawning nest at the Upper Bertrand Creek monitoring site. WSDA will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

### **Upper Big Ditch**

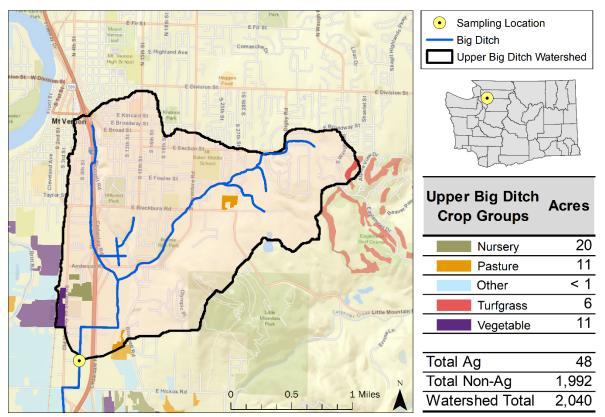


Figure 7 – Map of Upper Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2007, WSDA started monitoring the Upper Big Ditch in Skagit County. The entire Big Ditch watershed drains a mixture of non-agricultural and agricultural land. The Upper Big Ditch site consistently has the most pesticide detections each year compared to any other site WSDA has sampled. The upper monitoring site is located just upstream from the bridge crossing at Eleanor Lane in Mt. Vernon (latitude: 48.3882°, longitude: -122.3330°) (Figure 7).



Water from Big Ditch drains into Puget Sound. WDFW has documented winter steelhead, fall Chinook salmon,

Figure 8 – Upper Big Ditch upstream view

and coho salmon within the reach of ditch that encompasses the monitoring site (WDFW, 2019). A culvert that impeded fish passage upstream of the Upper Big Ditch monitoring site was removed in the fall of 2020. Coho were observed swimming through the reconstructed channel in late November (Skagit Conservation District, 2021). Staff frequently observed juvenile fish of unknown species at the site and identified one coho fry (Figure 8).

Precipitation events and commercial/residential irrigation influence streamflow in the ditch. Flows at the monitoring site were almost stagnant towards the end of the sampling season due to dense aquatic vegetation. The water sampling method was adapted to single point sampling where the highest velocity water was flowing in the ditch from June 18 until the end of the sampling season. Big Ditch stretches north approximately 3 miles from the monitoring site to its headwaters. Within the Upper Big Ditch drainage area, the agricultural land use is predominantly commercial nursery and greenhouse. No other watersheds WSDA monitors have nursery or greenhouse crop groups as their main agricultural commodity. The 'Other' crop group category was a seed crop in 2019 (Figure 7).

Below is a brief overview of the pesticide findings in Upper Big Ditch in 2019.

- WSDA tested for 159 unique pesticides in Upper Big Ditch.
- There were 688 total pesticide detections from eight different use categories: 30 types of herbicides, 14 insecticides, 13 fungicides, 11 degradates, 1 antimicrobial, 1 insect repellent, 1 synergist, and 1 wood preservative.
- Pesticides were detected at all 25 sampling events.
- Up to 54 pesticides were detected at the same time.
- Of the total pesticide detections, 24 were above WSDA's assessment criteria (Table 7).
  - The single detection of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 μg/L).

The Upper Big Ditch watershed POCs were bifenthrin, imidacloprid, sulfometuron-methyl, thiamethoxam, and fluvalinate. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- All six bifenthrin detection exceeded the invertebrate NOAEC (0.0013 µg/L).
- Out of 15 detections of imidacloprid, 14 detections approached the invertebrate NOAEC (0.01 μg/L).
- Out of seven fluvalinate detections, three exceeded the WSDA Endangered Species Level of Concern (0.009 μg/L). The detection on May 20 also exceeded the fish NOAEC (0.064 μg/L) and invertebrate NOAEC (0.1 μg/L).
- The 12 detections of sulfometuron-methyl and 21 detections of thiamethoxam did not exceed any assessment criteria in 2019, but these pesticides were still considered watershed POCs because of detections in 2017 that did exceed criteria.

The Upper Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 7). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

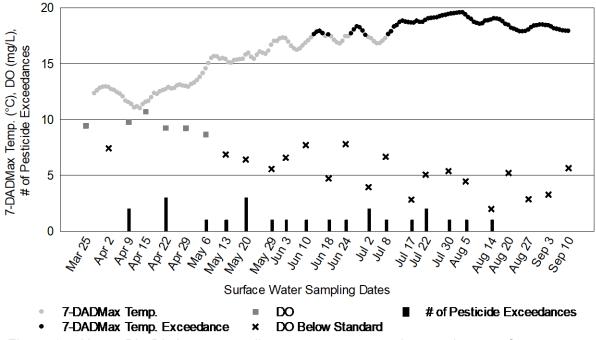
Table	/ -		μει	ыy		JΠμ	1000	lciu			uai,	μ <i>y</i> ,														
Month		Mar			Apr					ay				un				Jul					ug		Se	
Day of the Month	Use*	25	2	9	15	22	29	6	13	20	29	3	10	18	24	2	8	17	22	30	5	14	20	27	3	10
1-(3,4-Dichlorophenyl)-3-methylurea 2,4-D	D H			0.095						0.003						0.253	0.032		0.023		0.069	0.244	0.051	0.052		0.401
2,6-Dichlorobenzamide	D	0.149	0.142		0.273	0.202	0.168	0.137	0.126		0.104	0.118	0.121	0.131	0.094			0.134		0.136						
4,4'-DDE	D					0.002																				
4-Nitrophenol	D			0.518						0.392						0.036										
Acephate	1					0.390	1.230	0.041		0.007					0.007	0.032										
Acetamiprid	D																			0.013		0.002				
Acetochlor ESA Aminomethylphosphonic acid (AMPA)	Н	0.092		0.183		0.134		0.110		0.445		0.161		0.168		0.242		0.190		0.013		0.263		4.970		5.500
Atrazine	н	0.092		0.105		0.134		0.110	0.005			0.101		0.004		0.004		0.190	0.005	0.175		0.203		4.570		5.500
Azoxystrobin	F		0.005	0.005	0.002	0.031	0.112	0.123			0.006	0.024	0.019		0.011		0.007	0.187	0.075	0.043	0.134	0.219	0.016	0.009	0.006	0.006
Bifenthrin	I			0.006		0.010					0.005					0.005			0.006							
Boscalid	F		0.039						0.068	0.246	0.055								0.231						0.027	0.029
Bromacil	H	0.006	0.005	0.025	0.008	0.007	0.007	0.007		0.004	0.005		0.007	0.009	0.006	0.007	0.009	0.011	0.010	0.011	0.011	0.010	0.008	0.007	0.007	
Carbaryl Carbendazim				0.005	0.001	0.005	0.003	0.004		0.004	0.003	0.004	0.004	0.005		0.005		0.003	0.004	0.004	0.004	0.005	0.004	0.004	0.003	0.009
Chlorpropham	Н			0.005	0.001	0.003	0.003	0.004		0.004		0.004	0.004	0.005		0.005		0.003	0.004	0.004	0.004	0.005	0.004	0.004	0.003	0.000
Chlorpyrifos	1			0.000		0.000				0.005				0.005		0.003		0.005	0.004	0.004	0.005	0.004				
Clothianidin	i							0.003		0.009				0.004												
Cyprodinil	F		0.003			0.011				0.044	0.005	0.014	0.004	0.012			0.002	0.006			0.003			0.005		
Dicamba acid	Н			0.028																		0.012				0.051
Dichlobenil	H	0.006	0.009	0.039	0.016	0.006	0.004	0.007		0.019	0.004	0.002	0.003				0.006	0.003		0.004		<u> </u>	0.004	0.004	0.004	0.015
Dimethoate Dinotefuran		0 191	0 277	0.047	0.226	0 205	0.259	0 209	0.007	0.073	0.200	0.210	0 125	0 1 2 2	0.062	0.007	0.013	0.029	0.020	0.054	0.025	0.025	0.014	0.012	0.012	0.000
Dinoteruran Dithiopyr	н Н	0.101	0.211		0.226	0.090	0.338	0.398	0.107	0.006		0.310	0.135		0.003	0.0037		0.028	0.030	0.001	0.025	0.025	0.014	0.012	0.013	0.009
Diuron	Н		1		0.004		0.003	0.003	0.003		0.004	0.003				0.003		0.004	0.004			0.004		0.005	0.004	0.019
Eptam	Н			0.003						0.008																
Etridiazole	F	0.001	0.004					0.001		0.004					ſ	0.003										
Fenarimol	F	<u> </u>	0.004																							
Fipronil	1			0.005						0.004																
Fipronil sulfide	D D				0.006		0.004																			
Fipronil sulfone Fludioxonil	F	0 0/0	0.132	0.045		0 386	0.416	0.461	0 273	1 3/0	0.132	0 375	0 351	0 005	0 326	0.668	0 258	0.496	0.818	0 0/8	0.623	0.613	0 252	0 221	0 161	0 120
Flumioxazin	н	0.043	0.152	0.043	0.045	0.000	0.410	0.401	0.210	1.040	0.152	0.575	0.001	0.333		0.006		0.011	0.010	0.340	0.020	0.015	0.202	0.221	0.101	0.120
Glufosinate-ammonium	Н			0.031		0.482		0.020		0.189				0.039				0.031								
Glyphosate	Н	0.093		0.337		0.214		0.111		1.820		0.136		0.125		0.269		0.103		0.068		0.128		0.361		5.500
Imazapic	Н				0.006			0.005		0.019																0.010
Imazapyr	H	0.011	0.011	0.039			0.035		0.035		0.036				0.037								0.017	0.022	0.009	0.727
Imidacloprid	H H			0.005	0.002		0.010	0.011	0.010	0.032	0.005		0.008		0.005				0.020				0.006	0.000	0.003	0.007
Indaziflam Isoxaben	Н			0.001	0.004	0.034	0.010	0.014	0.010	0.008		0.007	0.005	0.013	0.005	0.013	0.007	0.017	0.012	0.006	0.013	0.017	0.006	0.008		0.007
Mecoprop (MCPP)	н			0.034						0.000																0.080
Metalaxyl	F	0.011	0.020			0.111	0.143	0.059	0.020	0.287	0.016															
Methamidophos	D					0.012	0.290				0.002				0.002	0.012	0.002			0.003	0.003	0.003	0.004	0.004	0.005	0.002
Metolachlor	Н			0.006			0.005	0.004	0.006		0.004		0.006	0.004				0.005	0.006							
Metribuzin	Н									0.007																
Metsulfuron-methyl N,N-Diethyl-m-toluamide (DEET)	H Ir			0.018		0.075				0.033													0.007		0.007	0.015
Napropamide	Н	0.007	0.017					0 008	0.007	0.025	0.005	0.007	0.005	0.012	0.005	0.008	0.005	0.012	0.011		0.015	0.007	0.007		0.007	0.015
Paclobutrazol	F	0.003					0.047				0.006									0.035			0.007	0.007	0.003	
Pentachlorophenol	Wp			0.036																						0.023
Phosmet	1					0.006																				
Picloram	Н			$\geq$	$\geq$	$\geq$	$\geq$	$\geq$			0.036	0.038		0.037					0.056				0.089	0.097		
Piperonyl butoxide (PBO)	Sy				<u> </u>	0.007				0.001	0.000	0.350	0.099	0.089					0.039			0.048	0.000			0.007
Prodiamine	H H	0.000	0.007	0.000	0.040	0.011	0.040	0.040	0.040		0.006	0.000	0.000	0.000					0.017						0.007	
Prometon Propiconazole	F	0.008	0.007	0.022	0.012	0.010	0.010	0.010	0.010	0.007		0.008	0.008	0.009	0.008	0.009	0.010	0.014	0.010	0.014	0.011	0.009	0.007	0.008	0.007	0.006
Pyraclostrobin	F			0.017						0.013				0.007				0.009	0.008			0.013				0.020
Pyridaben				0.006		0.005				0.008																
Sulfentrazone	Н			0.007	0.006	0.006																				0.009
Sulfometuron-methyl	Н						0.028				0.015					0.005			0.003							0.004
Tebuthiuron	Н	0.021	0.030	0.013	0.031	0.030	0.038				0.046	0.070	0.065	0.080	0.068	0.058	0.078	0.097	0.114	0.112	0.120	0.084	0.094	0.071	0.069	
Tetrahydrophthalimide (THPI)	D	0.007	0.045	0.000	0.000	0.004	0.045	0.003		0.007		0.000	0.040	0.040	0.000	0.040	0.000	0.044	0.007	0.000	0.000	0.040				
Thiamethoxam Total Fluvalinate	1	0.007	0.015	0.003	0.009	0.031	0.015	0.029		0.049	0.008	0.032	0.010		0.002	0.013		0.011	0.007	0.003	0.008	0.010				
Triadimefon	F		1	0.000		0.005	0.004	0.004		0.005					0.003				0.007					0.054		
Triazine DEA degradate	D		1	1					1	0.001																
Triazine HA degradate	D	0.005	0.006	0.003	0.006	0.007	0.008	0.008		0.009	0.008				0.009					0.010	0.010	0.007	0.009	0.008	0.008	0.005
Triclopyr acid	Н				0.025				0.100	0.608	0.098	0.041				0.146	0.066	0.025	0.056		0.122	0.138	0.019	0.057		0.500
Triclosan	A	<u> </u>	0.008		0.009		0.53	L		0.00	<u> </u>		0.014			<u> </u>	0.07	0.07								
Trifloxystrobin	F				<u> </u>		0.023	<u> </u>		0.009			0.006				0.005	0.007				<u> </u>				
Trifluralin Total suspended solids (mg/L)	Н	4	6	76	E	15	6	7	10	0.003		F	4	e	2	20	2	7		2	e	2	2	2		F
Streamflow (cubic ft/sec)		4	6 1.4	76 5.5	6 3.3	15 2.2	6 1.5	7 0.9	10 1.0	12 1.4	7 0.8	5 0.8	4	6 0.7	3 0.6	20 0.8	3 0.8	7 0.5	4 0.4	3 0.3	6 0.2	2	2 0.3	2	0.3	5 3.5
Precipitation (total in/week)†		0	0.17				0.04		0		0.33	0.8	0.93	0.7	0.04		0.0			0.3	0.2				0.3	
The "" signifies a sample that was not	collec														,								. ~			
- ·				-		·	-			_																
	C	lurre	nt_u	se e	xce	eda	nce			ח	DT/de	eare	date	ev	:eed	lanc	e		Г	Dete	ctio	n				
<u> </u>		and	nit-u	500		Judi	100				- 1/ U	Syra	aato				-				510	••				

#### Table 7 – Upper Big Ditch pesticide calendar, µg/L

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist, Wp: Wood preservative)

<sup>+</sup> Washington State University AgWeatherNet station: WSU Mt. Vernon, (latitude: 48.44°, longitude: -122.39°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet state standards at 14 of the 25 site visits (56%). Water quality at the Upper Big Ditch site is shown below (Figure 9).



*Figure 9 – Upper Big Ditch water quality measurements and exceedances of assessment criteria* 

All pH measurements met the state standard, ranging from 6.95 to 7.27 with an average of 7.08. DO measurements ranged from 2.00 mg/L to 10.70 mg/L with an average of 6.30 mg/L. More than half (76%) of the DO measurements did not meet the state standard in that 19 measurements were less than 8 mg/L. Fourteen of the DO measurements that did not meet the standard coincided with at least one pesticide exceedance. Upper Big Ditch had the lowest DO measurement than any other monitoring site in both 2018 and 2019. The 7-DADMax temperature standard of 17.5°C was exceeded 75 days of the sampling season, primarily from July 9 through the end of the season. A pesticide exceedance overlapped with both 7-DADMax temperature exceedances and DO measurements that did not meet the standard in six site visits.

Upper Big Ditch has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC, 2019). Flow in the ditch stopped almost completely due to constriction from aquatic vegetation towards the end of summer. WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs.

# **Lower Big Ditch**

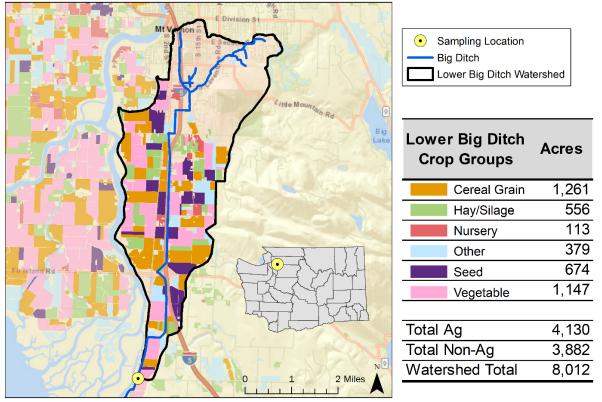


Figure 10 – Map of Lower Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2006, WSDA started sampling the Lower Big Ditch monitoring site in Skagit County. The entire Big Ditch watershed drains a mixture of non-agricultural and agricultural land. Currently, the lower monitoring site is located just upstream from the bridge crossing at Milltown Road near Mt. Vernon (latitude: 48.3085°, longitude: -122.3474°) (Figure 10).

WSDA only sampled this site when the tide gate located downstream of the monitoring site was open and the water was flowing from Big Ditch into Puget Sound to avoid sample contamination with saltwater or pooling backwater. Staff occasionally observed small fish and tadpoles. WDFW has documented winter steelhead, fall Chinook salmon, coho salmon, and chum salmon within the reach of ditch that encompasses the monitoring site (Figure 11) (WDFW, 2019).

Precipitation events and agricultural irrigation



Figure 11 – Lower Big Ditch upstream view

influence the streamflow in the ditch. Big Ditch stretches north approximately 8 miles from the monitoring site to its headwaters. Within the Lower Big Ditch drainage area, the

agricultural land use is predominantly potatoes, field corn, barley, grass hay, and ryegrass seed. The 'Other' crop group category consists mostly of fallow fields and wildlife feed (Figure 10).

Below is a brief overview of the pesticide findings in Lower Big Ditch in 2019.

- WSDA tested for 159 unique pesticides in Lower Big Ditch.
- There were 329 total pesticide detections from seven different use categories: 27 types of herbicides, 10 insecticides, 8 fungicides, 10 degradates, 1 antimicrobial, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 15 sampling events.
- Up to 33 pesticides were detected at the same time.
- Of the total pesticide detections, 17 were above WSDA's assessment criteria (Table 8).
  - Four detections of 4,4'-DDD and seven detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 μg/L). The 4,4'-DDD detection May 20 only approached the chronic criteria.
  - $\circ$  Both bifenthrin detections exceeded the invertebrate NOAEC (0.0013 µg/L).
  - Of the two clothianidin detections, the detection on April 15 approached the invertebrate NOAEC (0.05 μg/L).
  - One of the two detections of pyridaben exceeded the WSDA Endangered Species Level of Concern (0.018 μg/L).

The Lower Big Ditch watershed POCs were fipronil, imidacloprid and metolachlor. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- One of the four detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- The three detections of fipronil and 13 detections of metolachlor did not exceed any assessment criteria in 2019, but these pesticides were still considered watershed POCs because of detections in 2017 and 2018 that did exceed criteria.

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 8). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. In 2019, WSDA primarily collected samples during the spring due to historically infrequent pesticide detections during the summer and fall.

Month	- <u></u> -	Mar			Apr		, <u>- 9</u>	_	м	ay			. Ji	ın		Jul
Day of the Month	Use*		2	9	15	22	29	6	13	20	29	3	10	18	24	2
	-	25		-	15	22		0	-			3	-	10	24	2
2,4-D	Н	0.000	0.128		0.000	0.055	0.057	0.004	0.043		0.090	0.047	0.102	0.004	0.040	0.014
2,6-Dichlorobenzamide	D D	0.060	0.058	0.043				0.064		0.020	0.021	0.017	0.048	0.004	0.019	0.011
4,4'-DDD				0.004			0.003			< 0.001		0.000				
4,4'-DDE	D			0.004	0.003	0.003	0.002		0.003	0.002		0.003				
Acetochlor ESA	D	0.011		0.000		0.004	0.025			0.400		0.404		0.445		0.445
Aminomethylphosphonic acid (AMPA)		0.311		0.233		0.201		0.285		0.139		0.124		0.115		0.115
Atrazine	H	0.050	0.044	0.040	0.040	0.040	0.000			0.004		0.000	0.004	0.000	0.000	0.004
Azoxystrobin	F	0.056	0.044		0.048	0.018	0.020	0.029	0.009	0.016		0.006	0.019	0.002	0.003	0.004
Bifenthrin		0.010	0.040	0.005			0.040				0.004	0.007				0.040
Boscalid	F		0.013					0.007		0.026	0.028	0.007	0.028			0.012
Bromacil	H	0.006	0.005	0.005		0.006	0.006	0.007								
Carbendazim	F												0.003			
Chlorpropham	Н	ļ	0.003			0.003										
Chlorsulfuron	Н			0.019			0.012									
Clothianidin	I				0.037	0.003										
Cyprodinil	F									0.004						
Dichlobenil	Н	0.006		0.034		0.003					0.002		0.003			
Difenoconazole	F				0.005		0.008	0.011								
Dimethoate	I					0.006										
Dinotefuran	1	0.048	0.044	0.032	0.021	0.023	0.025	0.044	0.014	0.009	0.018	0.015	0.040			0.008
Diuron	Н	0.016	0.014	0.004	0.035	0.008	0.008	0.015		0.004	0.005		0.003			
Eptam	н	0.010	0.014	0.006	0.004	0.004	0.022	0.014	0.003	0.028	0.003					
Ethoprop	1						0.003									
Fipronil	li –						0.004			0.003			0.004			
Fipronil sulfide	D		0.004				0.004			0.003						
Fipronil sulfone	D		0.001					0.005		0.000						
Fludioxonil	F	0.055	0.055	0.038	0.013	0 158			0.055	0.062	0.054	0.025	0.081	0.016	0.058	0.020
Glufosinate-ammonium	Н	0.000		0.030		0.150		0.003		0.002		0.025		0.010		0.020
Glyphosate	Н	0.798		0.020		0.519		0.716		0.376		0.278		0.257		0.239
	Н	0.790	0.003	0.577		0.519		0.005		0.370		0.270		0.237		0.239
Hexazinone	Н	0.050		0.017	0.077	0.020			0.005	0.010	0.010	0.005	0.012	0.004	0.007	0.007
Imazapyr		0.059	0.057	0.017			0.044	0.046	0.005	0.010	0.010	0.005	0.013	0.004	0.007	0.007
Imidacloprid	<u> </u>			0.000				0.004		0.000	0.004					
Indaziflam	Н			0.003	0.003	0.003	0.002	0.004		0.002	0.004		0.01			
Isoxaben	Н			0.000									0.002			
MCPA	Н			0.063			-	0.004	0.011				0.019			
Metalaxyl	F								0.011		0.009					
Methamidophos	D									0.001			0.002		0.001	0.002
Metolachlor	Н								0.007	0.035				0.004		
Metribuzin	Н	0.005	0.013			0.006	0.004	0.007		0.014	0.008	0.004				
N,N-Diethyl-m-toluamide (DEET)	lr			0.008												
Napropamide	Н	0.005	0.005			0.005		0.005								
Norflurazon	Н							0.006								
Paclobutrazol	F							0.007	0.002	0.002	0.003		0.007			0.003
Piperonyl butoxide (PBO)	Sy			0.009									0.019		0.030	
Prometon	Н	0.006	0.005		0.004	0.005	0.006	0.007		0.003		0.003	0.003			
Pyridaben	1			0.020		0.005										
Simazine	Н	0.012	0.011		0.006	0.007	0.007	0.009								0.004
Sulfentrazone	Н					0.006										
Sulfometuron-methyl	Н							0.009	0.002	0.010	0.018		0.024			0.003
Tebuthiuron	Н	0.017	0.024	0.018							0.006			0.005	0.012	
Terbacil	Н		0.006					0.008					i			
Tetrahydrophthalimide (THPI)	D							0.008								
Thiamethoxam	1	0.008		0.002	0.016	0.031	0.008		0.003	0.036	0.026	0.002	0.007			
Total Fluvalinate	li	0.000		5.502	5.510	5.501	0.000	5.501	2.000	0.000	5.520	5.502	5.501	0.004	1	
Triazine DIA degradate	D	1			0.003		1							5.00-		
Triazine HA degradate	D	0.039	0.044	0.011		0 023	0.029	0.029	0.005	0.009	0.010	0.005	0.000	0.006	0.010	0.009
Triclopyr acid	Н	0.000	0.044	0.011	0.040	0.020	0.020	0.020	0.000		0.140	0.000	0.100	0.000	0.010	0.000
Triclopyr acid					0.007					0.142	0.140		0.100			
Total suspended solids (mg/L)	A	50	50	104	0.007	0.0	47	14	10	14	0	10	A		4	
		50	50	101	73	80	17	11	19	14	9	13	4	3	1	2
Streamflow (cubic ft/sec)		15.8	5.1	35.2	43.6		4.4	17.5	45.0	28.5	16.4	23.9	9.0	9.8	4.8	5.5
Precipitation (total in/week)†		0	0.11	0.14	0.02	0.01	0	0	0	0.24	0.25	0	0.50	0	0.03	0.30

Table 8 – Lower Big Ditch pesticide calendar, µg/L

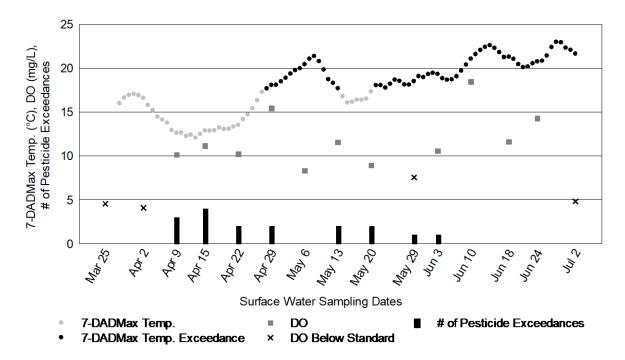
The "--" signifies a sample that was not collected.

Current-use exceedance

DDT/degradate exceedance

Detection

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist) † Washington State University AgWeatherNet station: Fir Island, (latitude: 48.36°, longitude: -122.42°) When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at four of the 15 site visits (27%). Water quality at the Lower Big Ditch site is shown below (Figure 12 and Figure 13).



*Figure 12 – Lower Big Ditch water quality measurements and exceedances of assessment criteria* 

DO measurements ranged from 4.09 mg/L to 18.43 mg/L with an average of 10.10 mg/L. Less than half (27%) of these measurements did not meet the DO standard in that four measurements were less than 8 mg/L. The 7-DADMax temperatures were greater than the 17.5°C standard for 59 days of the sampling season, from April 28 through May 13 and from May 21 through the rest of the season. A 7-DADMax temperature exceedance coincided with at least one pesticide exceedance in four site visits. On May 29, a pesticide exceedance overlapped with both a 7-DADMax temperature exceedance and a DO measurement that did not meet the standard.

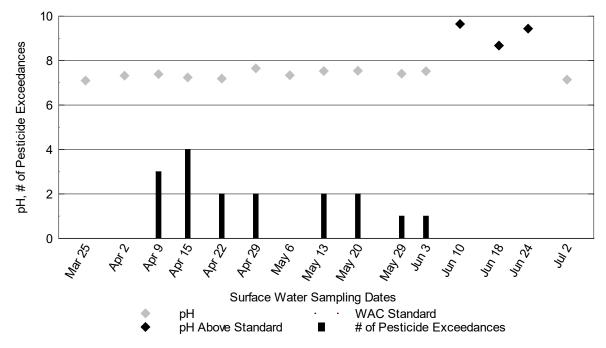


Figure 13 – Lower Big Ditch pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.10 to 9.65 with an average of 7.74. Of these measurements, three were greater than the pH standard of 8.5 (red-dashed line), (Figure 13). These pH exceedances also coincided with 7-DADMax temperature exceedances.

Lower Big Ditch is not only considered habitat for salmonid spawning, rearing and migration, but is also used as a corridor by migrating waterfowl (WAC, 2019). WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

## **Burnt Bridge Creek**

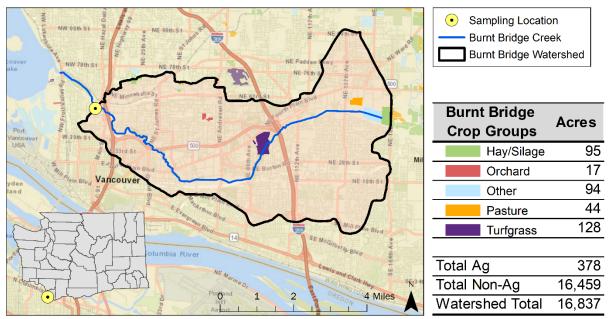


Figure 14 – Map of Burnt Bridge Creek and its drainage area with associated sampling location and crop groups identified

In 2017, WSDA started sampling the Burnt Bridge watershed in Clark County. The monitoring site selected on Burnt Bridge Creek is located approximately 10 meters downstream from the bridge crossing at Alki Road (latitude: 47.6614°, longitude: -122.6720°). Roughly 10 miles of Burnt Bridge Creek flows through the center of Vancouver, Washington making it the most urban site WSDA monitored. The watershed is highly impacted by residential, commercial, and industrial development as shown in Figure 14. The 'Other' crop group category includes mostly land used for conservation purposes.



Figure 15 – Burnt Bridge Creek upstream view

Burnt Bridge Creek flows into Vancouver Lake, which <sup>L</sup> drains into the Columbia River. Precipitation events

generally influence streamflow in this creek. In summer, inflow from groundwater, residential irrigation, and industrial discharge from a manufacturing facility near the headwaters maintain the creek's base flow. WDFW has documented winter steelhead and coho salmon within the Burnt Bridge watershed (WDFW, 2019). Staff frequently observe fish of unknown species at the site (Figure 15).

Below is a brief overview of the pesticide findings in Burnt Bridge Creek in 2019.

- WSDA tested for 159 unique pesticides in Burnt Bridge Creek.
- There were 242 total pesticide detections from seven different use categories: 27 types of herbicides, 8 insecticides, 7 fungicides, 8 degradates, 1 antimicrobial, 1 insect repellent and 1 synergist.
- Pesticides were detected at all 13 sampling events.
- Up to 25 pesticides were detected at the same time.
- Of the total pesticide detections, eight were above WSDA's assessment criteria (Table 9).
  - The three detections of 4,4'-DDD, one detection of 4,4'-DDE, and one detection of 4,4'-DDT were equal to or exceeding NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - $\circ~$  Out of five fipronil detections, one approached the invertebrate NOAEC (0.011  $\mu g/L).$
  - $_{\odot}$  Tefluthrin, detected once, exceeded the WSDA Endangered Species Level of Concern (0.0015  $\mu g/L).$
  - The single detection of trans-permethrin was greater than the invertebrate NOAEC (0.0014  $\mu$ g/L).

Diuron was the only Burnt Bridge watershed-specific POC. There were nine detections of this herbicide throughout the 2019 monitoring season; none of which exceeded assessment criteria. However, diuron is still considered a watershed POC because it was detected at this site in 2017 exceeding assessment criteria.

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 9). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month		Mar	Δ	pr	М	ay	Jı	ın		Jul		Δι	ıg	Sep
Day of the Month	Use*	27	10	24	8	22	5	19	1	16	31	12	28	11
2.4-D		21	10	24	0	22	5	19		10	51		20	
7	H	0.007	0.404	0.000	0.000	0.005	0.005	0.045	0.025	0.050	0.074	0.097	0.223	0.035
2,6-Dichlorobenzamide	D	0.207	0.194		0.223		0.205	0.245		0.256	0.271	0.201	0.223	0.171
4,4'-DDD	D			0.004		0.001			0.003					
4,4'-DDE	D			0.004		0.002								
4,4'-DDT	 			0.004						0.407				0 - 10
Aminomethylphosphonic acid (AMPA)	Н	0.075	0.069					0.098				0.302	3.020	3.540
Atrazine	H			0.005	0.006	0.004	0.004	0.005	0.006	0.007	0.007	0.004		
Azoxystrobin	F									0.000		0.001		
Boscalid	F									0.008				
Bromacil	H	0.006	0.006	0.007	0.008	0.004	0.005	800.0	0.007	0.010	0.010		0.006	
Carbendazim	F											0.003		0.003
Chlorothalonil	F	0.003												
Dichlobenil	Н		0.012			0.006				0.003			0.005	0.007
Dithiopyr	Н	0.008	0.006	0.005			0.003			0.007	0.006			
Diuron	Н		0.002		0.179	0.018	0.004	0.003	0.003	0.002		0.007		0.011
Ethoprop	1	0.008												
Fenarimol	F		0.007	0.004		0.005			0.003		0.002		0.005	
Fipronil	I	0.005	0.005			0.004			0.004			0.008		
Fipronil sulfide	D					0.003								
Fipronil sulfone	D					0.004								
Fludioxonil	F				0.006									
Glyphosate	Н	0.067	0.067	0.034	0.031	0.057	0.040	0.062	0.165	0.076	0.073	0.224	0.254	3.590
Hexazinone	Н					0.003								
Imazapyr	Н	0.006	0.016	0.018	0.018	0.016	0.022	0.026	0.025	0.026	0.027	0.023	0.021	0.022
Imidacloprid	I		0.003						0.004					
Isoxaben	Н		0.002									0.002		
Mecoprop (MCPP)	Н											0.028		
Methamidophos	D						0.001		0.001	0.001	0.001	0.002	0.002	0.003
Metolachlor	Н	0.006		0.004	0.003									0.009
N,N-Diethyl-m-toluamide (DEET)	lr		0.008					0.049		0.019		0.046		0.021
Norflurazon	н				0.006									
Oryzalin	н	0.020	0.012						0.012			0.019		
Pendimethalin	Н	0.007	0.012	0.008	0.007	0.008		0.005	0.006	0.012	0.011			0.007
Pentachloronitrobenzene (PCNB)	F		0.004											
Piperonyl butoxide (PBO)	Sy									0.013		0.009		
Prometon	н			0.003	0.004	0.002						0.006		
Prometryn	Н	0.010												
Propyzamide (Pronamide)	Н				0.004									
Pyridaben	1					0.004								
Pyriproxyfen	1	0.004		0.005										
Simazine	Н	0.030	0.025		0.007	0.009	0.006	0.005	0.007	0.007	0.006	0.017	0.012	0.096
Simetryn	н	0.01												
Sulfentrazone	Н		0.008		0.005				0.003	0.011		0.009		0.007
Sulfometuron-methyl	Н				0.015									
Tebuthiuron	H		0.009		0.007			0.006			0.005			
Tefluthrin	h i					0.002								
Terbacil	H	0.006	0.007	0.005	0.006				0.004					
Triazine DEA degradate	D				0.004			0.004		0.005	0.004	0.002	0.003	0.002
Triazine DIA degradate	D				0.003	2.300	0.000	0.00 1	0.002	5.500	5.50 T	0.002	2.000	0.002
Triclopyr acid	Н	0.004	0.00 1	0.016		0.037			0.036				0.061	
Triclosan	A	0.020	0.013	0.010		5.001	0.007		0.000			0.107	0.001	5.074
Trifluralin	H	0.020	0.010			0.003	0.001							
trans-Permethrin	1	0.004	0.006			0.000								
Total suspended solids (mg/L)	1	9	13	7	9	7	5	10	20	5	7	5	3	4
Streamflow (cubic ft/sec)		10.2	20.6	10.8	6.9	7.4	6.2	4.8	5.4	4.9	4.1	4.7	3.6	5.5
Precipitation (total in/week)†		0.36		0.22	0.9	0.97	0.2	4.0 0	0.36	4.9 0.37	4.1 0.16	4.7	3.0	
The "" signifies a sample or measure					-		-	-	0.30	0.37	0.10			

Table 9 – Burnt Bridge Creek pesticide calendar, µg/L

The "--" signifies a sample or measurement that was not collected or could not be analyzed.

Current-use exceedance

DDT/degradate exceedance

Detection

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist) † Washington State University AgWeatherNet station: WSU Vancouver RE, (latitude: 45.68°, longitude: -122.65°) When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at two of the 13 site visits (23%). Water quality at the Burnt Bridge Creek site is shown below (Figure 16).

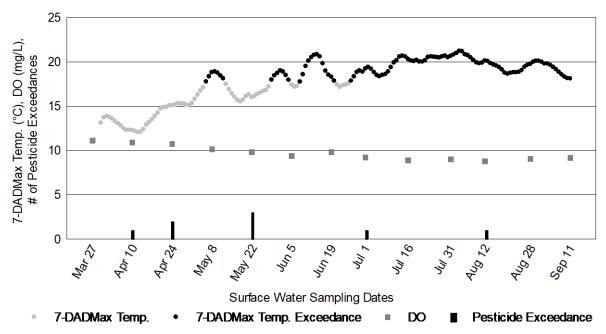


Figure 16 – Burnt Bridge Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.86 to 8.20 and averaging 8.04. All DO measurements also met the standard, ranging from 8.76 mg/L to 11.12 mg/L and averaging 9.68 mg/L. The 7-DADMax temperatures were greater than the 17.5°C temperature standard for 105 days of the sampling season, primarily from May 29 through the end of the season. Pesticide exceedances coincided with 7-DADMax temperature exceedances on July 1 and August 12.

Burnt Bridge Creek has been designated as a freshwater habitat for salmonid spawning, rearing, and migration (WAC, 2019). Historically, this urban creek has been one of the least healthy streams in Clark County, often exceeding total maximum daily loads for DO and temperature in certain reaches of the creek (Kardouni and Brock, 2008). In addition, the presence of invasive New Zealand mud snails has been confirmed in Burnt Bridge Creek.

Non-profits, volunteers, and government agencies such as the City of Vancouver have been actively implementing stream habitat and water quality improvement projects. This drainage will continue to be monitored because of its representative regional urban land use and consistent, yearly detections of POCs.

# **Indian Slough**

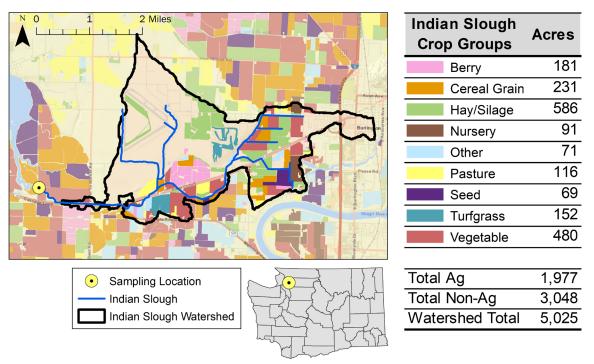


Figure 17 – Map of Indian Slough and its drainage area with associated sampling location and crop groups identified

In 2006, WSDA started sampling the Indian Slough watershed in Skagit County. The monitoring site is located just upstream from the tide gate at Bayview-Edison Road near Mt. Vernon (latitude: 48.4506°, longitude: -122.4650°) (Figure 17).

Indian Slough water drains directly into Puget Sound. Agricultural irrigation and precipitation events generally influence streamflow in the slough. WDFW has documented winter steelhead, Chinook salmon and coho salmon within the reach of slough that encompasses the Indian Slough site (WDFW, 2019). Staff frequently observed juvenile fish of unknown species at the site (Figure 18).

The Indian Slough watershed is a web of drainage ditches that pass through agricultural and industrial/residential areas. Indian Slough stretches approximately 6 miles from its sources to the



Figure 18 – Indian Slough upstream view

monitoring site. Within the watershed, the agricultural land use is predominantly potatoes, grass hay, field corn, blueberries and cucumber. The 'Other' crop group category consists mostly of fallow fields and assorted low-acreage crops (Figure 17). Indian Slough is another site where the presence of invasive New Zealand mud snails has been confirmed.

Staff only sampled this site when the tide gate was open and the water flowed from Indian Slough into Puget Sound to avoid contamination with saltwater or pooling backwater. Both of those conditions were avoided because they are not representative of conditions throughout the watershed.

Below is a brief overview of the pesticide findings in Indian Slough in 2019.

- WSDA tested for 159 unique pesticides in Indian Slough.
- There were 605 total pesticide detections from 7 different use categories: 33 types of herbicides, 13 insecticides, 8 fungicides, 11 degradates, 1 antimicrobial, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 24 sampling events.
- Up to 39 pesticides were detected at the same time.
- Of the total pesticide detections, 22 were above WSDA's assessment criteria (Table 10).
  - The three detections of 4,4'-DDD and three detections of 4,4'-DDE were equal to or exceeding NRWQC and WAC chronic criteria (both 0.001  $\mu$ g/L).
  - $_{\odot}$  Bifenthrin, detected once, exceeded the WSDA Endangered Species Level of Concern (0.00375  $\mu g/L)$  and invertebrate NOAEC (0.0013  $\mu g/L)$ .
  - Of the four tetramethrin detections, the detection on September 10 exceeded the WSDA Endangered Species Level of Concern (0.0925 μg/L).

The Indian Slough watershed POCs were diuron, fipronil, and imidacloprid. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Diuron was detected 23 times. The detection on June 3 approached the plant EC<sub>50</sub> (2.4 μg/L).
- Of the four fipronil detections, two approached the invertebrate NOAEC (0.011 µg/L).
- Out of 14 detections of imidacloprid, 11 detections approached or exceeded the invertebrate NOAEC (0.01 μg/L).

The Indian Slough monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 10). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month		Mar		Α	pr			M	ay			Jı	ın				Jul				A	ug		S	эр
	Jse*	25	9	15	22	29	6	13	20	29	3	10	18	24	2	8	17	22	30	5	14	19	27	3	10
	D			0.007				0.003			0.098	0.059			0.029		0.007	0.008							0.030
2,4-D H	H	0.059			0.055				0.062	0.214	0.293	0.309	0.032		0.026										2.550
2,6-Dichlorobenzamide		0.117	0.113	0.171	0.171		0.128	0.110		0.098	0.132	0.259	0.133	0.170	0.154	0.208	0.185	0.153	0.146	0.149	0.102	0.104	0.086	0.084	0.060
4,4'-DDD E	-					0.003		0.004	0.001																
4,4'-DDE [	_					0.002			0.002			0.003										<u> </u>			
4-Nitrophenol D	2								$\geq$			0.063										<b> </b>			
Acephate I											0.006						0.004					<b> </b>			
Acetamiprid		0.025	0.000		0.050		0.020		0.054		0.050		0.000		0.445		0.001		0.405		0 4 4 4	<u> </u>	1 700		2 4 2 0
Aminomethylphosphonic acid (AMPA) H Atrazine		0.035	0.039		0.050		0.038		0.054		0.058		0.068		0.115		0.073	 0.005	0.105		0.144		1.700		3.120
Azoxystrobin F		0.087	0 0 20	0.025	0 176	0.032	0 1 3 0	0.062	0.011	0.016	0.013	0.008	0.006	0.005	0.004		0.004		0.003		0.006	0.006	0.006	0.004	0.003
Bifenthrin	1	0.007	0.023	0.0020	0.170	0.002	0.150	0.002	0.011	0.010	0.015	0.000	0.000	0.000	0.004		0.004	0.005	0.005	0.004	0.000	0.000	0.000	0.004	0.000
Boscalid	=	0.008	0.008	0.012	0.010	0.008			0.019		0.006	0.009	0.007	0.044	0.010	0.012	0.056	0.031	0.024	0.018	0.030	0.013	0.009	0.007	0.006
Bromacil	н							0.026		0.110					0.064										
Carbendazim F					0.011																				0.027
Chlorantraniliprole I																						0.012			
Chlorpropham H	Н			0.003	0.005	0.003	0.007	0.035	0.005		0.003														
Chlorsulfuron H	Н				0.019																				
Clothianidin I					0.005							0.006													
	H	0.042	0.059				0.086		0.109	0.053	0.083			0.090	0.046	0.088	0.045	0.035	0.034	0.035	0.030	0.030			
Diazinon I				0.004	0.010	0.015	0.004	0.004				0.041	0.004									<u> </u>			0.047
Dicamba acid			0.000	0.001	0.040		<u> </u>		0.000	0.000	<u> </u>	0.041	0.000					<u> </u>	<u> </u>		<u> </u>	<u> </u>			0.018
Dichlobenil H	H F		0.006	0.024		0.005	0.015	0.000	0.003	0.003		0.043	0.003									<u> </u>			0.006
Bironocondeoro	<u>-</u> Н			0.000	0.024	0.005	0.015	0.008	-			0.002	0.005									<u> </u>			
		0.011	0.000			0.014	0.010	0.000	0.040	0.014	1 200		0 222	0.000	0.110	0.044	0.005	0.000	0.007	0.047	0.011	0.010	0.000		0.440
Diuron H Eptam H		0.001			0.020	0.011					0.004		0.333	0.099	0.110	0.041	0.025	0.020	0.027	0.017	0.011	0.010	0.009		0.119
Fenarimol F		0.003	0.004				0.035	0.005	0.019	0.010	0.004	0.004			0.007		0.002					<u> </u>			
Fipronil				0.006	0.006	0.005						0.004													
Fipronil sulfide	D			0.000	0.000	0.000			0.003			0.004													
Fipronil sulfone	_						0.005	0.005	0.004																
Fludioxonil		0.028	0.015	0.018	0.070	0.018				0.011	0.009	0.006	0.011	0.007	0.010	0.011	0.014	0.014	0.013	0.013	0.011	0.007	0.013	0.009	
	Н																0.006								
Glyphosate H	Н	0.034	0.043		0.048		0.032		0.038		0.039		0.043		0.046		0.034		0.063		0.055		0.250		7.140
Hexazinone H	H	0.019	0.020	0.014	0.020	0.024	0.020		0.020	0.016	0.023	0.021	0.021	0.016	0.017	0.019	0.024	0.025	0.022	0.015	0.010	0.010	0.010	0.010	0.006
Imazapic H	H			0.004								0.017													
	H														0.031	0.012		0.016	0.015	0.007	0.005	0.005	0.003	0.003	0.475
Imidacloprid I			0.004				0.009	0.013					0.011	0.008	0.004		0.008								
Indaziflam H					0.006	0.002			0.002	0.008	0.002		0.002					0.002				<u> </u>			0.08
Isoxaben H				0.002								0.004										<b> </b>			
	H								0.227	0.037	0.283	0.000					0.040		0.040			<b> </b>			
Malathion I Metalaxyl F	_									0.040		0.006					0.013		0.010			<u> </u>			
Metalaxyl F Methamidophos E									0.001	0.013	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.004	0.006	0.000	0.007	0.000
Methoxyfenozide				0.004	0.004				0.001	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.002	0.002	0.003	0.003	0.004	0.006	0.006	0.007	0.000
Metolachlor H	4	0 000	0.006			0 000	0.010	0.005	0.01/	0.013	0.017		0.014	0.006	0.007		0.006	0.006	0.005	0.005		<u> </u>			0.005
Metribuzin		0.003	0.000	0.007		0.003	0.010	0.000	0.006	0.015	0.005	0.021	0.005	0.000	0.007		0.000	0.000	0.005	0.000		<u> </u>			0.000
Metsulfuron-methyl				0.007					3.000		0.000		3.000												0.047
N,N-Diethyl-m-toluamide (DEET)	lr		0.005		0.000																			0.006	
	H	0.006			0.005		0.007		0.005					0.009		0.010									
	H											0.005													
	Wp			0.025	0.023																				
Phosmet I			0.011																						
	Н				0.005							0.003								0.006					0.004
Propiconazole F				0.162	0.081	0.030				0.091					0.098							<u> </u>			0.486
Simazine H			0.005		0.011	0.011		0.008			0.006		0.154	0.028	0.020	0.021	0.000	0.006	0.006	0.0.1	0.011	0.00	0.000	0.000	0.00
Sulfentrazone			0.012	0.011		0.014		0.018	0.012						0.011	0.025	0.022	0.018	0.024	0.011	0.014	0.008	0.008		
	H	0.044	0.057		0.013	0.001	0.002	0.000	0.000		0.003				0.003	0.070	0.077	0.001	0.007	0.077	0.040	0.040	0.000		0.086
	H	0.044	0.057	0.039	0.050	0.084	0.068	0.080	0.066	0.051	0.076	0.058	0.066	0.065	0.068	0.076	0.077	0.081	0.087	0.077	0.046	0.049	0.039	0.035	
Terbacil H Tetrahydrophthalimide (THPI)		0.014	0.013	0.008	0.011		0.016				0.014	0.013		0.018		0.022	0.017	0.014	0.014	0.015	0.008	0.008	0.007	0.009	
Tetramethrin				-		0.008	0.003	0.000		0.016		0.072		0.003								<u> </u>			0.102
Thiamethoxam		0.010	0.010	0.017	0.018	0.01/	0.018	0.013				0.020			0.009	0.012	0.011	0.008	0.008	0.003	0.002	0.002			0.102
Triazine DIA degradate	D	0.010	3.010		0.004	0.014	0.010	0.010	0.012	3.510	0.017	0.020			0.003		0.011	0.000	0.000	0.000	0.002	3.002			
Triazine HA degradate		0.009	0.007			0.011	0.010	0.011	0.012	0.012	0.010	0.011			0.013		0.010	0.012	0.009	0.010	0.006	0.006	0.008	0.006	0.005
	H	0.000	5.501	0.011	0.010	0.011	0.010	5.511			0.183			2.511	0.038	2.000	0.010	0.012	0.000	0.010	0.000	5.500	0.000	5.505	2.380
	A							0.008	0.042	2.100	0.100	0.100	0.015		5.500										2.500
Triclosan	H					0.004	0.004		0.003																
					<u> </u>						+		<u> </u>			~	-	<u> </u>	<u> </u>		1				0
		13	11	8	8	8	11	12	8	9	8	6	6	7	6	5	7	7	6	14	9	6	10	15	8
Trifluralin H		13 47.4	11 61.6		8 57.3			12 12.5				6	6	7	9.9	5		7	6	14 2.8	9 5.4	6 5.9	10 4.1	15 0.7	8 34.2
Trifluralin F Total suspended solids (mg/L)				83.7		44.3	24.5									-					5.4	5.9		0.7	34.2

#### Table 10 – Indian Slough pesticide calendar, µg/L

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Wp: Wood preservative)

Current-use exceedance

<sup>+</sup> Washington State University AgWeatherNet station: WSU Mt Vernon, (latitude: 48.44°, longitude: -122.39°)

DDT/degradate exceedance

Detection

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at seven of the 24 site visits (29%). Water quality at the Indian Slough site is shown below (Figure 19).

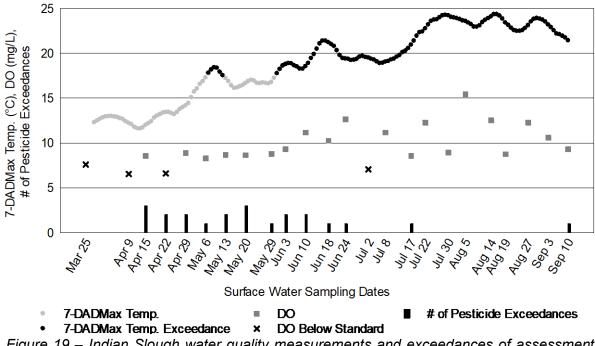


Figure 19 – Indian Slough water quality measurements and exceedances of assessment criteria

The pH measurements ranged from 6.83 to 8.63 and averaged 7.50. Of these measurements, one exceeded the state pH standard of 8.5 on August 5. DO measurements ranged from 6.54 mg/L to 15.41 mg/L with an average of 9.70 mg/L. Less than half (17%) of the measurements did not meet the DO standard in that four measurements were less than 8 mg/L. On April 22, a DO measurement that did not meet the standard coincided with two pesticide exceedances. The 7-DADMax temperatures were greater than the 17.5°C temperature standard for 109 days of the sampling season, primarily from May 31 through the end of the season. Pesticide exceedances overlapped with 7-DADMax temperature exceedances at six site visits.

Indian Slough is not only considered habitat for salmonid spawning, rearing and migration, but is also used as a corridor by migrating waterfowl. WSDA will continue to monitor this drainage because of its representative regional land use.

## **Woodland Creek**

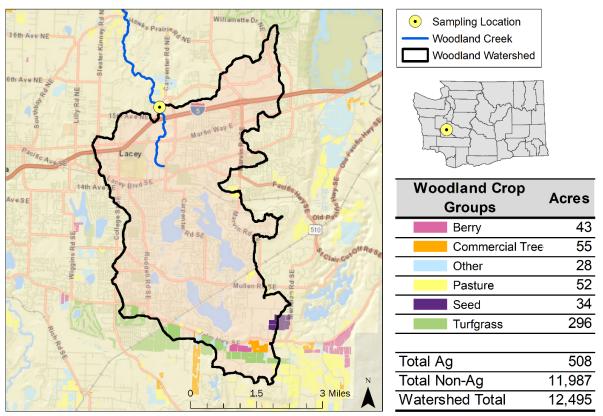


Figure 20 – Map of Woodland Creek and its drainage area with associated sampling location and crop groups identified

In 2017, WSDA started sampling the Woodland watershed in Thurston County. Most of Woodland Creek, where the Woodland monitoring site is located, flows directly through Lacey. The watershed is undergoing rapid urban development from prairie and wooded lands. The Woodland monitoring site is located just downstream of the open-bottom culvert under Draham Street NE (latitude: 47.0610°, longitude: -122.8044°). Within the Woodland drainage area, the land use is predominantly residential with a few ornamental nurseries, sod farms, golf courses, pastures, and low-acreage crops (Figure 20).



Figure 21 – Woodland Creek downstream view

Woodland Creek drains into Henderson Inlet, which is known for its shellfish harvesting beds. WDFW has documented winter steelhead, fall Chinook salmon, coho salmon, and chum salmon within the reach of creek that encompasses the monitoring site (WDFW, 2019). Staff observed adult salmon at the site during spawning season in 2017 (Figure 21).

The source of Woodland Creek is approximately 3 miles south of the monitoring site along a chain of lakes: Hicks Lake, Pattison Lake, Long Lake and Lake Lois. Precipitation events,

runoff, and residential irrigation generally influence streamflow in the creek. The city installed a storm water retention and treatment facility near the Saint Martin's University campus that controls some of the streamflow upstream of the monitoring site.

Below is a brief overview of pesticide findings in Woodland Creek in 2019.

- WSDA tested for 159 unique pesticides in Woodland Creek.
- There were 44 total pesticide detections from five different use categories: 10 types of herbicides, 5 insecticides, 3 fungicides, 1 degradates, and 1 antimicrobial.
- Pesticides were detected at all 13 sampling events.
- Up to nine pesticides were detected at the same time.
- Of the total pesticide detections, one was above WSDA's assessment criteria (Table 11).
  - Tefluthrin, detected once, approached the fish NOAEC (0.004 μg/L) and exceeded the WSDA Endangered Species Level of Concern (0.0015 μg/L).
- There were no watershed-specific POCs for the Woodland site and no statewide WSDA POCs detected.

The Woodland Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 11). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month			Apr		Μ	ay	Ju	ın	J	ul	Αι	Jg	Se	эр
Day of the Month	Use*	2	16	30	13	28	10	25	9	23	5	20	4	16
2,6-Dichlorobenzamide	D	0.049	0.069	0.062	0.050	0.040	0.046	0.047	0.052	0.057	0.053	0.035	0.028	0.026
Acetamiprid	I					0.002								
Alachlor	Н				0.004									
Aminomethylphosphonic acid (AMPA)	Н			0.006	0.007									0.148
Atrazine	Н				0.005									
Chlorothalonil	F				0.006									
Chlorpropham	Н	0.002												
Dinotefuran	I					0.002								
Fenarimol	F		0.005	0.003			0.012							
Glyphosate	Н			0.005	0.005									
Hexazinone	Н	0.003	0.006	0.005										
Imazapyr	Н		0.002		0.002	0.003		0.002						
Metolachlor	Н				0.004									
Metsulfuron-methyl	Н					0.004								
Propiconazole	F								0.007					
Sulfometuron-methyl	Н					0.002								
Tefluthrin	1									0.003				
Thiamethoxam	1					0.002								
Total Fluvalinate	I									0.006				
Triclosan	А		0.007		0.022		0.019							
Total suspended solids (mg/L)		3	3	3	2	2	2	2	2	2	2	2		1
Streamflow (cubic ft/sec)		15.2	17.4	15.6	12.0	10.0	8.5	8.2	7.5	7.4	6.6	6.5	6.1	6.2
Precipitation (total in/week)†		0.27	1.04	0	0	0.31	0.14	0	0.15	0.25	0.20	0	0.18	1.51
	Curr	ent-us	e exc	eedan	ce		De	tectior	ı					

Table 11 – Woodland Creek pesticide calendar, µg/L

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide)

<sup>†</sup> Washington State University AgWeatherNet station: Olympia East, (latitude: 46.95°, longitude: -122.84°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. However, no pesticide exceedances coincided with water quality measurements that did not meet state standards at this site. Water quality at the Woodland Creek site is shown below (Figure 22).

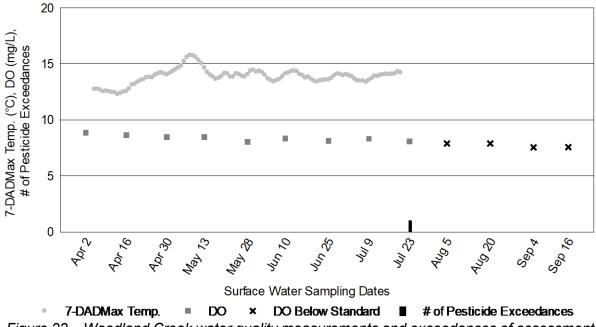


Figure 22 – Woodland Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.05 to 7.20 and averaging 7.13. DO measurements ranged from 7.56 mg/L to 8.87 mg/L and averaged 8.18 mg/L. Less than half (31%) of the DO measurements did not meet the standard in that four measurements were less than 8 mg/L. All 7-DADMax temperatures met state water quality standards up until at least July 21. The temperature data logger was lost from July 23 through September 18; therefore, 7-DADMax temperatures could not be calculated after July 21.

Woodland Creek provides habitat for salmonid spawning, rearing and migration. Many local, city, county, and state partners have been actively restoring and managing the urban stream with success. WSDA monitored the site through 2019, at which point it was dropped from the program due to lack of exceedances.

## **Brender Creek**

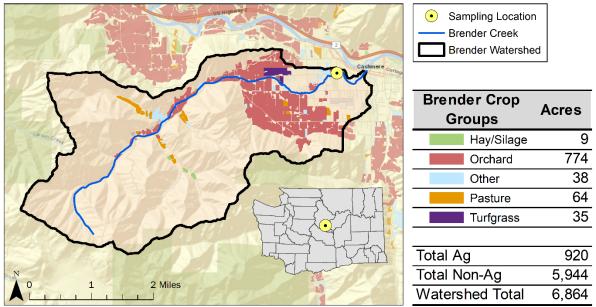


Figure 23 – Map of Brender Creek and its drainage area with associated sampling location and crop groups identified

In 2007, WSDA started sampling the Brender Creek watershed in Chelan County. This watershed is representative of agricultural practices used in tree fruit cultivation in Central Washington. The legacy pesticide, DDT, was widely used in orchard production until its banning in the U.S. in 1972. WSDA still detects it in the Brender Creek watershed due to its strong soil binding abilities, combined with soil erosion into the adjacent creek.

The Brender site is located in Cashmere, on the upstream side of the culvert at Evergreen Drive (latitude: 47.5211°, longitude: - 120.4863°) (Figure 23, Figure 24). Brender Creek is approximately 6.8 miles long and drains into the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence



Figure 24 – Brender Creek upstream view

streamflow in the creek. WDFW has documented spring Chinook salmon and summer steelhead within the lower reaches of the creek (WDFW, 2019).

The watershed terrain in the upper three-quarters is mountainous with a transition into lowlying, flat terrain in the bottom quarter where tree fruit crops are plentiful. The agricultural land use is predominately pears, apples, pasture, and cherries. The 'Other' crop group category mostly consists of fallow fields (Figure 23).

Below is a brief overview of the pesticide findings in Brender Creek in 2019.

- WSDA tested for 145 unique pesticides in Brender Creek.
  - This was 14 fewer pesticides analyzed for than many of the other sites. They were removed due to few detections at this site in recent years.
- Pesticides were detected at all 23 sampling events.
- There were 325 total pesticide detections from seven different use categories: 13 types of herbicides, 16 insecticides, 2 fungicides, 6 degradates, 1 antimicrobial, 1 insect repellent, and 1 synergist.
- Up to 19 pesticides were detected at the same time.
- Of the total pesticide detections, 78 were above WSDA's assessment criteria (Table 12).
  - DDT and its degradates accounted for 64 of these exceedances. The 21 detections of 4,4'-DDD, 21 detections of 4,4'-DDE, and 22 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - $\circ$  Tefluthrin, detected once, approached the fish NOAEC (0.004 µg/L) and exceeded the WSDA Endangered Species Level of Concern (0.0015 µg/L).
  - Both detections of fluvalinate exceeded the WSDA Endangered Species Level of Concern (0.009 μg/L).

The Brender Creek watershed POCs were chlorpyrifos, imidacloprid, malathion, and pyridaben. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Of the 19 detections of chlorpyrifos, six exceeded assessment criteria.
  - $_{\odot}$  Of these six, five exceeded the NRWQC and state WAC chronic criteria (both 0.041  $\mu g/L)$  and invertebrate NOAEC (0.04  $\mu g/L).$
  - The detections on April 10 and April 30 also exceeded the NRWQC and state WAC acute criteria (both 0.083  $\mu$ g/L) and invertebrate LC<sub>50</sub> (0.1  $\mu$ g/L).
  - $_{\odot}$  The May 14 detection of chlorpyrifos approached the invertebrate NOAEC (0.04  $\mu g/L).$
- Out of six imidacloprid detections, one detection approached the invertebrate NOAEC and another detection exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the nine malathion detections, three exceeded criteria.
  - ο The detection on April 10 exceeded the invertebrate NOAEC (0.06  $\mu$ g/L), the invertebrate LC<sub>50</sub> (0.098  $\mu$ g/L), WSDA Endangered Species Level of Concern (0.103  $\mu$ g/L), and the NRWQC chronic criterion (0.1  $\mu$ g/L). This was the highest concentration of malathion detected in 2019.
  - $_{\odot}$  The April 2 and April 30 detections approached the invertebrate NOAEC (0.06  $\mu g/L).$
- The single detection of pyridaben in 2019 did not exceed any assessment criteria, but this pesticide was still classified as a watershed POC because of 2017 and 2018 detections that did exceed criteria.

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 12). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month				Apr				M	ay			Ju	un				Jul				Α	ug		Sep
Day of the Month	Use*	2	10	16	23	30	7	14	21	29	4	11	18	25	2	8	16	23	30	6	13	20	27	3
1-(3,4-Dichlorophenyl)-3-methylurea	D									0.006					0.005									
2,6-Dichlorobenzamide	D	0.010	0.012	0.015	0.016	0.016	0.015	0.010	0.008	0.008	0.010	0.017	0.015	0.010	0.010	0.011	0.015	0.021	0.016	0.022	0.011		0.012	0.009
4,4'-DDD	D	0.004	0.005	0.005	0.005	0.007	0.004	0.007	0.004	0.004	0.004	0.004	0.005		0.005	0.006	0.008	0.007	0.005	0.005	0.008		0.005	0.004
4,4'-DDE	D	0.013	0.010	0.010	0.007	0.016		0.028	0.021	0.021	0.013	0.012	0.013	0.013	0.019	0.022	0.028	0.022	0.010	0.012	0.030		0.022	0.015
4,4'-DDT	I	0.008	0.006	0.007	0.005	0.006	0.008	0.014	0.010	0.011	0.007	0.007	0.009	0.009	0.010	0.013	0.017	0.013	0.010	0.005	0.016		0.009	0.007
Acetamiprid	1				0.009	0.009	0.006	0.006	0.004	0.002	0.005	0.004	0.002					0.001				0.002		[
Aminomethylphosphonic acid (AMPA	)H						0.003				0.059		0.012		0.015		0.006						0.104	
Atrazine	Н																					0.009		
Boscalid	F		0.006	0.006		0.005											0.008	0.011						
Carbendazim	F		0.002	0.001									0.044							0.003		0.003	0.007	0.005
Chlorantraniliprole	1										0.026	0.007		0.006		0.007								
Chlorpyrifos	I	0.004	0.203	0.060	0.079	0.111	0.048	0.032	0.019		0.011	0.009	0.010	0.006	0.006	0.006	0.006	0.006	0.005	0.005	0.005			(
Clothianidin	1		0.003	0.004	0.004	0.002	0.003	0.002				0.007	0.003	0.003	0.003		0.003	0.004		0.005			0.003	0.003
Diazinon	I	0.006	0.005		0.008	0.003										0.003								
Diuron	Н									0.007		0.002			0.005									
Etoxazole	1									0.007			0.005		0.011	0.008	0.007	0.004		0.004	0.005			
Fipronil	1		0.005																					
Glyphosate	Н						0.004				0.020		0.008		0.049		0.004				0.022			
Hexazinone	Н					0.004	0.005		0.004															
Imazapyr	Н		0.003			0.008	0.007	0.007																
Imidacloprid	1					0.004									0.002					0.015	0.009	0.003	0.003	
Malaoxon	D		0.005	< 0.001	0.001	0.002	< 0.001																	1
Malathion	1	0.038					0.009	0.009	0.004					0.005										[
N,N-Diethyl-m-toluamide (DEET)	Ir																	0.047		0.015	0.021	0.005		
Norflurazon	Н	0.009	0.010	0.011	0.013	0.010	0.012	0.011	0.008	0.010	0.010	0.017	0.011	0.015	0.015	0.016	0.024	0.025	0.018	0.027	0.014		0.009	0.008
Oryzalin	Н		0.024				0.006		0.020	0.007	0.012		0.009		0.004		0.005	0.009		0.006				
Pendimethalin	Н	0.005	0.006	0.006	0.006	0.008	0.006	0.007	0.005		0.003	0.003	0.005	0.005			0.014	0.011	0.011					
Piperonyl butoxide (PBO)	Sy	0.017						0.679	0.264	0.103	0.023	0.013	0.019	0.020	0.016	0.013	0.019	0.017	0.013	0.011	0.006		0.005	0.006
Prometon	Н				0.004		0.004																	
Pyridaben	1								0.004															
Pyriproxyfen	1					0.004			0.005															
Simazine	Н							0.011	0.004		0.007	0.008	0.017		0.005		0.007	0.007	0.006	0.007				0.005
Spirotetramat	1												0.071											
Sulfentrazone	Н		0.007		0.006	0.005	0.005	0.007		0.006		0.007		0.005			0.012			0.005	0.006	0.007		
Tefluthrin	I								0.002															
Thiamethoxam	I					0.005	0.035	0.003	0.004		0.002	0.004	0.045	0.003	0.005	0.005	0.006	0.008		0.007		0.003	0.002	
Total Fluvalinate	I								0.019					0.012										
Triazine DIA degradate	D												0.007											1
Triclosan	А			0.006													0.013							
Trifluralin	Н								0.003															(
Total suspended solids (mg/L)		19	14	20	9	40	16	61	30	37	19	12	24	21	40	39	52	35	13	21	71	35	52	24
Streamflow (cubic ft/sec)		1.5	0.9	1.3	1.1	3.0	1.7	4.4	7.1	6.1	2.0	1.6	3.4	2.1	4.3	4.5	4.1	2.5	1.9	1.3	5.5	3.9	3.8	4.4
Precipitation (total in/week)†		0	0.48	0.10	0	0.01	0	0	0.47	0.54	0.01	0.06	0	0	0.46	0.04	0.07	0	0.15	0	0.50	0.0	0.0	0
The "" signifies a sample that was no		-			. ~		. <u> </u>	~					~					. ~		. <u> </u>		, <u> </u>	<u> </u>	

#### Table 12 – Brender Creek pesticide calendar, µg/L

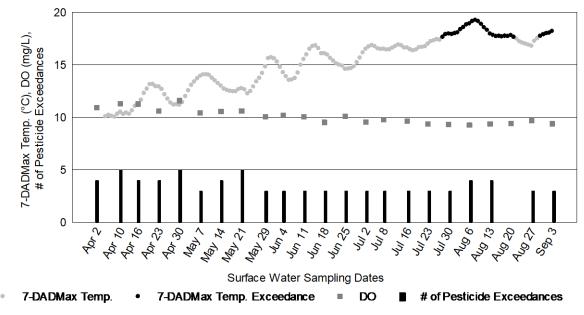
The "--" signifies a sample that was not collected.

Current-use exceedance

DDT/degradate exceedance

Detection

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist) † Washington State University AgWeatherNet station: N. Cashmere, (latitude: 47.51°, longitude: -120.43°) When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at four of the 23 site visits (17%). Water quality at the Brender site is shown below (Figure 25).



*Figure 25 – Brender Creek water quality measurements and exceedances of assessment criteria* 

All pH measurements met state standards, ranging from 7.89 to 8.42 with an average of 8.07. All DO measurements also met state standards, ranging from 9.26 mg/L to 11.59 mg/L with an average of 10.09 mg/L. The 7-DADMax temperatures exceeded the 17.5°C temperature standard for 30 days of the sampling season from July 28 through August 21 and August 30 through the rest of the season. Pesticide exceedances coincided with 7-DADMax temperature exceedances on July 30, August 6, August 13, and September 3.

The lower portion of Brender Creek has been designated as a freshwater body that provides habitat for salmonids spawning, rearing, and migration by the WAC (WAC, 2019). Staff observed juvenile fish of unknown species. WSDA will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

## Lower Crab Creek

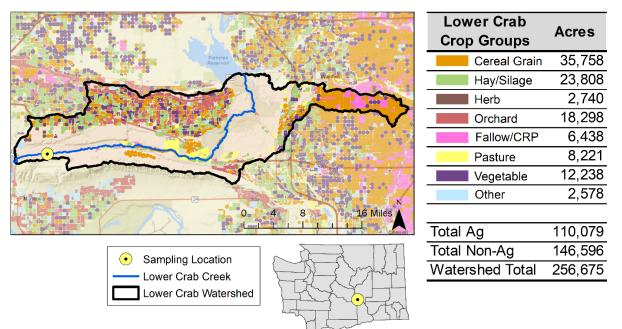


Figure 26 – Map of Lower Crab Creek and its drainage area with associated sampling location and crop groups identified

In 2017, WSDA started sampling the Lower Crab watershed in Grant County. WSDA selected the watershed for its diverse agricultural land uses and large watershed drainage area. The Lower Crab Creek monitoring site is located just upstream of the bridge crossing the Lower Crab Creek Road SW (latitude: 46.8298°, longitude: -119.8309°) (Figure 26).

The Columbia Basin Irrigation Project created a series of reservoirs and irrigation canals that provide Lower Crab Creek with perennial sources of water. Lower Crab Creek is predominately groundwater fed just below Potholes Reservoir and down through the Columbia National Wildlife Refuge. Below the refuge, irrigation inflows, runoff, and seeps resupply water to the creek before it drains into the Columbia River. WDFW has documented summer steelhead and fall Chinook salmon within the reach of the creek that encompasses the monitoring site (WDFW, 2019) downstream view (Figure 27). Data suggests the fall Chinook salmon in the



Figure 27 – Lower Crab Creek

creek are genetically diverse from hatchery salmon in the area (Small et al., 2011).

The watershed that contains the approximately 48-mile-long Lower Crab Creek has desertlike habitat with a deeply incised stream channel from historically large flows. The irrigation projects in the region have allowed the sagebrush steppe environment to become agriculturally productive. Within the Lower Crab Creek drainage area, land use is predominantly wheat, alfalfa hay, apples, field corn, and ranch grazing. The 'Other' crop group category is an assortment of vineyards, seed crops, turf grass, melon, and berry fields (Figure 26).

Below is a brief overview of pesticide findings in Lower Crab Creek in 2019.

- WSDA tested for 159 unique pesticides in Lower Crab Creek.
- There were 328 total pesticide detections from six different use categories: 22 types of herbicides, 15 insecticides, 4 fungicides, 10 degradates, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 14 sampling events (March 26 and April 2 events combined).
- Up to 34 pesticides were detected at the same time.
- Of the total pesticide detections, four were above WSDA's assessment criteria (Table 13).
  - The single detection of 4,4'-DDD and single detection of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - $_{\odot}$  Tefluthrin, detected once, approached the fish NOAEC (0.004  $\mu g/L$ ) and exceeded the WSDA Endangered Species Level of Concern (0.0015  $\mu g/L$ ).
  - The single fluvalinate detetection exceeded the WSDA Endangered Species Level of Concern (0.009 μg/L).
- Malathion was the only 2019 watershed-specific POC at this site. The two detections of malathion did not exceed any assessment criteria in 2019, but this pesticide was still considered a watershed POC because of detections in 2017 that did exceed criteria. None of the nine detections of chlorpyrifos, a statewide POC; exceeded WSDA assessment criteria.

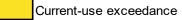
The Lower Crab Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 13). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Staff sampled for only three analytes (glyphosate, AMPA, and glufosinate-ammonium) on April 2 that weren't sampled March 26. In this report, these two sampling dates were combined into one sampling event for summarized sampling event analysis. Also, a planned June 4 sample collection was postponed to June 11 due to wildfire.

Month		Mar		Apr		M	av	Jı	In		Jul		Δ	ug	S	ер
Day of the Month	Use*	26	2	9	23	7	21	11	18	2	16	30	13	27	10	24
	-			-							-		-	21	10	24
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.01		0.03	0.02	0.03	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.040	0 4 4 5	0.045
2,4-D	Н	0.070		0.007								0.160		0.246		
2,6-Dichlorobenzamide	D	0.078		0.007		0.007		0.005	0.007	0.006	0.007	0.007	0.006	0.005	0.004	$\diamond$
4,4'-DDD	D						0.001									$\diamond$
4,4'-DDE	D						0.002			0.000			0.000	0.007		$\sim$
Acephate	1						0.004			0.003			0.006	0.007		
Acetamiprid				0.000			0.001								0.042	0.040
Acetochlor ESA	D			0.033	0.040	0.040	0.031	0.000	0.070	0.040	0 4 4 2	0.044	0.000	0.400		0.046
Aminomethylphosphonic acid (AMPA)	Н											0.641				
Atrazine	H F			0.010	0.009	0.013			0.001	0.015	0.014	0.015	0.014	0.011	0.008	$\sim$
Azoxystrobin	F			0.012	0.012					0.012	0.027	0.029	0 1 1 2	0.026	0.019	
Boscalid					0.012	0.010						0.028				
Bromacil	H			0.019	0.019			0.015	0.019	0.014	0.019	0.015	0.015	0.011	0.010	$\sim$
Carbaryl						0.002	0.007							0.000		
Carbendazim	F										0.007			0.003		
Chlorantraniliprole				0.004							0.007					
Chlorpropham	Н			0.004	0.040	0.000	0.007	0.004	0.005	0.004	0.004	0.004				$\Leftrightarrow$
Chlorpyrifos	1			-	0.013	0.008	-	0.004		-			0.000		0.005	
Clothianidin	1	0.407		0.003	0.050	0.407	0.002	0.040		0.004			0.006	0.444		0.006
Dacthal (DCPA)	Н	0.197				0.197	0.228	0.243	0.215	0.054		0.215	0.046	0.144	0.053	0.136
Diazinon	1	0.000		0.004	0.003		0.044	0.004	0.054	0.050		0.005	0.000	0.005	0.004	
Dicamba acid	Н	0.009					0.044	0.061	0.054		0.017	0.012	0.032	0.035	0.031	0.010
Dimethoate	1	0.005		0.400	0.070	0.074	0.040	0.000	0.040	0.005	0.000	0.000	0.014	0.004	0.000	
Diuron	Н	0.035		0.180	0.076					0.017	0.008	0.009	0.011	0.004	0.003	0.003
Eptam	Н			0.005	0.045		0.029			0.407	0.000	0.040	4 000	4 740	0.700	
Glyphosate	Н		0.077									3.810				
Hexazinone	Н	0.005				0.043								0.009		
Imazapyr	Н	0.035		0.041	0.030	0.019	0.020			0.016	0.023	0.011	0.015	0.015	0.013	0.020
Malathion						0.007		0.002	0.007							$\Leftrightarrow$
Metalaxyl	F			0.004	0.004	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.004	
Methamidophos	D			0.001	0.001	0.001	0.002					0.003			0.004	0.003
Methomyl								0.002	0.003		0.040	0.012	0.003	0.001		
Methomyl oxime	D						0.004	0.004		0.01		0.01				
Methoxyfenozide	1			0.004	0.005	0.000	0.004		0.040	0.044	0.040	0.000	0.000			
Metolachlor	Н							0.022	0.018	0.011		0.008			0.005	$\Leftrightarrow$
Metribuzin	Н		-	0.005		0.004	0.004	0.040	0.005	0.000	0.006	0.005	0.008	0.004	0.005	$\sim$
Metsulfuron-methyl	H			0.000			0.023	0.010	0.035	0.022						
N,N-Diethyl-m-toluamide (DEET) Norflurazon	lr			0.006	0.005											$\diamond$
	Н		-					0.040	0.000	0.000	0.000	0.010	0.004	0.011		$\frown$
Oxamyl oxime	D			0.000		0.007	0.000					0.018	0.021	0.011		
Pendimethalin Piperonyl butoxide (PBO)	H			0.006	0.006	0.007	0.006	0.005	0.004	0.005	0.012					$\diamond$
	Sy				0.004	0.004				0.009						$\bigcirc$
Prometon	Н				0.004	0.004	0.007									$\bigcirc$
Pyridaben	1			0.005			0.007		0.005	0.005	0.000	0.000				$\bigcirc$
Simazine	Н			0.005			0.004		0.005	0.005	0.006	0.006				
Sodium bentazon Sulfentrazone	Н			0.000	0.006	0.000		0.006					0.006		0.005	0.043
	H			0.000	0.000	0.000	0.000	0.000					0.000		0.005	$\bowtie$
Tefluthrin Terbaail				0.000	0.044	0.040	0.002	0.000	0.040	0.000	0.014	0.016	0.040	0.014	0.000	$\Leftrightarrow$
Terbacil Thiamathayam	H			0.008	0.041	0.040		0.009	0.013		0.011					0.002
Thiamethoxam							0.003			0.002		0.003		0.002	0.002	0.002
Total Fluvalinate		0.040		0.000	0.007	0.000	0.031	0.007	0.000	0.000	0.040	0.044	0.000	0.000	0.000	
Triazine DEA degradate	D	0.010		0.006	0.007		0.007	0.007				0.011	0.008	0.008	0.008	0.007
Triazine DIA degradate	D	0-				0.003	4.4-	4.2				0.003				
Total suspended solids (mg/L)		35		36	63	108	117	48	65	70	37	32	52	31	31	12
Streamflow (cubic ft/sec)		173	177	244	209	172	193	153	118	141	170	149	209	201	214	
Precipitation (total in/week)†		0.16	0.03	0.36	0	0	0.54	0.08	0	0.12	0	0.21 mance		0	0.15	0.07

#### Table 13 – Lower Crab Creek pesticide calendar, µg/L

The "--" signifies a sample that was not collected. The "X" signifies data rejected by failing quality assurance performance measures.



DDT/degradate exceedance

Detection

\* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist)

<sup>+</sup> Washington State University AgWeatherNet station: Royal City W, (latitude: 46.97°, longitude: -119.83°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at one of the 15 site visits (7%). Water quality at the Lower Crab Creek site is shown below (Figure 28).

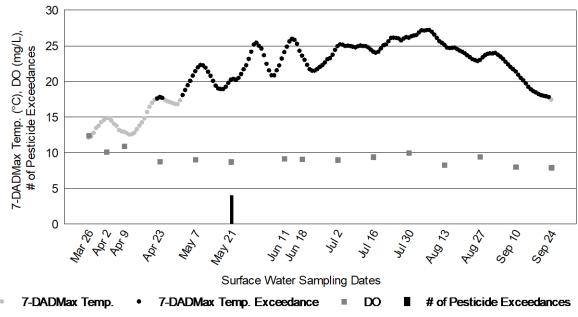


Figure 28 – Lower Crab Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 7.58 to 8.48 with an average of 8.24. All DO measurements also met the state standard, ranging from 7.90 mg/L to 12.39 mg/L with an average of 9.34 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard for 148 days of the sampling season, primarily from May 2 through September 23. Four pesticide exceedances coincided with a 7-DADMax temperature exceedance on May 21.

Lower Crab Creek has been designated as a freshwater body that provides habitat for salmonid rearing and migration by the WAC (WAC, 2019). Staff frequently observed juvenile fish of unknown species at the site. WSDA also monitored this location in 2020, at which point it will be evaluated for continued monitoring efforts.

## **Marion Drain**

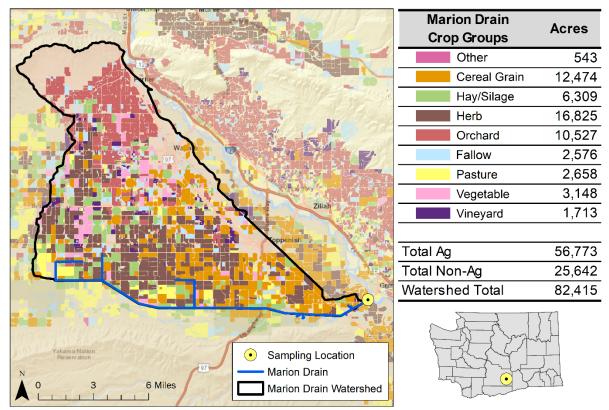


Figure 29 – Map of Marion Drain and its drainage area with associated sampling location and crop groups identified

In 2003, WSDA started sampling the Marion Drain watershed in Yakima County. The monitoring site is located near Granger, approximately 140 meters upstream from the bridge crossing at Indian Church Road (latitude: 46.3306°, longitude: -120.2000°) (Figure 29, Figure 30). WSDA selected this watershed to represent irrigated agricultural practices in Eastern Washington.

Marion Drain flows directly into the Yakima River. Melting snowpack, precipitation events, groundwater, and irrigation generally influence flows in the stream. There was a large amount of



Figure 30 – Marion Drain upstream view

aquatic vegetation growing in the streambed in 2019. WDFW and the Yakama Nation have documented fall Chinook salmon, coho salmon, and summer steelhead within the Marion Drain watershed (WDFW, 2019).

The Marion Drain watershed has low-lying and flat terrain. Marion Drain is a highly modified waterway that travels straight about 18 miles through many irrigated agricultural fields. The agricultural land use in the area is dominated by hops (grouped with the 'Herb' crop group),

field corn, apples, mint and wheat. The 'Other' crop group category consists of nurseries, melons, berries and other assorted crops (Figure 29).

Samples were collected at this site in the spring and summer and again in the late fall because of a history of low pesticide detections during early fall. Sampling events extended into November only at this site in order to capture pesticide detections during the peak fall Chinook salmon migration and spawning in Marion Drain.

Below is a brief overview of the pesticide findings in Marion Drain in 2019.

- WSDA tested for 159 unique pesticides in Marion Drain.
- There were 535 total pesticide detections from six different use categories: 23 types of herbicides, 23 insecticides, 6 fungicides, 10 degradates, 1 antimicrobial, and 1 synergist.
- Pesticides were detected at all 28 sampling events.
- Up to 34 pesticides were detected at the same time.
- Of the total pesticide detections, 27 were above WSDA's assessment criteria (Table 14).
  - The three detections of 4,4'-DDD, six detections of 4,4'-DDE, and two detections of 4,4'-DDT were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 μg/L).
  - $_{\odot}$  The single fluvalinate detection exceeded the WSDA Endangered Species Level of Concern (0.009  $\mu g/L).$
  - $_{\odot}$  The detection of fipronil at this site approached the invertebrate NOAEC (0.011  $\mu g/L).$

The Marion Drain watershed POCs were chlorpyrifos, clothianidin, imidacloprid, and tefluthrin. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- The eight detections of chlorpyrifos did not exceed any assessment criteria in 2019, but this pesticide was still considered a watershed POC because of detections in 2018 that did exceed criteria.
- Of the 28 detections of clothianidin, 11 approached the invertebrate NOAEC (0.05 µg/L).
- Two of the four imidacloprid detections approached the invertebrate NOAEC (0.01 µg/L).
- Tefluthrin, detected once, exceeded the WSDA Endangered Species Level of Concern (0.0015 µg/L).

The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 14). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

		. 10			Jiai		-31				uur,	μġ	-																	
Month		Mar			Apr				M	lay			Jı	un				Jul				Au	ug		S	ер	$\overline{\ }$	0	ct	Nov
Day of the Month	Use*	27	1	9	15	22	29	6	13	20	28	3	10	17	24	1	9	15	22	29	5	12	19	26	4	9		21	29	5
1-(3,4-Dichlorophenyl)-3-methylurea	D								0.003					0.004								0.006					$\setminus$			
2,4-D	Н			0.058			0.020		0.060			0.045	0.065	0.040	0.032	0.034	0.089	0.048	0.112	0.049	0.035	0.158	0.019	0.014			/			
2,6-Dichlorobenzamide	D							0.004		0.003				0.003	0.005			0.004					0.012				$\rightarrow$			
4,4'-DDD	D						0.003			< 0.001													0.005				<			
4,4'-DDE	D					0.002	0.003		0.003	0.002													0.021				>			0.002
4,4'-DDT							0.004									0.044	0.000		0.000				0.011				<		<u> </u>	
Acephate Aminomethylphosphonic acid (AMPA)			0.013		0.009		0.023		0.096		0.067		0.113		0.138	0.011	0.003		0.008		0.170		0.275		2.120		>	0.659		0.595
Atrazine	н	0.006		0.008			0.023		0.096	0.013					0.138			0.008	0.008		0.007	0.011	0.275	0.006		0.005	<		0.007	
Azoxystrobin	F	0.000	0.003	0.000	0.010		0.005	0 004	0.005		0.007							0.013			0.004		0.025		0.001	0.003	>	0.001		0.000
Boscalid	F	0.006		0.006	0.005	0.006		0.001	0.000	0.025			0.009		0.002	0.011		0.021			0.013	0.039	0.020			0.009	<	0.006		
Bromacil	H	0.005	0.006	0.006			0.004	0.010	0.011						0.007			0.006			0.006	0.025					$\geq$			
Bromoxynil	н								0.029																		$\leq$			
Carbaryl	I	0.007							0.005	0.006												0.003								
Chlorantraniliprole	I	0.005								0.007				0.011		0.010		0.011	0.010	0.008	0.007			0.010	0.007	0.013		0.018	0.015	0.015
Chlorpyrifos	I			0.006					0.006	0.004		0.003		0.004													/			
Clothianidin	I	0.021	0.022	0.025	0.022	0.011		0.018	0.020		0.011		0.019	0.025	0.028	0.028			0.035		0.024	0.020		0.021	0.026	0.021	$\searrow$	0.052	0.046	0.047
Dicamba acid	Н						0.009		0.012	0.014	0.014					0.009	0.042	0.017	0.011			0.038					$\langle$			
Dichlobenil	Н																												$\square$	0.001
Dicofol	1	L	L	-	<u> </u>				-				L										0.005	L	<u> </u>		$\langle \rangle$			
Dimethoate	1	L	I		<u> </u>					0.019									0.021	L	0.011				<u> </u>		>			
Diuron	Н		I	-		0.002	0.006	0.025		0.013				0.007	0.005			0.005	0.003			0.019	0.004		I		$\langle$			
Eptam	H									0.026	0.010	0.005	0.003			0.005	0.003										>			
Ethoprop	1				-			0.004																	-		<		<u> </u>	
Etoxazole					-				1	-						-	-	0.003	0.003		-				-		>	0.000		
Fenarimol	F																					0.000					<	0.003	$\vdash$	
Fipronil									0.005													0.006					>		<b>⊢</b> −−−	
Fipronil sulfone	D					0.017	0.012	0.015	0.005	0.024	0.026	0.020	0.000	0.011	0.010	0.000	0.012	0.016	0.016	0.012	0.016	0.015		0.011	0.005	0.000	<	0.000	0.000	0.000
Fludioxonil	н		0.010	0.029	0.012	0.017	0.013		0.029		0.026		0.022		0.010	0.008	0.269		0.016		0.016		0.215		0.005	0.006	>	0.009	0.008	0.008
Glyphosate	Н		0.012	0.029	0.013		0.034		0.201	0.003			0.420		0.330		0.209		0.401	-	0.205		0.215		0.927		<	0.792		0.403
Hexazinone Imazapyr	Н			0.004	0.003	0.002				0.003	0.003		0.003			0.002						0.003					>		— I	0.002
Imidacloprid	1			0.004	0.003	0.003	0.003				0.003		0.005	0.008		0.002		0.003				0.003					<		<b>—</b>	
MCPA	Н				1				0 237	0.144	0.015		0.005	0.000				0.005	0.055		0.036	0.003					>		$ \rightarrow$	
Malathion	i								0.201	0.144	0.010							0.012	0.000		0.000						<		<u> </u>	
Methamidophos	D				1												0.002	0.012	0.001								$\geq$			
Methomyl	1								0.002																		<			
Metolachlor	н																		0.004											
Metribuzin	н	0.005			0.003			0.004										0.005									$\leq$			
Norflurazon	H		0.007	0.007	0.006	0.005	0.002				0.005			0.005	0.007	0.009	0.010	0.004			0.012	0.008	0.010	0.005	0.005	0.006		0.006	0.006	0.006
Oxamyl	1															< 0.001		0.011		0.001		0.003					<			
Oxamyl oxime	D																	0.006												
Pendimethalin	н	0.004	0.006	0.008	0.006	0.009	0.006	0.027	0.047	0.044	0.038	0.036	0.029	0.014	0.008	0.006	0.011	0.013	0.013		0.011						$\leq$			
Phosmet	1																			0.006										
Piperonyl butoxide (PBO)	Sy				1										0.007												$\leq$			
Prometon	H					0.004		0.004		0.003																				
Propargite	1					0.001		0.001		0.029																	<		<u> </u>	
Propiconazole	F			+		-		0.008	0.036			0.009							-								$\geq$			
Pyridaben	i.			+				5.000	3.000	0.004		5.005							-								$ \langle  $		$\rightarrow$	
Pyrimethanil	F			+		0.002	0.005	0.021		0.004		0.000	0.004	<u> </u>			-					0.005		0.004	-		>	$\vdash$		
Pyriproxyfen	li -		L	-		0.003	0.005	0.021		0.004	-	0.000	0.004				-	-	-	-		0.000		0.004			$ \langle$	<u> </u>		0.002
Simazine	Н			0.008			0.004		0.027			0.018	0.012	0.023	0.012	0.009	0 008	0.010	0 000	0.011		0.020		0.008	0.007	0.008	>	0.010	0.011	
Sodium bentazon	н	<u> </u>	<u> </u>	0.000			<u> </u>	<u> </u>	0.027		0.023	0.010	0.012	0.023	0.012	0.009					0 152	0.020			0.007				0.011	
Spirotetramat									0.150				0.000	0.009	0.000		0.110	0.105	0.140	0.174	0.155	0.102		0.000	0.070		>	0.002	0.000	0.043
Sulfentrazone	Н		0.000	0.010	0.008	0.007	0.006	0.000	0.018	0.007	0.005	-	0.008	0.009	0.000	0.004	0.015	0.016		0.010	0.009	0.010		0.007	0.000	0.012	<	$\bigtriangledown$		
Tefluthrin	11		0.008	0.010	0.008	0.007	0.006	0.006	0.018	0.007	0.005		0.008		0.009	0.004	0.015	0.016		0.010	0.009	0.019		0.007	0.009	0.012	>	$\sim$	$\frown$	$\frown$
	Н	0.010	<u> </u>	0.000	0.006	0.004		0.007	0.301	0.002	0.044	0.405	0.445	0 1 4 4	0.000	0.450	0.100	0 470	0.225	0.005	0.050	0.144		0.060	0.020	0.290	<	0.000	0.008	0.000
Terbacil Thiamethoxam		0.010	<u> </u>	0.009			0.005		0.301		0.211	0.105	0.115	0.144	0.066	0.153		0.173				0.144				0.380	>		0.008	
Total Fluvalinate	Ľ		l	0.008	0.010	0.005	0.005	0.008	0.009	0.009	0.004	0.012	0.010	0.019	0.015	0.015	0.022	0.021	0.023	0.017	0.015	0.013	0.018	0.018	0.018	0.023	<	0.003	0.000	0.003
	D	0.007	0.007	0.005	0.000	0.000	0.000	0.005	0.000		0.004	0.004	0.004	0.000	0.000	0.005	0.005	0.005	0.000	0.005	0.004	0.000	0.004	0.000	0.004	0.004	>	0.005	0.000	0.005
Triazine DEA degradate		0.007			0.006	0.003	0.003		0.006	0.005			0.004			0.005	0.005	0.005	0.006	0.005		0.003	0.004	0.003			$ \langle$	0.005	0.006	0.005
Triazine DIA degradate	D		0.003	5	I				0.004	0.000	0.003			0.003	0.003						0.003	0.000			0.003		>	<u> </u>	<u> </u>	
Triazine HA degradate	D			-		<u> </u>		0.002		0.002												0.003	ļ		<u> </u>	<b> </b>	$\langle \rangle$	L	<u> </u>	
Triclosan	A		0.008	3	0.006	L																			<u> </u>					0.035
Trifluralin	Н								0.012		0.010																$\langle$			
Total suspended solids (mg/L)		39	21	29	14	67	32	4	6	4	5	4	2	1	1	2				2	1	2	2	2		2		7	5	12
Streamflow (cubic ft/sec)		253.9	206.3	3 223.3	205.3			26.5		30.0			53.8				12.3		12.9	12.0	11.1	17.5	22.8	24.2				-		220.5
Precipitation (total in/week)†		0	0	0	0.41	0.06	0	0	0.03	0.23		0.01		0.04				0.17	0.25	0.19	0.35	0.92	0.44	0.15	0.13	0.02		0	0	0
The "" signifies a sample or measure					d or cou						a data a	in the set of a	i ber fait		1.11		nerform				-		-	-	-					

#### Table 14 – Marion Drain pesticide calendar, μg/L

The "--" signifies a sample or measurement that was not collected or could not be analyzed. The "X" signifies data rejected by failing quality assurance performance measures.

Current-use exceedance

ce DDT/deg

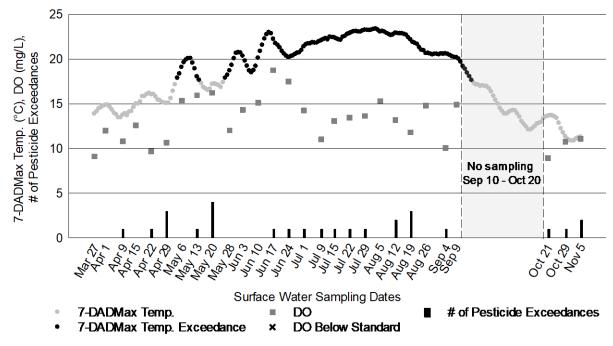
DDT/degradate exceedance

Detection

<sup>†</sup> Washington State University AgWeatherNet station: Toppenish, (latitude: 46.37°, longitude: -120.39°)

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Sy: Synergist)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 12 of the 28 site visits (43%). Water quality at the Marion Drain site is shown below (Figure 31 and Figure 32).



*Figure 31 – Marion Drain water quality measurements and exceedances of assessment criteria* 

All DO measurements met the state standard, ranging from 8.93 mg/L to 18.75 mg/L with an average of 13.08 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard for 125 days of the sampling season, from May 4 through May 14 and May 26 through September 16. Pesticide exceedances coincided with 7-DADMax temperature exceedances at 11 site visits.

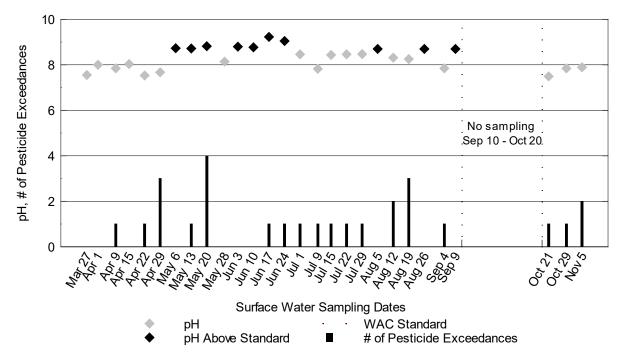


Figure 32 – Marion Drain pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.49 to 9.23 with an average of 8.29. Less than half (36%) of these measurements exceeded the state standard in that 10 measurements were above 8.5 (red-dashed line in Figure 32). Out of the 10 pH exceedances, four coincided with at least one pesticide exceedance. Pesticide exceedances overlapped with both pH and 7-DADMax temperature exceedances on May 13, June 17, and June 24.

Marion Drain has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC, 2019). NRAS staff at the site frequently observed juvenile fish of an unknown species. WSDA will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

#### **Mission Creek**

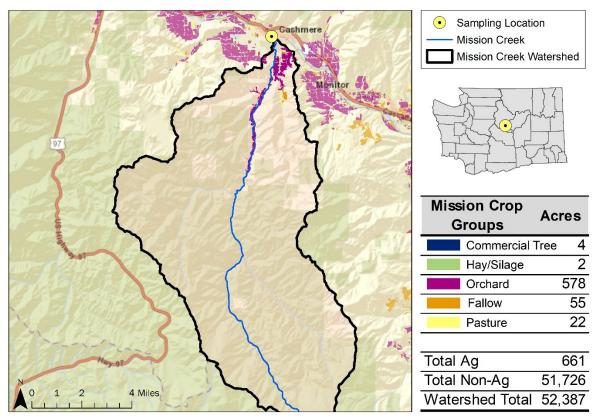


Figure 33 – Map of Mission Creek and its drainage area with associated sampling location and crop groups identified

In 2007, WSDA started sampling the Mission Creek watershed in Chelan County. The site is located in Cashmere, approximately 10 meters downstream from the bridge crossing of Sunset Highway where the Department of Ecology manages a stream gauging station (latitude: 47.5212°, longitude: -120.4760°) (Figure 33). The watershed that contains the 18.5-mile-long Mission Creek has mountainous terrain. The agricultural land use is predominately tree fruit production of pears, cherries, and apples.

Mission Creek joins Brender Creek approximately 130 meters upstream of its confluence with the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. At the headwaters of Mission Creek, WDFW has documented summer spawning of steelhead (WDFW, 2019). Staff at the site frequently observed juvenile fish of unknown species (Figure 34).

The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides



Figure 34 – Mission Creek downstream view

detected during the 2019 monitoring season and a visual comparison to the WSDA

assessment criteria (Table 15). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. Staff collected samples at Mission Creek only during early spring due to historically few pesticide detections during the late spring, summer and fall.

Month				Apr				M	ay	
Day of the Month	Use*	2	10	16	23	30	7	14	21	29
2,6-Dichlorobenzamide	D			0.004		0.003	0.004	0.003	0.003	
4,4'-DDD	D					0.004		0.004	<0.001	
4,4'-DDE	D			0.003	0.002	0.004		0.004	0.003	
4,4'-DDT	1			0.005				0.005		
Chlorpyrifos	1		0.248	0.013	0.005	0.008	0.005	0.005	0.004	
Diazinon	1				0.003					
Hexazinone	Н	0.007	0.010	0.011		0.007	0.007		0.006	
Malathion	1	0.011	0.497	0.012	0.005	0.009	0.005	0.005		
Norflurazon	Н			0.006	0.004	0.005	0.006		0.005	
Pendimethalin	Н			0.005	0.005	0.006	0.007	0.007	0.005	
Piperonyl butoxide (PBO)	Sy							0.053	0.009	0.007
Pyridaben	I			0.032						
Pyriproxyfen	1		0.190	0.008						
Simetryn	Н						0.004			
Triadimefon	F								0.004	
Triclosan	А			0.006						
Total suspended solids (m	ig/L)	36	32	22	45	23	32	25	22	271
Streamflow (cubic ft/sec)		78.6	85.3	60.4	85.4	50.0	56.8	48.9	37.7	84.9
Precipitation (total in/week)	)†	0	0.48	0.10	0	0.01	0	0	0.47	0.54
	nondono	~		/dograda	to over	odonoo		Dotor	tion	

Table 15 – Mission Creek pesticide calendar, µg/L

Current-use exceedance

DDT/degradate exceedance

Detection

Below is a brief overview of the pesticide findings in Mission Creek in 2019.

- WSDA tested for 90 unique pesticides.
  - This was 66 fewer pesticides analyzed for than many of the other sites. They were removed due to few detections at this site in recent years.
- There were 56 total pesticide detections from six different use categories: four types of herbicides, six insecticides, one fungicide, three degradates, one antimicrobial, and one synergist.
- Pesticides were detected all nine sampling events.
- Up to 11 pesticides were detected at the same time.
- Of the total pesticide detections, 15 were above WSDA's assessment criteria (Table 15).
  - $_{\odot}$  The three detections of 4,4'-DDD, five detections of 4,4'-DDE, and two detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

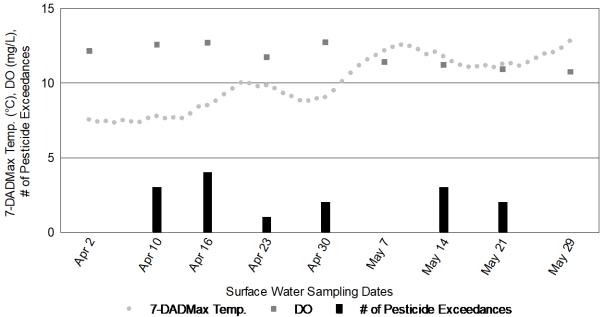
<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Sy: Synergist)

<sup>&</sup>lt;sup>†</sup> Washington State University AgWeatherNet station: N. Cashmere, (latitude: 47.51°, longitude: -120.43°)

The Mission Creek watershed POCs were chlorpyrifos, malathion, pyridaben and pyriproxyfen. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Of the seven chlorpyrifos detections, one exceeded assessment criteria.
  - The detection on April 10 exceeded the NRWQC and state WAC chronic criteria (both 0.041 μg/L), the invertebrate NOAEC (0.04 μg/L), the NRWQC and state WAC acute criteria (both 0.083 μg/L), and invertebrate LC<sub>50</sub> (0.1 μg/L).
- Out of the seven malathion detections, one exceeded assessment criteria.
  - The detection on April 10 exceeded the invertebrate NOAEC (0.06  $\mu$ g/L), the invertebrate LC<sub>50</sub> (0.098  $\mu$ g/L), WSDA Endangered Species Level of Concern (0.103  $\mu$ g/L), and the NRWQC chronic criterion (0.1  $\mu$ g/L).
- Pyridaben, detected once on April 16, approached the invertebrate NOAEC (0.044  $\mu$ g/L) and the WSDA Endangered Species Level of Concern (0.018  $\mu$ g/L).
- The detection of pyriproxyfen on April 10 exceeded the invertebrate NOAEC (0.015 μg/L) and plant EC<sub>50</sub> (0.18 μg/L). The detection on April 16 approached the invertebrate NOAEC.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Water quality at the Mission Creek site is shown below (Figure 35).



*Figure 35 – Mission Creek water quality measurements and exceedances of assessment criteria* 

All pH measurements met the state standard, ranging from 8.16 to 8.40 with an average of 8.26. All DO measurements also met the state standard, ranging from 10.75 mg/L to 12.73

mg/L with an average of 11.80 mg/L. All 7-DADMax temperatures throughout the 2019 sampling season met the state standard by not exceeding 17.5°C.

Mission Creek provides habitat for salmonid spawning, rearing and migration. Dense riparian vegetation for most of the creek's length helps prevent pesticide contamination from runoff and application drift. WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as chlorpyrifos and malathion.

## **Naneum Creek**

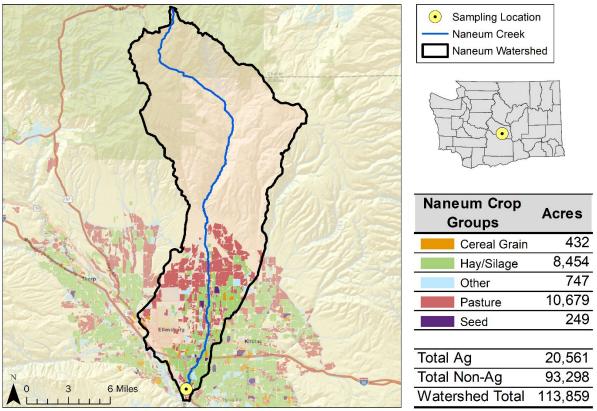


Figure 36 – Map of Naneum Creek and its drainage area with associated sampling location and crop groups identified

In 2017, WSDA started sampling the Naneum watershed in Kittitas County. WSDA selected the watershed to represent hay production (specifically timothy hay) and mixed agricultural land use in the heavily irrigated Kittitas Valley. The monitoring site is located at the Fiorito Ponds public access road, approximately 700 feet south of the restroom (latitude: 46.9380°, longitude: -120.5062°) (Figure 36, Figure 37).

The 35-mile-long Naneum Creek drains indirectly into the Yakima River through Wilson Creek. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. WDFW has documented spring Chinook salmon, coho salmon, and summer steelhead within the reach of the creek that encompasses the monitoring site (WDFW, 2019).

The watershed has mountainous terrain in the upper half with a transition into low-lying, flat terrain in the bottom half of the watershed where crops are plentiful. The agricultural



Figure 37 – Naneum Creek downstream view

land use is predominately pasture, timothy hay, alfalfa hay, grass hay, and sudangrass. The 'Other' crop group category consists of tilled and idle fallow fields, oilseed, and other assorted low-acreage crops (Figure 36).

The Naneum Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 16). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month			Apr		M	ay	Ju	JN	J	ul	Αι	Jg	Se	ep
Day of the Month	Use*	2	16	30	14	29	11	25	8	23	6	20	3	17
2,4-D	Н				0.498	0.097	0.087		0.180		0.219	0.034	0.404	0.061
2,6-Dichlorobenzamide	D		0.003			0.003					0.005			
Aminomethylphosphonic acid (AMPA)	н	0.019											12.000	7.710
Atrazine	н	0.006	0.005					0.007					0.019	
Boscalid	F											0.008		
Bromacil	Н			0.003	0.006					0.005				
Bromoxynil	Н			0.043			0.146		0.012					
Carbaryl	1				0.003									0.004
Chlorantraniliprole	1						0.010		0.007					
Chlorpyrifos	1									0.003				
Chlorsulfuron	Н			0.011										
Clopyralid	Н			0.093	0.072					0.099				
Clothianidin	1									0.003				
Dicamba acid	Н			0.794	0.192	0.034	0.036	0.031	0.064	0.142	0.067	0.020	0.281	0.022
Dimethoate	1				0.019						0.039			
Diuron	Н				0.020		0.002		0.004					
Eptam	Н				0.133									
Ethalfluralin	Н				0.006					0.006				
Fludioxonil	F											0.011		
Fluroxypyr 1-methylheptyl ester	Н			0.088	0.007									
Glyphosate	Н	0.017	0.018	0.241	0.675	0.184	0.160	4.380	0.244	2.060	1.250	0.323	12.300	18.400
Hexazinone	Н			0.003				0.004						
Imazapyr	Н		0.003	0.006	0.006	0.006	0.004	0.005	0.005	0.010	0.009	0.004	0.004	0.006
Imidacloprid	1							0.017						
Indaziflam	Н													0.002
МСРА	Н			0.909	0.053		0.211		0.039					
Metalaxyl	F			0.013										
Methamidophos	D												0.002	0.001
Metolachlor	Н				0.009		0.039	0.003	0.019	0.009	0.005			
N,N-Diethyl-m-toluamide (DEET)	lr												0.005	
Norflurazon	Н											0.005		
Pendimethalin	Н			0.027	0.037	0.006	0.005	0.008	0.036	0.032	0.030		0.119	0.012
Simazine	Н											0.007		
Sulfentrazone	Н			0.017	0.014	0.022	0.008	0.007	0.015	0.018	0.009	0.007	0.007	0.008
Terbacil	Н											0.056		
Thiamethoxam	1				0.004		0.003		0.005	0.005	0.003		0.006	0.002
Total Fluvalinate	1									0.006				
Triazine DEA degradate	D	0.004	0.003	0.003	0.005	0.003	0.005	0.007	0.011	0.015	0.011	0.005	0.015	0.006
Triazine DIA degradate	D										0.006		0.008	
Triazine HA degradate	D			0.026	0.015	0.010	0.007	0.016	0.023	0.032	0.022	0.005	0.018	0.007
Triclopyr acid	Н			1.220	0.128	0.160	0.120	0.198	0.056	0.136	0.029		0.188	0.036
Triclopyr butoxyethyl ester	Н			0.226										
Triclosan	А										0.017			
Total suspended solids (mg/L)		22	22	21	35	32	19	6	27	6	6	6	6	11
Streamflow (cubic ft/sec)		70.5	86.6	65.7	101.6		60.4	41.4	64.7	23.7	47.8	67.5	60.7	88.8
Precipitation (total in/week)†		0	0.06	0	0	0.19	0	0	0	0	0	0	0.03	0.19

Table 16 – Naneum Creek pesticide calendar, µg/L

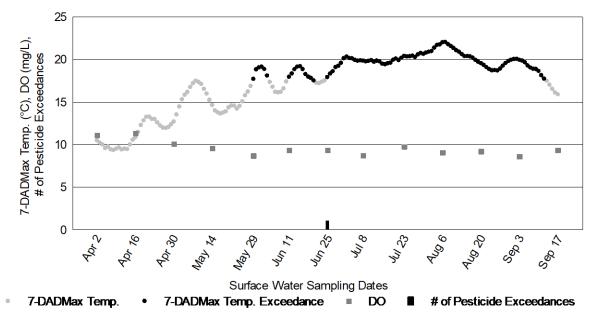
\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent)

<sup>†</sup> Washington State University AgWeatherNet station: Broadview, (latitude: 46.97°, longitude: -120.5°)

Below is a brief overview of the pesticide findings in Naneum in 2019.

- WSDA tested for 159 unique pesticides in Naneum Creek.
- There were 199 total pesticide detections from six different use categories: 25 types of herbicides, 8 insecticides, 3 fungicides, 5 degradates, 1 antimicrobial, and 1 insect repellent.
- Pesticides were detected at all 13 sampling events.
- Up to 23 pesticides were detected at the same time.
  - Of the total pesticide detections, one was above WSDA's assessment criteria (Table 16). • The single imidacloprid detection exceeded the invertebrate NOAEC (0.01 µg/L).
- There were no watershed-specific POCs for the Naneum site and no statewide WSDA POCs detected in exceedance of WSDA assessment criteria. However, chlorpyrifos, a statewide POC, was detected once in the summer below assessment criteria.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at one of the 13 site visits (8%). Water quality at the Naneum Creek site is shown below (Figure 38).



*Figure 38 – Naneum Creek water quality measurements and exceedances of assessment criteria* 

All pH measurements met the state water quality standard, ranging from 7.55 to 7.97 with an average of 7.74. All DO measurements also met the state standard, ranging from 8.59 mg/L to 11.30 mg/L with an average of 9.53 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard for 96 days of the sampling season, primarily from June 11 through September 12. On June 25, a pesticide exceedance coincided with a 7-DADMax temperature exceedance.

Naneum Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC, 2019). Staff observed fish of unknown species upstream of the sampling site. WSDA monitored the site through 2019 at which point it was dropped from the program due to lack of exceedances.

### **Snipes Creek**

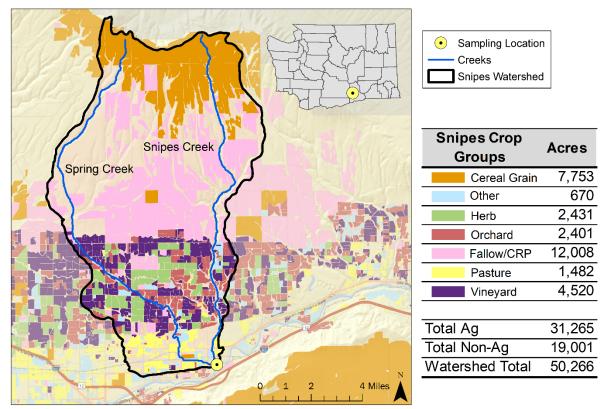


Figure 39 – Map of Snipes Creek and its drainage area with associated sampling location and crop groups identified

In 2016, WSDA started monitoring the Snipes Creek watershed in Benton County. A monitoring site within the Snipes Creek watershed on Spring Creek was sampled from 2003 to 2015. WSDA moved the monitoring site downstream in order to incorporate a larger watershed capture area. Currently, the site is located near Prosser, approximately 20 meters downstream from the confluence of Spring Creek and Snipes Creek (latitude: 46.2332°, longitude: -119.6774°) (Figure 39, Figure 40).

The Snipes watershed contains the almost 15-mile-long Snipes Creek and 19-mile-long Spring Creek that drain

Figure 40 – Snipes Creek upstream view with average streamflow

directly into the Yakima River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creeks. Roza Irrigation District releases water from the Roza Canal into Snipes Creek at times during the irrigation season. WDFW has documented Chinook salmon, coho salmon, and steelhead within the reach of creek that encompasses the monitoring site (WDFW, 2019).

The watershed has hilly terrain in the upper half that is protected through conservation programs or used for growing cereal grains. The lower half transitions into low-lying, flat terrain where crop diversity increases substantially. The agricultural land use in Snipes

Creek watershed is predominantly wheat, wine and juice grapes, hops, and apples. The 'Other' crop group category consists of berries, hay/silage and other assorted low-acreage crops (Figure 39).

Below is a brief overview of pesticide findings in Snipes Creek in 2019.

- WSDA tested for 159 unique pesticides in Snipes Creek.
- There were 398 total pesticide detections from eight different use categories: 22 types of herbicides, 12 insecticides, 4 fungicides, 7 degradates, 1 antimicrobial, 1 insect repellent, 1 synergist, and 1 wood preservative.
- Pesticides were detected at all 21 sampling events.
- Up to 30 pesticides were detected at the same time.
- Of the total pesticide detections, 20 were above WSDA's assessment criteria (Table 17).
  - The five detections of 4,4'-DDD and eight detections of 4,4'-DDE were found at concentrations equal to or exceeding NRWQC and WAC chronic criteria (both 0.001 µg/L).

The three statewide POCs in 2019, chlorpyrifos, imidacloprid and malathion, were also watershed-specific POCs in Snipes Creek. Below, each POC detected is compared to its corresponding assessment criteria that were exceeded.

- Of the 12 chlorpyrifos detections, 3 exceeded WSDA assessment criteria.
  - The detections on April 9 and April 15 exceeded the NRWQC and state WAC chronic criteria (both 0.041  $\mu$ g/L), NRWQC and state WAC acute criteria (0.083  $\mu$ g/L), the invertebrate NOAEC (0.04  $\mu$ g/L), and the invertebrate EC<sub>50</sub> criterion (0.1  $\mu$ g/L).
  - $\circ$  On April 22, the detection approached the invertebrate NOAEC (0.04 µg/L).
- There were eight detections of imidacloprid. Two detections approached the invertebrate NOAEC, one detection was equal to the invertebrate NOAEC, and one detection exceeded the invertebrate NOAEC (0.01 µg/L).
- The three detections of malathion did not exceed any assessment criteria in 2019, but malathion was still considered a watershed-specific POC because of detections in 2018 that did exceed criteria.

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 17). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month		Mar	<u> </u>		Apr					ay			. li	un	-		Jul				Aug		Sep
	Use*	27		9	<b>רקר</b> 15	22	29	6	13		20	3	10	17	24	1	9	15	$\rightarrow$	12	<b>709</b>	26	4
Day of the Month		21	1	-	-	22	29	0	-	20	28	3	10	17	24		9	15	$\leftarrow$		19	20	4
. (.,	D		0.005	0.004	0.005	0.015	0.004	0.004	0.004		0.004	0.070	0.000	0.050	0.040	0.000	0.045	0.000	$\rightarrow$	0.003	0.000	0.004	0.044
2,4-D	н D	0.040	0.007	0.030	0.000			0.084		0.118									<			0.021	
2,6-Dichlorobenzamide 4,4'-DDD	ם ח	0.018	0.007	0.006	0.006		0.004	0.006	0.006	0.005	0.007	0.009	0.006	0.009	0.008	0.012	0.013	0.014	$\rightarrow$	0.009	0.022	0.016	0.014
	D		0.003	0.004		0.002			0.003	0.001			0.003						<			┟───┦	<b>├</b> ──┤
Acetamiprid	U I		0.003	0.003		0.002	0.003		0.004	0.002	0.003	0.003	0.003						$\rightarrow$				$\vdash$
•	Н		0.061		0.077		0.058		0.089		0.115		0.093		0.091		0.090		<		0.214		3.610
Atrazine	н		0.001		0.077				0.009			0.005		0.006					$\rightarrow$		0.214	0.005	3.010
Boscalid	F			0.007	0 008	0 000		0.005	0.007	0.003	0.000	0.003				0.000			<	0.053	0.024	0.005	0.012
	Н			0.003				0.012	0.010	0.006	0.007	0.000	0.006			0.007			$\geq$			0.007	
Carbaryl	1	0.002	0.010	0.010	0.024	0.012	0.011		0.011	0.000			0.000	0.007	0.010	0.007	0.000	0.007	$\leq$	0.011	0.005	0.007	0.007
Chlorantraniliprole		0.008						0.000	0.011	0.014	0.000		0.008	0.009			0 009	0.009	$\geq$	0.008	0.005	0.005	
Chlorpyrifos		0.000		0.143	0 117	0.032	0.010	0.006	0.006	0.004	0.004	0.003	0.000	0.004			0.000	0.003	$\leq$	0.000	0.000	0.000	
Clothianidin			0.001	00	0	0.002	0.0.0	0.000	0.000	0.001	0.001	0.000		0.001				0.000	$\geq$			0.003	0.003
Diazinon															0.004			0.015	$\leq$			0.000	0.000
Dicamba acid	H							0.016	0.013	0.079	0.023				0.00.		0.013		$\geq$	0.048			
Dichlobenil	Н			0.004		0.002	0.002											0.003	$\leq$				
Dimethoate	1							0.007	0.012	0.009									$\geq$				
	Н	0.010	0.040	0.021	0.063	0.115				0.012	0.010	0.006	0.005	0.006	0.005	0.002		0.005	$\leq$				
Eptam	Н		0.003			-				0.003									$\geq$				
Etoxazole	1																0.008	0.004	$\leq$				
Fenarimol	F	0.005																	$\geq$				
Fludioxonil	F	0.006	0.028	0.013	0.013	0.018	0.014	0.027	0.026	0.021	0.008	0.016	0.028	0.027	0.027	0.020	0.027	0.022		0.033	0.019	0.016	0.014
	Н		0.072		0.414		0.127		0.206		0.149		0.290		0.247		0.113				0.116		0.608
Hexazinone	Н			0.005			0.003					0.004											
Imazapyr	Н			0.002	0.003	0.003				0.003								0.002		0.003	0.003	0.002	
Imidacloprid	_	0.008								0.009			0.004	0.048	0.004	0.004		0.010				0.003	
Isoxaben	Н					0.003		0.004	0.004	0.003													
Malathion	1			0.005										0.005	0.003				$\searrow$				
mounannaoprioo	D					0.001					0.002										0.001	0.001	0.002
Methomyl	1								0.017										$\searrow$				
Metolachlor	Н							0.003	0.004	0.003				0.004				0.005	$\langle$				
Metsulfuron-methyl	Н				0.006														$\rightarrow$				
N,N-Diethyl-m-toluamide (DEET)	lr																		$\langle$				0.006
Norflurazon	Н	0.010	0.006	0.007	0.005	0.006	0.002	0.009	0.008	0.006		0.008	0.005	0.006	0.009	0.010	0.011	0.007	$\rightarrow$	0.008	0.006	0.006	0.006
Oryzalin	Н									0.032									$\langle$				
Pendimethalin	Н			0.017	0.011	0.011	0.013	0.013	0.014	0.012	0.007	0.004	0.003	0.006	0.007	0.006	0.013	0.015	$\rightarrow$	0.014	-		
Pentachlorophenol	Wp	0.013																	$\langle$				
Piperonyl butoxide (PBO)	Sy		0.006								0.005								$\searrow$	0.007			
Prometon	Н					0.004		0.005															
Pyrimethanil	F		0.013	0.005		0.004	0.003	0.021		0.006			0.008	0.007					$\searrow$	0.014	0.004	0.012	
Simazine	Н	0.006					0.008		0.009	0.012		0.009		0.006	0.005	0.005		0.007	$\langle$				0.005
Sulfentrazone	Н		0.006	0.006	0.005	0.006		0.005			0.004								$\searrow$			0.005	0.005
Terbacil	Н	0.004				0.004		0.011	0.011	0.010	0.004	0.005	0.004	0.005		0.004	0.005	0.010		0.007	0.005		
Thiamethoxam	1								0.002	0.002	0.003	0.014	0.004	0.010	0.007	0.005		0.002		0.002	0.002	0.002	
Triazine DEA degradate	D	0.014	0.003	0.002	0.002	0.002	0.002	0.002	0.003	0.002	0.004	0.004	0.004	0.004	0.004	0.005	0.004	0.005		0.002	0.003	0.003	0.004
Triazine HA degradate	D									0.002													
Triclopyr acid	н							0.025	0.023	0.042	0.031								$\geq$				
Triclosan	A			0.008	0.007														$\leq$				
Total suspended solids (mg/L)		12	95	36	24	21	26	32	41	28	60	18	16	13	31	14	11	15	$\rightarrow$	82	12	8	7
Streamflow (cubic ft/sec)		6.6	82.2				76.0	82.9	68.2	67.5	23.8	26.8	43.6	34.2	50.5	34.6	30.2	35.4	$\leq$		33.7	39.9	47.7
Precipitation (total in/week)†		0.0	0.03			0.02	0	02.9	00.2	07.5	0.23	20.0	0.01	0	0.02	0.18		0	$\rightarrow$	0.57	0	0.09	0
The " " cignifica a comple or moscuro		-		0.09		d not h			U	0.01	0.23	0	0.01	0	0.02	0.10	0.01	U		0.07	U	0.03	<u> </u>

#### Table 17 – Snipes Creek pesticide calendar, µg/L

The "--" signifies a sample or measurement that was not collected or could not be analyzed.

Current-use exceedance

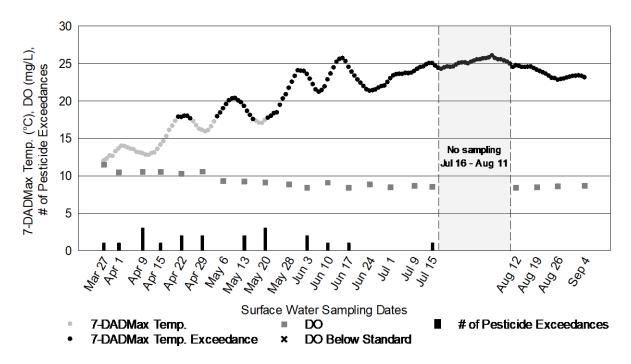
DDT/degradate exceedance

Detection

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist, Wp: Wood preservative)

<sup>&</sup>lt;sup>†</sup> Washington State University AgWeatherNet station: WSU Prosser, (latitude: 46.26°, longitude: -119.74°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at nine of the 21 site visits (43%). Water quality at the Snipes Creek site is shown below (Figure 41, Figure 42).



*Figure 41 – Snipes Creek water quality measurements and exceedances of assessment criteria* 

All DO measurements met state water quality standards, ranging from 8.39 mg/L to 11.51 mg/L with an average of 9.28 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard for 125 days of the sampling season, primarily from May 4 through the end of the season. Pesticide exceedances coincided with 7-DADMax temperature exceedances at six site visits.

The pH measurements ranged from 7.77 to 8.86 with an average of 8.41. Less than half (29%) of these measurements exceeded the state standard in that six pH measurements were greater than 8.5 (red-dashed line), (Figure 42); all of these pH exceedances coincided with at least one pesticide exceedance. Pesticide exceedances overlapped with both pH and 7-DADMax temperature exceedances at four site visits.

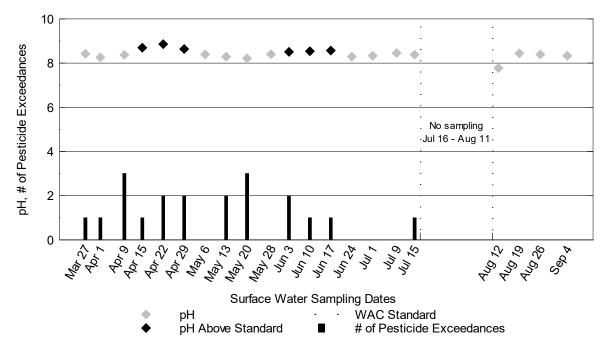


Figure 42 – Snipes Creek pH measurements and exceedances of assessment criteria

Snipes Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC, 2019). Staff observed juvenile fish of an unknown species during the sampling season. A fish passage blockage restricts salmonids from migrating beyond Spring Creek's crossing with Hess Road. Snipes Creek is believed to be uninhibited from fish passage blockages. WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as chlorpyrifos.

### **Stemilt Creek**

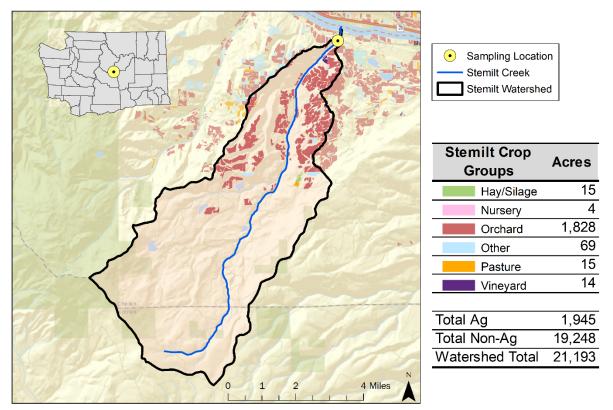


Figure 43 – Map of Stemilt Creek and its drainage area with associated sampling location and crop groups identified

In 2013, WSDA started sampling the Stemilt Creek watershed in Chelan County. The site is located near Wenatchee, approximately 30 meters upstream of the bridge over the creek on Old West Malaga Road (latitude: 47.3748°, longitude: -120.2496°) (Figure 43, Figure 44). Stemilt Creek water drains directly into the Columbia River. Melting snowpack, precipitation events, and irrigation generally influenced streamflow in the creek. Within the reach of the creek that encompasses the monitoring site, WDFW has documented spring Chinook salmon and summer steelhead (WDFW, 2019). In 2019, a WDFW fish



Figure 44 – Stemilt Creek upstream view

biologist identified a salmonid fry as a Chinook salmon at the monitoring site. WDFW also note that the inlet of Stemilt Creek provides rearing habitat for salmon.

The watershed that contains the 12-mile-long Stemilt Creek has mountainous terrain. WSDA selected the watershed to be representative of agricultural practices used in tree fruit cultivation in Central Washington. The agricultural land use is predominately tree fruit production of cherries, apples, and pears. The 'Other' crop group category consists of fallow fields (Figure 43).

The Stemilt Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 18). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. Staff collected samples only during the spring due to historically few pesticide detections at this site during the summer and fall.

Month				Apr		-		M	ay	
Day of the Month	Use*	2	10	16	23	30	7	14	21	29
2,6-Dichlorobenzamide	D	0.030	0.032	0.025	0.016	0.029	0.033	0.015	0.012	0.006
4,4'-DDD	D			0.003	0.003	0.003		0.004	0.001	
4,4'-DDE	D							0.003	0.002	
4,4'-DDT	1			0.004	0.004	0.005		0.005		0.006
Boscalid	F	0.036	0.024	0.014	0.011	0.011			0.018	
Chlorpyrifos	1	0.007	0.010	0.015	0.011	0.007	0.004	0.006	0.004	
Diazinon	1			0.005	0.012	0.016	0.004	0.004	0.003	
Dichlobenil	Н		0.006		0.002	0.002			0.002	
Hexazinone	Н					0.003			0.003	
Malathion	1		0.012		0.004					
Pendimethalin	Н				0.005	0.004		0.006		
Pyriproxyfen	I	0.004							0.004	
Sulfentrazone	Н	0.013	0.015	0.013	0.010	0.013	0.023	0.011		0.009
Tefluthrin	1								0.002	
Total suspended solids	(mg/L)	8	9	7	21	10	6	18	25	98
Streamflow (cubic ft/sec	)	4.3	7.1	6.0	12.0	5.5	1.4	10.3	19.8	
Precipitation (total in/wee	0.75	0.03	0	0.01	0	0	0.56	0.97		
	ek)†	0	0.75	0.03	0	0.01	0	0	0.56	 0.97

Table 18 – Stemilt Creek pesticide calendar, µg/L	Table 18 – Ste	emilt Creek pe	esticide cale	endar, µg/L
---	----------------	----------------	---------------	-------------

The "--" signifies a measurement that was not collected or could not be analyzed.

Current-use exceedance

DDT/degradate exceedance

Detection

Below is a brief overview of pesticide findings in Stemilt Creek in 2019.

- WSDA tested for 90 unique pesticides in Stemilt Creek.
  - This was 66 fewer pesticides analyzed for than many of the other sites. They were removed due to few detections at this site in recent years.
- There were 63 total pesticide detections from four different use categories: four types of herbicides, six insecticides, one fungicide, and three degradates.
- Pesticides were detected at all nine sampling events.
- Up to 10 pesticides were detected at the same time.
- Of the total pesticide detections, 13 were above WSDA's assessment criteria (Table 18).
  - The five detections of 4,4'-DDD, two detections of 4,4'-DDE, and five detections of 4,4'-DDT were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

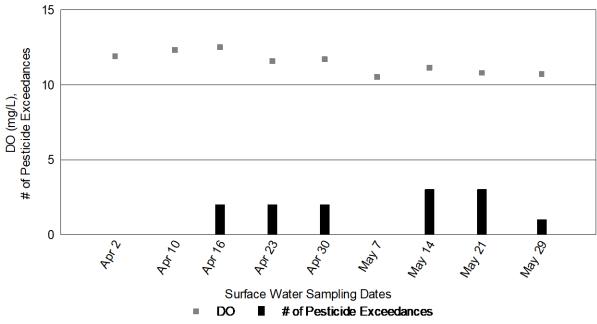
<sup>&</sup>lt;sup>\*</sup> (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide)

<sup>&</sup>lt;sup>†</sup> Wash. State Univ. AgWeatherNet station: Wenatchee Heights, (latitude: 47.37°, longitude: -120.31°)

 $_{\odot}$  Tefluthrin, detected once, exceeded the WSDA Endangered Species Level of Concern (0.0015  $\mu g/L).$ 

The Stemilt Creek watershed-specific POCs were chlorpyrifos, diazinon, and malathion. The eight detections of chlorpyrifos, six detections of diazinon, and three detections of malathion did not exceed any assessment criteria in 2019, but these pesticides were still considered watershed POCs because of detections in 2017 and 2018 that exceeded criteria.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Water quality at the Stemilt Creek site is shown below (Figure 45).



*Figure* 45 – *Stemilt Creek dissolved oxygen measurements and exceedances of assessment criteria* 

All pH measurements met the state standard, ranging from 7.86 to 8.48 with an average of 8.16. All DO measurements also met the state standard, ranging from 10.52 mg/L to 12.51 mg/L with an average of 11.47 mg/L. The temperature data logger was lost during extremely high streamflow; therefore, no 7-DADMax temperatures were calculated.

Stemilt Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC, 2019). Staff observed fish believed to be juvenile salmonids frequently during site visits. WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as chlorpyrifos and malathion.

### Sulphur Creek Wasteway

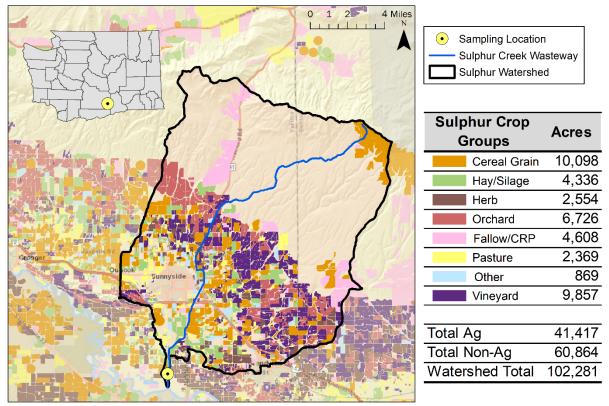


Figure 46 – Map of Sulphur Creek Wasteway and its drainage area with associated sampling location and crop groups identified

In 2003, WSDA started sampling the Sulphur Creek Wasteway watershed in Yakima County as one of the first monitoring locations in the program. The monitoring site is located near Sunnyside, just on the downstream side of the bridge crossing of Holaday Road, adjacent to the intersection of Midvale Road (latitude: 46.2510°, longitude: -120.0200°) (Figure 46, Figure 47).

Sulphur Creek Wasteway water drains directly into the Yakima River approximately 0.8 miles Figure 47 – Sulphur Creek Wasteway downstream of the monitoring site. Precipitation downstream view events, irrigation, and groundwater generally



influence streamflow in the wasteway. The majority of the water in the wasteway comes from the Yakima River through irrigation return flows from the Roza and Sunnyside canal systems. WDFW has documented Chinook salmon, coho salmon, and steelhead within the reach of wasteway that encompasses the monitoring site downstream of the fish barrier near the Holaday Road crossing (WDFW, 2019). The local irrigation districts constructed a fish barrier in order to restrict salmon from migrating further upstream in the irrigation return channel due to unfavorable habitat conditions.

The watershed that contains the 23-mile-long Sulphur Creek Wasteway has flat, low-lying terrain. The agricultural land use is predominately field corn, juice grapes, apples, wine grapes, and alfalfa hay. The 'Other' crop group category consists of vegetables, turf grass, nurseries and other assorted low-acreage crops (Figure 46).

Below is a brief overview of pesticide findings in Sulphur Creek Wasteway in 2019.

- WSDA tested for 159 unique pesticides in Sulphur Creek Wasteway.
- There were 504 total pesticide detections from seven different use categories: 26 types of herbicides, 15 insecticides, 9 degradates, 5 fungicides, 1 antimicrobial, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 21 sampling events.
- Up to 34 pesticides were detected at the same time.
- Of the total pesticide detections, 21 were above WSDA's assessment criteria (Table 19).
  - $_{\odot}$  The five detections of 4,4'-DDD, eight detections of 4,4'-DDE, and one detection of 4,4'-DDT were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Sulphur Creek Wasteway watershed-specific POCs were chlorpyrifos and imidacloprid. Below, each POC detection is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Three of the nine detections of chlorpyrifos exceeded assessment criteria.
  - $\circ$  The detections on April 1, April 9, and April 15 were equal to or exceeded the NRWQC and state WAC chronic criteria (both 0.041 µg/L) and invertebrate NOAEC (0.04 µg/L).
  - $_{\odot}$  The detection on April 9 exceeded the WSDA Endangered Species Level of Concern (0.045  $\mu g/L).$
- Of the six detections of imidacloprid, three approached the invertebrate NOAEC (0.01 µg/L). The detection on September 9 exceeded the invertebrate NOAEC.

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 19). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. Staff collected samples during the early spring and again from midsummer through the fall due to historically few pesticide detections during the late spring and early summer.

Month         Mar         Apr         May         Jul         Lug         Sep           0.0 of the Month         0         1         2         1         1         2         2         0         1         2         0         1         0         <	Month		Mar			_				May				/ 10	Jul				Δ.	IG			Sep	
1 - 3.6 Journey - Sametyues         D         Image: Same Same Same Same Same Same Same Same		Lloo*		1	0		22	20	6		20		1			22	20	F		<u> </u>	26	4		16
2.4-0         0.001 <td< td=""><td>,</td><td>-</td><td>21</td><td></td><td>9</td><td>15</td><td>22</td><td>29</td><td>0</td><td>-</td><td></td><td><math>\leftarrow</math></td><td>1</td><td>-</td><td></td><td>22</td><td></td><td>5</td><td></td><td>19</td><td>20</td><td>4</td><td>-</td><td>10</td></td<>	,	-	21		9	15	22	29	0	-		$\leftarrow$	1	-		22		5		19	20	4	-	10
24-0-000         0         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001         0.000         0.001							0.000	0.000	0 457			>	0.054			0.070		0 440		0.440	4 4 0 0	0.400		0.004
4.4-000         0         0000 <th< td=""><td></td><td>_</td><td></td><td>0.011</td><td>0.000</td><td>0.000</td><td></td><td></td><td></td><td></td><td></td><td>&lt;</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></th<>		_		0.011	0.000	0.000						<												
44-000         0         0000				0.011	0.009		0.011					>	0.014	0.015	0.018	0.018	0.014	0.017	0.008	0.011	0.011	0.011	0.009	0.010
44-0071       0 </td <td></td> <td></td> <td>0.006</td> <td>0.002</td> <td></td> <td></td> <td>0.002</td> <td></td> <td>0.003</td> <td></td> <td></td> <td> &lt;</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>0.005</td> <td></td> <td></td> <td></td> <td></td> <td></td>			0.006	0.002			0.002		0.003			<							0.005					
Accelerators ESA         D         EGAS         EGAS         D         DG28         D         DG28         D         DG28         D         DG28         DG28 <thdg28< td=""><td>*</td><td></td><td>0.000</td><td>0.003</td><td></td><td>0.003</td><td>0.003</td><td></td><td></td><td>0.004</td><td>0.004</td><td>  &gt;</td><td></td><td></td><td></td><td></td><td></td><td>-</td><td>0.005</td><td></td><td></td><td></td><td></td><td></td></thdg28<>	*		0.000	0.003		0.003	0.003			0.004	0.004	>						-	0.005					
Aminomethylophone and (AMPA)         I         -         0.33         -         0.356         -         0.226         -         0.026         -         0.226         -         0.026         0.00         0.000<	-			0.025								<	0.004		0.024	0.040		0.000			0.044			0.000
Aname         H         0.068         0.010         0.020         0.006         0.006         0.007         0.0		-				0.450				0.000		>	0.061	0.000	0.031					4 200		10 700		
Boscaid         F         0.008         0.019         0.000         0.010         0.000         0												<												
Bormani         H         0.019         0.201         0.020         0.020         0.021         0									0.009	0.034		>							0.000					
Carbandari         F         0.008 <t< td=""><td></td><td>-</td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.000</td><td>0.005</td><td></td><td>&lt;</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>		-							0.000	0.005		<												
Carbundamino         F         0.001         0.02         0.002         0.003         0.004         0.004           Chiorytrifus         1         0.043         0.064         0.002         0.000         0.003         0.003         0.004         0.003           Chiorytrifus         1         0.043         0.043         0.002         0.000         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.005         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.004         0.007         0.003         0.003         0.003         0.003         0.003         0.001 <td< td=""><td></td><td>н</td><td>0.019</td><td>0.020</td><td>0.019</td><td>0.017</td><td>0.021</td><td>0.018</td><td></td><td></td><td></td><td>  &gt;</td><td>0.023</td><td>0.024</td><td>0.033</td><td>0.027</td><td>0.019</td><td>0.028</td><td>0.017</td><td>0.021</td><td>0.019</td><td>0.018</td><td>0.017</td><td>0.018</td></td<>		н	0.019	0.020	0.019	0.017	0.021	0.018				>	0.023	0.024	0.033	0.027	0.019	0.028	0.017	0.021	0.019	0.018	0.017	0.018
Odoregring         I         Outer         Outer <t< td=""><td></td><td></td><td></td><td></td><td>0.004</td><td></td><td></td><td></td><td>0.008</td><td>0.008</td><td>0.013</td><td>&lt;</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.004</td><td></td></t<>					0.004				0.008	0.008	0.013	<											0.004	
Categoryan         1         0.041         0.043         0.046         0.003         0.003         0 <th< td=""><td></td><td>F</td><td></td><td></td><td>0.001</td><td></td><td></td><td></td><td></td><td></td><td></td><td>&gt;</td><td></td><td>0.007</td><td></td><td>0.000</td><td></td><td></td><td></td><td></td><td></td><td></td><td>0.004</td><td></td></th<>		F			0.001							>		0.007		0.000							0.004	
Containing         I		1		0.044	0.004	0.040	0.040	0.007	0.000	0.005	0.005	<		0.007										
Dacharino         H         Dech         0.032         0.022         0.022         0.022         0.022         0.022         0.023         0.03		1		0.041	0.064	0.043	0.016	0.007				>	0.011	0.047	0.040		0.044	0.040	0.005	0.000	0.011	0.040	0.000	0.007
Diazono         I<         I<<         I<		1					-		0.003		0.003	<		_	0.018				0.005	0.008	0.011		0.009	0.007
Decembe auci         H         I         0.013         0.020         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.021         0.022         0.025         0.021         0.021         0.020         0.020         0.020         0.021		H								0.032		>	0.028		0.005		0.028	0.024				0.030		
Dichobenii         H         0.007         0.007         0.008         0.008         0.008         0.007         0.007           Duron         H         0.022         0.026         0.026         0.026         0.028         0.008         0.008         0.008         0.008         0.007         0.008         0.007         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.007         0.008         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.007         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008         0.008<		1					-	0.040	0.000	0.040	0.004	$\langle$	0.047	0.040			0.070	0.040	0.004	0.040	0.011	0.000		
Onemboale         1         0									0.032	0.012	0.064	$\rightarrow$	0.017	0.018			0.073	0.013	0.031	0.010	0.011	0.009		
Drunn         H         0.022         0.028         0.007         0.029         0.028         0.008         0.0		H			0.004		0.007	0.002				$\langle$			0.003	0.003								
Eptam         H         0.002         0.003         0.003         0.003         0.007         Image: Control of the state of th		1										$\rightarrow$												
Eloxacole         I						0.020	0.024	0.018	0.019			$\langle \rangle$		0.009	0.015	0.008	0.008	0.007	0.011	0.003	0.004		0.014	
Fudiowali         F         0.026         0.02         0.026         0.006         0.037         0.023         0.025         0.026         0.016         0.011         0.014           Glufosited-momlum         H         -        -         -		Н	0.002	0.003	0.003		-			0.003	0.002	$\rightarrow$	0.007					-						
Clufostate-ammonium         H         -         -         0         -		1										$\langle$												
Gypbosate         H         -         0.150         -         0.153         -         0.300         -         0.451         -         0.705         -         2.140         -         6.859           Imazapyr         H         0.005         0.005         0.005         0.007         0.007         0.007         0.007         0.007         0.006         0.008         0.009         0.008         0.009         0.008         0.009         0.008         0.007         0.007         0.007         0.006         0.008         0.009         0.008         0.009         0.008         0.009         0.008         0.009         0.004         0.008         0.009         0.004         0.008         0.009         0.004         0.001         0.009         0.004         0.001         0.009         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002 <td></td> <td>-</td> <td>0.026</td> <td>0.021</td> <td>0.018</td> <td>0.012</td> <td>0.009</td> <td>0.009</td> <td>0.013</td> <td>0.016</td> <td>0.014</td> <td><math>\rightarrow</math></td> <td>0.014</td> <td>0.017</td> <td>0.023</td> <td></td> <td>0.024</td> <td>0.023</td> <td>0.025</td> <td>0.016</td> <td>0.015</td> <td>0.011</td> <td>0.011</td> <td>0.014</td>		-	0.026	0.021	0.018	0.012	0.009	0.009	0.013	0.016	0.014	$\rightarrow$	0.014	0.017	0.023		0.024	0.023	0.025	0.016	0.015	0.011	0.011	0.014
Hermitorine         H         0.008         0.009         0.005         0.005         0.005         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.008         0.008         0.001         0.000         0.008         0.001         <	Glufosinate-ammonium																							
Imazayr         H         0.005         0.013         0.008         0.011         0.006         0.007         0.007         0.006         0.008         0.008           Imidacloprid         I         0         0.008         0.008         0.008         0.008         0.008         0.008         0.004         0.004         0.008         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.001         0.002         0.003         0.002         0.003         0.003         0.004         0.003         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004<	Glyphosate	Н		0.150		0.125		0.153		3.300				0.922		0.859		0.541		0.705		2.140		6.930
Initiaciprid         I         Image	Hexazinone			0.008																				
Indexition       H       B       B       D       D       D       D       D       D         Malation       1       0.005       0       0.001       0.002       0.002       0.001       0.002       0.003       0.006	Imazapyr	Н	0.005		0.013	0.008	0.013	0.009	0.008	0.011	0.006	$\sim$	0.009	0.010	0.010			0.007	0.007	0.006	0.006	0.009	0.006	0.008
Nalathon         I         0.005         0         0         0.001         0.002 <td>Imidacloprid</td> <td>I</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>0.006</td> <td></td> <td></td> <td></td> <td>0.008</td> <td>0.009</td> <td>0.004</td> <td></td> <td>0.004</td> <td></td> <td></td> <td></td> <td>0.018</td> <td></td>	Imidacloprid	I									0.006				0.008	0.009	0.004		0.004				0.018	
Methamidophos         D         0.001         0.001         0.003         0.002         0.002         0.001         0.002         0.002         0.001         0.002         0.002         0.001	Indaziflam	Н								0.002		$\sim$												
Nethonyi         I<	Malathion	1			0.005										0.011									
Metolachior         H         0.003         0.008         0.039         0.005         0.006         0.006         0.006         0.006           Metolachior         H         0.003         0         0.003         0         0         0         0         0.005         0.006         0.006         0.006         0.006         0.006         0.007         0.008         0.006         0.007         0.008         0.006         0.007         0.008         0.006         0.007         0.008         0.006         0.006         0.006         0.006         0.008         0.006         0.006         0.006         0.007         0.008         0.006         0.007         0.008         0.006         0.007         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.006         0.008         0.001         0.008	Methamidophos	D						0.001	0.001	0.003	0.002	$\sim$	0.001		0.002	0.002	0.001	0.002	0.001	0.002	0.001	0.002	0.003	0.002
Metribuzin         H         0.003         0           Myclobutanii         F         0 <td>Methomyl</td> <td>1</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>0.004</td> <td></td>	Methomyl	1								0.004														
Myclobutanii         F         0.008         0	Metolachlor	Н	0.003						0.008	0.039	0.003	$\left \right\rangle$	0.005		0.008	0.006			0.005					
N.P.Diethyl-m-toluamide (DEET)         Ir         0.008         0.002         0.007         0.008         0.006         0.007         0.008         0.006           Norflurazon         H         0.006         0.006         0.006         0.006         0.006         0.008         0.008         0.006           Oxamyl         I         0         0.019         0.022         0.008         0.001         0.008         0.006         0.006         0.007         0.008         0.006           Oxyfluorfen         H         0.009         0.021         0.019         0.022         0.008         0.012         0.013         0.018         0.012         0.013         0.018         0.012         0.013         0.018         0.012         0.013         0.018         0.012         0.013         0.018         0.012         0.013         0.018         0.012         0.011         0.018         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.001         0.005         0.006         0.006         0.001         0.005         0.006         0.006         0.001         0.001         0.005         0.001         0.005         0.001	Metribuzin	Н				0.003																		
Norflurazón         H         0.006         0.006         0.006         0.005         0.007         0.009         0.013         0.008         0.006         <	Myclobutanil	F										$\sim$				0.034								
Oxamyl         I <td>N,N-Diethyl-m-toluamide (DEET)</td> <td>lr</td> <td></td> <td></td> <td>0.008</td> <td></td> <td>0.006</td> <td></td> <td>0.007</td> <td>0.008</td> <td>0.006</td>	N,N-Diethyl-m-toluamide (DEET)	lr			0.008															0.006		0.007	0.008	0.006
Oxyfliorfen         H         0.009         0.0019         0.022           Pendimethalin         H         0.009         0.003         0.043         0.043         0.043         0.043         0.019         0.022           Prometon         H         0.009         0.008         0.012         0.013         0.013         0.016         0.012         0.006         0.006           Prometon         H         0.003         0.004         0.004         0.004         0.004         0.004         0.004         0.001         0.004         0.001         0.004         0.001<		Н	0.006	0.006	0.006	0.004	0.005	0.002	0.007	0.009	0.005	$\langle \rangle$	0.010	0.013	0.008	0.009		0.013	0.008	0.006	0.006	0.008	0.006	0.006
Pendimethalin         H         0.009         0.002         0.011         0.013         0.043         0.047         0.018         0.015         0.013         0.018         0.006         0.005           Propergite         I         0.004         0.004         0.004         0.004         0.004         0.001         0.013         0.018         0.012         0.018         0.012         0.018         0.012         0.005         0.005           Propergite         I         0.004         0.004         0.004         0.004         0.004         0.004         0.001         0.011         0.011         0.006         0.005         0.005           Primethanil         F         0.003         0.005         0.004         0.004         0.004         0.004         0.001         0.006         0.0	Oxamyl	1													0.006									
Piperonyl butoxide (PBO)         Sy         0.008         0.008         0.012         0.012         0.012         0.005           Prometon         H         0.004         0.004         0.004         0.009         0.012         0.012         0.005           Propargite         I         0.005         0.004         0.004         0.004         0.004         0.001         0.005           Primethanil         F         0.005         0.004         0.005         0.004         0.004         0.004         0.001         0.006		Н							0.019	0.022		$\langle \rangle$												
Piperonyl butoxide (PBO)         Sy         0.008         0.008         0.012         0.012         0.012         0.005           Prometon         H         0.004         0.004         0.004         0.004         0.004         0.005           Propargite         I         0.005         0.004         0.004         0.004         0.004         0.004           Primerthanil         F         0.003         0.005         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.004         0.006         0.004         0.011         0.006         0.001         0.007         0.004           Sufferstractine         H         0.008         0.010         0.009         0.006	Pendimethalin	Н	0.009	0.008	0.021	0.010	0.013	0.043	0.040	0.047	0.018		0.007	0.013	0.016	0.015		0.013	0.018	0.006	0.005		0.006	
Prometon         H         0.004         0.004           Propagite         I         0.003         0.004         0.004           Pyrimethanil         F         0.003         0.005         0.004         0.003         0.004         0.004           Pyrimethanil         F         0.003         0.005         0.004         0.004         0.004         0.011         0.006         0.011         0.007           Pyrimethanil         F         0.005         0.005         0.004         0.004         0.010         0.008         0.006         0.007         0.006         0.007         0.006         0.007 </td <td></td> <td>Sv</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td> </td> <td></td>		Sv																						
Propargite         I							0.004																	
Pyrimethanil         F         0.003         0.005         0.004         0.003         0.004         0.004         0.004         0.001         0.006         0.004         0.007           Pyriproxyfen         I         0.005         0.005         0.004         0.007         0.004         0.006         <		1										$\langle$						-	0.010					
Pyriproxyfen         I         0.005         0.004         Image: Constraint of the second		F	0.003	0.005	0 004			0.003	0.010	0 004	0 004		0.010	0.003	0 004			0.011		0 004	0 0 1 1	0.005	0.011	0 007
Simazine         H         0.004         0.005         0.007         0.004           Sodium bentazon         H         0.008         0.009         0.006         0.007 <t< td=""><td></td><td>i.</td><td>0.000</td><td>0.000</td><td></td><td>0.005</td><td></td><td></td><td>0.0.0</td><td>0.001</td><td>0.001</td><td> </td><td>0.0.0</td><td>0.000</td><td>0.001</td><td></td><td></td><td>0.011</td><td>0.000</td><td>0.001</td><td>0.011</td><td>0.000</td><td>0.0.1</td><td>0.001</td></t<>		i.	0.000	0.000		0.005			0.0.0	0.001	0.001		0.0.0	0.000	0.001			0.011	0.000	0.001	0.011	0.000	0.0.1	0.001
Sodium bentazon         H         0.008         0.010         0.009         0.006         0.008         0.015         0.005         0.007         0.008         0.009         0.008         0.009           Sulfentrazone         H         0.008         0.011         0.018         0.017         0.013         0.005         0.009         0.009         0.008         0.009           Terbacil         H         0.008         0.011         0.018         0.077         0.072         0.037           Thiamethoxam         I         0.004         0.007         0.004         0.007         0.004         0.007         0.004         0.007         0.004         0.007 <td< td=""><td></td><td>н. Н</td><td></td><td></td><td></td><td>0.000</td><td></td><td>0.001</td><td>0.005</td><td>0.007</td><td>0 004</td><td></td><td>0.006</td><td>0.006</td><td>0 009</td><td></td><td>0.006</td><td>0.006</td><td></td><td></td><td>0.006</td><td>0.006</td><td>0.006</td><td>0.006</td></td<>		н. Н				0.000		0.001	0.005	0.007	0 004		0.006	0.006	0 009		0.006	0.006			0.006	0.006	0.006	0.006
Sulfentrazone         H         0.008         0.010         0.009         0.006         0.008         0.015         0.005         0.001         0.003         0.009         0.009         0.009         0.008         0.009         0.009         0.008         0.009         0.007					0.001				0.000	0.001	0.001	<	0.000	0.000	0.000						0.000	0.000	0.000	0.000
Terbacii       H       0.008       0.018       0.019       0.011       0.018       0.074       0.072       0.037         Thiamethoxam       I       0       0.014       0.007       0.004       0.005       0.003       0.002       0.041       0.042       0.019       0.019       0.015       0.233       0.338       0.095         Triazine DEA degradate       D       0.014       0.007       0.004       0.005       0.007       0.010       0.005         Triazine DIA degradate       D       0.005       0       0.002       0.004       0.003       0.003       0.003       0.007<				0.008	0.010		0 000	0.006	0 008	0.015	0.005		0.004	0.017	0.013				0 000	0 000	0.008	0 000	0.008	0 000
Thiamethoxam         I <t< td=""><td></td><td></td><td>0 000</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>&lt;</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>			0 000									<												
Triazine DEA degradate       D       0.014       0.007       0.004       0.005       0.005       0.001       0.010       0.011       0.011       0.009       0.007 </td <td></td> <td></td> <td>0.000</td> <td>0.010</td> <td>0.013</td> <td>0.011</td> <td>0.010</td> <td>0.074</td> <td>0.070</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>0.037</td> <td>0.005</td> <td>0.041</td> <td>0.042</td> <td>0.021</td> <td>0.013</td> <td>0.015</td> <td>0.200</td> <td>0.550</td> <td>0.035</td>			0.000	0.010	0.013	0.011	0.010	0.074	0.070						0.037	0.005	0.041	0.042	0.021	0.013	0.015	0.200	0.550	0.035
Triazine DIA degradate         D         0.005         Image: model of the system of the sys			0.014	0.007	0.004	0.004	0.005	0.005	0.007						0.011	0.011	0.000	0.007	0.004	0.007	0.007	0.007	0.007	0.006
Triazine HA degradate         D         0.002         0.004         0.003           Triclopyr acid         H         0.008         0.042         0.043           Triclosan         A         0.008         0.005         0.043           Trifluralin         H         0.005         0.004         0.010         0.005           Total suspended solids (mg/L)         526         102         66         81         42         24         46         20         86           Streamflow (cubic ft/sec)         175.3         162.0         216.3         145.5         91.8         130.0         112.6         75.4         181.2           Precipitation (total in/week)†         0.13         0.09         0.73         0.23         0.26         0.12         0.47         0.51         0.22	v				0.004	0.004	0.005	0.005	0.007	0.010	0.005	>	0.010						0.004		0.007	0.007	0.007	
Triclopyr acid         H         0.008         0.005         0.042         0.043           Triclosan         A         0.008         0.005         0.004         0.010         0.005         0.001         0.005         0.009         0.009         0.009         0.005         0.001         0.001         0.009         0.009         0.005         0.001         0.001         0.005         0.001         0.0001         0.001         0.001         <			0.005						0.000	0.004	0.000	<		0.002	0.004	0.003	0.003	0.003		0.003				0.004
Triclosan         A         0.008         0.005         Image: Constraint of the constraint of th										0.004		>							0.004					
Trifluralin         H         0.004         0.006         0.005         0.004         0.010         0.005         0         0.009         Image: Constraint of the state of the st		-		0.000	<u> </u>	0.005			0.042		0.043								0.021					
Total suspended solids (mg/L)       526       102       66       81       42       62       46       20       86       8       8       9       6       58       11       13       10       8         Streamflow (cubic ft/sec)       175.3       162.0       216.3       145.5       91.8       130.0       112.6       75.4       181.2       91.8       86.9       86.9       96.5       58       11       13       10       8         Precipitation (total in/week)†       0.13       0.09       0.73       0.23       0.26       0.12       0.47       0.51       0.22       0.30       0.43       0.20       0.21       0.56       0.83       0.28       0.17       0.18       0.09       0.35       0.38			0.001			0.005		0.005	0.001	0.010	0.005	>		-		-		0.000						
Streamflow (cubic ft/sec)         175.3         162.0         216.3         145.5         91.8         130.0         112.6         75.4         181.2         91.8         86.9         98.4         95.8         92.7.4         120.2         128.3         115.5         130.0         136.7           Precipitation (total in/week)†         0.13         0.09         0.73         0.23         0.26         0.12         0.47         0.51         0.22         0.30         0.43         0.20         0.21         0.56         0.83         0.28         0.17         0.18         0.09         0.35         0.38		ΙH										$\leftarrow$				-								
Precipitation (total in/week)† 0.13 0.09 0.73 0.23 0.26 0.12 0.47 0.51 0.22 \ 0.30 0.43 0.20 0.21 0.56 0.83 0.28 0.17 0.18 0.09 0.35 0.38												$>$												
												$\langle$												
The "" signifies a sample that was not collected.				0.09	0.73	0.23	0.26	0.12	0.47	0.51	0.22		0.30	0.43	0.20	0.21	0.56	0.83	0.28	0.17	0.18	0.09	0.35	0.38
	The "" signifies a sample that was no	t colle	cted.							_														-

#### Table 19 – Sulphur Creek Wasteway pesticide calendar, µg/L

Current-use exceedance

DDT/degradate exceedance

Detection

\* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent, Sy: Synergist) <sup>+</sup> Washington State Univ. AgWeatherNet station: Port of Sunnyside, (latitude: 46.28°, longitude: -120.01°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at nine of the 21 site visits (43%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 48).

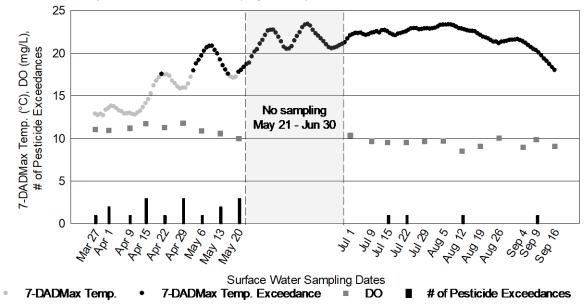


Figure 48 – Sulphur Creek Wasteway water quality measurements and exceedances of assessment criteria

All DO measurements met the state standard, ranging from 8.52 mg/L to 11.79 mg/L with an average of 10.16 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard for 135 days of the sampling season, primarily from May 3 through the rest of the season. Pesticide exceedances coincided with 7-DADMax temperature exceedances at seven site visits.

The pH measurements ranged from 7.55 to 8.69 with an average of 8.22. Less than a quarter (14%) of these measurements exceeded the state standard in that three measurements were greater than 8.5. The pH exceedances on April 15 and April 29 coincided with three pesticide exceedances each. On May 6, a pesticide exceedance overlapped with both a pH exceedance and a 7-DADMax temperature exceedance.

Sulphur Creek Wasteway provides habitat for salmonid rearing and migration. During particularly warm weather periods, Sulphur Creek Wasteway contributes cooler water to the Yakima River, which acts as a thermal refuge for salmon as they travel up the Yakima River to their spawning grounds (A. Gendaszek, USGS, personal communication, 2019). Exceedances of the 7-DADMax standard during this time may further negatively affect these endangered species in the region. WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly exceedances of chlorpyrifos.

## **Touchet River**

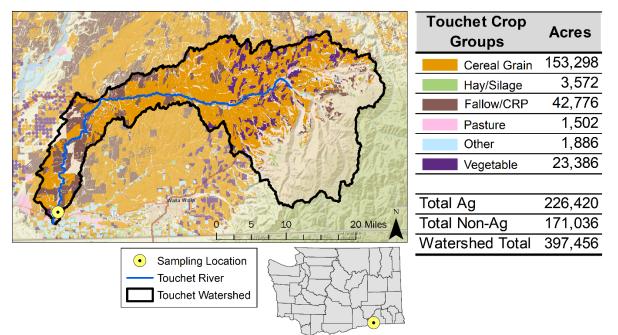


Figure 49 – Map of Touchet River and its drainage area with associated sampling location and crop groups identified

In 2018, WSDA started sampling the Touchet River watershed in Walla Walla County. Staff selected the watershed to represent typical Eastern Washington dryland agricultural practices and to expand the monitoring further east where WSDA sampling had not taken place before. The site is located on the upstream side of the bridge crossing of Cummins Road near Touchet (latitude: 46.056877°, longitude: -118.668973°) (Figure 49, Figure 50).



Figure 50 - Touchet River downstream view

The approximately 65-mile-long Touchet River drains into the Walla Walla River almost 3 miles downstream of the monitoring site. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the river. WDFW has documented spring Chinook salmon and summer steelhead throughout the main stem of Touchet River (WDFW, 2019).

The Touchet River headwaters are located in the Blue Mountains within the Umatilla National Forest. The majority of the watershed has mountainous terrain; however, the monitoring site is within flatter, low-lying terrain. The agricultural land use is predominately wheat, dry peas, garbanzo beans, grass hay, and barley. The 'Other' crop group category consists of oilseed, seed crops, nurseries and other assorted low-acreage crops (Figure 49).

The Touchet River monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2019 monitoring season and a visual comparison to the WSDA assessment criteria (Table 20). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Month			Apr		M	ay	Ju	ın	J	ul	A	ug	Sep		
Day of the Month	Use*	1	15	29	13	28	10	24	9	22	5	19	4	16	30
1-(3,4-Dichlorophenyl)-3-methylurea	D											0.01			
2,4-D	н			0.024			0.033					0.036		0.044	
2,6-Dichlorobenzamide	D		0.003	0.004	0.003				0.002						
4,4'-DDD	D		0.021	0.003											
4,4'-DDE	D		0.003												
4,4'-DDT	I		0.004												
Aminomethylphosphonic acid (AMPA)	Н	0.020	0.039	0.020	0.023	0.021	0.022	0.022	0.030	0.048	0.041	0.247	1.670	4.180	4.160
Atrazine	Н			0.004					0.004	0.005					
Azoxystrobin	F													0.002	
Boscalid	F														0.004
Bromacil	Н	0.007	0.006	0.011	0.010	0.008	0.009	0.010	0.011	0.013	0.012	0.007	0.006	0.005	
Carbendazim	F								0.012					0.003	
Chlorpyrifos	1		0.003												
Dacthal (DCPA)	Н														0.028
Dicamba acid	Н						0.011					0.010			
Dichlobenil	Н			0.004											
Diuron	Н											0.015			
Eptam	Н				0.002										
Glyphosate	Н	0.027	0.019	0.019	0.026	0.018	0.020	0.014	0.012	0.068	0.015	0.054	0.179	0.924	0.414
Hexazinone	Н	0.006	0.006	0.005											
Imazapyr	Н		0.011	0.005	0.003										
Methamidophos	D						0.001			0.002	0.004	0.004	0.004	0.003	0.002
Metolachlor	Н				0.005			0.003		0.004					
Metribuzin	Н	0.005	0.005	0.005											
N,N-Diethyl-m-toluamide (DEET)	lr										0.015	0.013			
Pendimethalin	Н	0.006	0.006	0.005	0.006					0.011					
Propiconazole	F								0.008						
Sodium bentazon	Н						0.045					0.057			
Sulfentrazone	Н	0.006	0.007	0.006											>>
Tebuthiuron	Н				0.007		0.016	0.005			0.005				
Thiamethoxam	1			0.002											
Triallate	Н			0.003											
Triclosan	А	0.009													
Total suspended solids (mg/L)		104	1,120	235	23	12	5	4	1						
Streamflow (cubic ft/sec)		549	1,490	515	277	183	105	61		22				24	41
Precipitation (total in/week)†															
The "" signifies a sample or measure	ment t	hat was	s not co	llected	or cou	Id not b	he anal	vzed T	'he "X"	signifie	es data	rejecte	d by fa	ilina au	ality

Table 20 – Touchet River pesticide calendar, µg/L

The "--" signifies a sample or measurement that was not collected or could not be analyzed. The "X" signifies data rejected by failing quality assurance performance measures.

DDT/degradate exceedance

Detection

Below is a brief overview of pesticide findings in Touchet River in 2019.

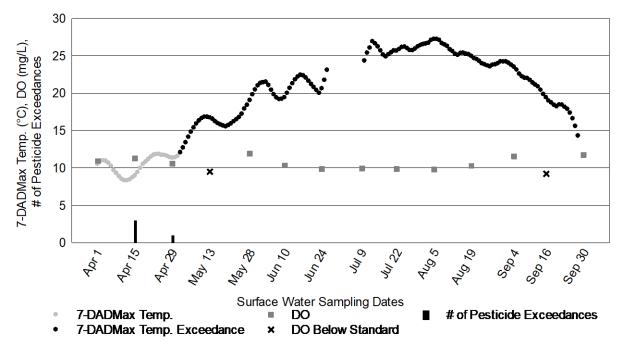
- WSDA tested for 159 unique pesticides in Touchet River.
- There were 107 total pesticide detections from six different use categories: 19 types of herbicides, 3 insecticides, 4 fungicides, 5 degradates, 1 antimicrobial and 1 insect repellent.

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, Ir: Insect repellent)

<sup>&</sup>lt;sup>†</sup> Washington State University AgWeatherNet station: Touchet, (latitude: 46.02°, longitude: -118.68°)

- Pesticides were detected at all 14 sampling events.
- Up to 15 pesticides were detected at the same time.
- Of the total pesticide detections, four were above WSDA's assessment criteria (Table 20).
  - The single detection of 4,4'-DDE, two detections of 4,4'-DDD, and single detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 μg/L).
- There were no watershed-specific POCs for the Touchet site and no statewide WSDA POCs detected in exceedance of WSDA assessment criteria. However, chlorpyrifos, a statewide POC, was detected below assessment criteria once on April 15.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. However, no pesticide exceedances coincided with water quality measurements that did not meet state standards at this site. Several water quality measurements at the Touchet River site are shown below (Figure 51 and Figure 52).



*Figure 51 – Touchet River water quality measurements and exceedances of assessment criteria* 

DO measurements ranged from 9.22 mg/L to 11.90 mg/L with an average of 10.48 mg/L. Less than half (14%) of these measurements did not meet the state standard in that two measurements were less than 9.5 mg/L. The 7-DADMax temperatures exceeded the 12°C standard for at least 137 days of the sampling season, from May 2 through the rest of the season. There was a temperature data gap resulting in missing 7-DADMax temperature calculations from June 27 through July 9; however, the temperatures likely exceeded the standard since there were exceedances before and after the gap.

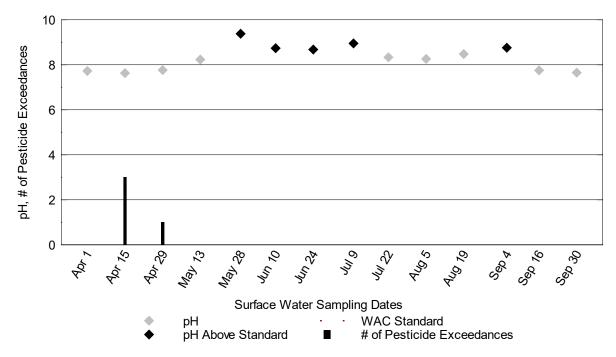


Figure 52 – Touchet River pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.63 to 9.38 with an average of 8.31. Less than half (36%) of these measurements exceeded the state water quality standard in that three measurements were above 8.5 (red-dashed line), (Figure 52).

The Touchet River has been designated as a freshwater body that provides habitat for char spawning and rearing by the WAC (WAC, 2019). Staff observed juvenile fish of unknown species at the monitoring site. WSDA will continue to monitor this drainage because of its representative regional land use.

# **Statewide Results**

WSDA selects sites where, based on land use or historic pesticide detections, pesticide contamination and poor water quality are expected. Sites are not compared on the basis of total detections or exceedances due to variability in site characteristics and site-specific sampling practices. Each of the 16 current monitoring sites has distinct watershed and land-use characteristics that dictate the pesticides detected. Different sites are sampled for different periods of time (9 to 28 sampling events) and samples from several sites are tested for a subset of pesticides compared to the majority of sites (90 to 159 analytes). In addition, WSDA monitoring sites are not representative of all Washington streams in terms of levels of pesticide contamination or other characteristics. Statewide summary information (Table 21) provides a useful overview but should be used with caution.

Pesticide general use category	# of analytes tested for	# of analytes detected	# of analytes with detections above assessment criteria	# of individual detections
Antimicrobial	1	1		27
Legacy pesticides	5	4	3	168
Degradate	16	14	1	912
Fungicide	20	17		730
Glyphosate, AMPA and glufosinate-ammonium	3	3		324
Herbicide	56	49	1	2,452
Insect repellent	1	1		30
Insecticide	54	31	13	908
Synergist	2	1		50
Wood preservative	1	1		5
Total analytes	159	122	18	5,606

There were 122 different analytes detected in 2019 (Table 21). Across 16 monitoring sites, WSDA identified 5,606 detections. Every monitoring site had detections of at least one herbicide, one fungicide, and one insecticide. To determine if the concentration of the detections could negatively affect aquatic life, WSDA compared each detection to WSDA assessment criteria.

There were 308 instances where detections exceeded the WSDA assessment criteria listed in Appendix A: Assessment Criteria for Pesticides. The Monitoring Site Results section in this report discusses the individual exceedances in more detail while the Pesticide Detection Summary below divides the detections and associated exceedances by pesticide general use category.

Of the 308 individual exceedances, 154 (50%) were currently registered pesticides or their associated degradates. The other 154 (50%) were detections of the legacy insecticide DDT

or its associated degradates. Approximately half of the exceedances, 181 (59%), occurred at monitoring sites in Eastern Washington including many of the statewide exceedances of DDT or its degradates (130). Imidacloprid, a neonicotinoid insecticide, accounted for 83 (27%) of the individual pesticide exceedances with 70 of the exceedances found in Western Washington monitoring sites. WSDA found at least one pesticide that exceeded WSDA assessment criteria at each site monitored.

### **Pesticide Detection Summary**

Below, statewide detections are summarized by pesticide general use categories. This subsection only presents analytes detected in 2019. Appendix B: 2019 Quality Assurance Summary provides a list of all analytes tested.

#### **Herbicide Detections**

Herbicides were the most frequently detected group of current-use pesticide making up approximately 44% (2,452 detections) of the total pesticide detections. Of the 56 herbicides included in the laboratory analysis, 49 were detected in surface water samples. Table 22 provides a statewide summary of the detected herbicides.

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Bromacil	292	183 (63%)	-	12		0.00326 - 0.353
Sulfentrazone	292	152 (52%)		14		0.00309 - 0.0708
Imazapyr	274	151 (55%)		13		0.0021 - 0.727
Terbacil	292	150 (51%)		10		0.00344 - 0.38
Diuron	274	149 (54%)	1	13	1	0.00221 - 1.29
Simazine	292	127 (43%)		11		0.00381 - 0.764
Metolachlor	292	122 (42%)		13		0.00272 - 0.127
2,4-D	251	121 (48%)		12		0.0137 - 3.26
Pendimethalin	292	116 (40%)		12		0.0029 - 0.119
Norflurazon	292	115 (39%)		11		0.00151 - 0.0266
Atrazine	292	112 (38%)		13		0.00353 - 0.0544
Hexazinone	292	105 (36%)		15		0.00203 - 0.0428
Dichlobenil	292	100 (34%)		11		0.00102 - 0.0956
Tebuthiuron	292	83 (28%)		7		0.00343 - 0.12
Dicamba acid	251	67 (27%)		10		0.009 - 0.794
Prometon	292	60 (21%)		10		0.00233 - 0.0219
Triclopyr acid	251	51 (20%)		7		0.0161 - 2.38
Eptam	292	46 (16%)		9		0.00209 - 0.133

Table 22 – Statewide summary of herbicides with one or more detections in 2019

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Indaziflam	274	43 (16%)		5		0.00165 - 0.0762
Napropamide	292	41 (14%)		4		0.00447 - 0.0416
Dacthal (DCPA)	251	40 (16%)		4		0.0241 - 0.253
Sulfometuron methyl	274	35 (13%)		7		0.00189 - 0.129
Metribuzin	292	34 (12%)		8		0.00326 - 0.0141
Oxadiazon	292	29 (10%)		3		0.00341 - 0.0168
Trifluralin	292	23 (8%)		6		0.00321 - 0.0119
MCPA	251	21 (8%)		6		0.0153 - 0.909
Sodium bentazon	251	19 (8%)		4		0.0435 - 0.174
Dithiopyr	292	18 (6%)		3		0.00221 - 0.00798
Oryzalin	292	17 (6%)		4		0.00415 - 0.0315
Chlorpropham	292	16 (5%)		5		0.00205 - 0.0347
Prodiamine	292	14 (5%)		1		0.00562 - 0.0283
Mecoprop (MCPP)	251	13 (5%)		4		0.0216 - 0.132
Picloram	251	13 (5%)		1		0.0361 - 0.0972
Isoxaben	274	12 (4%)		5		0.00156 - 0.00827
Metsulfuron-methyl	274	10 (4%)		5		0.00328 - 0.0468
Chlorsulfuron	274	7 (3%)		3		0.0108 - 0.0469
Imazapic	274	7 (3%)		2		0.00351 - 0.0186
Flumioxazin	292	7 (2%)		3		0.00494 - 0.0111
Bromoxynil	251	6 (2%)		2		0.0121 - 0.146
Clopyralid	251	4 (2%)		2		0.0353 - 0.0988
Ethalfluralin	292	2 (1%)		1		0.00606 - 0.0065
Fluroxypyr 1- methylheptyl ester	292	2 (1%)		1		0.00663 - 0.0885
Oxyfluorfen	292	2 (1%)		1		0.0191 - 0.022
Simetryn	292	2 (1%)		2		0.00426 - 0.0103
Alachlor	292	1 (0%)		1		0.00413 - 0.00413
Prometryn	292	1 (0%)		1		0.00975 - 0.00975
Propyzamide	292	1 (0%)		1		0.00395 - 0.00395
Triallate	292	1 (0%)		1		0.00288 - 0.00288
Triclopyr butoxyethyl ester	292	1 (0%)		1		0.226 - 0.226

Bromacil, sulfentrazone, and imazapyr were the most frequently detected herbicides that WSDA annually tests for with 183, 152, and 151 detections, respectively. There were 16 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Only one herbicide, diuron, was detected above the assessment criteria, accounting for less than 1% of the total exceedances in 2019. Diuron is used mostly for broadleaf and grassy weed control in agricultural and non-agricultural locations. WSDA finds this herbicide at many of the monitoring sites across the state annually.

Several of the herbicides detected break down into chemicals that may also negatively affect aquatic life. Below is a list of herbicides with a corresponding degradate that WSDA tests for.

- Atrazine  $\rightarrow$  triazine DEA (detected at nine monitoring sites),
  - $\circ \rightarrow$  triazine HA (detected at nine monitoring sites),
  - $\circ \rightarrow$  triazine DIA (detected at 10 monitoring sites),
- Dichlobenil  $\rightarrow$  2,6-dichlorobenzamide (detected at 16 monitoring sites),
- Diuron  $\rightarrow$  1-(3,4-Dichlorophenyl)-3methylurea (detected at nine monitoring sites).

#### **Fungicide Detections**

Fungicides were the third most frequently detected group of current-use pesticides making up 730 detections, or 13%, of the total number of detections. In 2017 and 2018, fungicides were the second most frequently detected group of pesticides. Out of 20 fungicides included in the laboratory analysis, 17 were detected in surface water samples. Table 23 provides a statewide summary of the detected fungicides.

Analyte	# of samples collected*	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (μg/L)
Boscalid	292	189 (65%)		14		0.00256 - 0.341
Fludioxonil	292	164 (56%)		10		0.00358 - 1.34
Azoxystrobin	274	97 (35%)		9		0.00114 - 0.219
Carbendazim	274	62 (23%)		10		0.00128 - 0.044
Pyrimethanil	274	47 (17%)		5		0.00314 - 0.0214
Propiconazole	274	37 (14%)		7		0.00742 - 0.486
Metalaxyl	292	31 (11%)		7		0.00652 - 0.287
Paclobutrazol	274	29 (11%)		4		0.00227 - 0.0596
Cyprodinil	274	21 (8%)		3		0.00187 - 0.0444
Myclobutanil	274	12 (4%)		3		0.00392 - 0.048
Triadimefon	292	10 (3%)		2		0.00342 - 0.054
Difenoconazole	274	9 (3%)		2		0.00493 - 0.0237
Chlorothalonil	292	6 (2%)		4		0.00274 - 0.00592
Etridiazole	292	5 (2%)		1		0.0012 - 0.00406
Pyraclostrobin	274	5 (2%)		1		0.00731 - 0.0132

Table 23 – Statewide summary of fungicides with one or more detections in 2019

Analyte	# of samples collected*	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (μg/L)
Trifloxystrobin	274	5 (2%)		1		0.00545 - 0.0228
PCNB	292	1 (0%)		1		0.0035 - 0.0035

Boscalid, fludioxonil, and azoxystrobin were the most commonly detected fungicides with 189, 164, and 97 detections, respectively. Boscalid and fludioxonil were among the most commonly detected fungicides each year since 2015. Carbendazim, detected the fourth most commonly, is rarely used as a fungicide and is more often found in the environment as a degradate (Montague et al., 2014). However, it is registered in Washington as a fungicide and is categorized as a fungicide in this program. Its parent compound, thiophanate-methyl is a fungicide that WSDA does not test for and degrades very quickly into carbendazim in surface water. Detections of fungicides occur primarily at Western Washington sampling sites (approximately 68% of 2019 fungicide detections). The wetter climate of Western Washington drives the usage of more fungicides than in Eastern Washington. No fungicide detections exceeded WSDA assessment criteria in 2019.

WSDA detected the following fungicides in at least 50% of the monitoring sites throughout the sampling season:

• Azoxystrobin

Carbendazim

Boscalid

• Fludioxonil

#### **Insecticide Detections**

Current-use insecticides were the second most frequently detected group of pesticides representing approximately 16% (908 detections) of the total pesticide detections. Of the 54 current-use insecticides included in the laboratory analysis, 31 were detected in surface water samples. Table 24 provides a statewide summary of the detected insecticides.

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (μg/L)
Thiamethoxam	274	170 (62%)		13		0.00158 - 0.0889
Imidacloprid	274	104 (38%)	83	11	10	0.00231 - 0.29
Clothianidin	274	103 (38%)	12	11	2	0.00229 - 0.0522
Chlorpyrifos	292	82 (28%)	13	10	4	0.00287 - 0.248
Malathion	292	53 (18%)	9	10	3	0.00209 - 0.874
Dinotefuran	274	51 (19%)		4		0.00206 - 0.973

#### Table 24 – Statewide summary of insecticides with one or more detections in 2019

Ambient Monitoring for Pesticides in Washington State Surface Water: 2019 Technical Report | 85

Analyte	# of samples collected	# of detections (% samples)	s) assessment detections exceeding detections		with exceeding	Concentration range (μg/L)	
Diazinon	292	45 (15%)	1	9	1	0.00263 - 0.133	
Acephate	274	40 (15%)		6		0.0031 - 1.23	
Oxamyl	274	39 (14%)		4		0.000876 - 0.0853	
Chlorantraniliprole	274	32 (12%)		7		0.00528 - 0.0264	
Acetamiprid	274	22 (8%)		8		0.00127 - 0.00914	
Dimethoate	292	22 (8%)		8		0.0048 - 0.039	
Fipronil	292	17 (6%)	4	7	3	0.00329 - 0.00829	
Carbaryl	274	16 (6%)		6		0.00247 - 0.0144	
Methomyl	274	15 (5%)		6		0.000855 - 0.0401	
Pyriproxyfen	292	15 (5%)	2	7	1	0.0018 - 0.19	
Total fluvalinate	292	15 (5%)	8	8	5	0.00191 - 0.164	
Etoxazole	292	13 (4%)		4		0.00282 - 0.0105	
Pyridaben	292	10 (3%)	2	7	2	0.00388 - 0.0315	
Bifenthrin	292	9 (3%)	9	3	3	0.00418 - 0.0131	
Phosmet	292	8 (3%)		5		0.00553 - 0.0891	
Tefluthrin	292	6 (2%)	6	6	6	0.00169 - 0.00256	
Methoxyfenozide	274	5 (2%)		2		0.00359 - 0.00419	
Tetramethrin	292	4 (1%)	1	1	1	0.0159 - 0.102	
Ethoprop	292	3 (1%)		3		0.00277 - 0.00766	
Propargite	292	3 (1%)		3		0.00648 - 0.029	
Spirotetramat	274	2 (1%)		2		0.00869 - 0.0706	
Permethrin (cis & trans)	292	1 (0%)	1	1	1	0.01626 - 0.01626	
Permethrin (trans)	292	1 (0%)	1	1	1	0.00559 - 0.00559	
Chlorpyrifos-methyl	292	1 (0%)		1		0.00485 - 0.00485	
Dicofol	292	1 (0%)		1		0.00516 - 0.00516	

WSDA identified bolded analytes to be statewide POCs.

Thiamethoxam, imidacloprid, and clothianidin were the most commonly detected insecticides with 170, 104, and 103 detections, respectively. The insecticides thiamethoxam and imidacloprid have been among the most commonly detected insecticides every year since 2015. Several neonicotinoid pesticides such as thiamethoxam, imidacloprid, and clothianidin have low laboratory method detection limits, which is one reason for their high frequency of detection.

WSDA detected the following insecticides in at least 50% of the monitoring sites throughout the sampling season:

• Chlorpyrifos

• Clothianidin

Diazinon

Malathion

Imidacloprid

Thiamethoxam

Detections of current-use insecticides accounted for almost 50% (152 detections) of all exceedances in 2019. All detections of bifenthrin, tefluthrin and permethrin were at concentrations above the WSDA assessment criteria. Of the 31 current-use insecticides that WSDA detected, 42% (13 insecticides) had a concentration detected that exceeded WSDA assessment criteria at least once.

The three statewide POCs identified in 2019 were chlorpyrifos, malathion, and imidacloprid. Chorpyrifos has been a WSDA POC since 2009 and is most often applied on fruit trees. Every exceeding detection in 2019 was found in Eastern Washington, where most of the state's fruit trees are located. Malathion has been a POC since 2015. Malathion is applied most frequently to control fruit flies and mosquitos. It is applied to a wide range of crops from tree fruit and berries to yards and even has indoor uses. Most detections and exceedances of malathion were found in Eastern Washington. Imidacloprid has been a POC since 2017. This insecticide can be applied to over 250 commercial crop types and has residential uses; the majority of the exceedances and detections were found in Western Washington sites. It is unknown by WSDA if the detections of imidacloprid that exceeded WSDA criteria were the result of applications to crops or residential uses.

Several of the insecticides detected break down into chemicals that may also negatively affect aquatic life. Below is a list of insecticides with corresponding degradates that WSDA tests for.

- Acephate  $\rightarrow$  methamidophos (detected at 12 monitoring sites),
- Malathion  $\rightarrow$  malaoxon (detected at three monitoring sites),
- Fipronil  $\rightarrow$  fipronil sulfide (detected at four monitoring sites),
  - $\circ \rightarrow$  fipronil sulfone (detected at five monitoring sites),
- Oxamyl  $\rightarrow$  oxamyl oxime (detected at four monitoring sites),
- Methomyl  $\rightarrow$  methomyl oxime (detected at one monitoring site),
- Thiamethoxam → clothianidin. Although thiamethoxam degrades into clothianidin, both insecticides are registered independently in Washington.

#### Glyphosate, AMPA and Glufosinate-ammonium Detections

WSDA conducted a special herbicide project in 2019 in conjunction with the regular surface water monitoring. Glyphosate, aminomethylphosphonic acid (AMPA) (a glyphosate breakdown product), and glufosinate-ammonium, were tested for at 14 of the 16 monitoring sites every two weeks for the duration of the sampling season. The two sites excluded were Mission Creek and Stemilt Creek due to their shortened sampling season schedules. WSDA does not typically test for the three chemicals in this special study due to the cost of lab analysis. We tested for these three chemicals previously in 2015, but sampling only took place during the first five weeks of spring.

The three chemicals accounted for 6% (324 detections) of the total pesticide detections. All three of the chemicals included in the lab analysis for the special project were detected. A statewide summary of glyphosate, AMPA and glufosinate-ammonium is shown below in Table 25.

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Glyphosate	173	156 (90%)		14		0.00353 - 18.4
AMPA	173	155 (90%)		14		0.00346 - 16.7
Glufosinate- ammonium	173	13 (8%)		6		0.00331 - 0.482

Table 25 – Statewide summary of glyphosate, AMPA and glufosinate-ammonium in 2019

Glyphosate was the most frequently detected chemical in the study with 156 detections closely followed by a degradate of glyphosate, AMPA, with 155 detections. Glyphosate and AMPA were found at every monitoring site where they were tested for. Even though they were frequently detected, their concentrations were below WSDA assessment criteria levels of concern.

#### **Degradate and Other Pesticide Product Detections**

This group includes degradates of current-use pesticides as well as several other pesticiderelated chemicals. Current-use degradates represented 16% (912 detections) and pesticide-related chemicals represented 2% (112 detections) of total detections. Of the 16 degrades from current-use chemicals included in the laboratory analysis, 13 were detected in surface water samples. Only one of the two synergists tested for was detected. Each antimicrobial, wood preservative, and insect repellent tested for had at least one detection. Table 26 provides a statewide summary of the detected degradates and other pesticide product ingredients.

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)	
Degradates:							
2,6-Dichlorobenzamide	292	245 (84%)		16		0.00175 - 0.273	
Methamidophos	274	135 (49%)		12		0.00116 - 0.29	
Triazine DEA degradate	274	127 (46%)		9		0.00138 - 0.0155	
Triazine HA degradate	274	104 (38%)		9		0.0016 - 0.0442	
Triazine DIA degradate	274	87 (32%)		10		0.00244 - 0.0715	

Table 26 – Statewide summary of degradates and other pesticide products in 2019

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Oxamyl oxime	274	53 (19%)		4		0.0065 - 0.132
1-(3,4-Dichlorophenyl)-3 methylurea	274	52 (19%)		9		0.00295 - 0.0976
Tetrahydrophthalimide	292	43 (15%)		5		0.00255 - 0.469
Malaoxon	274	24 (9%)	1	3	1	0.000409 - 0.0325
Acetochlor ESA	274	22 (8%)	5			0.00991 - 0.0628
Fipronil sulfone	292	8 (3%)	5			0.00373 - 0.00561
Fipronil sulfide	292	6 (2%)	4			0.00303 - 0.0044
4-Nitrophenol	251	4 (2%)	2			0.0365 - 0.518
Methomyl oxime	274	2 (1%)	1			0.00686 - 0.00845
Antimicrobial:						
Triclosan	292	27 (9%)		14		0.00522 - 0.0348
Insect repellent:						
DEET	292	30 (10%)		12		0.00489 - 0.0747
Synergist:						
Piperonyl butoxide	292	50 (17%)		10		0.00519 - 0.679
Wood preservative:						
Pentachlorophenol	251	5 (2%)		3		0.0135 - 0.0361

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 245 detections, followed by methamidaphos (degradate of the insecticide acephate) with 135 positive detections. Detections of 2,6-dichlorobenzamide may be from either dichlobenil or fluopicolide; WSDA only tests samples for the presence of dichlobenil. The degradate, 2,6-dichlorobenzamide, was found ubiquitously throughout the season at all monitoring sites. Degradates detected that did not have a parent compound detected at any of the monitoring sites were acetochlor ESA, tetrahydrophthalimide and 4-nitrophenol. Acetochlor ESA is the breakdown product of the herbicide acetochlor, tetrahydrophthalimide is the main breakdown product of the fungicide captan, and 4-nitrophenol is a breakdown product of several natural and synthetic products.

A single detection of malaoxon exceeded WSDA assessment criteria at Lower Bertrand Creek on April 8. We detected malathion, the parent compound of malaoxon, exceeding WSDA assessment criteria at the same sampling event as well.

Other associated pesticide ingredients detected were pentachlorophenol, triclosan and piperonyl butoxide. Pentachlorophenol's main usage is for wood preservation. Also, the insect repellent DEET (N,N-Diethyl-m-toluamide), detected 30 times, was found at every monitoring site but three. The only federally registered uses of DEET are for application to horses, the human body, and clothing.

#### **Legacy Pesticide Detections**

WSDA tested for three legacy pesticides in order to document the pesticide prevalence in surface waters after the products were banned. The U.S. EPA banned products containing the insecticide DDT in 1972, the fungicide fenarimol in 2013, and the insecticide tralomethrin in 2011. DDT, DDT degradates and fenarimol may be detected in areas where products containing these chemicals were historically used because of their persistence in soils. Contaminated soil can enter surface water as a result of runoff or when sediment is disturbed. Fenarimol is allowed to be applied until all stock is gone.

Detected legacy pesticides and associated degradates accounted for 3% (168 detections) of the total pesticide detections. Table 27 provides a statewide summary of the detected legacy pesticides and degradates.

Table 27 – Statewide summary of legacy pesticides and their degradate detections in 2019											
Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (μg/L)					
4,4'-DDE	292	64 (22%)	64	12	12	0.0016 - 0.0304					
4,4'-DDD	292	56 (19%)	56	11	11	0.000807 - 0.0205					
4,4'-DDT	292	34 (12%)	34	7	7	0.00421 - 0.0166					
Fenarimol	292	14 (5%)		6		0.0021 - 0.0153					

There were detections of four of the five legacy analytes. DDT's degradate, 4,4'-DDE, was the most frequently detected legacy chemical with 64 detections closely followed by 4,4'-DDD with 56 detections. DDT or an associated degradate were found in four of seven Western Washington sites and all but one Eastern Washington monitoring sites.

The parent compound 4,4'-DDT and its degradates (4,4'-DDE and 4,4'-DDD) accounted for 50% of the total exceedances detected in 2019. Of the 154 combined DDT exceedances, 64 (42%) were detected at the monitoring site on Brender Creek. Although every detection of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD exceeded the state water quality standards, these detections are not a result of current pesticide usage patterns.

### **Toxic Unit Analysis**

A study by Broderius and Kahl (1985) found when a large number of chemicals are included in mixture experiments on organisms; 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 toxic units (TUs). For this report, TUs were used to estimate the additive effects of pesticide mixtures, as described by Faust et al. in 1993 (in Lydy et al., 2004). To determine a TU for a sample, a criteria ratio is calculated for each pesticide detected in the sample by dividing the pesticide concentration by the corresponding pesticides  $LC_{50}$ assessment criteria. Then, each of those ratios is summed to obtain an estimated TU for the whole sample. In this report, WSDA analyzed TU using the fish  $LC_{50}$ , invertebrate  $EC_{50}$  and plant  $EC_{50}$  assessment criteria with WSDA's safety factor for a more conservative approach. If the TU ratio is above or equal to one, there is a higher possibility of lethal or sublethal effects on aquatic life. Of the 289 samples analyzed using TUs, there were 32 samples that had a TU above or equal to one. In all 32 samples this was primarily due to an elevated concentration of one or two pesticides. The pesticides that contributed significantly to high TU values were chlorpyrifos, diazinon, diuron, imidacloprid, malathion, pyriproxyfen, and fluvalinate. All of these chemicals were found in concentrations above WSDA assessment criteria at least once throughout the sampling season, often coinciding with the samples with TUs greater than or equal to one. These samples came from Upper Bertrand Creek, Lower Bertrand Creek, Upper Big Ditch, Brender Creek, Indian Slough, Mission Creek, Snipes Creek, and Sulphur Creek Wasteway.

# Conclusions

Staff collected surface water monitoring data at 16 locations across Eastern and Western Washington in 2019. Water samples were collected during the peak pesticide application season (March – November) a total of 292 times. Samples taken from 13 of the monitoring sites were tested in a lab for 159 pesticide and pesticide-related chemicals, while one monitoring site was tested for a subset of 145 chemicals, and two more monitoring sites were tested for a subset of 90 chemicals.

- Of 159 pesticides tested for, 122 unique pesticides were detected.
- WSDA detected pesticides in water samples a total of 5,606 times.
- In a special 2019 project, we tested for glyphosate, AMPA (a glyphosate degradate), and glufosinate-ammonium at 14 of the 16 monitoring sites every other week. Both glyphosate and AMPA were detected at a 90% frequency with 156 detections and 155 detections, respectively. All concentrations were below levels of concern.
- Bromacil, sulfentrazone, and imazapyr were the most frequently detected herbicides that weren't tested for in the special study (183, 152, and 151 times, respectively).
- Thiamethoxam, imidacloprid, and clothianidin were the most frequently detected insecticides (170, 104, and 103 times, respectively).
- Boscalid, fludioxonil, and azoxystrobin were the most frequently detected fungicides (189, 164, and 97 times, respectively).
- We detected more fungicides at Western Washington sites (499 total detections) than Eastern Washington sites (231 total detections).
- Only 11 chemicals were detected in over 50% of sampling events they were tested for. Glyphosate, AMPA, and 2,6-dichlorobenzamide (a degradate) were detected each in more than 80% of sampling events.

In 2019, monitoring sites commonly contained mixtures of pesticides in samples. Of the 16 monitoring sites, 14 sites had two or more pesticide detections at every sampling event during the entire field season. Only the Woodland Creek and Mission Creek monitoring sites had sampling events with less than two detections. The maximum number of detections (54) at a single sampling event occurred May 20 at the Upper Big Ditch site. Although studies on the effects of pesticide mixtures are limited, there is evidence that indicates certain combinations of pesticides can have compounding adverse effects in aquatic systems (Broderius and Kahl, 1985).

In order to assess the potential effects of pesticide exposure to aquatic life and endangered species, WSDA compared detected pesticide concentrations to WSDA assessment criteria. There were 308 exceedances total with at least one exceedance at every site monitored (16) (Table 28). Half of the total exceedances (154 exceedances) were from 14 current-use pesticides and one degradate (resulting from current usage of parent compound). Every detection of bifenthrin, tefluthrin and permethrin exceeded WSDA assessment criteria. However, not every detection of the other 12 pesticides did. A summary of current-use pesticides with exceedances is below in Table 28. Imidacloprid had substantially more detections exceeding criterion than other pesticides in part due to low laboratory method

detection limits and low WSDA assessment criterion. Detections of DDT and associated degradates accounted for the remaining half (154 exceedances) of the total exceedances. DDT and/or one of its degradates was detected at four Western Washington sites, ranging from one exceeding detection at the Upper Big Ditch site to a maximum of 12 exceeding detections at the Lower Big Ditch site. In Eastern Washington, DDT and/or one of its degradates was detected at every monitoring site but Naneum Creek; detections ranged from two exceedances at Lower Crab Creek to a maximum of 64 exceedances at Upper Brender Creek alone. Every detection of DDT exceeded WSDA assessment criteria.

Analyte	# of detections	# of detections above assessment criteria
Imidacloprid	104	83 (80%)
Chlorpyrifos	82	13 (16%)
Clothianidin	103	12 (12%)
Malathion	53	9 (17%)
Bifenthrin	9	9 (100%)
Total fluvalinate	15	8 (53%)
Tefluthrin	6	6 (100%)
Fipronil	17	4 (24%)
Pyriproxyfen	15	2 (13%)
Pyridaben	10	2 (20%)
Permethrin (cis &/or trans)	2	2 (100%)
Diuron	149	1 (1%)
Diazinon	45	1 (2%)
Tetramethrin	4	1 (25%)

Table 28 – Summary of WSDA assessment criteria exceedances from current-use pesticides

Exceedances by current-use pesticide types are as follows.

- Out of 2,452 total herbicide detections, one detection exceeded criteria (<1%).
- Out of 730 total fungicide detections, no detection exceeded criteria (0%).
- Out of 908 total insecticide detections, 152 detections exceeded criteria (17%).

WSDA maintains and updates a POC list annually, consisting solely of current-use pesticides, in order to identify the highest priority pesticides for education and outreach programs. The agricultural community, regulatory community, and public may also reference the POC list to keep informed about current pesticide trends in Washington State. In 2019, WSDA and all other Region 10 states adopted a new decision matrix for selecting watershed and statewide POCs. The decision matrix provides a uniform methodology for selecting POCs and significantly reduced the number of POCs identified. With the new decision matrix, the statewide POC list went from 21 pesticides to three. Identifying a smaller number of pesticides as statewide POCs will allow for more consistent communication to pesticide applicators across the state. Maintaining watershed POC lists still allows WSDA to communicate watershed-specific priorities based on results from each monitoring site.

WSDA's statewide POCs were the insecticides chlorpyrifos, imidacloprid and malathion. The Monitoring Site Results section in this report lists each watershed's individual POCs. Even though DDT and its degradates exceeded assessment criteria, they are not considered POCs because they are legacy chemicals that have not been registered for use in the U.S. since 1972.

Washington State had approximately 870 pesticide active ingredients (including pesticides, synergists, adjuvants, and additives) registered for use in 2019 (WSPMRS, 2019). Surface water samples in 2019 were tested for roughly 18% of the total registered pesticide active ingredients. WSDA selects pesticides annually to test for based on lab capabilities, grower usage practices, pesticide characteristics, and toxicity to aquatic life. Staff may add or remove pesticides from the testing list based on new registrations, label changes, changes in usage, changes in analytical equipment, and information from local and federal partners.

Generally speaking, pesticides are becoming more specific to the target organisms they are intended for. Insecticides usually have a low toxicity towards aquatic plants and vertebrates and a higher toxicity towards aquatic invertebrates. Meanwhile, herbicides and fungicides are often less toxic to fish and invertebrates but more toxic to aquatic plants. However, any pesticide at high enough concentrations in surface water can directly or indirectly effect ESA-listed salmonids. Invertebrates are the main food source of juvenile salmonids, and those invertebrates rely on aquatic plants to sustain their populations. If a pesticide is causing impairment to any organism, food webs and ecosystem functions can be potentially disrupted. Pesticide monitoring in Washington waterways is essential for understanding the fate and transport of pesticides that can cause water quality concerns. WSDA POCs should be given additional prioritization for management by WSDA and partners to ensure their concentrations are maintained or reduced below WSDA assessment criteria. WSDA will continue to implement the Pesticide Management Strategy as a way to identify and address specific pesticide issues, as well as promote public education and outreach efforts through presentations, reports, and watershed-specific fact sheets in order to support appropriate pesticide use.

## **Program Changes**

Several changes occurred between the 2019 and 2020 sampling seasons. In Western Washington, sampling was discontinued after the 2019 season at the Woodland Creek monitoring site due to few pesticide detections exceeding WSDA assessment criteria. For the 2020 sampling season as a replacement of Woodland Creek, a new urban tier 1 site was established on Juanita Creek located in the city of Kirkland. Staff sampled the remaining six Western Washington monitoring sites sampled in 2019, in 2020. In Eastern Washington, sampling of Naneum Creek was discontinued after the 2019 monitoring season due to few pesticide detections exceeding WSDA assessment criteria as well. Staff sampled the remaining eight Eastern Washington sites sampled in 2019, in 2020. In an effort to expand sampling across Eastern Washington, WSDA partnered with the Palouse Conservation District to monitor Dry Creek, located near Colfax starting in the 2020 sampling season.

The 159 analytes tested for in 2019 were tested for in 2020 with the addition of 10 analytes (Table 29). WSDA only tested for the special 2019 project analytes (glyphosate, AMPA, and glufosinate-ammonium) in Dry Creek during 2020 to expand the special project to another region of Washington.

Analytes added	CAS number	General Use
Aminocyclopyrachlor	858956-08-8	Herbicide
Azinphos-ethyl	2642-71-9	Insecticide
Azinphos-methyl	86-50-0	Insecticide
Cyantraniliprole	736994-63-1	Insecticide
Fenpropathrin	39515-41-8	Insecticide
Fluopicolide	239110-15-7	Fungicide
Gamma-cyhalothrin	76703-62-3	Insecticide
Lambda-cyhalothrin	91465-08-6	Insecticide
Pyroxasulfone	447399-55-5	Herbicide
Thiram	137-26-8	Fungicide

Table 29 – Additional analytes tested for in 2020

The 2020 sampling season was the first time WSDA sampled for nutrients in Upper Big Ditch, Marion Drain, Sulphur Creek Wasteway, and Dry Creek. We started sampling nutrients to understand if chemicals other than pesticides may be affecting water quality in each monitored watershed. The nutrients sampled for were total phosphorus, orthophosphate, ammonia, and nitrate-nitrite as N.

# References

[CFR] Code of Federal Regulations. 2007. Data Requirements for Pesticides.

[CWA] U.S. Code. 1972. Federal Water Pollution Control Act Amendments of 1972.

[Ecology] Washington State Department of Ecology. 2018. Water Quality Program Policy 1-11 Chapter 1: Washington's Water Quality Assessment Listing Methodology to Meet Clean Water Requirements. Publication No. 18-10-035. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

[EPA] U.S. Environmental Protection Agency. 2017. National Functional Guidelines for Organic Superfund Methods Data Review (SOM02.4). EPA-540-R-2017-002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation.

[EPA] U.S. Environmental Protection Agency. 2019a. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. Washington, D.C.: U.S. Environmental Protection Agency.

[EPA] U.S. Environmental Protection Agency. 2019b. National Recommended Water Quality Criteria - Aquatic Life Criteria. Washington, D.C.: U.S. Environmental Protection Agency.

[ESA] U.S. Code. 1973. Endangered Species Act.

[FIFRA] U.S. Code. 1947. Federal Insecticide, Fungicide, and Rodenticide Act.

[WAC] Washington State Legislature. 2019. Water Quality Standards for Surface Waters of the State of Washington.

[WDFW] Washington Department of Fish and Wildlife. 2019. "SalmonScape." Retrieved (http://apps.wdfw.wa.gov/salmonscape/map.html).

[WPAA] Washington State Legislature. 1971. Washington Pesticide Application Act.

[WPCA] Washington State Legislature. 1971. Washington Pesticide Control Act.

[WSPMRS] Washington State Pest Management Resource Service. 2019. "Pesticide Information Center Online." Retrieved (http://cru66.cahe.wsu.edu/labels/Labels.php?SrchType=c).

Bahr, Gary. 2019. Quality Assurance Project Plan: Ambient Monitoring for Pesticides in Washington State Surface Water, Revision 2.0. Olympia, WA: Washington State Department of Agriculture, Natural Resources Assessment Section.

Bischof, Matthew. 2019. Standard Operating Procedure: Water Quality and Pesticides Monitoring Programs Revision 1.1. Yakima, WA: Washington State Department of Agriculture, Natural Resources Assessment Section.

Broderius, Steven and Michael Kahl. 1985. "Acute Toxicity of Organic Chemical Mixtures to the Fathead Minnow." Aquatic Toxicology 6(4):307–22.

Cook, Kirk V. and Jim Cowles. 2009. Washington State Pesticide Management Strategy, Version 2.22. Olympia, WA: Washington State Department of Agriculture, Pesticide Management Division.

Kardouni, James and Stephanie Brock. 2008. Burnt Bridge Creek, Fecal Coliform Bacteria, Dissolved Oxygen, and Temperature Total Maximum Daily Load. Publication No. 08-03-110. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

Lydy, M., J. Belden, C. Wheelock, B. Hammock, D. Denton. 2004. Challenges in Regulating Pesticide Mixtures. Ecology and Society 9(6): 1.

Mathieu, Nuri. 2006. Replicate Precision for 12 TMDL Studies and Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters. Publication No. 06-03-044. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

Mathieu, Nuri. 2019. Standard Operating Procedure EAP024, Version 3.1: Measuring Streamflow for Water Quality Studies. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

Montague, Brian, Michael Barrett, and Jim Carleton. 2014. Preliminary Problem Formulation for the Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments in Support of the Registration Review of Thiophanate Methyl and Carbendazim. Memorandum. EPA-HQ-OPP-2014-0004-0012. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

Payne, Sabrina. 2011. Waters Requiring Supplemental Spawning and Incubation Protection for Salmonid Species. Publication No. 06-10-038. Olympia, WA: Washington State Department of Ecology, Water Quality Program.

Skagit Conservation District. 2021. Skagit Conservation News: Plant Sale Edition. 37(1): 8.

Small, Maureen P., Dave Burgess, Cheryl Dean, and Kenneth I. Warheit. 2011. "Does Lower Crab Creek in the Eastern Washington Desert Have a Native Population of Chinook Salmon?" Transactions of the American Fisheries Society 140(3):808–21.

Ward, William J. 2018. Standard Operating Procedures, EAP080, Version 2.1: Continuous Temperature Monitoring of Fresh Water Rivers and Streams. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

YSI. 2018. ProDSS User Manual, Revision F. Document #626973-01REF.

# **Appendix A: Assessment Criteria for Pesticides**

For this report, assessment criteria include data taken from studies determining hazards to non-target organisms and refer to acute and chronic hazard levels for fish, aquatic invertebrates, and aquatic plants. Staff reviewed various EPA derived risk assessments to determine the most comparable and up-to-date toxicity guidelines for freshwater species.

WSDA applies a 0.5x safety factor to state and national water quality standards and criteria in order to be adequately protective of aquatic life. This safety factor was applied to each criteria found in Table 30a. The most recent versions of WAC 173-201A and EPA's NRWQC were included in the development of the assessment criteria. Pesticide detections at all monitoring sites were evaluated using freshwater assessment criteria.

The following acronyms describe testing details or organisms (spp.) used for testing.

- Fish:
  - o AS-Atlantic salmon
  - o AG-astacopsis
  - gouldi (crayfish)
  - BS-bluegill sunfish
  - BT-brook trout
  - Invertebrate:
    - ACR-acute to chronic ratio
    - CG-chloroperia grammatical (stonefly)
    - CR-chironomus riparius
    - CT-chironomus tentans (midge)
  - Aquatic plant:
    - AF-anabaena flos-aquae (cyanobacteria)
    - o LG- lemna gibba
    - o LM-Lemna minor
    - o ND-not described
    - o NP-navicula pelliculosa

- o DM-daphnia magna
- o DP-daphnia pulex
- o GF-gammarus fasciatus (scud)
- o ND-not described
- o PC-pteronarcys californica (stonefly)
- OL-oscillatoria lutea (blue-green algae)
- SC-pseudokirchneriella subcapitata
- SP-scenedesmus pannonicus
- SS-scendesmus subspicatus (green algae)

In cases where different organisms were used for acute and chronic toxicity tests, the organism used for the acute test is noted first and the organism used for the chronic test is second. Table 30a contains only chemicals detected in 2019. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2019 Quality Assurance Summary.

- CC-carp
- CF-catfish
- o FF-flagfish
  - FM-fathead
    - minnow

- JM-Japanese medaka
- ND-not described
- o RT-rainbow trout
- SB-striped bass

		Fish				<b>Invertebrate</b>			Plant	N	/AC	NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Son	Acute	Chronic	Snn	Acute	Snn	Acuto	Chronic	СМС	ссс
1-(3,4-Dichlorophenyl)-3-	Acute	Acule	CIIIOIIIC	Spp.	Acule	CIIIOIIIC	Spp.	Acule	Shh	Acule	CIIIOIIIC		
methylurea													
2,4-D <sup>1</sup> , <sup>b</sup>	2,040	20,400	11,800	RT/FM	6,250	8,025	DM	149.6	LG				
2,6-Dichlorobenzamide <sup>2</sup>	3,000	30,000	5,000	BS/RT	46,000	160,000	DM	50,000	SP				
4,4'-DDD <sup>3, 4</sup>										0.55ª	0.0005ª	0.55ª	0.0005ª
4,4'-DDE <sup>3, 4</sup>										0.55ª	0.0005ª	0.55ª	0.0005ª
4,4'-DDT <sup>3, 4</sup>										0.55ª	0.0005ª	0.55ª	0.0005ª
4-Nitrophenol <sup>5</sup>	100	1,000		RT	1,250		DM						
Acephate <sup>6</sup>	20,800	208,000	2,880	RT	275	75	DM	25,000	SD				
Acetamiprid <sup>7</sup>	2,500	25,000	9,600	RT/FM	5.25	1.05	CR/ACR	500	LG				
Acetochlor ESA <sup>8</sup>	4,500	45,000		RT	31,250		DM	4,950	SC				
Alachlor <sup>9</sup>	45	450	93.5	RT	625	55	DM	0.82	SC				
AMPA <sup>10</sup>	12,475	124,750		RT	170,750		DM						
Atrazine <sup>11</sup>	132.5	1,325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin <sup>12</sup>	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Bifenthrin <sup>13</sup>	0.00375	0.0375	0.02	RT/FM	0.4	0.00065	DM						
Boscalid <sup>14</sup>	67.5	675	58		1,333	395		670					
Bromacil <sup>15</sup>	900	9,000	1,500	RT	30,250	4,100	DM	3.4	SC				
Bromoxynil <sup>16</sup>	52.5	525		RT	4,805		DM						
Carbaryl <sup>4, 17</sup>	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	330	NP			1.05	1.05
Carbendazim <sup>18</sup>	0.25	2.5	0.495		27.5	1.55							
Chlorantraniliprole 19	345	3,450	55	RT/RT	2.9	2.235	DM/DM	890	SC				
Chlorothalonil 20	0.2625	2.625	1.5	RT/AG	0.9	0.3	DM	3.4	SC				
Chlorpropham <sup>21</sup>	75.25	752.5		RT	927.5		DM						
Chlorpyrifos <sup>3, 4, 22</sup>	0.045	0.45	0.285	RT/FM	0.025	0.02	DM	70		0.0415	0.0205	0.0415	0.0205
Chlorpyrifos-methyl <sup>23</sup>	0.35	3.5			0.0425								

Table 30a – WSDA Freshwater assessment criteria (WSDA safety factors applied,  $\mu g/L$ )

		<u>Fis</u> t	<u>1</u>		<u> </u>	nvertebrate	2	Aquatio	Plant	WAC	NRV	NQC
	Endangered Species											
Pesticide	Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute Chronic	СМС	CCC
Chlorsulfuron <sup>24</sup>	7,500	75,000	16,000	RT	92,500	10,000	DM	0.175	LG			
cis-Permethrin <sup>25</sup>	0.01975	0.1975	0.02575	BS/FM	0.00975	0.0007	DM	34	SC			
Clopyralid <sup>26</sup>	2,588	25,875		RT	58,250		DM	3,450	SC			
Clothianidin 27	2,538	25,375	4,850	RT/FM	5.5	0.025	CR	32,000				
Cyprodinil <sup>28</sup>	54.5	545	115	BS/FM	8	4.1	DM	985	AF			
Dacthal (DCPA) <sup>29</sup>	165	1,650		RT	4,505		DM					
Diazinon <sup>4, 30</sup>	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1,850	SC		0.085	0.085
Dicamba acid <sup>31</sup>	700	7,000		RT	25,000		DM	30.5	AF			
Dichlobenil <sup>2</sup>	123.25	1,232.5	165	RT	1,550	280	DM	15	LG			
Dicofol 32	1.325	13.25	2.2		35	9.5		2,500				
Difenoconazole 33	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP			
Dimethoate <sup>34</sup>	155	1,550	215	RT	10.75	0.25	PC	10,000	AF			
Dinotefuran <sup>35</sup>	2,478	24,775	3,180	CC/RT	242,075	47,650	DM	48,800	SC			
Dithiopyr <sup>36</sup>	11.75	117.5	28	BS/RT	425	40.5	DM	10	SC			
Diuron <sup>37</sup>	10	100	13.2	SB/FM	40	100	GF/DM	1.2	SC			
Eptam <sup>38</sup>	350	3,500	20	BS/FM- ACR	1,625	400	DM	700	SC			
Ethalfluralin <sup>39</sup>	0.8	8	0.2	BS/RT	15	12	DM	3.65	LG			
Ethoprop 40	7.5	75	12	RT/FM	11	0.4	DM	4,200				
Etoxazole 41	9.25	92.5	7.5	RT	1.825	0.065	DM	25.95	NP			
Etridiazole <sup>42</sup>	30.25	302.5	60	RT	770	185	DM	36	SC			
Fenarimol <sup>43</sup>	22.5	225	90	RT	1,700	56.5	DM	50	SC			
Fipronil 44	2.075	20.75	3.3	BS	0.055	0.0055	DM/ACR	50				
Fipronil Sulfide 44	2.075	20.75	3.3		0.5325	0.055		50	ND			
Fipronil Sulfone 44	0.625	6.25	0.335	RT/ND	0.18	0.0185	DM/ND	50	ND			
Fludioxonil <sup>45</sup>	11.75	117.5	9	RT/FM	225	7	DM	140	SC			
Flumioxazin <sup>46</sup>	57.5	575	3.85	RT	1375	14	DP/DM	0.245	LG			

	Endangered	<u>Fis</u> t	<u>1</u>		<u> </u>	<u>nvertebrate</u>		Aquatic	Plant	WAC	NRV	VQC
Pesticide	Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute Chronic	СМС	ссс
Fluroxypyr 1-methylheptyl ester 47	15.75	157.5		BS	150	30.25	DM	28	NP			
Glufosinate-ammonium 48	7,800	78,000	25,000	RT	162,750	15,500	DM	36	AF			
Glyphosate <sup>10</sup>	1,075	10,750	12,850	BS/FM	13,300	24,950	CP/DM	5,950	LG			
Hexazinone 49	6,850	68,500	8,500	RT/FM	37,900	10,000	DM	3.5	SC			
Imazapic <sup>50</sup>	2,500	25,000	48,000	RT/FM	25,000	48,000	DM	3.11	LM			
Imazapyr <sup>51</sup>	2,500	25,000	21,550	RT/FM	25,000	48,550	DM	12	LM			
Imidacloprid 52	5,725	57,250	4,500	RT	0.1925	0.005		5,000	ND			
Indaziflam												
Isoxaben 53	25	250	200	RT	325	345	DM	5	LG			
Malaoxon <sup>54</sup>	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1,020				0.05
Malathion <sup>4, 54</sup>	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1,020				0.05
MCPA 55								85	SC			
Mecoprop (MCPP) 56	2,325	23,250		RT	22,750	25,400	DM	7	SC			
Metalaxyl <sup>57</sup>	3,250	32,500	4,550	RT/FM	7,000	600	DM	42,500	LG			
Methamidophos 58	625	6,250	86.8	RT	6.5	2.25	DM	25,000	SD			
Methomyl <sup>59</sup>	8	80	6	CF	1.25	0.35	DM					
Methomyl Oxime												
Methoxyfenozide 60	105	1,050	265	RT/FM	14.25	1.55	CR	1,700	SC			
Metolachlor 61	95	950	15	RT	275	0.5	DM	4	SC			
Metribuzin <sup>62</sup>	1,050	10,500	1,500	RT	1,050	645	DM	4.05				
Metsulfuron-methyl 63	3,750	37,500	2,250	BS	37,500		DM	0.18	LG			
Myclobutanil <sup>64</sup>	60	600	490	BS/FM	2,750		DM	415	SC			
N,N-Diethyl-m-toluamide 65	1,875	18,750		RT	18,750		DM					
Napropamide 66	160	1,600	550	RT	3,575	550	DM	1,700	SC			
Norflurazon 67	202.5	2,025	385	RT	3,750	500	DM	4.85	SC			
Oryzalin <sup>68</sup>	72	720	110	BS/FM	375	179	DM	6.5	LG			

		Fist	<u>1</u>			Invertebrate	2	Aquatio	: Plant	WAC	NRV	NQC
	Endangered											
Pesticide	Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute Chronic	СМС	ccc
Oxadiazon <sup>69</sup>	30	300	16.5	RT/FM	545	16.5	DM	2.6	SC			
Oxamyl <sup>70</sup>	105	1,050	250	RT/FM	45	13.5	ACR	60	SC			
Oxamyl oxime <sup>70</sup>	105	1,050	250	RT/FM	45	13.5	ACR	60	SC			
Oxyfluorfen 71	5	50	0.65	BS/FM	375	6.5	DM	0.145	SC			
Paclobutrazol 72	397.5	3,975	24.5	GC/RT	60	4.5	DM	4	LG			
Pendimethalin <sup>73</sup>	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC			
Pentachloronitrobenzene 74	2.5	25	6.5		192.5	9						
Pentachlorophenol 4, 75	0.375	3.75	5.5	RT	23	2.05	DM	25	SC		9.5	7.5
Phosmet <sup>76</sup>	1.75	17.5	1.6	RT	0.5	0.4	DM					
Picloram 77	137.5	1,375	275	RT	8,600	5,900	DM	17,450	SC			
Piperonyl butoxide 78	47.5	475	20	RT	127.5	15	DM					
Prodiamine <sup>79</sup>	0.325	3.25		BS	3.25	0.75	DM					
Prometon <sup>80</sup>	300	3,000	9,850	RT/FM	6,425	1,725	DM	49	SC			
Prometryn <sup>81</sup>	72.75	727.5	310	RT/FM	2,425	500	DM	0.52	NP			
Propargite <sup>82</sup>	2.025	20.25	8	BS/FM	3.5	4.5	DM	9.7	SC			
Propiconazole <sup>83</sup>	21.25	212.5	47.5	RT/FM	325	130	DM	10.5	ND			
Propyzamide <sup>84</sup>	265	2,650	112	RT/FM	1,400	300	DM	380	SC			
Pyraclostrobin <sup>85</sup>	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP			
Pyridaben <sup>86</sup>	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG			
Pyrimethanil <sup>87</sup>	252.5	2,525	10	RT	750	500	DM	900	ND			
Pyriproxyfen <sup>88</sup>	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG			
Simazine <sup>89</sup>	160	1,600	30	FM	250	20	DM/ACR	3	SC			
Simetryn												
Sodium bentazon <sup>90</sup>	4,750	47,500	4,915	RT/FM	15,575	50,600	CR/DM	2,250	SC			
Spirotetramat <sup>91</sup>	35.25	352.5	267	RT/FM	165	50	СТ	2,025	NP			
Sulfentrazone <sup>92</sup>	2,345	23,450	1,475	BS/RT	15,100	100	DM	14.4	SC			
Sulfometuron methyl 93	3,700	37,000		RT	37,500	48,500	DM	0.225	LG			

	Endongorod	<u>Fish</u>	<u>1</u>		<u> </u>	nvertebrate	<u>)</u>	Aquatic	<u>Plant</u>	WAC	NRV	VQC
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute Chronic	СМС	ссс
Tebuthiuron <sup>94</sup>	2,650	26,500	4,650	FM	74,250	10,900	DM	25	SC			
Tefluthrin <sup>95</sup>	0.0015	0.015	0.002	RT/FM	0.0175	0.004	DM					
Terbacil <sup>96</sup>	1,155	11,550	600	RT	16,250	25	DM	5.5	NP			
Tetrahydrophthalimide 97	3,150	31,500		RT	28,250		DM	90,500	SC			
Tetramethrin <sup>98</sup>	0.0925	0.925		RT								
Thiamethoxam <sup>99</sup>	2,850	28,500	10,000	BS/RT	8.75	0.37	CR	45,100	LM			
Total fluvalinate <sup>100</sup>	0.00875	0.0875	0.032	CC/FM	0.235	0.05	DM					
Tralomethrin <sup>101</sup>	0.04	0.4	0.044	RT/FM	0.00975	0.0022	DM					
trans-Permethrin <sup>25</sup>	0.01975	0.1975	0.02575	BS/FM- ACR	0.00975	0.0007	DM/FM- ACR	34	SC			
Triadimefon <sup>102</sup>	102.5	1,025	85	RT	400	26	DM	1,000	SC			
Triallate <sup>103</sup>	30	300	19	RT	22.75	7	DM	10.5	SC			
Triazine DEA degradates <sup>11</sup>								500				
Triazine DIA degradates <sup>11</sup>	425	4,250			31,500			1,250				
Triazine HA degradates <sup>11</sup>	75	750		RT	1,025		DM	5,000	AI			
Triclopyr acid <sup>104</sup>	2,925	29,250	52,000	RT/FM	33,225	40,350	DM	2,950	SC			
Triclopyr butoxyethyl ester	9	90	13	BS/RT	425		DM	50	NP			
Triclosan <sup>105</sup>	7.2	72		FM	97.5		DM	0.35	SS			
Trifloxystrobin <sup>106</sup>	0.3575	3.575	2.15	RT	6.325	1.38	DM	18.55	SC			
Trifluralin <sup>107</sup>	0.4625	4.625	0.95		62.75	1.2		10.95				

CMC: Criteria Maximum Concentration

CCC: Criteria Continuous Concentration

<sup>a</sup> Criteria is specific to total DDT but is used here for individual metabolites as well.
 <sup>b</sup> 2,4-D criteria reflect toxicity of the 2,4-D acids and salts. Toxicity values for the individual forms of 2,4-D are available in the referenced document.

# **Assessment Criteria References**

- 1. Radtke, Meghan, and Faruque Khan. 2013. EFED Registration Review Problem Formulation 2,4-D-REVISED. Memorandum EPA-HQ-OPP-2012-0330-0025. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 2. Garber, Kristina, and Greg Orrick. 2012. Revised EFED Registration Review Problem Formulation for Dichlobenil. Memorandum EPA-HQ-OPP-2012-0395-0019. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 3. Washington State Legislature. 2020. Toxic Substances. Vol. WAC 173-201A-240.
- 4. U.S. Environmental Protection Agency. 2019. National Recommended Water Quality Criteria Aquatic Life Criteria. Washington, D.C.: U.S. Environmental Protection Agency.
- Cottrill, Michele, Ghulam Ali, Mary Frankenberry, Gail Maske-Love, Paul Mastradone, Jim Goodyear, Paula A. Deschamp, et al. 1998. Reregistration Eligibility Decision (RED) Paranitrophenol. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 6. Mason, Tiffany, Michael Davy, and William P. Eckel. 2009. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment of Acephate. Memorandum EPA-HQ-OPP-2008-0915-0006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- White, Katrina, and Cathryn Britton. 2012. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Acetamiprid. Memorandum EPA-HQ-OPP-2012-0329-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Barrett, Michael R., Ronald Parker, and Gabe Patrick. 2006. Section 3 Environmental Risk Assessment for the New Use Registration of Acetochlor on Sorghum and Sweet Corn. Memorandum EPA-HQ-OPP-2009-0081-0043. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- Panger, Melissa, and Reuben Baris. 2009. Potential Risks of Alachlor Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii) and Delta Smlet (Hypomesus transpacificus). EPA-HQ-OPP-2009-0081. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 10. Hetrick, James, and Amy Blankinship. 2015. Registration Review Preliminary Ecological Risk Assessment for Glyphosate and Its Salts. Memorandum EPA-HQ-OPP-2009-0361-0077. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Farruggia, Frank T., Colleen M. Rossmeisl, James A. Hetrick, Melanie Biscoe, Rosanna Louie-Juzwiak, and Dana Spatz. 2016. Refined Ecological Risk Assessment for Atrazine. Memorandum EPA-HQ-OPP-2013-0266-0315. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 12. Carey, Stephen, and James K. Wolf. 2009. Registration Review Preliminary Problem Formulation for the Ecological Risk and Drinking Water Exposure Assessments for Azoxystrobin. Memorandum EPA-HQ-OPP-2009-0835-0008. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 13. Melendez, Jose L., and N.E. Federoff. 2010. EFED Registration Review Problem Formulation for Bifenthrin. Memorandum EPA-HQ-OPP-2010-0384-0006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 14. Aubee, Catherine, and Katrina White. 2014. Registration Review: Draft Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water

Exposure Assessments for Boscalid. Memorandum EPA-HQ-OPP-2014-0199-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 15. Baris, Reuben, and Nathan Miller. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Bromacil and Bromacil Lithium Salt. Memorandum EPA-HQ-OPP-2012-0445-0005. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Federoff, N.E., and Elyssa Gelmann. 2013. EFED Registration Review Problem Formulation for Bromoxynil and Bromoxynil Esters. Memorandum EPA-HQ-OPP-2012-0896-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 17. Jones, R. David, and Thomas Steeger. 2010. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Carbaryl. Memorandum EPA-HQ-OPP-2010-0230-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 18. Montague, Brian, Michael Barrett, and Jim Carleton. 2014. Preliminary Problem Formulation for the Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments in Support of the Registration Review of Thiophanate Methyl and Carbendazim. Memorandum EPA-HQ-OPP-2014-0004-0012. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Odenkirchen, Ed, and James Hetrick. 2009. Ecological Risk Assessment for Section 3 Registration for Fruit, Vegetable, Selected Field Crop, Turf and Ornamental Uses of Chlorantraniliprole. EPA-HQ-OPP-2009-0081-0120. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- Bohaty, Rochelle F. H., and Donna R. Judkins. 2010. Ecological Assessment for the IR-4 Registration of Chlorothalonil (Bravo Weather Stik/Bravo 720,54%; EPA Reg. 50534-188) and the Degradation Product, 4-Hydroxy-2,5,6-trichloro-1,3-dicyanobenzene (SDS-3701) for the New Uses On: Bulb Vegetables, Bushberries, and Low Growing Berries. Memorandum EPA-HQ-OPP-2009-0081-0213. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 21. Jones, R. David, and Brian D. Kiernan. 2010. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Chlorpropham. Memorandum EPA-HQ-OPP-2010-0923-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 22. Corbin, Mark, and Colleen Flaherty. 2008. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species and Drinking Water Assessments for Chlorpyrifos. Memorandum EPA-HQ-OPP-2008-0850-0007. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 23. Judkins, Donna, and Mark Corbin. 2009. Registration Review Problem Formulation for Chlorpyrifosmethyl. Memorandum EPA-HQ-OPP-2010-0119-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 24. Clock-Rust, Mary, and Katrina White. 2012. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Chlorsulfuron. Memorandum EPA-HQ-OPP-2012-0878-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Melendez, Jose L., Amanda Solliday, and Keith Sappington. 2011. EFED Registration Review Preliminary Problem Formulation for Permethrin. Memorandum EPA-HQ-OPP-2011-0039-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 26. Arnold, Elyssa, and James Lin. 2014. EFED Registration Review Problem Formulation for Clopyralid. Memorandum EPA-HQ-OPP-2014-0167-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 27. Wagman, Michael, Nathan Miller, and William Eckel. 2011. Registration Review: Problem Formulation for the Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments of Clothianidin. Memorandum EPA-HQ-OPP-2011-0865-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 28. Melendez, Jose, and Justin Housenger. 2013. Environmental Fate and Ecological Risk Assessment Preliminary Problem Formulation In Support of REgistration Review of Cyprodinil. PC288202. Washington, DC: U.S. Environmental Protection Agency.
- Wendel, Christina, and Wm. J. Shaughnessy. 2011. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment of Dimethyl 2,3,5,6-Tetrachloroterephthalate (DCPA). Memorandum EPA-HQ-OPP-2011-0374-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- Garber, Kristina, and Thomas Steeger. 2008. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species and Drinking Water Assessments for Diazinon. Memorandum EPA-HQ-OPP-2008-0351-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 31. Maher, Iwona L., and Michael Wagman. 2011. Ecological Risk Assessment for Dicamba and its Degradate, 3,6-dichlorosalicylic acid (DCSA), for the Proposed New Use on Dicamba-Tolerant Soybean. Memorandum EPA-HQ-OPP-2016-0187-0008. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 32. Garber, Kristina, and Charles Peck. 2009. Risks of Dicofol Use to Federally Threatened California Red-legged Frog. Washington, DC: U.S. Environmental Protection Agency.
- 33. Lowit, Michael, Faruque Khan, and Sujatha Sankula. 2015. Difenoconazole: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments in Support of Registration Review. Memorandum EPA-HQ-OPP-2015-0401-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Yingling, Hannah, Jose Melendez, and Keith Sappington. 2015. Registration Review Preliminary Ecological Risk Assessment for Dimethoate. Memorandum EPA-HQ-OPP-2009-0059-0029. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Donovan, Elizabeth, and Rochelle F.H. Bohaty. 2017. Preliminary Ecological Risk Assessment (excluding terrestrial invertebrates) for the Registration Review of Dinotefuran. Memorandum EPA-HQ-OPP-2011-0920-0616. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 36. Sternberg, Robin, and Christopher M. Koper. 2013. Registration Review Problem Formulation for Dithiopyr. Memorandum EPA-HQ-OPP-2013-0750-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Dean, Ron, Tiffany Mason, and Bill Shaughnessy. 2009. Risks of Diuron Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii). EPA-HQ-OPP-2009-0081-0140. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- Flaherty, Colleen, Pamela Hurley, James K. Wolf, Lucy Shanaman, and James A. Hetrick. 2008. Risks of EPTC Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii). EPA-HQ-OPP-2009-0081-0053. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.

- Sinclair, Geoffrey, and Michael Barrett. 2016. Preliminary Environmental Fate and Ecological Risk Assessment for Registration Review of Ethalfluralin. Memorandum EPA-HQ-OPP-2011-0094-0019. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 40. Sinclair, Geoffrey, and Michael Barrett. 2015. Environmental Fate and Ecological Risk Assessment for the Registration Review of Ethoprop. Memorandum EPA-HQ-OPP-2008-0560-0030. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 41. Melendez, Jose, and Justin Housenger. 2014. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment and Drinking Water Exposure Assessment to Be Conducted for Etoxazole. Memorandum EPA-HQ-OPP-2014-0133-0009. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 42. Milians, Karen, and Catherine Aubee. 2014. Registration Review: Draft Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments for Etridiazole. Memorandum EPA-HQ-OPP-2014-0414-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 43. Panger, Melissa, and Greg Orrick. 2007. Ecological Risk Assessment for the Fenarimol Section 3 Use on Hops. Memorandum EPA-HQ-OPP-2009-0081-0222. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 44. Odenkirchen, Edward, and Stephen Wente. 2011. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Fipronil. Memorandum EPA-HQ-OPP-2011-0448-0006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 45. Randall, Donna M., and Cheryl Sutton. 2011. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Fludioxonil. Memorandum EPA-HQ-OPP-2010-1067-0008. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 46. DeCant, Joseph, and Larry Liu. 2011. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Flumioxazin. Memorandum EPA-HQ-OPP-2011-0176-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 47. Mastrota, Nicholas, and Rochelle F. Bohaty. 2014. Problem Formulation for the Ecological Risk and Drinking Water Exposure Assessments to be Conducted in Support of the Registration Review for Fluroxypyr-MHE. Memorandum EPA-HQ-OPP-2014-0570-0008. Washington, D.C.: U.S. Environmental Protection Agency, Environmental Fate and Effects Division.
- 48. Aubee, Catherine, and Chuck Peck. 2013. Environmental Fate and Ecological Risk Assessment for the Registration Review of Glufosinate. EPA-HQ-OPP-2008-0190-0023. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 49. Woodard, Valerie, and Jose Melendez. 2010. EFED Registration Review Problem Formulation for Hexazinone. Memorandum EPA-HQ-OPP-2009-0755-0007. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 50. Wagman, Michael, and Iwona L. Maher. 2014. Registration Review Preliminary Problem Formulation for Ecological Risk and Environmental Fate, Endangered Species, and Drinking Water Assessments for Imazapic and its Ammonium Salt. Memorandum EPA-HQ-OPP-2014-0279-0009. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 51. Hetrick, James A., and Tanja Crk. 2014. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment and Drinking Water Exposure Assessment to be Conducted for Imazapyr and Imazapyr Isoporopylamine. Memorandum EPA-HQ-OPP-2014-0200-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 52. Sappington, Keith G., Mohammed A. Ruhman, and Justin Housenger. 2016. Preliminary Aquatic Risk Assessment to Support the Registration Review of Imidacloprid. Memorandum EPA-HQ-OPP-2008-0844-1086. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 53. Shelby, Andrew, and Amy Blankinship. 2014. Transmittal of the Preliminary Environmental Fate and Ecological Risk Assessment in Support of the Registration Review of Isoxaben. Memorandum EPA-HQ-OPP-2007-1038-0024. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 54. Mastrota, Nicholas, and Stephen P. Wente. 2009. Registration Review Preliminary Problem Formulation for Ecological Risk, Environmental Fate, and Endangered Species Assessments for Malathion. Memorandum EPA-HQ-OPP-2009-0317-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 55. E.P.A. Environmental Fate and Effects Division. 2009. Risk Assessment for the Reregistration Eligibility Document for 2-methyl-4-chlorophenoxyacetic acid (MCPA). EPA-HQ-OPP-2009-0081-0061. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 56. Carey, Steve, and Ibrahim Abdel-Saheb. 2014. Problem Formulation for the Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments in Support of the Registration Review of Mecoprop-p (MCPP-p). Memorandum EPA-HQ-OPP-2014-0361-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 57. Mastrota, Nicholas, James Lin, and Yan Donavan. 2009. Registration Review Preliminary Problem Formulation for Environmental Fate, Ecological Risk, and Endangered Species for Metalaxyl and Mefenoxam. Memorandum EPA-HQ-OPP-2009-0863-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 58. Davy, Michael, William P. Eckel, and Tiffany Mason. 2008. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment of Methamidophos. Memorandum EPA-HQ-OPP-2008-0842-0006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 59. Panger, Melissa, and Greg Orrick. 2010. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Methomyl. Memorandum EPA-HQ-OPP-2010-0751-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Milians, Karen, and Mary Clock-Rust. 2013. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments for Methoxyfenozide. Memorandum EPA-HQ-OPP-2012-0663-0008. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 61. Sternberg, Robin, and Christopher Koper. 2014. Registration Review Problem Formulation for Metolachlor and S-Metolachlor. Memorandum EPA-HQ-OPP-2014-0772-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 62. Carey, Stephen, and Andrew Shelby. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Metribuzin. Memorandum EPA-HQ-OPP-2012-0487-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 63. Kiernan, Brian D., and Reuben Baris. 2011. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Metsulfuron-methyl. Memorandum EPA-HQ-OPP-2011-0375-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 64. Wolf, James K., Michael Lowit, and Rebecca Daiss. 2009. Risks of Myclobutanil Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii). EPA-HQ-OPP-2009-0081-0171. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 65. Hartless, Christine, and James Lin. 2012. Registration Review Ecological Risk, Environmental Fate, and Endangered Species Assessment for N,N-diethyl-meta-toluamide (DEET). Memorandum EPA-HQ-OPP-2012-0162-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 66. Rim, Elisa, Monisha Kaul, Nicole Zinn, Sunil Ratnayake, Fred Jenkins, Jim Breithaupt, Shannon Borges, et al. 2005. Reregistration Eligibility Decision for Napropamide. Decision EPA-HQ-OPP-2009-0081-0037. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 67. Kiernan, Brian D., and Amy A. McKinnon. 2008. Risks of Norflurazon Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii). EPA-HQ-OPP-2009-0081-0048. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 68. Koper, Christopher M., Anita Ullagaddi, and Nancy Andrews. 2010. Registration Review: Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Oryzalin. Memorandum EPA-HQ-OPP-2010-0940-0005. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 69. Yingling, Hannah, and Mohammed Ruhman. 2014. EFED Registration Review Problem Formulation for Oxadiazon. Memorandum EPA-HQ-OPP-2014-0782-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 70. Korol, Alicia, Greg Orrick, and Kristina Garber. 2009. Risks of Oxamyl Use to Federally Threatened California Red-legged Frog (Rana aurora draytonii). EPA-HQ-OPP-2009-0081-0174. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 71. Sternberg, Robin, and He Zhong. 2014. Registration Review Problem Formulation for Oxyfluorfen. Memorandum EPA-HQ-OPP-2014-0778-0006. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 72. Radtke, Meghan, and Faruque Khan. 2013. Registration Review Ecological Risk Assessment and Effects Determination of Paclobutrazol. Memorandum EPA-HQ-OPP-2006-0109-0020. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 73. Riley, Elizabeth, and Ibrahim Abdel-Saheb. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Pendimethalin. Memorandum EPA-HQ-OPP-2012-0219-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 74. Garber, Kristina. 2010. 2008 Science Advisory Panel Meeting Follow Up: Assessment of the Bioaccumulation and Long-Range Transport Potential (LRTP) and of Pentachloronitrobenzene (PCNB) and Associated Ecological Risks. Memorandum EPA-HQ-OPP-2009-0081-0225. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 75. Chen, Jonathan, Nathan Mottl, Bill Erickson, Najm Shamim, Siroos Mostaghimi, Jaclyn Pyne, Sandra O'Neill, et al. 2015. Pentachlorophenol Final Work Plan. EPA-HQ-OPP-2014-0653-0023. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 76. Kiernan, Brian D., and Reuben Baris. 2009. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Assessments for Phosmet. Memorandum EPA-HQ-OPP-2009-0316-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 77. Wagman, Michael, and Andrew Shelby. 2013. Problem Formulation for the Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments in Support of the Registration Review of Picloram. Memorandum EPA-HQ-OPP-2013-0740-0005. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 78. Judkins, Donna, and Ibrahim Abdel-Saheb. 2010. EFED Registration Review Problem Formulation for Piperonyl Butoxide (PBO). Memorandum EPA-HQ-OPP-2010-0498-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 79. Wagman, Michael, and Ibrahim Abdel-Saheb. 2010. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment of Prodiamine. Memorandum EPA-HQ-OPP-2010-0920-0004. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 80. Sternberg, Robin, Stephen Wente, and Ed Odenkirchen. 2013. Registration Review Problem Formulation for Prometon. Memorandum EPA-HQ-OPP-2013-0068-0002. U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 81. Ruhman, Mohammed, and Nicholas Mastrota. 2013. EFED Registration Review Preliminary Problem Formulation for Prometryn. Memorandum EPA-HQ-OPP-2013-0032-0007. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 82. Sternberg, Robin, and Stephen Wente. 2014. Registration Review Problem Formulation for Propargite. Memorandum EPA-HQ-OPP-2014-0131-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 83. Abdel-Saheb, Ibrahim, and Steve Carey. 2012. Updated Ecological Risk Assessment for the Proposed New Use of Propiconazole on Sugarcane. Memorandum EPA-HQ-OPP-2011-0772-0009. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 84. Milians, Karen, and Andrew Sayer. 2015. Preliminary Ecological Assessment for the Registration Review of the Herbicide Propyzamide and Proposed New Use on Leaf Lettuce. Memorandum EPA-HQ-OPP-2009-0326-0015. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 85. Radtke, Meghan, and Christopher Koper. 2014. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Pyraclostrobin. Memorandum EPA-HQ-OPP-2014-0051-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 86. Garber, Kristina, and Reuben Baris. 2010. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Pyridaben. Memorandum EPA-HQ-OPP-2010-0214-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 87. Crk, Tanja, Silvia C. Termes, and James A. Hetrick. 2010. Pyrimethanil New Uses on Small Berries (Caneberries and Bushberries) in the Co-Formulated End-Use Product Fluopyram/Pyrimethanil 500 SC. Memorandum EPA-HQ-OPP-2009-0081-0217. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 88. Mastrota, Nick, James Hetrick, and Dana Spatz. 2011. Registration Review Problem Formulation for Pyriproxyfen. Memorandum EPA-HQ-OPP-2011-0677-0005. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Farruggia, Frank T., and Melanie Biscoe. 2013. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment for Simazine. Memorandum EPA-HQ-OPP-2013-0251-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 90. Zhong, He, and Stephen Wente. 2014. Registration Review Ecological Risk Assessment and Effects Determination for Sodium Bentazon. Memorandum EPA-HQ-OPP-2010-0117-0016. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 91. DeCant, Joseph, and Christina deMariano. 2009. EFED Environmental Risk Assessment for the Proposed Uses of Spirotetramat on the Production of Cotton, Soybean, Legume Vegetables, Tropical Fruit, Pistachio, Okra, and Dried Prunes, Review of Risk to Pollinators, and Groundwater Label

Requirement Revision. Memorandum EPA-HQ-OPP-2009-0263-0015. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.

- 92. Sinclair, Geoffrey, and Michael Barrett. 2014. Preliminary Ecological Risk Assessment for the Registration Review of Sulfentrazone and Proposed New Uses on Apples. Memorandum EPA-HQ-OPP-2009-0624-0017. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 93. Sternberg, Robin, and Michael Barrett. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments for Sulfometuron Methyl. Memorandum EPA-HQ-OPP-2012-0501-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 94. Abdel-Saheb, Ibrahim, and Steve Carey. 2014. Transmittal of the Draft Environmental Fate and Ecological Risk Assessment in Support of the Registration Review of Tebuthiuron. Memorandum EPA-HQ-OPP-2009-0327-0042. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 95. Abdel-Saheb, Ibrahim, and Brian D. Kiernan. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Tefluthrin. Memorandum EPA-HQ-OPP-2012-0501-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 96. Panger, Melissa, Michael Wagman, and Stephanie Syslo. 2011. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Terbacil. Memorandum EPA-HQ-OPP-2011-0054-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 97. Sternberg, Robin, and Faruque Khan. 2013. Registration Review Problem Formulation for Captan. Memorandum EPA-HQ-OPP-2013-0296-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- Gelmann, Elyssa, and Wm. J. Shaughnessy. 2011. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment for Tetramethrin. Memorandum EPA-HQ-OPP-2011-0907-0003. Washington, D.C.: U.S. Environmental Protection Agency, Environmental Fate and Effects Division.
- 99. Mroz, Ryan, Christopher Koper, and Kristina Garber. 2017. Thiamethoxam Transmittal of the Preliminary Aquatic and Non-Pollinator Terrestrial Risk Assessment to Support Registration Review. Memorandum EPA-HQ-OPP-2011-0581-0093. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 100. Hurley, Pamela, and Rochelle F. H. Bohaty. 2010. Registration Review Preliminary Problem Formulation for the Ecological Risk and Drinking Water Exposure Assessments for Tau-Fluvalinate. Memorandum EPA-HQ-OPP-2010-0915-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 101. Melendez, Jose L., and Amanda Solliday. 2010. EFED Revised Registration Review Problem Formulation for Tralomethrin. Memorandum EPA-HQ-OPP-2010-0116-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 102. Angier, Jonathan, and Michelle Embry. 2005. Environmental Fate and Ecological Risk Assessment for Triadimeton. EPA-HQ-OPP-2005-0258-0018. Washington, D.C.: U.S. Environmental Protection Agency, Environmental Fate and Effects Division.
- 103. Zhong, He, Faruque Khan, and Edom Seifu. 2014. Registration Review Problem Formulation for Triallate. Memorandum EPA-HQ-OPP-2014-0573-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.

- 104. Montague, Brian, and Larry Liu. 2014. Registration Review; Preliminary Problem Formulation for Environmental Fate, Ecological Risk, Endangered Species, and Human Health Drinking Water Exposure Assessments for Triclopyr [Triclopyr Acid, Triclopyr Triethylamine Salt, and Triclopyr Butoxyethyl Ester]. Memorandum EPA-HQ-OPP-2014-0576-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 105. Hazel, William, Timothy Leighton, Tim McMahon, James Breithaupt, Srinivas Gowda, Pat Jennings, William Erickson, et al. 2013. Triclosan Registration Review Preliminary Work Plan. EPA-HQ-OPP-2012-0811-0002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 106. Mastrota, Nick, and James K. Wolf. 2013. Registration Review Preliminary Problem Formulation for the Ecological Risk Assessment in Support of Registration Review for Trifloxystrobin. Memorandum EPA-HQ-OPP-2013-0074-0008. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.
- 107. Ullagaddi, Anita, and Faruque Khan. 2012. Registration Review: Problem Formulation for the Environmental Fate, Ecological Risk, Endangered Species, and Drinking Water Exposure Assessments for Trifluralin. Memorandum EPA-HQ-OPP-2012-0417-0003. Washington, D.C.: U.S. Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention.
- 108. Hurley, Pamela, Michael Lowit, and James Hetrick. 2009. Registration Review Preliminary Problem Formulation for the Ecological Risk and Drinking Water Exposure Assessments for Glyphosate and Its Salts. Memorandum EPA-HQ-OPP-2009-0361-0007. Washington, D.C.: U.S. Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances.
- 109. Garber, Kristina, and Charles Peck. 2009. Risks of Dicofol Use to Federally Threatened California Red-legged Frog. EPA-HQ-OPP-2009-0081-0136. Washington, D.C.: U.S. Environmental Protection Agency, Office of Pesticide Programs.

# **Appendix B: 2019 Quality Assurance Summary**

Quality assurance (QA) elements and quality control (QC) samples assure consistency and accuracy throughout sample collection, sample analysis, and the data reporting process. For this project, QC samples used in analysis of pesticides, total suspended solids (TSS), and specific conductivity include field replicates, field blanks, matrix spike/matrix spike duplicates (MS/MSD), laboratory control samples/laboratory control sample duplicates (LCS/LCSD), surrogate spikes, and method blanks.

In 2019, QA/QC samples were 11% of all the samples collected in the field. There were 169 QC samples in total: 73 field replicates, 45 field blanks, 44 MS/MSD samples and 7 conductivity check samples. The lab contributed the remaining LCS/LCSD and method blank samples.

# **Data Qualification**

Performance measures were used to determine when data should be qualified. Performance measures for this program consist of percent recovery control limits and relative percent difference (RPD) control limits of QC data. Control limits may be specified by the EPA method or provided by the lab. Percent recovery was used to assess bias in an analysis by adding a known amount of chemical to a sample before analysis and comparing it to the amount detected during analysis. Systematically low percent recoveries show analytical bias. The analytical method named GCMS-Pesticide in this report had analyte-specific percent recovery control limits. All other percent recovery limits are default limits specified by the EPA method. RPD was used to assess analytical precision; the difference between replicate pairs (matrix spike duplicates, laboratory control sample duplicates, and field replicates) is compared. The RPD was calculated by dividing the absolute value of the difference between the consistently identified replicate pair concentrations by their mean and then multiplying by 100 for a percent value. When RPDs and percent recoveries are outside control limits, analytical results may be qualified.

The Manchester Environmental Laboratory qualify all sample results based on the analysis of LCS/LCSDs, MS/MSDs, surrogates, and method blanks. LCS/LCSD were generated by adding analytes at known concentrations to purified water free of all organics. An LCS/LCSD pair was extracted and analyzed with every batch of field samples and other QC samples. They were used to evaluate method performance for a specific analyte and to check for bias and precision of the lab's extraction and analytical processes. Detections from a batch may be qualified based on high/low recovery and/or high RPD between the paired LCS and LCSD. Similarly, samples collected in the field that had analytes added at known concentrations and analyzed are MS/MSD samples. The analysis of this type of QC sample can assess the potential for matrix interactions or interaction between analytes within field samples that can affect analytical results. Staff collected an MS/MSD sample once during the season at each site for each analysis method, except in a few cases where budgetary restrictions were prohibitive. In 2019, almost all analytes tested for during the season were used to spike MS/MSDs and LCS/LCSDs, although the lab rotated between two spike

mixtures for the GCMS-Pesticides analytical method to avoid coelution of analytes. Surrogates are analytes not normally found in environmental samples that were spiked into all field and QC samples to evaluate recoveries for groups of organic compounds. Results of surrogates can evaluate extraction efficiency and matrix interference within the sample.

WSDA staff qualify the remainder of the field sample data based on field replicates, field blanks, and MS/MSD results. Field replicates were used to evaluate variability in analytical results. No field sample results were qualified due solely to field replicate results in 2019. Field blank results were used to examine bias caused by contamination in the field during transport to the lab and during processing at the lab. Two detections of tralomethrin, a legacy insecticide, were qualified to non-detects due to poor MS/MSD and LCS/LCSD recoveries.

MEL reports the lower limit of quantitation (LLOQ) which is the lowest concentration at which the laboratory has demonstrated analytes can be reliably reported with a level of confidence. The LLOQ was adjusted for each individual sample according to sample volume and dilution (if needed). Results outside the instrument calibration range may be qualified as estimates (*J*). Mean LLOQ (calculated for each individual sample in 2019) and standard deviation are presented in Table *31*b.

Analyte	CAS number	Analytical method	Pesticide type	Mean LLOQ	Standard deviation
1-(3,4-Dichlorophenyl)-3- methylurea	3567-62-2	LCMS-Pesticides	Degradate	1.01E+01	8.56E-01
2,4-D	94-75-7	GCMS-Herbicides	Herbicide	6.20E+01	3.01E+01
2,6-Dichlorobenzamide	2008-58-4	GCMS-Pesticides	Degradate	5.40E+00	1.73E+00
2-Hydroxyatrazine	2163-68-0	LCMS-Pesticides	Degradate	6.97E+00	3.37E+00
3,5-Dichlorobenzoic acid	51-36-5	GCMS-Herbicides	Degradate	5.99E+01	7.74E-01
4,4'-DDD	72-54-8	GCMS-Pesticides	Degradate	5.37E+00	2.09E+00
4,4'-DDE	72-55-9	GCMS-Pesticides	Degradate	5.30E+00	1.20E+00
4,4'-DDT	50-29-3	GCMS-Pesticides	Insecticide	5.52E+00	1.54E+00
4-Nitrophenol	100-02-7	GCMS-Herbicides	Degradate	5.99E+01	7.74E-01
Acephate	30560-19-1	LCMS-Pesticides	Insecticide	3.05E+01	6.47E+00
Acetamiprid	135410-20-7	LCMS-Pesticides	Insecticide	1.89E+01	4.58E+00
Acetochlor	34256-82-1	GCMS-Pesticides	Herbicide	1.33E+01	2.65E+01
Acetochlor ESA	187022-11-3	LCMS-Pesticides	Degradate	4.03E+01	3.43E+00
Afidopyropen	915972-17-7	LCMS-Pesticides	Insecticide	7.40E+01	1.34E+01
Alachlor	15972-60-8	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02
Aldicarb sulfoxide	1646-87-3	LCMS-Pesticides	Degradate	1.01E+01	8.56E-01
AMPA	1066-51-9	LCMS-Glyphos	Herbicide	2.35E+01	4.84E+01
Atrazine	1912-24-9	GCMS-Pesticides	Herbicide	5.17E+00	9.48E-01
Azoxystrobin	131860-33-8	LCMS-Pesticides	Fungicide	1.41E+01	8.90E+00
Baygon	114-26-1	LCMS-Pesticides	Insecticide	1.01E+01	8.59E-01
Benefin	1861-40-1	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02

Table 31b – Mean performance of method reporting limits (LLOQ) in ng/L

AnalyteCAS numberMarytourFootolideIndiamethodtypeLLOOBensulide741-58-2LCMS-PesticidesHerbicide2.15E+Bentazon25057-89-0GCMS-HerbicidesHerbicide5.99E+	
Bentazon 25057-89-0 GCMS-Herbicides Herbicide 5.99E+	
	01 7.56E+00
	01 7.74E-01
Bifenazate 149877-41-8 GCMS-Pesticides Insecticide 6.69E+	00 4.16E+00
Bifenthrin 82657-04-3 GCMS-Pesticides Insecticide 4.99E+	00 5.99E-02
Boscalid 188425-85-6 GCMS-Pesticides Fungicide 1.03E+	01 1.25E+01
Bromacil 314-40-9 GCMS-Pesticides Herbicide 4.99E+	00 5.99E-02
Bromoxynil 1689-84-5 GCMS-Herbicides Herbicide 5.99E+	01 7.74E-01
Captan 133-06-2 GCMS-Pesticides Fungicide 6.46E+	00 4.12E+00
Carbaryl 63-25-2 LCMS-Pesticides Insecticide 1.92E+	01 4.32E+00
Carbendazim 10605-21-7 LCMS-Pesticides Fungicide 5.24E+	00 3.83E+00
Chlorantraniliprole 500008-45-7 LCMS-Pesticides Insecticide 2.01E+	01 1.71E+00
Chlorethoxyfos 54593-83-8 GCMS-Pesticides Insecticide 9.97E+	00 1.21E-01
Chlorothalonil (Daconil) 1897-45-6 GCMS-Pesticides Fungicide 5.20E+	00 1.01E+00
Chlorpropham 101-21-3 GCMS-Pesticides Herbicide 5.26E+	00 1.67E+00
Chlorpyrifos 2921-88-2 GCMS-Pesticides Insecticide 4.99E+	00 5.99E-02
Chlorsulfuron 64902-72-3 LCMS-Pesticides Herbicide 4.91E+	01 8.65E+00
cis-Permethrin 54774-45-7 GCMS-Pesticides Insecticide 4.99E+	00 5.99E-02
Clopyralid 1702-17-6 GCMS-Herbicides Herbicide 5.99E+	01 7.74E-01
Clothianidin 210880-92-5 LCMS-Pesticides Insecticide 9.59E+	01 2.23E+01
Coumaphos 56-72-4 GCMS-Pesticides Insecticide 8.90E+	00 1.01E+01
Cycloate 1134-23-2 GCMS-Pesticides Herbicide 1.50E+	01 1.85E-01
Cyfluthrin 68359-37-5 GCMS-Pesticides Insecticide 5.40E+	00 1.38E+00
Cypermethrin 52315-07-8 GCMS-Pesticides Insecticide 6.39E+	00 4.24E+00
Cyprodinil 121552-61-2 LCMS-Pesticides Fungicide 9.98E+	00 1.10E+00
Dacthal 1861-32-1 GCMS-Herbicides Herbicide 5.99E+	01 7.74E-01
Deisopropyl atrazine 1007-28-9 LCMS-Pesticides Degradate 1.01E+	01 8.56E-01
Deltamethrin 52918-63-5 GCMS-Pesticides Insecticide 7.37E+	00 9.60E+00
Desethylatrazine 6190-65-4 LCMS-Pesticides Degradate 9.60E+	00 2.13E+00
Diazinon 333-41-5 GCMS-Pesticides Insecticide 4.99E+	00 5.99E-02
Dicamba 1918-00-9 GCMS-Herbicides Herbicide 5.99E+	01 7.74E-01
Dichlobenil 1194-65-6 GCMS-Pesticides Herbicide 5.39E+	00 1.71E+00
Dichlorprop 120-36-5 GCMS-Herbicides Herbicide 5.99E+	01 7.74E-01
Dichlorvos (DDVP) 62-73-7 GCMS-Pesticides Insecticide 4.99E+	00 5.99E-02
Difenoconazole 119446-68-3 LCMS-Pesticides Fungicide 9.13E+	00 2.12E+00
Diflubenzuron 35367-38-5 LCMS-Pesticides Insecticide 7.05E+	01 5.99E+00
Dimethoate 60-51-5 GCMS-Pesticides Insecticide 5.52E+	00 1.54E+00
Dinotefuran 165252-70-0 LCMS-Pesticides Insecticide 1.96E+	01 2.90E+00
Dithiopyr 97886-45-8 GCMS-Pesticides Herbicide 5.38E+	00 2.08E+00
Diuron 330-54-1 LCMS-Pesticides Herbicide 9.19E+	00 2.47E+00
Eptam 759-94-4 GCMS-Pesticides Herbicide 4.99E+	00 5.99E-02
Ethalfluralin (Sonalan) 55283-68-6 GCMS-Pesticides Herbicide 4.99E+	00 5.99E-02

		Analytical	Pesticide	Mean	Standard
Analyte	CAS number	method	type	LLOQ	deviation
Ethoprop	13194-48-4	GCMS-Pesticides	Insecticide	4.99E+00	5.99E-02
Etoxazole	153233-91-1	GCMS-Pesticides	Insecticide	1.50E+01	1.85E-01
Etridiazole	2593-15-9	GCMS-Pesticides	Fungicide	5.18E+00	9.71E-01
Fenarimol	60168-88-9	GCMS-Pesticides	Fungicide	6.39E+00	3.99E+00
Fenbuconazole	114369-43-6	LCMS-Pesticides	Fungicide	2.01E+01	1.71E+00
Fenbutatin oxide	13356-08-6	LCMS-Pesticides	Insecticide	2.18E+01	8.24E+00
Fenvalerate	51630-58-1	GCMS-Pesticides	Insecticide	8.23E+00	6.60E+00
Fipronil	120068-37-3	GCMS-Pesticides	Insecticide	5.52E+00	1.54E+00
Fipronil desulfinyl	205650-65-3	GCMS-Pesticides	Degradate	5.73E+00	1.78E+00
Fipronil sulfide	120067-83-6	GCMS-Pesticides	Degradate	6.25E+00	3.36E+00
Fipronil sulfone	120068-36-2	GCMS-Pesticides	Degradate	9.97E+00	1.21E-01
Fludioxonil	131341-86-1	GCMS-Pesticides	Fungicide	6.40E+00	3.23E+00
Flumioxazin	103361-09-7	GCMS-Pesticides	Herbicide	2.49E+01	3.02E-01
Fluroxypyr-meptyl	81406-37-3	GCMS-Pesticides	Herbicide	2.49E+01	3.02E-01
Glufosinate-ammonium	77182-82-2	LCMS-Glyphos	Herbicide	2.71E+01	3.90E+01
Glyphosate	1071-83-6	LCMS-Glyphos	Herbicide	1.70E+01	3.15E+01
Hexazinone	51235-04-2	GCMS-Pesticides	Herbicide	7.08E+00	5.03E+00
Hexythiazox	78587-05-0	LCMS-Pesticides	Insecticide	9.91E+00	9.07E+00
Imazapic	104098-48-8	LCMS-Pesticides	Herbicide	9.33E+01	2.67E+01
Imazapyr	81334-34-1	LCMS-Pesticides	Herbicide	9.81E+01	1.80E+01
Imidacloprid	138261-41-3	LCMS-Pesticides	Insecticide	1.94E+01	3.48E+00
Imidan	732-11-6	GCMS-Pesticides	Insecticide	6.92E+00	2.43E+00
Indaziflam	950782-86-2	LCMS-Pesticides	Herbicide	8.81E+00	2.92E+00
Isoxaben	82558-50-7	LCMS-Pesticides	Herbicide	9.65E+00	2.03E+00
Kelthane	115-32-2	GCMS-Pesticides	Insecticide	2.49E+01	4.96E-01
Linuron	330-55-2	LCMS-Pesticides	Herbicide	7.05E+01	5.99E+00
Malaoxon	1634-78-2	LCMS-Pesticides	Degradate	9.40E+00	2.43E+00
Malathion	121-75-5	GCMS-Pesticides	Insecticide	5.58E+00	1.81E+00
MCPA	94-74-6	GCMS-Herbicides	Herbicide	5.99E+01	7.74E-01
MCPP	93-65-2	GCMS-Herbicides	Herbicide	5.99E+01	7.74E-01
Metalaxyl	57837-19-1	GCMS-Pesticides	Fungicide	9.97E+00	1.21E-01
Methamidophos	10265-92-6	LCMS-Pesticides	Insecticide	2.95E+01	5.30E+00
Methidathion	950-37-8	LCMS-Pesticides	Insecticide	1.01E+01	8.56E-01
Methiocarb	2032-65-7	LCMS-Pesticides	Insecticide	3.02E+01	2.57E+00
Methomyl	16752-77-5	LCMS-Pesticides	Insecticide	1.01E+01	8.56E-01
Methomyl oxime	13749-94-5	LCMS-Pesticides	Degradate	1.01E+02	8.56E+00
Methoxyfenozide	161050-58-4	LCMS-Pesticides	Insecticide	1.01E+01	8.56E-01
Methyl chlorpyrifos	5598-13-0	GCMS-Pesticides	Insecticide	4.99E+00	5.99E-02
Metolachlor	51218-45-2	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02
Metribuzin	21087-64-9	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02
Metsulfuron-methyl	74223-64-6	LCMS-Pesticides	Herbicide	4.82E+01	1.01E+01

Analyte	CAS number	Analytical method	Pesticide type	Mean LLOQ	Standard deviation
MGK264	113-48-4	GCMS-Pesticides	Synergist	5.16E+00	9.17E-01
Myclobutanil	88671-89-0	LCMS-Pesticides	Fungicide	1.04E+01	2.32E+00
N,N-Diethyl-m-toluamide	134-62-3	GCMS-Pesticides	Insect Repellent	1.15E+01	1.87E+01
Naled	300-76-5	GCMS-Pesticides	Insecticide	4.99E+01	5.99E-01
Napropamide	15299-99-7	GCMS-Pesticides	Herbicide	5.90E+00	1.92E+00
Norflurazon	27314-13-2	GCMS-Pesticides	Herbicide	6.28E+00	2.19E+00
Oryzalin	19044-88-3	GCMS-Pesticides	Herbicide	2.79E+01	1.45E+01
Oxadiazon	19666-30-9	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02
Oxamyl	23135-22-0	LCMS-Pesticides	Insecticide	9.41E+00	2.42E+00
Oxamyl oxime	30558-43-1	LCMS-Pesticides	Degradate	3.02E+01	2.57E+00
Oxyfluorfen	42874-03-3	GCMS-Pesticides	Herbicide	4.99E+01	5.99E-01
Paclobutrazol	76738-62-0	LCMS-Pesticides	Fungicide	9.72E+00	1.63E+00
Pendimethalin	40487-42-1	GCMS-Pesticides	Herbicide	6.07E+00	2.06E+00
Pentachloronitrobenzene	82-68-8	GCMS-Pesticides	Fungicide	4.99E+00	5.99E-02
Pentachlorophenol	87-86-5	GCMS-Herbicides	Wood Preservative	5.99E+01	7.74E-01
Phenothrin	26002-80-2	GCMS-Pesticides	Insecticide	9.97E+00	1.21E-01
Phorate	298-02-2	GCMS-Pesticides	Insecticide	1.10E+02	2.98E+01
Picloram	1918-02-1	GCMS-Herbicides	Herbicide	3.11E+02	9.49E+01
Piperonyl butoxide (PBO)	51-03-6	GCMS-Pesticides	Synergist	6.18E+00	2.13E+00
Prallethrin	23031-36-9	GCMS-Pesticides	Insecticide	4.99E+00	5.99E-02
Prodiamine	29091-21-2	GCMS-Pesticides	Herbicide	2.49E+01	3.02E-01
Prometon	1610-18-0	GCMS-Pesticides	Herbicide	5.48E+00	1.50E+00
Prometryn	7287-19-6	GCMS-Pesticides	Herbicide	1.13E+01	4.18E+00
Pronamide (Kerb)	23950-58-5	GCMS-Pesticides	Herbicide	5.52E+00	1.54E+00
Propargite	2312-35-8	GCMS-Pesticides	Insecticide	9.97E+00	1.21E-01
Propiconazole	60207-90-1	LCMS-Pesticides	Fungicide	4.69E+01	1.20E+01
Pyraclostrobin	175013-18-0	LCMS-Pesticides	Fungicide	4.74E+01	1.13E+01
Pyraflufen-ethyl	129630-19-9	GCMS-Pesticides	Herbicide	5.93E+00	1.95E+00
Pyrethrins	121-21-1	GCMS-Pesticides	Insecticide	9.97E+01	1.23E+00
Pyridaben	96489-71-3	GCMS-Pesticides	Insecticide	5.14E+00	8.48E-01
Pyrimethanil	53112-28-0	LCMS-Pesticides	Fungicide	9.97E+00	1.07E+00
Pyriproxyfen	95737-68-1	GCMS-Pesticides	Insecticide	1.20E+01	8.35E+00
Simazine	122-34-9	GCMS-Pesticides	Herbicide	1.01E+01	2.15E+00
Simetryn	1014-70-6	GCMS-Pesticides	Herbicide	2.49E+01	3.02E-01
Specific conductivity		SCOND		15 µS/cm	0.00E+00
Spirotetramat	203313-25-1	LCMS-Pesticides	Insecticide	2.28E+01	9.52E+00
Sulfentrazone	122836-35-5	GCMS-Pesticides	Herbicide	1.05E+01	1.82E+01
Sulfometuron-methyl	74222-97-2	LCMS-Pesticides	Herbicide	1.96E+01	3.22E+00
Tau-fluvalinate	102851-06-9	GCMS-Pesticides	Insecticide	9.96E+00	1.04E+01

Ambient Monitoring for Pesticides in Washington State Surface Water: 2019 Technical Report | 117

Analyte	CAS number	Analytical method	Pesticide type	Mean LLOQ	Standard deviation
Tebuthiuron	34014-18-1	GCMS-Pesticides	Herbicide	9.97E+00	1.21E-01
Tefluthrin	79538-32-2	GCMS-Pesticides	Insecticide	4.99E+00	5.99E-02
Terbacil	5902-51-2	GCMS-Pesticides	Herbicide	4.99E+00	5.99E-02
Tetrachlorvinphos	961-11-5	GCMS-Pesticides	Insecticide	6.52E+00	4.13E+00
Tetrahydrophthalimide	27813-21-4	GCMS-Pesticides	Degradate	5.18E+00	9.71E-01
Tetramethrin	7696-12-0	GCMS-Pesticides	Insecticide	5.46E+00	2.50E+00
Thiacloprid	111988-49-9	LCMS-Pesticides	Insecticide	9.87E+00	1.24E+00
Thiamethoxam	153719-23-4	LCMS-Pesticides	Insecticide	1.96E+01	2.97E+00
Total suspended solids		TSS		2.45 mg/L	2.29E+00
Tralomethrin	66841-25-6	GCMS-Pesticides	Insecticide	7.15E+00	9.59E+00
trans-Permethrin	61949-77-7	GCMS-Pesticides	Insecticide	7.48E+00	9.16E+00
Treflan (Trifluralin)	1582-09-8	GCMS-Pesticides	Herbicide	8.58E+00	2.24E+00
Triadimefon	43121-43-3	GCMS-Pesticides	Fungicide	5.68E+00	1.73E+00
Triallate	2303-17-5	GCMS-Pesticides	Herbicide	5.26E+00	1.45E+00
Triclopyr	55335-06-3	GCMS-Herbicides	Herbicide	6.20E+01	3.01E+01
Triclopyr-butoxyl	64700-56-7	GCMS-Pesticides	Herbicide	9.97E+00	1.21E-01
Triclosan	3380-34-5	GCMS-Pesticides	Antimicrobial	1.78E+01	1.55E+01
Trifloxystrobin	141517-21-7	LCMS-Pesticides	Fungicide	2.03E+01	1.88E+00
Zoxamide	156052-68-5	LCMS-Pesticides	Fungicide	1.00E+01	9.33E-01

Data qualifiers describe the level of confidence associated with the data points. Laboratory data was qualified according to the National Functional Guidelines for Organic Data Review (EPA, 2017), Manchester Environmental Lab's data qualification criteria and professional judgement. The Manchester Environmental Lab provides a list of data qualifiers and their definitions in Table 32b that are used for sample analysis of pesticides, TSS, and specific conductivity (MEL, 2016).

Qualifier	Definition
	The analyte was positively identified and was detected at the reported concentration.
Е	Reported result is an estimate because it exceeds the calibration range.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
Ν	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a "tentative identification".
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified," and the associated numerical value represents its approximate concentration.

Qualifier	Definition
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.

Laboratory data points that were not assigned a qualifier are equivalent to having "No qualifier" which is the traditionally accepted method of assigning the highest level of confidence. Laboratory data assigned a qualifier of E or J are considered confirmed pesticide detections. Laboratory data qualified with NJ, N, U, or UJ are considered non-detects. A non-detect is a typical qualifier for no chemical detected, but can also include chemicals that were potentially detected below reported sample quantitation limits that cannot be confirmed. All pesticide laboratory results that were not assigned a qualifier or assigned a qualifier of E or J were compared to the WSDA assessment criteria that were developed for this report.

# Analytical Quality Assurance and Quality Control Sample Summaries

In this section of the report, quality control data is summarized from field replicate, field blank, MS/MSD, laboratory duplicate, surrogate and LCS/LCSD results. Overall, analyte recoveries and RPDs were of acceptable data quality.

#### **Field Replicate Results**

Staff collected field replicate samples in order to assess the potential for variation in sample homogeneity and the entire process of sampling and analysis. Replicate pairs were analyzed by taking into consideration the qualifier of both the sample *and* field replicate. If the sample and replicate were consistently identified, then the higher concentration was chosen as the concentration of the confirmed detection. If the sample and replicate were inconsistently identified, then the sample or replicate with the unqualified, *J* or *E* qualification was chosen with its respective concentration as the positive detection.

During 2019, 5% of pesticide and TSS samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 280 consistently identified pairs for pesticide analysis and 14 consistently identified pairs for TSS analysis. Consistently identified pairs are those where the analytes were identified in both the original sample and field replicate with unqualified, J and E results. Conversely, inconsistently identified replicate pairs are those where the analyte was detected in only one of the two samples collected. Only 42 inconsistently identified pairs for pesticide analysis and no inconsistently identified pairs for TSS were found.

Of the 160 analytes tested for, 55% (88 analytes) were detected in field replicates. Table 33b presents the variability of detections in field replicates with at least one detection in a replicate pair. RPDs were only calculated for consistently identified replicate pairs. Variability of detection and RPDs could not be calculated for the 72 analytes without replicate detections and, therefore, are not found in Table 33b.

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Bentazon	GCMS-Herbicides	11	0	-	1	100	100
Chlorothalonil (Daconil)	GCMS-Pesticides	16	0		1	100	100

#### Table 33b – Variability of pesticide detections in field replicates and mean RPDs

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Chlorsulfuron	LCMS-Pesticides	12	0		1	100	100
Cyprodinil	LCMS-Pesticides	12	0		1	100	100
Fipronil	GCMS-Pesticides	16	0		1	100	100
Fluroxypyr-meptyl	GCMS-Pesticides	16	0		1	100	100
Myclobutanil	LCMS-Pesticides	12	0		1	100	100
Pentachlorophenol	GCMS-Herbicides	11	0		1	100	100
Tefluthrin	GCMS-Pesticides	16	0		1	100	100
Triclosan	GCMS-Pesticides	15	0		2	100	100
4,4'-DDE	GCMS-Pesticides	14	1	1	2	67	97
Tau-fluvalinate	GCMS-Pesticides	14	1	10	2	67	97
Acetochlor ESA	LCMS-Pesticides	11	1	33	1	50	95
MCPP	GCMS-Herbicides	10	1	7	1	50	95
Methomyl	LCMS-Pesticides	11	1	3	1	50	95
Oryzalin	GCMS-Pesticides	15	1	13	1	50	95
Pyriproxyfen	GCMS-Pesticides	15	1	1	1	50	95
Sulfometuron-methyl	LCMS-Pesticides	11	1	29	1	50	95
4,4'-DDD	GCMS-Pesticides	16	1	1	0	0	90
Bifenthrin	GCMS-Pesticides	16	1	11	0	0	90
Chlorantraniliprole	LCMS-Pesticides	12	1	22	0	0	90
Flumioxazin	GCMS-Pesticides	16	1	5	0	0	90
Glufosinate-ammonium	LCMS-Glyphos	14	1	0	0	0	90
Imidan	GCMS-Pesticides	16	1	2	0	0	90
Indaziflam	LCMS-Pesticides	12	1	13	0	0	90
Malaoxon	LCMS-Pesticides	12	1	9	0	0	90
Metalaxyl	GCMS-Pesticides	16	1	14	0	0	90
Metribuzin	GCMS-Pesticides	16	1	4	0	0	90
Metsulfuron-methyl	LCMS-Pesticides	12	1	54	0	0	90

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Paclobutrazol	LCMS-Pesticides	12	1	11	0	0	90
Picloram	GCMS-Herbicides	11	1	4	0	0	90
Prometon	GCMS-Pesticides	16	1	2	0	0	90
Propiconazole	LCMS-Pesticides	12	1	4	0	0	90
Pyridaben	GCMS-Pesticides	16	1	8	0	0	90
Tetramethrin	GCMS-Pesticides	16	1	10	0	0	90
Triadimefon	GCMS-Pesticides	16	1	1	0	0	90
Diazinon	GCMS-Pesticides	14	2	4	1	33	80
Eptam	GCMS-Pesticides	14	2	11	1	33	80
Malathion	GCMS-Pesticides	14	2	5	1	33	80
Tetrahydrophthalimide	GCMS-Pesticides	14	2	5	1	33	80
4,4'-DDT	GCMS-Pesticides	15	2	9	0	0	68
Acetamiprid	LCMS-Pesticides	11	2	26	0	0	68
Carbendazim	LCMS-Pesticides	11	2	1	0	0	68
Dimethoate	GCMS-Pesticides	15	2	1	0	0	68
Dinotefuran	LCMS-Pesticides	11	2	4	0	0	68
Ethalfluralin (Sonalan)	GCMS-Pesticides	15	2	4	0	0	68
Etoxazole	GCMS-Pesticides	15	2	12	0	0	68
Oxadiazon	GCMS-Pesticides	15	2	6	0	0	68
Oxamyl	LCMS-Pesticides	11	2	2	0	0	68
Pyrimethanil	LCMS-Pesticides	11	2	6	0	0	68
Imidacloprid	LCMS-Pesticides	9	3	10	1	25	68
Simazine	GCMS-Pesticides	10	5	24	2	29	60
2,4-D	GCMS-Herbicides	2	7	19	3	0.3	55
1-(3,4-Dichlorophenyl)-3-							
methylurea	LCMS-Pesticides	10	3	23	0	0	54
Acephate	LCMS-Pesticides	10	3	6	0	0	54

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Azoxystrobin	LCMS-Pesticides	10	3	4	0	0	54
Dacthal	GCMS-Herbicides	9	3	15	0	0	54
N,N-Diethyl-m-toluamide	GCMS-Pesticides	13	3	3	0	0	54
Napropamide	GCMS-Pesticides	14	3	7	0	0	54
Oxamyl oxime	LCMS-Pesticides	10	3	10	0	0	54
Dicamba	GCMS-Herbicides	6	5	8	1	0.2	51
Norflurazon	GCMS-Pesticides	11	5	4	1	0.2	51
Thiamethoxam	LCMS-Pesticides	7	5	8	1	0.2	51
Boscalid	GCMS-Pesticides	7	7	4	2	0.2	49
Pendimethalin	GCMS-Pesticides	7	8	8	2	0.2	45
2-Hydroxyatrazine	LCMS-Pesticides	9	4	4	0	0	44
Clothianidin	LCMS-Pesticides	9	4	9	0	0	44
Deisopropyl atrazine	LCMS-Pesticides	9	4	5	0	0	44
Hexazinone	GCMS-Pesticides	12	4	14	0	0	44
Tebuthiuron	GCMS-Pesticides	13	4	23	0	0	44
Triclopyr	GCMS-Herbicides	8	4	13	0	0	44
Dichlobenil	GCMS-Pesticides	12	5	9	0	0	37
Piperonyl butoxide	GCMS-Pesticides	12	5	8	0	0	37
Diuron	LCMS-Pesticides	4	8	15	1	0.1	37
Bromacil	GCMS-Pesticides	4	11	9	2	0.2	36
Chlorpyrifos	GCMS-Pesticides	11	6	2	0	0	32
Methamidophos	LCMS-Pesticides	7	6	3	0	0	32
Atrazine	GCMS-Pesticides	10	7	8	0	0	28
Desethylatrazine	LCMS-Pesticides	6	7	5	0	0	28
Fludioxonil	GCMS-Pesticides	10	7	9	0	0	28
Imazapyr	LCMS-Pesticides	6	7	7	0	0	28
Terbacil	GCMS-Pesticides	10	7	20	0	0	28

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
2,6-Dichlorobenzamide	GCMS-Pesticides	2	14	9	1	0.1	24
Sulfentrazone	GCMS-Pesticides	8	9	12	0	0	23
Metolachlor	GCMS-Pesticides	7	10	7	0	0	21
Glyphosate	LCMS-Glyphos	2	13	10	0	0	16
AMPA	LCMS-Glyphos	1	14	19	0	0	15
Total Suspended Solids	TSS	2	14	5	0	0	15

Staff used two methods to estimate the uncertainty of replicate variability. The first was the percentage of inconsistently identified replicate pairs and the second was an evaluation of the upper confidence bound associated with the percentage of inconsistently identified replicate pairs. If the percentage of inconsistently identified replicate pairs out of the total count of consistently and inconsistently identified replicate pairs was 25% or less, a low variability of detection was assumed; whereas, a percentage of 50% or greater was indicative of high variability of detection (Martin, 2002). Almost 74% of analytes (65 analytes) with inconsistently identified replicate pairs had percentages of equal to or less than 25%. This analysis of variability can be useful when there are many replicate pairs with identified detections. In the second method, the 90% upper confidence bound was evaluated alongside the percentage of inconsistently identified replicate pairs as an additional estimate in the uncertainty of replicate variability. Evaluating variability using a one-sided confidence limit can increase the assurances of the data user that the analyte detections are reproducible. It also provides an upper limit of the likelihood that a pesticide detected in a field sample would fail to be detected in a replicate sample (Martin, 2002). The replicate results evaluated in 2019 using the second method indicate only six analytes have a low detection variability rather than the 65 analytes estimated through the first method. These six were 2,6-dichlorobenzamide, sulfentrazone, metolachlor, glyphosate, AMPA, and TSS. All six of these analytes were frequently detected throughout the season at most monitoring sites. This analysis shows that there was not a high reproducibility of detections between replicates for most analytes. Likely, some of the high variability was due in part to a small number of replicate pairs with at least one detection.

The RPD of analytes for consistently identified pairs was good overall. For pesticide analysis, the mean RPD of the consistently identified replicate-paired analytes was 10%. Only 15 of the 280 consistently identified replicate pairs for pesticides had RPDs that were equal to or greater than the 40% RPD criterion. For TSS analysis, the mean RPD of the consistently identified replicate-paired analyte was 5%. No consistently identified replicate pairs for TSS had an RPD that was equal to or greater than the 20%

RPD criterion. Results for pesticide and TSS field sample and replicate detections were not qualified because RPD has limited effectiveness in assessing variability at low levels (Mathieu, 2006). When concentrations are low, the RPD may be large even though the actual difference between the pairs is low. The remaining data for pesticide and TSS field replicates are of acceptable data quality.

The majority of the 42 inconsistently identified pairs were detections at concentrations between the LLOQ and the method detection limit (MDL) (below which the laboratory is unable to distinguish between instrument response due to the presence of analytes or background noise). Most of these replicate pairs consisted of a *J* qualified detection and a *U* or *UJ* qualified detection. There were no sample detections qualified due solely to inconsistent field replicate results.

## Laboratory Duplicates

MEL uses split sample duplicates to evaluate the precision of TSS and conductivity analyses. In 2019, there were 96 laboratory duplicate pairs for TSS and seven duplicate pairs for conductivity (Table 34b). No field TSS samples were qualified due solely to RPD exceedances. Overall, laboratory duplicate results were of acceptable data quality.

Parameter	pecific conductivity 7	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Specific conductivity	7	20	0	0
Total suspended solids	96	20	1	1

## **Field Blank Results**

Field blank detections indicate the potential for sample contamination in the field and laboratory or the potential for false detections due to analytical error. In 2019, there were 11 detections in the 45 field blank samples collected for TSS and pesticide analysis (Table 35b). If a detection occurred in a field blank, all sample detections of the same analyte in the analytical batch were reviewed for qualification. Sample detection concentrations that were greater than five times the field blank detection concentration were not qualified. Sample detection concentrations that were lower than five times the field blank detection concentration were qualified to *U*. There were 22 sample detections qualified to U in 2019 due to field blank detections.

Sampling date	Monitoring Site	Analytical method	Analyte	Result (ng/L)	LLOQ (ng/L)	MDL (ng/L)	Qualifier
3/25	Indian Slough	GCMS-Pesticides	Acetochlor	15.3	4.9	3.44	
3/25	Indian Slough	GCMS-Pesticides	Chlorpropham	3.11	4.9	0.961	J
4/01	Upper Bertrand	GCMS-Pesticides	Acetochlor	20	5.05	3.54	
4/01	Upper Bertrand	GCMS-Pesticides	N,N-Diethyl-m-toluamide	3.47	5.05	1.35	J
4/22	Lower Big Ditch	GCMS-Pesticides	Acetochlor	22.4	5.05	3.54	
5/14	Stemilt Creek	GCMS-Pesticides	N,N-Diethyl-m-toluamide	23.9	4.98	1.33	J
5/20	Snipes Creek	GCMS-Pesticides	N,N-Diethyl-m-toluamide	13.8	4.98	1.33	
5/20	Snipes Creek	GCMS-Pesticides	Triclosan	4.44	9.95	1.72	J
7/22	Upper Big Ditch	GCMS-Pesticides	Triclosan	15.7	10	1.73	
7/30	Brender Creek	GCMS-Pesticides	N,N-Diethyl-m-toluamide	76.4	4.98	1.33	
9/03	Naneum Creek	TSS	Total suspended solids	1 mg/L	1 mg/L		

#### Table 35b – Analyte detections in field blanks

#### Matrix Spike/Matrix Spike Duplicate Results

Summary MS/MSD results for each analyte are shown in Table 36b, with control limits, percent recoveries, and RPDs. The table describes the number of MS/MSD recoveries that were above or below the laboratory control limits set for each analyte and the number of detections from all grab samples throughout the season for each analyte. Only the MS/MSD recoveries that were unqualified, *E*, or *J* qualified are included in the table. Some RPDs were unable to be calculated because of a *U*, *NAF*, or *NC* qualified MS/MSD recovery result. The summary table excluded the uncalculated RPDs. Parameters that were not spiked into MS/MSD samples but were tested for in field samples include pyrethrins, TSS and specific conductivity.

Analyte	MS/MSD recoveries (n)		Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)		Total detections (n)
1-(3,4-Dichlorophenyl)-3-											
methylurea	26	40	130	108	84 - 152	0	4	13	5	0.2 - 18	52
2,4-D	16	10	150	75	56 - 86	0	0	8	7	0.09 - 18	121
2,6-Dichlorobenzamide	20	30	140	119	84 - 144	0	1	10	4	0.08 - 18	245
2-Hydroxyatrazine	26	40	130	113	85 - 140	0	2	13	3	0.02 - 6	104
3,5-Dichlorobenzoic acid	16	21	144	65	58 - 74	0	0	8	7	0.7 - 11	
4,4'-DDD	20	49	143	120	108 - 136	0	0	10	4	0.2 - 9	56
4,4'-DDE	20	40	130	85	72 - 101	0	0	10	3	0.5 - 9	64
4,4'-DDT	20	42	120	95	82 - 106	0	0	10	5	0.2 - 20	34
4-Nitrophenol	16	10	172	79	40 - 101	0	0	8	11	0.7 - 23	4
Acephate	26	40	130	89	77 - 99	0	0	13	3	0.8 - 8	40
Acetamiprid	26	70	122	116	82 - 147	0	10	13	3	0.5 - 7	22
Acetochlor	20	30	130	108	90 - 123	0	0	10	3	0.4 - 11	
Acetochlor ESA	26	40	130	98	69 - 115	0	0	13	6	0.6 - 20	22
Afidopyropen	26	40	130	99	74 - 125	0	0	13	15	4 - 31	
Alachlor	20	16	181	123	104 - 140	0	0	10	4	0.9 - 14	1
Aldicarb sulfoxide	26	68	119	96	84 - 112	0	0	13	2	0.03 - 5	
AMPA	25	50	150	88	40 - 123	4	0	12	4	0.04 - 11	155
Atrazine	20	13	172	103	95 - 112	0	0	10	3	0.3 - 8	112
Azoxystrobin	26	63	130	104	90 - 122	0	0	13	3	0.5 - 7	97
Baygon	26	62	120	100	90 - 109	0	0	13	3	0.3 - 6	
Benefin	20	50	151	113	103 - 125	0	0	10	4	0.2 - 11	
Bensulide	26	40	130	105	82 - 131	0	1	13	6	1 - 13	
Bentazon	16	25	159	75	64 - 86	0	0	8	7	0.6 - 17	19
Bifenazate	20	50	150	294	186 - 525	0	20	10	7	0.05 - 29	
Bifenthrin	20	30	130	113	92 - 134	0	2	10	6	3 - 14	9
Boscalid	20	50	150	167	127 - 202	Ő	16	10	5	0.9 - 18	189
Bromacil	20	55	181	152	131 - 175	0	0	10	5	0.1 - 16	183
Bromoxynil	16	28	138	73	64 - 82	0	0 0	8	7	2 - 17	6

Table 36b – Summary statistics for MS/MSD recoveries and RPD

Analyte	MS/MSD recoveries (n)	Lower control limit (%)		Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
Captan	20	10	219	89	20 - 120	0	0	10	9	2 - 22	
Carbaryl	26	29	139	103	87 - 117	0	0	13	5	1 - 7	16
Carbendazim	26	40	130	103	84 - 117	0	0	13	3	0.2 - 7	62
Chlorantraniliprole	26	53	130	97	80 - 113	0	0	13	4	1 - 13	32
Chlorethoxyfos	20	30	130	109	97 - 119	0	0	10	6	0.04 - 17	
Chlorothalonil	20	57	227	97	73 - 108	0	0	10	5	0.2 - 15	6
Chlorpropham	20	53	181	122	106 - 134	0	0	10	3	0.04 - 9	16
Chlorpyrifos	20	52	152	125	107 - 140	0	0	10	4	1 - 10	82
Chlorsulfuron	26	10	125	98	65 - 139	0	3	13	13	0.03 - 36	7
cis-Permethrin	20	17	201	148	116 - 184	0	0	10	4	1 - 11	1
Clopyralid	16	10	106	45	25 - 54	0	0	8	11	0.1 - 53	4
Clothianidin	26	29	148	145	87 - 198	0	13	13	6	2 - 27	103
Coumaphos	20	10	487	252	191 - 341	0	0	10	3	0.8 - 12	
Cycloate	20	49	151	120	100 - 140	0	0	10	5	0.6 - 17	
Cyfluthrin	20	50	150	192	146 - 459	0	19	10	7	1 - 19	
Cypermethrin	20	30	130	149	111 - 214	0	14	10	6	1 - 18	
Cyprodinil	26	72	130	95	78 - 115	0	0	13	4	0.004 - 7	21
Dacthal	16	38	173	79	67 - 96	0	0	8	9	1 - 28	40
Deisopropyl atrazine	26	10	146	110	86 - 131	0	0	13	3	0.6 - 7	87
Deltamethrin	20	30	130	195	130 - 303	0	19	10	5	0.5 - 14	
Desethylatrazine	26	21	131	115	92 - 131	0	0	13	3	0.07 - 15	127
Diazinon	20	59	168	138	118 - 150	0	0	10	3	0.4 - 7	45
Dicamba	16	10	146	72	64 - 81	0	0	8	7	0.8 - 15	67
Dichlobenil	20	34	153	98	80 - 115	0	0	10	5	1 - 21	100
Dichlorprop	16	22	160	75	67 - 84	0	0	8	6	0.1 - 15	
Dichlorvos (DDVP)	20	27	169	129	85 - 166	0	0	10	8	2 - 29	
Difenoconazole	26	44	153	92	72 - 118	0	0	13	4	0.6 - 9	9
Diflubenzuron	26	45	127	154	97 - 373	0	14	13	10	0.6 - 61	
Dimethoate	20	65	217	137	113 - 151	0	0	10	4	0.3 - 13	22
Dinotefuran	26	36	175	112	78 - 146	0	0	13	3	0.04 - 12	51

Analyte	MS/MSD recoveries (n)	Lower control limit (%)		Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Rando of	Total detections (n)
Dithiopyr	20	30	130	126	104 - 150	0	8	10	5	0.7 - 14	18
Diuron	26	75	115	103	88 - 116	0	1	13	4	0.3 - 9	149
Eptam	20	41	159	106	83 - 127	0	0	10	6	0.2 - 28	46
Ethalfluralin (Sonalan)	20	6	243	113	104 - 123	0	0	10	4	0.2 - 13	2
Ethoprop	20	10	263	139	119 - 154	0	0	10	3	0.08 - 10	3
Etoxazole	20	50	150	133	110 - 147	0	0	10	4	0.02 - 12	13
Etridiazole	20	50	150	100	82 - 111	0	0	10	5	0.03 - 22	5
Fenarimol	20	30	130	146	124 - 168	0	18	10	3	0.2 - 15	14
Fenbuconazole	26	34	152	95	69 - 117	0	0	13	5	0.3 - 20	
Fenbutatin oxide	26	40	130	64	32 - 117	5	0	13	12	2 - 25	
Fenvalerate	20	30	130	175	127 - 263	0	16	10	4	0.6 - 10	
Fipronil	20	30	130	159	145 - 176	0	20	10	6	0.9 - 19	17
Fipronil desulfinyl	20	30	130	156	134 - 191	0	20	10	6	0.3 - 16	
Fipronil sulfide	20	30	130	135	118 - 154	0	14	10	5	2 - 15	6
Fipronil sulfone	20	30	130	152	137 - 188	0	20	10	4	0.9 - 14	8
Fludioxonil	20	50	150	122	66 - 137	0	0	10	4	0.8 - 11	164
Flumioxazin	20	50	150	163	60 - 187	0	16	10	5	0.004 - 12	7
Fluroxypyr-meptyl	20	50	150	120	110 - 137	0	0	10	3	0.3 - 12	2
Glufosinate-ammonium	27	50	150	104	44 - 227	4	3	13	6	0.1 - 22	13
Glyphosate	25	50	150	100	37 - 149	4	0	12	5	0.3 - 17	156
Hexazinone	20	41	183	138	117 - 156	0	0	10	4	0.2 - 15	105
Hexythiazox	26	40	130	106	82 - 137	0	2	13	3	0.1 - 7	
Imazapic	26	45	141	125	92 - 178	0	7	13	4	0.0003-11	7
Imazapyr	26	40	109	124	85 - 174	0	16	13	4	0.8 - 7	151
Imidacloprid	26	58	135	209	89 - 317	0	20	13	3	0.006 - 11	104
Imidan	20	32	203	155	104 - 202	0	0	10	4	0.8 - 9	8
Indaziflam	26	40	130	108	100 - 123	0	0	13	3	0.2 - 9	43
Isoxaben	26	59	138	106	92-118	0	0	13	3	0.07 - 6	12
Kelthane	20	10	265	21	11 - 38	0	0	10	6	0.6 - 15	1
Linuron	26	35	144	101	82 - 128	0	0	13	5	2 - 9	

Analyte	MS/MSD recoveries (n)	Lower control limit (%)		Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
Malaoxon	26	10	145	103	87 - 119	0	0	13	2	0.6 - 6	24
Malathion	20	50	147	139	126 - 151	0	2	10	4	2 - 13	53
MCPA	16	14	148	71	63 - 80	0	0	8	6	0.4 - 15	21
MCPP	16	23	162	76	68 - 85	0	0	8	7	2 - 16	13
Metalaxyl	20	56	149	113	88 - 129	0	0	10	5	0.7 - 13	31
Methamidophos	26	40	130	81	64 - 98	0	0	13	3	0.2 - 7	135
Methidathion	26	40	130	104	79 - 128	0	0	13	4	0.001 - 17	
Methiocarb	26	10	154	105	87 - 124	0	0	13	2	0.3 - 7	
Methomyl	26	65	119	99	88 - 112	0	0	13	3	0.7 - 7	15
Methomyl oxime	26	13	164	83	75 - 96	0	0	13	4	0.02 - 12	2
Methoxyfenozide	26	62	134	112	86 - 140	0	3	13	5	0.04 - 14	5
Methyl chlorpyrifos	20	50	144	111	88 - 128	0	0	10	7	0.5 - 26	1
Metolachlor	20	55	180	118	107 - 139	0	0	10	5	2 - 17	122
Metribuzin	20	30	130	84	54 - 106	0	0	10	7	0.3 - 18	34
Metsulfuron-methyl	26	10	119	117	65 - 172	0	10	13	7	0.4 - 18	10
MGK264	20	49	193	114	96 - 129	0	0	10	4	1 - 8	
Myclobutanil	26	59	123	95	81 - 110	0	0	13	5	0.4 - 14	12
N,N-Diethyl-m-toluamide	20	50	150	121	100 - 138	0	0	10	4	0.08 - 12	30
Naled	20	10	220	158	120 - 219	0	0	10	4	0.4 - 11	
Napropamide	20	70	180	134	115 - 150	0	0	10	4	0.8 - 13	41
Norflurazon	20	70	168	144	122 - 160	0	0	10	4	0.08 - 14	115
Oryzalin	20	10	230	136	99 - 171	0	0	10	9	3 - 17	17
Oxadiazon	20	50	150	100	83 - 109	0	0	10	2	0.3 - 6	29
Oxamyl	26	10	173	100	86 - 114	0	0	13	3	0.8 - 7	39
Oxamyl oxime	26	37	189	113	68 - 162	0	0	13	3	0.4 - 12	53
Oxyfluorfen	20	51	153	162	140 - 186	0	16	10	6	2 - 19	2
Paclobutrazol	26	40	130	98	79 - 111	0	0	13	3	0.03 - 7	29
Pendimethalin	20	39	163	117	95 - 135	0	0	10	7	2 - 24	116
Pentachloronitrobenzene	e 20	50	150	95	86 - 107	0	0	10	4	0.2 - 8	1
Pentachlorophenol	16	32	136	75	60 - 84	0	0	8	7	0.5 - 16	5

Analyte	MS/MSD recoveries (n)	Lower control limit (%)		Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
Phenothrin	20	22	130	78	54 - 123	0	0	10	9	0.05 - 23	
Phorate	20	12	130	136	105 - 157	0	13	10	5	0.1 - 16	
Picloram	16	10	110	40	23 - 57	0	0	8	21	3 - 63	13
Piperonyl butoxide	20	30	130	388	283 - 458	0	20	10	3	0.2 - 8	50
Prallethrin	20	30	130	155	125 - 178	0	18	10	6	0.2 - 20	
Prodiamine	20	30	130	133	117 - 153	0	11	10	6	2 - 18	14
Prometon	20	55	164	122	106 - 135	0	0	10	3	0.6 - 10	60
Prometryn	20	62	165	128	110 - 143	0	0	10	4	1 - 14	1
Pronamide (Kerb)	20	63	169	121	104 -134	0	0	10	3	0.1 - 11	1
Propargite	20	30	130	292	257 - 327	0	20	10	3	0.9 - 8	3
Propiconazole	26	47	146	92	74 - 112	0	0	13	4	0.2 - 12	37
Pyraclostrobin	26	64	142	102	85 - 120	0	0	13	2	0.04 - 4	5
Pyraflufen-ethyl	20	50	150	165	146 - 187	0	18	10	4	0.6 - 9	
Pyridaben	20	50	150	145	123 - 170	0	7	10	4	0.3 - 16	10
Pyrimethanil	26	78	122	98	87 - 107	0	0	13	3	0.04 - 8	47
Pyriproxyfen	20	30	130	118	110 - 135	0	2	10	4	0.3 - 12	15
Simazine	20	72	192	99	89 - 109	0	0	10	3	0.4 - 10	127
Simetryn	20	61	171	111	95 - 124	0	0	10	3	0.6 - 10	2
Spirotetramat	26	17	133	94	68 - 132	0	0	13	8	0.1 - 17	2
Sulfentrazone	20	50	150	117	31 - 160	2	4	10	17	0.7 - 55	152
Sulfometuron-methyl	26	41	122	104	83 - 128	0	7	13	4	0.1 - 8	35
Tau-fluvalinate	20	50	150	271	120 - 575	0	14	10	12	2 - 37	15
Tebuthiuron	20	10	235	144	122 - 164	0	0	10	4	0.3 - 13	83
Tefluthrin	20	30	130	91	71 - 109	0	0	10	4	0.3 - 9	6
Terbacil	20	27	237	155	133 - 176	0	0	10	4	0.2 - 13	150
Tetrachlorvinphos	20	70	196	189	166 - 213	0	6	10	5	1 - 14	
Tetrahydrophthalimide	20	50	150	110	66 - 146	0	0	10	6	0.1 - 25	43
Tetramethrin	20	30	130	140	82 - 190	0	12	10	6	0.7 - 15	4
Thiacloprid	26	64	121	112	85 - 136	0	8	13	4	0.5 - 8	
Thiamethoxam	26	58	131	160	87 - 231	0	18	13	5	0.3 - 31	170

Analyte	MS/MSD recoveries (n)	Lower control limit (%)		Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
Tralomethrin	20	30	130	195	130 - 303	0	19	10	5	0.5 - 14	0
trans-Permethrin	20	30	130	134	102 - 178	0	11	10	5	0.7 - 15	2
Treflan (Trifluralin)	20	58	174	124	107 - 144	0	0	10	5	0.1 - 13	23
Triadimefon	20	61	178	132	113 - 148	0	0	10	5	0.09 - 13	10
Triallate	20	52	128	104	80 - 122	0	0	10	4	0.2 - 10	1
Triclopyr	16	10	190	80	66 - 89	0	0	8	6	0.3 - 14	51
Triclopyr-butoxyl	20	50	150	119	103 - 126	0	0	10	4	0.8 - 9	1
Triclosan	20	30	130	153	136 - 181	0	20	10	6	3 - 16	27
Trifloxystrobin	26	41	142	105	83 - 135	0	0	13	3	0.6 - 13	5
Zoxamide	26	56	111	122	91 - 206	0	11	13	2	0.005 - 8	

\* RPD control limit for every analyte in this table was 40%.

There were a total of 3,433 spiked results (1,715 MS/MSD pairs) from MS and MSD recoveries that were unqualified or J qualified. Overall, the mean recovery was 121% with a standard deviation of 50 ng/L. The percentage of analyte recoveries from MS/MSD samples that were above, below, or fell within the laboratory control limits are as follows:

- 1) 1% of analyte recoveries (19 recoveries) fell below the control limits for MS/MSD samples,
- 2) 82% of analyte recoveries (2,825 recoveries) were within the control limits for MS/MSD samples,
- 3) 17% of analyte recoveries (589 recoveries) were above the control limits for MS/MSD samples.

RPDs calculated for 1,715 MS/MSD pairs were below the 40% RPD control limit 99% of the time; only five pairs had RPDs above the control limit. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 5% with a standard deviation of 5 ng/L. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 55% with a standard deviation of 8 ng/L.

If an MS/MSD sample exceeded MEL QC criteria, sample results were not qualified unless other QC criteria for that analyte was exceeded in the laboratory batch.

# Laboratory Blanks

MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. Lab blanks also provide a method to measure the response of an analytical process to the analyte at a theoretical concentration of zero, helping to determine at what concentration samples can be distinguished from background noise. If lab blank detections occur, the sample LLOQ may be increased, and detections may be qualified as estimates. Table *37*b lists the analyte detections that occurred in the laboratory blanks (254 detections). Regular field sample detections corresponding to the lab blank samples in the same batch were qualified if the regular sample result was less than 5 times the lab blank result.

Analyte	Analytical method	# of detections	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
2,6-Dichlorobenzamide	GCMS-Pesticide	2	2.5	2.08	2.86	<u>    (</u> <b>3</b> , 5	1.28
2-Hydroxyatrazine	LCMS-Pesticide	19	0.7	0.486	1.19	10	1.55
4,4'-DDD	GCMS-Pesticide	1	3.4	3.36	3.36	5	0.657
4,4'-DDE	GCMS-Pesticide	2	2.0	1.96	2.01	5	1.37
Acetamiprid	LCMS-Pesticide	4	1.0	0.351	1.52	20	1.25
Afidopyropen	LCMS-Pesticide	3	24.4	21.5	27.3	70	20.3
Azoxystrobin	LCMS-Pesticide	14	0.3	0.236	0.501	20	1.12
Baygon	LCMS-Pesticide	1	2.2	2.15	2.15	10	1.21
Bensulide	LCMS-Pesticide	1	12.1	12.1	12.1	20	4.21
Boscalid	GCMS-Pesticide	7	6.0	1.7	12.8	5	0.547
Carbaryl	LCMS-Pesticide	2	0.6	0.426	0.807	20	2.39
Carbendazim	LCMS-Pesticide	25	0.5	0.254	0.714	10	1.17
Chlorsulfuron	LCMS-Pesticide	1	1.2	1.2	1.2	50	9.54
Clothianidin	LCMS-Pesticide	3	1.9	1.86	2	100	2.21
Cyprodinil	LCMS-Pesticide	2	1.8	1.28	2.24	10	1.52
Desethylatrazine	LCMS-Pesticide	2	0.3	0.301	0.355	10	1.28
Dichlobenil	GCMS-Pesticide	5	1.5	0.49	2.67	5	1.4
Difenoconazole	LCMS-Pesticide	8	1.2	0.804	1.63	10	3.9

Table 37b – Analyte detections in laboratory blanks

Analyte	Analytical method	# of detections	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
Dinotefuran	LCMS-Pesticide	3	1.8	1.57	2.35	20	1.85
Dithiopyr	GCMS-Pesticide	1	3.3	3.27	3.27	5	1.66
Diuron	LCMS-Pesticide	6	0.7	0.466	0.883	10	2.15
Fenarimol	GCMS-Pesticide	5	2.8	1	4.08	5	1.07
Fenbutatin oxide	LCMS-Pesticide	18	4.9	2.29	12	20	4.12
Fenvalerate	GCMS-Pesticide	2	5.3	4.46	6.13	5	0.86
Fipronil sulfide	GCMS-Pesticide	1	4.3	4.29	4.29	5	0.863
Glufosinate-ammonium	LCMS-Glyphos	10	16.8	0.933	59.7	10.142	3.626
Hexazinone	GCMS-Pesticide	6	3.5	2.13	4.91	5	1.04
Hexythiazox	LCMS-Pesticide	10	1.7	0.397	11	10	1.97
Imazapic	LCMS-Pesticide	4	1.6	0.834	2.53	100	2.94
Imazapyr	LCMS-Pesticide	1	0.7	0.706	0.706	100	2.03
Imidacloprid	LCMS-Pesticide	3	1.7	1.03	2.34	20	2.29
Indaziflam	LCMS-Pesticide	8	0.5	0.318	0.74	10	1.58
Isoxaben	LCMS-Pesticide	2	0.4	0.325	0.378	10	1.53
Kelthane	GCMS-Pesticide	1	4.5	4.54	4.54	25	16
Malaoxon	LCMS-Pesticide	3	0.4	0.256	0.633	10	0.37
Methamidophos	LCMS-Pesticide	1	0.3	0.335	0.335	30	1.15
Metsulfuron-methyl	LCMS-Pesticide	3	2.0	1.36	2.55	50	2.99
Myclobutanil	LCMS-Pesticide	3	1.9	1	2.4	10	3.7
N,N-Diethyl-m-toluamide	GCMS-Pesticide	21	2.9	1.72	4.21	5	1.33
Oxamyl	LCMS-Pesticide	4	0.4	0.204	0.459	10	0.82
Paclobutrazol	LCMS-Pesticide	3	0.8	0.649	1.03	10	2.18
Propiconazole	LCMS-Pesticide	3	2.2	1.88	2.57	50	10.7
Pyraclostrobin	LCMS-Pesticide	3	2.8	1.06	6.19	50	11.7
Pyrimethanil	LCMS-Pesticide	2	1.4	0.992	1.77	10	2.99
Pyriproxyfen	GCMS-Pesticide	2	8.5	6.51	10.5	10	1.4
Spirotetramat	LCMS-Pesticide	2	2.3	1.69	2.84	20	6.06

Analyte	Analytical method	# of detections	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
Sulfentrazone	GCMS-Pesticide	1	5.2	5.15	5.15	5	2.4
Sulfometuron-methyl	LCMS-Pesticide	2	1.3	1.2	1.36	20	1.82
Thiacloprid	LCMS-Pesticide	3	1.2	0.983	1.39	10	1.69
Thiamethoxam	LCMS-Pesticide	3	1.8	1.33	2.19	20	1.53
Triallate	GCMS-Pesticide	1	2.6	2.58	2.58	5	1.26
Triclosan	GCMS-Pesticide	9	6.9	1.22	14.3	10	1.73
Trifloxystrobin	LCMS-Pesticide	1	4.9	4.89	4.89	20	4.67
Zoxamide	LCMS-Pesticide	1	1.6	1.61	1.61	10	1.52

# Surrogates

Surrogates are analytes used to assess recovery for a group of structurally related chemicals. Surrogates specific to the list of analytes were spiked into all field samples and QC samples such as blanks and LCS/LCSD samples. For instance, triphenyl phosphate is a surrogate for organophosphate insecticides. Table 38b presents summary statistics for surrogate recoveries.

Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
	-	-	-		
LCMS-Pesticides	407	101	99.5	67	132
GCMS-Herbicides	376	69	99.7	41	116
GCMS-Herbicides	376	73	100.0	31	149
GCMS-Pesticides	434	91	99.5	41	135
	LCMS-Pesticides GCMS-Herbicides GCMS-Herbicides	Analytical method(n)LCMS-Pesticides407GCMS-Herbicides376GCMS-Herbicides376	Analytical methodResults (n)recovery (%)LCMS-Pesticides407101GCMS-Herbicides37669GCMS-Herbicides37673	Analytical methodResults (n)recovery (%)control limits (%)LCMS-Pesticides40710199.5GCMS-Herbicides3766999.7GCMS-Herbicides37673100.0	Analytical methodResults (n)Mean recovery (%)Results within control limits (%)Control Limit (%)LCMS-Pesticides40710199.567GCMS-Herbicides3766999.741GCMS-Herbicides37673100.031

*Table 38b – Pesticide surrogates* 

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
Chlorinated pesticides:						
4,4'-DDE-13C12	GCMS-Pesticides	434	84	99.5	20	117
Decachlorobiphenyl (DCB)	GCMS-Pesticides	434	82	85.5	13	98
Glyphosate related pesticides:						
AMPA-C13N15	LCMS-Glyphos	287	69	97.9	20	200
Glyphosate-C13N15	LCMS-Glyphos	287	69	100.0	20	200
Organophosphate pesticides:						
Chlorpyrifos-D10	GCMS-Pesticides	434	111	99.3	30	178
Triphenyl phosphate	GCMS-Pesticides	434	121	85.7	45	137
Chlorine and nitrogen containing pesticides:						
Trifluralin-D14	GCMS-Pesticides	434	102	100.0	26	180
Atrazine-D5	GCMS-Pesticides	434	109	98.6	45	167

In 2019, the overall mean recovery for surrogates was 92% and 97% of surrogate recoveries were within control limits.

### Laboratory Control Samples

Table 39b shows the summary LCS/LCSD results for each analyte with control limits, percent recoveries, and RPDs. The table describes the number of LCS/LCSD recoveries that were above or below the laboratory control limits set for each analyte and the number of detections from all grab samples throughout the season for each analyte. Only the LCS/LCSD recoveries that were unqualified, *E*, or *J* qualified are included in the table. Some RPDs were unable to be calculated because of a *U*, *NAF*, or *NC* qualified LCS/LCSD recovery result. The summary table excludes the uncalculated RPDs.

· · · · ·						LCS/LCSD	LCS/LCSD			
Analyte	LCS/LCSD recoveries (n)	control	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	recoveries below control limits	recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
1-(3,4-Dichlorophenyl)-3- methylurea	56	40	130	109	91 - 156	0	7	28	4	0.6 - 30
2,4-D	62	10	147	74	51 - 95	0	0	31	8	0.7 - 29
2,6-Dichlorobenzamide	62	30	140	101	22 - 134	2	0	31	4	0.03 - 11
2-Hydroxyatrazine	56	40	130	111	86 - 142	0	6	28	4	0.3 - 33
3,5-Dichlorobenzoic acid	62	14	135	70	52 - 95	0	0	31	7	0.008 - 2
4,4'-DDD	62	64	138	109	91 - 142	0	1	31	3	0.06 - 7
4,4'-DDE	62	43	140	89	74 - 101	0	0	31	3	0.03 - 7
4,4'-DDT	62	49	148	99	58 - 116	0	0	31	2	0.004 - 7
4-Nitrophenol	62	11	187	69	5 - 111	2	0	31	12	0.3 - 40
Acephate	56	40	130	100	83 - 132	0	1	28	4	0.02 - 34
Acetamiprid	56	79	129	99	71 - 124	5	0	28	4	0.09 - 28
Acetochlor	62	30	130	103	86 - 116	0	0	31	3	0.7 - 9
Acetochlor ESA	56	40	130	104	66 - 148	0	3	28	8	0.09 - 40
Afidopyropen	56	40	130	95	70 - 120	0	0	28	9	0.2 - 20
Alachlor	62	13	184	107	89 - 125	0	0	31	3	0.1 - 8
Aldicarb sulfoxide	56	55	145	103	80 - 153	0	1	28	3	0.2 - 26
AMPA	34	50	150	75	13 - 138	9	0	17	14	0.4 - 65
Atrazine	62	14	178	96	74 - 109	0	0	31	3	0.2 - 8
Azoxystrobin	56	73	130	102	82 - 128	0	0	28	5	0.4 - 32
Baygon	56	72	127	105	90 - 168	0	2	28	3	0.2 - 20
Benefin	62	44	143	98	80 - 119	0	0	31	5	1 - 31
Bensulide	56	40	130	100	68 - 157	0	4	28	8	0.2 - 47
Bentazon	62	35	152	87	72 - 116	0	0	31	5	0.1 - 24
Bifenazate	60	50	150	169	0 - 586	2	28	29	7	0.004 - 4
Bifenthrin	62	30	130	109	85 - 128	0	0	31	4	0.2 - 13
Boscalid	62	50	150	129	102 - 207	0	9	31	5	0.2 - 36
Bromacil	62	58	170	130	102 - 152	0	0	31	3	0.2 - 9
Bromoxynil	62	32	128	76	59 - 106	0	0	31	6	0.04 - 22

Table 39b – Summary statistics for LCS/LCSD recoveries and RPD

Analyte	LCS/LCSD recoveries (n)			Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Captan	62	36	168	36	4 - 96	36	0	31	14	0.3 - 30
Carbaryl	56	67	127	108	92 - 143	0	2	28	5	0.1 - 16
Carbendazim	56	40	130	107	85 - 159	0	1	28	4	0.1 - 33
Chlorantraniliprole	56	56	146	99	77 - 131	0	0	28	6	0.06 - 33
Chlorethoxyfos	62	30	130	95	76 - 111	0	0	31	5	0.4 - 23
Chlorothalonil	62	86	221	92	70 - 105	12	0	31	5	0.1 - 14
Chlorpropham	62	58	150	107	86 - 128	0	0	31	4	0.7 - 12
Chlorpyrifos	62	64	146	111	78 - 131	0	0	31	3	0.03 - 9
Chlorsulfuron	56	10	142	87	49 - 136	0	0	28	9	0.2 - 34
cis-Permethrin	62	48	178	134	106 - 166	0	0	31	4	0.4 - 16
Clopyralid	62	10	119	37	18 - 56	0	0	31	17	0.2 - 59
Clothianidin	56	52	146	98	75 - 126	0	0	28	5	0.2 - 33
Coumaphos	62	65	207	165	106 - 333	0	8	31	3	0.1 - 18
Cycloate	62	50	141	113	82 - 151	0	1	31	6	0.3 - 29
Cyfluthrin	62	30	130	130	97 - 310	0	24	31	8	0.04 - 73
Cypermethrin	62	30	130	123	88 - 234	0	22	31	8	0.5 - 55
Cyprodinil	56	66	133	101	72 - 141	0	1	28	6	0.2 - 41
Dacthal	62	40	154	84	67 - 115	0	0	31	6	0.6 - 25
Deisopropyl atrazine	56	31	144	106	81 - 133	0	0	28	5	0.05 - 30
Deltamethrin	62	30	130	131	94 - 249	0	26	31	5	0.3 - 26
Desethylatrazine	56	31	151	114	92 - 136	0	0	28	5	0.2 - 30
Diazinon	62	70	142	118	75 - 141	0	0	31	3	0.04 - 9
Dicamba	62	12	138	73	54 - 103	0	0	31	6	0.1 - 23
Dichlobenil	62	44	139	92	70 - 108	0	0	31	5	0.5 - 18
Dichlorprop	62	16	153	74	58 - 102	0	0	31	7	0.08 - 24
Dichlorvos (DDVP)	62	39	145	107	69 - 162	0	2	31	6	0.08 - 18
Difenoconazole	56	10	190	98	77 - 120	Ō	0	28	5	0.06 - 33
Diflubenzuron	56	42	139	125	75 - 263	Ō	10	28	9	0.4 - 48
Dimethoate	62	48	206	113	77 - 136	Ō	0	31	3	0.05 - 10
Dinotefuran	56	66	138	94	75 - 123	Ō	0	28	5	0.2 - 32

Analyte	LCS/LCSD recoveries (n)	control	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Dithiopyr	62	30	130	105	80 - 130	0	0	31	3	0.09 - 18
Diuron	56	76	124	105	91 - 141	0	2	28	3	0.03 - 9
Eptam	62	48	142	99	67 - 128	0	0	31	5	0.06 - 18
Ethalfluralin (Sonalan)	62	31	167	98	81 - 121	0	0	31	5	0.3 - 29
Ethoprop	62	55	163	119	86 - 153	0	0	31	4	0.04 - 11
Etoxazole	62	50	150	117	95 - 136	0	0	31	3	0.02 - 9
Etridiazole	62	30	130	94	70 - 110	0	0	31	5	0.2 - 17
Fenarimol	62	30	130	122	99 - 152	0	14	31	3	0.5 - 9
Fenbuconazole	56	33	163	98	75 - 124	0	0	28	5	0.2 - 31
Fenbutatin oxide	56	40	130	57	25 - 110	15	0	28	10	0.02 - 24
Fenvalerate	62	30	130	127	86 - 227	0	19	31	4	0.04 - 20
Fipronil	62	30	130	122	95 - 150	0	16	31	5	0.2 - 21
Fipronil desulfinyl	62	30	130	120	83 - 154	0	23	31	5	0.03 - 17
Fipronil sulfide	62	30	130	110	81 - 129	0	0	31	3	0.01 - 11
Fipronil sulfone	62	30	130	126	91 - 161	0	27	31	3	0.09 - 14
Fludioxonil	62	30	130	110	90 - 128	0	0	31	3	0.02 - 13
Flumioxazin	62	30	130	69	12 - 129	5	0	31	11	0.5 - 48
Fluroxypyr-meptyl	62	30	130	112	90 - 134	0	4	31	3	0.2 - 10
Glufosinate-ammonium	34	50	150	131	36 - 220	2	9	17	11	1 - 30
Glyphosate	34	50	150	89	31 - 137	8	0	17	8	0.03 - 25
Hexazinone	62	69	150	125	97 - 139	0	0	31	3	0.1 - 11
Hexythiazox	56	40	130	102	72 - 131	0	1	28	6	0.1 - 38
Imazapic	56	57	133	104	77 - 159	0	2	28	5	0.03 - 18
Imazapyr	56	35	153	104	86 - 126	0	0	28	6	0.3 - 21
Imidacloprid	56	66	134	100	69 - 133	0	0	28	5	0.05 - 24
Imidan	62	44	190	99	35 - 154	4	0	31	5	0.6 - 18
Indaziflam	56	40	130	111	97 - 140	0	1	28	3	0.1 - 26
Isoxaben	56	67	137	105	83 - 126	0	0	28	5	0.6 - 31

Analyte	LCS/LCSD recoveries (n)	control	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Kelthane	60	31	179	68	11 - 410	35	7	30	8	0.3 - 29
Linuron	56	35	154	105	82 - 132	0	0	28	8	0.05 - 40
Malaoxon	56	67	124	103	81 - 131	0	1	28	4	0.1 - 32
Malathion	62	61	138	117	93 - 140	0	1	31	3	0.1 - 8
MCPA	62	13	139	70	55 - 85	0	0	31	7	0.5 - 21
MCPP	62	23	148	79	63 - 107	0	0	31	6	0.3 - 24
Metalaxyl	62	59	153	104	83 - 120	0	0	31	4	0.02 - 21
Methamidophos	56	40	130	98	66 - 139	0	1	28	4	0.006 - 33
Methidathion	56	40	130	106	82 - 140	0	5	28	6	0.09 - 33
Methiocarb	56	58	131	109	88 - 144	0	5	28	6	0.5 - 32
Methomyl	56	71	128	103	83 - 140	0	1	28	3	0.2 - 25
Methomyl oxime	56	14	160	105	82 - 199	0	1	28	5	0.1 - 32
Methoxyfenozide	56	69	140	106	76 - 159	0	3	28	6	0.1 - 29
Methyl chlorpyrifos	62	58	135	101	86 - 120	0	0	31	4	0.4 - 9
Metolachlor	62	68	158	106	89 - 122	0	0	31	3	0.4 - 9
Metribuzin	62	30	130	79	50 - 107	0	0	31	7	0.4 - 35
Metsulfuron-methyl	56	10	141	90	51 - 144	0	1	28	8	0.1 - 30
MGK264	62	71	169	100	84 - 118	0	0	31	4	0.4 - 11
Myclobutanil	56	50	143	100	77 - 130	0	0	28	5	0.8 - 31
N,N-Diethyl-m-toluamide		30	130	109	82 - 129	0	0	31	3	0.006 - 12
Naled	62	22	159	112	53 - 274	0	3	31	7	0.5 - 49
Napropamide	62	82	176	117	101 - 141	0	0	31	3	0.06 - 9
Norflurazon	62	85	143	120	99 - 148	0	1	31	4	0.2 - 20
Oryzalin	62	10	277	92	10 - 197	0	0	31	14	0.2 - 107
Oxadiazon	62	30	130	100	84 - 109	0	0	31	3	0.1 - 19
Oxamyl	56	64	135	103	81 - 141	Ō	1	28	3	0.2 - 28
Oxamyl oxime	56	61	149	92	67 - 152	Ō	1	28	7	0.2 - 25
Oxyfluorfen	62	42	154	129	102 - 161	Ō	2	31	5	0.2 - 20
Paclobutrazol	56	40	130	101	81 - 139	Ō	1	28	4	0.5 - 30
Pendimethalin	62	49	159	105	82 - 117	Ō	0 0	31	4	0.4 - 22

Analyte	LCS/LCSD recoveries (n)		Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Pentachloronitrobenzene	-	30	130	89	75 - 100	0	0	31	3	0.06 - 12
Pentachlorophenol	62	32	125	75	52 - 109	0	0	31	6	0.1 - 23
Phenothrin	62	20	95	66	22 - 101	0	1	31	8	0.006 - 29
Phorate	62	13	114	111	65 - 163	0	28	31	7	0.08 - 40
Picloram	62	10	110	20	2 - 69	9	0	31	26	3 - 88
Piperonyl butoxide	62	30	130	263	106 - 432	0	39	31	2	0.5 - 9
Prallethrin	62	30	130	122	88 - 292	0	13	31	6	0.07 - 71
Prodiamine	62	30	130	109	94 - 134	0	1	31	5	0.6 - 24
Prometon	62	59	161	108	83 - 129	0	0	31	3	0.1 - 8
Prometryn	62	60	160	111	86 - 129	0	0	31	2	0.03 - 6
Pronamide (Kerb)	62	74	150	109	86 - 127	0	0	31	3	0.007 - 7
Propargite	62	30	130	215	95 - 313	0	40	31	2	0.04 - 7
Propiconazole	56	29	175	96	77 - 129	0	0	28	5	0.1 - 34
Pyraclostrobin	56	55	156	102	74 - 122	0	0	28	5	0.6 - 33
Pyraflufen-ethyl	62	30	130	126	82 - 162	0	26	31	3	0.09 - 19
Pyrethrins	42	30	130	54	0 - 113	20	0	12	11	2 - 52
Pyridaben	62	30	130	129	103 - 158	0	25	31	3	0.02 - 19
Pyrimethanil	56	68	138	107	89 - 156	0	1	28	5	0.1 - 31
Pyriproxyfen	62	30	130	112	97 - 142	0	2	31	3	0.1 - 10
Simazine	62	80	184	94	78 - 109	1	0	31	3	0.2 - 7
Simetryn	62	44	168	100	77 - 114	0	0	31	3	0.2 - 7
Specific conductivity	6	95	105	100	97 - 101	0	0			
Spirotetramat	56	39	152	89	65 - 117	0	0	28	8	0.9 - 23
Sulfentrazone	62	30	130	61	0 - 125	16	0	30	28	0.5 - 200
Sulfometuron-methyl	56	42	134	92	73 - 125	0	0	28	6	0.03 - 30
Tau-fluvalinate	62	30	130	148	85 - 453	0 0	27	31	10	0.5 - 35
Tebuthiuron	62	10	94	115	73 - 151	0 0	54	31	5	0.08 - 15
Tefluthrin	62	30	130	88	71 - 101	0 0	0	31	4	0.07 - 11
Terbacil	62	57	183	123	89 - 153	Ō	0	31	5	0.4 - 13
Tetrachlorvinphos	62	84	176	137	80 - 181	2	1	31	4	0.4 - 17

Analyte	LCS/LCSD recoveries (n)	control	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	recoveries	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Tetrahydrophthalimide	62	50	150	76	12 - 105	2	0	31	6	0.2 - 18
Tetramethrin	62	30	130	89	50 - 134	0	1	31	10	0.2 - 44
Thiacloprid	56	71	131	101	77 - 138	0	1	28	5	0.1 - 30
Thiamethoxam	56	61	144	98	72 - 128	0	0	28	5	0.1 - 27
Total suspended solids	54	80	120	97	85 - 105	0	0			
Tralomethrin	62	30	130	131	94 - 249	0	26	31	5	0.3 - 26
trans-Permethrin	62	30	130	129	96 - 159	0	34	31	4	0.6 - 15
Treflan (Trifluralin)	62	41	173	101	81 - 129	0	0	31	5	0.2 - 31
Triadimefon	62	74	166	112	90 - 128	0	0	31	3	0.4 - 10
Triallate	62	58	126	97	67 - 120	0	0	31	4	0.04 - 10
Triclopyr	62	10	183	79	57 - 102	0	0	31	7	0.5 - 26
Triclopyr-butoxyl	62	30	130	111	86 - 135	0	2	31	3	0.005 - 12
Triclosan	62	30	130	108	66 - 138	0	7	31	5	0.2 - 19
Trifloxystrobin	56	46	165	106	71 - 136	0	0	28	5	0.008 - 34
Zoxamide	56	49	136	116	88 - 195	0	6	28	5	0.1 - 29

\*RPD control limit for all pesticide analytes was 40% and RPD control limits for TSS and conductivity was 20%.

There were a total of 9,498 spiked results from LCS and LCSD recoveries that were unqualified or J qualified. Overall, the mean recovery was 104% with a standard deviation of 35 ng/L. The percentage of analyte recoveries from LCS/LCSD samples that were above, below, or fell within the laboratory control limits are as follows:

- 1) 2% of analyte recoveries (187 recoveries) fell below the control limits for LCS/LCSD samples,
- 2) 91% of analyte recoveries (8,664 recoveries) were within the control limits for LCS/LCSD samples,
- 3) 7% of analyte recoveries (647 recoveries) were above the control limits for LCS/LCSD samples.

RPDs calculated for 4,708 LCS/LCSD pairs were below the 40% RPD control limit 99% of the time; only 34 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 5% with a standard deviation of 6 ng/L. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 63% with a standard deviation of 33 ng/L.

Whenever the RPD or analyte recoveries fell outside of the control limits for a given analyte, all detections of that analyte in field samples that were associated with that analytical batch were qualified as estimates.

# **Field Data Quality Control Measures**

A YSI ProDSS field meter was used at every Eastern and Western Washington sampling event. The field meters were calibrated the evening before, or the morning of the first field day of the week according to manufacturer's specifications described in the YSI ProDSS User Manual (YSI, 2018). Both field meters were post-checked, using known standards, at the end of the sampling week.

To check conductivity meter results, surface water grab samples were obtained and sent to MEL for conductivity analysis. Approximately 5% of the conductivity meter readings were checked with MEL conductivity results.

A new calibration method for dissolved oxygen was initiated this year as described in the NRAS *SOP: Water Quality and Pesticides Monitoring Program* (Bischof, 2019). The air-saturated (100%) water bath calibration method was implemented to discontinue the Winkler method.

Streamflow measurements were taken with OTT MF pro flow meters and top-setting wading rods for both Eastern and Western Washington monitoring sites. Each flow meter was calibrated the morning of the first day of the week as described in the OTT MF pro Basic User Manual (OTT, 2018). A replicate streamflow measurement was taken once a week at a randomly selected site for each flow meter.

Measurement quality objectives (MQOs) for meter post-checks and replicate comparisons are described in the *NRAS Quality Assurance Project Plan (QAPP), Revision 2.0* (Bahr, 2019). Data that did not meet MQOs were qualified.

## **Field Data Collection Performance**

Quality control results for two different conventional water quality parameter replicates are shown below in Table 40b. Precision of the conductivity and streamflow replicates was gauged by the relative standard deviation (RSD).

Replicate meter parameter	MQO	Western \	<b>Washington</b>	Eastern Washington		
Replicate meter parameter	NIQU	Mean	Maximum	Mean	Maximum	
Conductivity (field meter vs. laboratory)	10% RSD	1% RSD	2% RSD	1% RSD	2% RSD	
Streamflow	10% RSD	2% RSD	6% RSD	4% RSD	10% RSD	

Table 40b – Quality control results for conventional water qualiter parameter replicates

The field meters for laboratory conductivity comparisons and the streamflow replicates met MQOs for all Eastern and Western Washington monitoring locations.

Table 41b describes data quality objectives for field meter post-checks as described in the *WSDA QAPP* (Bahr, 2019).

Parameter	Units	Accept	Qualify	Reject
рН	standard units	≤ ± 0.25	> ± 0.25 and ≤ ± 0.5	> ± 0.5
Conductivity <sup>1</sup>	μS/cm	≤ ± 5%	> ± 5% and ≤ ± 15%	> ± 15%
Dissolved Oxygen	% saturation	≤±5%	> ± 5% and ≤ ± 10%	> ± 10%

Table 41b – Data quality objectives for YSI ProDSS or other field meter post-checks

<sup>1</sup>Criteria expressed as a percentage of readings; for example, buffer or post-calibration value = 1,000  $\mu$ S/cm and post-check YSI = 987.2  $\mu$ S/cm; [(1,000-987.2)/1,000]\*100 = 1.28% variation, which would fall into the acceptable data criteria of equal to or less than 5%.

Post-checks of the Westside and Eastside YSI meters met data quality objectives for all parameters except the following:

 Eastside YSI meter conductivity 100 μS/cm check, May 6 (pre-check YSI = 99.2 μS/cm and post-check YSI = 104.6 μS/cm; 5.4% difference)

The seven field conductivity readings taken by the Eastside YSI meter between the precheck and post-check were qualified as estimates.

## **Field Audit**

The purpose of the field audit was to ensure sampling methodologies were consistent for all field teams. For field audits, both the Western and Eastern Washington field teams met at a wadeable stream. The teams measured general water quality parameters and streamflow. Results and methods were compared to ensure field teams were using consistent sampling methodologies resulting in comparable data.

On May 2, staff conducted a field audit at Raging River near North Bend in King County, Washington. Both teams performed the field audit simultaneously. Results are displayed in Table 42b.

Equipment and location	Temperature (°C)	рН	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Field meter – West 1	8.1	7.47	48.7	99.4	11.74	
Field meter – West 2	8.1	7.35	50.3	97.6	11.55	
Field meter – East	8.1	7.29	51.1	98.3	11.58	
Flow – West						59.05
Flow – East						54.39
RSD (%)	0.0	1.24	2.44	0.92	0.88	5.81

Table 42b - Conventional water quality parameter and flow data from field audit

All meter results were acceptable based on the Measurement Quality Objectives described in the QAPP (Bahr, 2019). Table 40b shows some of the MQOs for conventional field parameters.

The Westside staff calibrated their YSI ProDSS field meter #1 on April 29 in Olympia at the Natural Resources Building's Entomology Lab. Eastside staff calibrated the Eastside YSI ProDSS on April 29 and the Westside YSI ProDSS field meter #2 on May 1 at the WSDA Yakima office in the NRAS lab. All three YSI meter post-checks passed Data Quality Objectives found in Table 41b.

# **Quality Assurance Summary References**

[EPA] U.S. Environmental Protection Agency. 2017. National Functional Guidelines for Organic Superfund Methods Data Review (SOM02.4). EPA-540-R-2017-002. Washington, D.C.: U.S. Environmental Protection Agency, Office of Superfund Remediation and Technology Innovation.

[MEL] Manchester Environmental Laboratory. 2016. Manchester Environmental Laboratory Lab User's Manual. Tenth. Manchester, WA: Washington State Department of Ecology.

Bahr, Gary. 2019. Quality Assurance Project Plan: Ambient Monitoring for Pesticides in Washington State Surface Water, Revision 2.0. Olympia, WA: Washington State Department of Agriculture, Natural Resources Assessment Section.

Bischof, Matthew. 2019. Standard Operating Procedure: Water Quality and Pesticides Monitoring Programs Revision 1.1. Yakima, WA: Washington State Department of Agriculture, Natural Resources Assessment Section.

Martin, Jeffrey D. 2002. Variability of Pesticide Detections and Concentrations in Field Replicate Water Samples Collected for the National Water-Quality Assessment Program, 1992-97. Water-Resources Investigations Report 01-4178. Indianapolis, IN: United States Geological Survey, National Water-Quality Assessment Program.

Mathieu, Nuri. 2006. Replicate Precision for 12 TMDL Studies and Recommendations for Precision Measurement Quality Objectives for Water Quality Parameters. Publication No. 06-03-044. Olympia, WA: Washington State Department of Ecology, Environmental Assessment Program.

OTT. 2018. OTT MF Pro Basic User Manual, Edition 7. Document #026.53.80211.

YSI. 2018. ProDSS User Manual, Revision F. Document #626973-01RE