

# Ambient Monitoring for Pesticides in Washington State Surface Water

2018 Technical Report

August 2020

Washington State Department of Agriculture
Natural Resources Assessment Section

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Publication No. 102-629 (R/8/20)

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Washington State Department of Agriculture Natural Resources Assessment Section

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# **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
- 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.

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# **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 degree of pesticide presence in surface water across a diverse cross section of land use 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 2018, WSDA's Natural Resources Assessment Section (NRAS) collected surface water samples weekly or biweekly from March through November at 16 monitoring sites. Sites were selected where pesticide contamination and poor water quality conditions were expected based on land use with high pesticide usage or historic pesticide detections. 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. 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 contribution to the economy, cultural significance, and function in the ecosystem. All of the watersheds sampled in 2018 have either 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 qualify as either statewide or watershed Pesticides of Concern (POC) by evaluating the most recent 3 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, pyridaben, pyriproxyfen, sulfometuron methyl, tefluthrin and thiamethoxam.

This report summarizes activities and data from the 16 separate sites selected for the 2018 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 289 surface water sampling events between March 7 and November 5.
- Out of 144 pesticide active ingredients and breakdown products tested for, there were 106 unique pesticides detected.

- There were 4,860 positively identified pesticide detections.
- At 286 of the 289 sampling events, mixtures of 2 or more pesticides were detected.
- Boscalid was the most frequently detected fungicide (242 times), thiamethoxam and chlorpyrifos were the most frequently detected insecticides (104 and 103 times, respectively), and dichlobenil was the most frequently detected herbicide (164 times).
- Boscalid was the most frequently detected chemical followed by 2,6-dichlorobenzamide, a breakdown product of dichlobenil, with 238 detections. Detections of these analytes occurred in over 80% of samples.
- There were 364 unique pesticide detections with concentrations exceeding WSDA assessment criteria (7.5% of total detections), approaching levels that could adversely affect aquatic life.
  - The legacy insecticide DDT and its breakdown products accounted for 191 of the exceedances (52% of exceedances).
  - Current-use pesticides accounted for 173 of the exceedances (48% of total exceedances). The chemicals include:
    - bifenthrin (10 exceedances),
    - chlorpyrifos (28 exceedances),
    - cis-permethrin (1 exceedance),
    - clothianidin (10 exceedances),
    - diazinon (2 exceedances),
    - dichlorvos (3 exceedances),
    - etoxazole (1 exceedance),
    - fipronil (7 exceedances).

- malathion (9 exceedances),
- imidacloprid (87 exceedances),
- metolachlor (1 exceedance),
- pentachlorophenol (1 exceedance),
- pyraclostrobin (1 exceedance),
- pyridaben (9 exceedances),
- sulfometuron methyl (2 exceedances), and
- thiamethoxam (1 exceedance).
- Lower Crab Creek was the only monitoring site where no detections were above WSDA assessment criteria.

Of the 364 detections that exceeded WSDA assessment criteria, many (83% or 303 detections) also exceeded state, national, or toxicity study criteria. Current-use pesticides accounted for 38% (114 detections) of these exceedances. Chlorpyrifos (20 exceedances) and/or malathion (6 exceedances) were detected above toxicity study criteria, state standards, or national water standards at 5 monitoring sites in Eastern Washington and 1 site in Western Washington. Imidacloprid, found at 64% of the monitoring sites, exceeded the invertebrate toxicity study criterion every detection (87 detections). Other pesticides detected less often that still exceeded state, national, or toxicity study criteria included bifenthrin, cis-permethrin, dichlorvos, fipronil and pyridaben. Legacy pesticide DDT and its associated degradates accounted for the remaining 62% (189 detections) of the total detected exceedances of state or national standards.

WSDA collected samples for total suspended solids analysis and tested dissolved oxygen, pH, conductivity, and streamflow in the field at sampling events. WSDA also collected continuous temperature measurements during the entire monitoring season in situ. Dissolved oxygen, pH, and temperature measurements were compared to Water Quality Standards for Surface Waters of the State of Washington (WAC, 2019). At least 1 conventional water quality parameter exceeded state water quality standards at 15 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: 2018 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 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 US Environmental Protection Agency (EPA) 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 3 kinds of information:

- pesticide usage data: types of pesticides used on different crops, application rate, and frequency,
- agricultural land use data: crop types grown and their locations in the state, and
- 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 2018,
- 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, and
- 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 2018 from March through November throughout the state. During the first year of monitoring (2003) WSDA sampled at 9 monitoring sites in agricultural and urban areas. By 2018, the program had expanded to 16 monitoring sites, including 2 of the 9 original sites. WSDA has monitored surface water in 20 unique watersheds since the start of the program. Site changes from 2017 to 2018 include the addition of 1 new site on the Touchet River in Eastern Washington and the removal of 1 site in Eastern Washington (Lower Brender Creek).

WSDA sent water samples to the Manchester Environmental Lab (MEL) for analysis of pesticides and pesticide-related chemicals such as insecticides, herbicides, fungicides, degradates, an antimicrobial, a wood preservative, an insect repellent, and synergists. In 2018, WSDA tested for 144 chemicals, of which 106 were detected in surface water samples.

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 adequately 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 2018, identified by their WRIA codes and corresponding subbasin names.

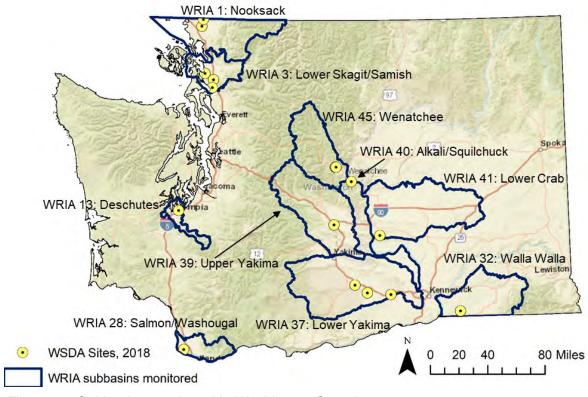


Figure 1 – Subbasins monitored in Washington State in 2018

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 endangered species including pacific salmonids. The other 8 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 MEL analyzed for 144 pesticide active ingredients and pesticide breakdown products. The sampling schedule 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 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 methods are described in the Quality Assurance Project Plan (Johnson and Cowles, 2003), and subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009; Anderson, 2011; Anderson, 2012; Sargeant, 2013).

## **Field Procedures**

Surface water samples were collected using a 1-liter glass jar by hand grab or pole grab as described in the Washington State Department of Ecology's (Ecology) *Standard Operating Procedure for Sampling of Pesticides in Surface Waters* (Anderson and Sargeant, 2012). Before delivery to MEL, staff labeled and preserved all samples according to the Quality Assurance Project Plan (Johnson and Cowles, 2003).

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, 2014). 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, 2015). Mission Creek, Lower Bertrand Creek, and Touchet River temperature data was obtained from Ecology gauging stations present at those monitoring sites. The 2018 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* (Shedd, 2014). WSDA obtained streamflow data for the remaining 5 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.

Table 1 – Summary of laboratory methods

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

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

MEL installed a new gas chromatography/triple quadrupole mass spectrometry (GC/MS/MS) instrument before the start of the 2018 sampling season, reducing detection and reporting limits for many analytes in the GCMS-Pesticides method.

## 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

GC/MS/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

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 2018, 11% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2018 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 1 of the 2 samples collected. Replicate pairs where both sample and field replicate were non-detects were not used in the WSDA analysis. As of 2018, 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. Previously, WSDA averaged consistently or inconsistently identified replicate pair concentrations for comparison to assessment criteria.

Precision between identified replicate pairs was evaluated using relative percent difference (RPD). 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. Only 13 of the 256 consistently identified replicate pairs detected for pesticide and TSS analysis exceeded an RPD criterion. The results were not qualified for the 13 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 2,4-D, 2,6-dichlorobenzamide, dichlobenil and metolachlor had low replicate variability among the 73 analytes detected in replicate pairs. There was not a high reproducibility of detections between replicate pairs for analytes detected in 2018. The analytes, in part, had high variability because of the small number of replicate pairs with at least 1 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.

#### **Blanks**

Field and laboratory blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were 13 detections in field blanks and 63 detections in laboratory blanks. Detections included dichlobenil, 2,6-dichlorobenzamide, fenarimol and TSS. No 2018 detections were qualified based on field blank detections. If lab blank detections occurred outside MEL QC criteria, MEL reviewed regular sample detections corresponding to the lab blank samples in the same batch for qualification.

## 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 (98%) of surrogate recoveries fell within the control limits established by MEL in 2018. 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 interference 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 88% 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 were 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 95% 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.

#### 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, 2019), 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 adequately 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 (ECY, 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, 2018).

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<sub>50</sub> (concentration causing death to 50% of the organisms, in the case of fish) or EC<sub>50</sub> (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 aguatic 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). This 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 repeated applications.

WSDA applies another 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 1/20th 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, 2019). 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 1-hour average concentration not to be exceeded more than once every 3 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 4-day average concentration not to be exceeded more than once every 3 years on average.

Acute and chronic numeric criteria for fish, invertebrates, and aquatic plants from the WAC, with the WSDA 0.5x safety factor, are 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 select WSDA assessment criteria. Table 2 provides a summary of how WSDA uses different sources to develop WSDA assessment criteria used in this report.

Table 2 -Safety factors applied to toxicity study data, NRWQC, and WAC criteria to generate WSDA assessment criteria

WSDA assessment 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	≥ 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	≥ 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

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

Annually, WSDA identifies Pesticides of Concern and Pesticides of Interest (POIs) using the most recent surface water data. Starting with the 2018 data, Washington and the other EPA Region 10 states (Oregon, Idaho, and Alaska) adopted the same method to identify statewide and watershed-specific POCs. For current-use pesticides detected in 2018, WSDA used the past 3 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 2 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 are current-use pesticides that were POCs in more than 30% of monitored watersheds. In 2018, 3 watershed POCs were found in 5 or more of the 16 monitored watersheds, making them statewide POCs.

For comparison, the statewide POC list went from 21 pesticides to 3 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.

Table 3 - WSDA watershed POC and POI decision matrix

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

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 monitored in 2018 was fresh water and was compared to WAC fresh water criteria.

WSDA measured and compared conventional parameters including 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.

Table 4 – Water Quality Standards for Washington State by aquatic life use

WAC aquatic life uses	7-DADMax (°C), highest allowable	DO (mg/L), lowest 1-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

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 1 WSDA monitoring site in 2018 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 1-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 2018, 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 2018 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.

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 1 WSDA assessment criteria; however, this scenario cannot be shown in the pesticide calendars. If multiple criteria exceedances of 1 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**

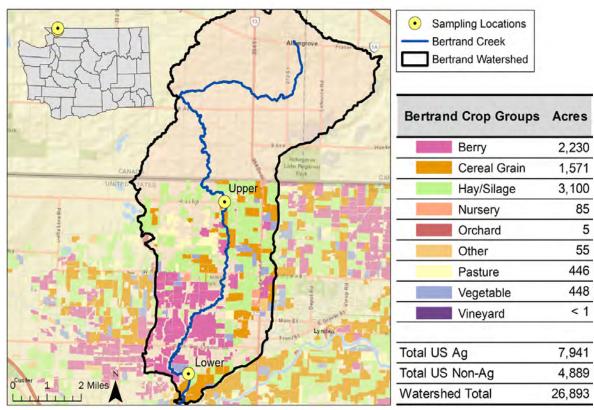


Figure 2 – Map of Bertrand Creek and its drainage area with associated sampling locations and crop groups identified

In 2013, WSDA started sampling the Bertrand watershed in Whatcom County. Monitoring takes place at 2 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 0.25 miles 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 Creek site is



Figure 3 – Upper Bertrand Creek site upstream view

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 1 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). Staff have frequently observed juvenile fish of unknown species and freshwater lamprey at the Upper Bertrand Creek monitoring site (Figure 3). Between August 7 and August 14, a beaver family created a dam several hundred yards downstream of the Upper Bertrand monitoring site. It visibly raised the water level at the upper monitoring site but did not stop downstream flow. The beaver dam remained intact the rest of the sampling season. This change in flow pattern may have resulted in unknown effects to pesticide detections or conventional water quality parameters.



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 2018.

- WSDA tested for 144 unique pesticides in Upper and Lower Bertrand Creek.
- Pesticides were detected at all 26 sampling events at each monitoring site.
- Up to 29 pesticides were detected at the same time in Upper Bertrand Creek and up to 33 in Lower Bertrand Creek.
- In both Upper and Lower Bertrand Creek, WSDA found 43 unique pesticides. At Upper Bertrand Creek, 2 unique pesticides were detected that were not found at Lower Bertrand Creek; 17 were found at Lower Bertrand Creek but not at Upper Bertrand Creek.
- There were 450 total pesticide detections in Upper Bertrand Creek from 7 different use categories: 18 types of herbicides, 9 fungicides, 8 insecticides, 7 degradates, 1 antimicrobial, 1 insect repellent, and 1 wood preservative.
- Of the total pesticide detections found at Upper Bertrand Creek, 30 were above WSDA's assessment criteria (Table 5).
  - o The single detection of 4,4'-DDD and single detection of 4,4'-DDE, degradates of DDT, were found at concentrations equal to or exceeding NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - Bifenthrin, detected once, was found greater than the invertebrate NOAEC (0.0013 μg/L) and greater than the WSDA Endangered Species Level of Concern (ESLOC),  $(0.00375 \mu g/L)$ .

- There were 643 total pesticide detections in Lower Bertrand Creek from 6 different use categories: 26 types of herbicides, 11 fungicides, 12 insecticides, 9 degradates, 1 insect repellent, and 1 wood preservative.
- Of the total pesticide detections found at Lower Bertrand Creek, 30 were above WSDA's assessment criteria (Table 6).
  - o The 2 detections of 4,4'-DDD and 3 detections of 4,4'-DDE were found at concentrations equal to or exceeding NRWQC and WAC chronic criteria (both  $0.001 \mu g/L$ ).
  - The single pentachlorophenol detection was found above the WSDA ESLOC  $(0.375 \mu g/L)$ .

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.

- Only 1 of the 4 diazinon detections was approaching the invertebrate NOAEC (0.17 μg/L).
- All 26 detections of imidacloprid were equal to or greater than the invertebrate NOAEC  $(0.01 \mu g/L)$ .
- The 4 detections of malathion did not exceed any assessment criteria in 2018, but it was still classified as a watershed POC because of 2017 detections that did exceed criteria.

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

- All 3 bifenthrin detections were greater than the invertebrate NOAEC (0.0013 µg/L).
- Only 1 of the 11 diazinon detections was approaching the invertebrate NOAEC (0.17  $\mu g/L$ ).
- All 18 detections of imidacloprid were approaching the invertebrate NOAEC (0.01 µg/L). Of those, 12 detections exceeded the invertebrate NOAEC (0.01 µg/L).
- Out of 9 malathion detections, 2 were approaching the invertebrate EC<sub>50</sub> (0.098 µg/L). The detection June 25 also exceeded the invertebrate EC<sub>50</sub> (0.098 µg/L).
- The 26 detections of thiamethoxam in 2018 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.

The Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2018 monitoring season and a visual comparison to 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.

Table 5 – Upper Bertrand Creek pesticide calendar (µg/L)

Month		Mar		Apr				Mav					Jun				Jul					Aug				Sep	
Day of the Month	Use*	20	27	3	10	16	24	1	8	15	22	30	5	11	19	25	3	9	16	24	30	7	14	20	28	4	11
2.4-D	ы	20	0.047		0.036			0.048	<u> </u>	Ü		- 50	- 5	0.080	15	20		0.249	10	27	- 50	-	17	20		-	<del></del>
2,6-Dichlorobenzamide	D	0.105		0.101				0.120	0.097	0 127	വ വരവ	0 08Q	0.102		0.003	0.083	0.092	0.249	0.096	0.068	0.040	0.035	0.031	0.025	0.027	0.023	0.020
4.4'-DDD	ח	0.103	0.073	0.101	0.102	0.037	0.107	0.120	0.037	0.127	0.000	0.003	0.102	0.104	0.000	0.003	0.032	0.120	0.030	0.000	0.040	0.000	0.001	0.023	0.021	0.025	0.020
4,4'-DDE	D			0.001																							0.002
Bifenthrin	ī			0.001	0.006																						
Boscalid	F	0.046	0.077	0.045		0.089	0.048	0.064	0.044	0.173	0.094	0.071	0.064	0.086	0.066	0.062	0.058	0.142	0.069	0.046	0.045	0.040	0.038	0.035	0.036	0.031	0.036
Carbendazim	F	0.003															0.011			0.007		0.006		0.004			
Chlorantraniliprole	li				0.004			0.002																			
Chlorothalonil	F			0.005																							
Diazinon	ı				0.098	0.018	0.004		0.002																		
Dicamba acid	Н		0.009			0.014		0.010						0.016				0.032									
Dichlobenil	Н	0.045	0.153	0.039	0.089	0.053	0.026	0.112	0.024	0.040	0.017	0.011	0.009	0.015	0.009	0.006	0.005	0.017	0.005	0.003	0.003	0.003	0.002	0.002	0.002		
Diuron	Н		0.004															0.004									
Eptam	Н							0.002																			
Ethoprop	I							0.002																			
Fludioxonil	F											0.004		0.006	0.004	0.004	0.003	0.011	0.005		0.004	0.003	0.004	0.004	0.004	0.003	
Hexazinone	Н		0.004	0.004	0.004		0.002		0.003			0.003	0.004	0.003	0.004	0.004	0.004	0.005	0.005	0.004	0.004	0.004	0.004		0.003	0.003	
Imazapyr	Н									0.007																	
Imidacloprid	I	0.070	0.029	0.043	0.028	0.048	0.035	0.077	0.039	0.055	0.048	0.040	0.051	0.010	0.114	0.040	0.036	0.138	0.039	0.019	0.018	0.016	0.012	0.011	0.010	0.012	0.013
Isoxaben	Н													0.005	0.009	0.004	0.003	0.004	0.002								
MCPA	Н		0.071					0.269		0.018				0.120				0.145									
Malathion	I															0.005	0.009	0.007		0.004							
Mecoprop (MCPP)	Н		0.037		0.038	0.068		0.072						0.064				0.150									
Metalaxyl	F	0.009				0.035					0.012					0.057	0.021	0.033		0.014		0.009		0.007			
Metolachlor	Н	0.005	0.046	0.026	0.080	0.057	0.024	0.010	0.007	0.007	0.007	0.006	0.006	0.010	0.006	0.005		0.006	0.004	0.002		0.001		0.001	0.001		
Metribuzin	Н					0.005		0.003		0.011																	
Myclobutanil	F	0.004		0.004				0.019			0.015	0.012	0.011			0.009	0.008		0.008	0.005		0.004	0.004				
N,N-Diethyl-m-toluamide		0.005				0.003			0.002	0.003				0.015				0.067			0.004		0.002				$oxed{oxed}$
Napropamide	Н					0.005																					
Oxadiazon	Н		0.009			0.012		0.013						0.012		0.004	0.003	0.014	0.004	0.003							
Oxamyl	I	0.003		0.002	0.001		0.003	0.002		0.003			0.002		0.002			0.002									
Charryr Chiric	D								0.019	0.026	0.023	0.031	0.033		0.055	0.030	0.026	0.022									
	WP		0.012																								
Propiconazole	F		0.014	0.008	0.078	0.059	0.013	0.013	0.007	0.007								0.012									
Pyrimethanil	F											0.006						0.007									
Simazine	Н	0.026				0.460	0.054	0.168	0.087	0.222	0.053	0.113	0.083	0.950	0.252	0.159	0.102	0.129	0.120	0.065	0.041	0.035	0.031	0.024	0.024	0.020	
Sulfentrazone	Н		0.025		0.013																						
Terbacil	Н	0.044		0.030	0.036		0.031	0.044											0.029	0.011	0.004						
Tetrahydrophthalimide	D		0.004			0.004		0.004					0.005	0.034			0.002								0.002		0.002
Thiamethoxam	I .			0.015			0.006	0.022	0.068	0.028	0.024	0.016	0.024		0.028	0.012	0.028	0.077	0.026	0.013	0.008	0.005					
Triadimefon	F																			0.003						0.003	
Triazine DEA degradate		0.001	0.55			0.55		0.5	0.001	0.5	0.65	0.0	0.0	0.5	0.53	0.55	0.5=:	0.003		0.55	0.5-	0.5	0.5	0.5	0.53	0.5-:	0.55
Triazine DIA degradate	D		0.006			0.007		0.012	0.020	0.049	0.022	0.046	0.045	0.016	0.097	0.067	0.052	0.065	0.076	0.031	0.022	0.016	0.015	0.014	0.008	0.007	0.005
Triclosan	Α	0.55	0.65	0.55		0.55				0.55	0.004					ļ	-										—
Trifluralin	IH	0.005		0.006		0.002				0.003					<u> </u>	L -	L		<u> </u>	<u> </u>	1.5		<b> </b>				₩
Total suspended solids			4.0	18.0		18.0		3.0	99.0	3.0	2.0	1.0	2.0	1.0	1.0	2.0	1.0	3.0	1.0	7.0	19.0	2.0			1.0		
Streamflow (cubic ft/sec		<u> </u>			65.25			27.09			14.94		5.90		4.33		2.09	1.44	1.72	1.01	0.85	0.95	0.95	0.68	0.75	1.09	0.98
Precipitation (total in/wee		1.14		1.21				0.86					0.36	0.41	0	0	0 ality ass	0	0.08	0	0	0.03	0	0	0	0.04	0.32

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.

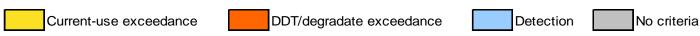


<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent, WP: Wood Preservative)

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

Table 6 – Lower Bertrand Creek pesticide calendar (μg/L)

Month		M	ar		Α	pr				May				Ju	ın				Jul				Αι	ıg		S	ер
Day of the Month	Use*	20	27	3	10	16	24	1	8	15	22	30	5	11	19	25	3	9	16	24	30	7	14	20	28	4	11
_	Н		0.027		0.027	0.042	$\sim$	0.035	$\overline{}$	$\sim$				0.016		0.021		0.012									
2,6-Dichlorobenzamide	D	0.118	0.065	0.121	0.141	0.053	0.125	0.135	0.109	0.128	0.111	0.120	0.119	0.138	0.118	0.110	0.122	0.154	0.137	0.127	0.125	0.127	0.125	0.118	0.132	0.114	0.114
	D																			0.001							0.002
	D	0.001	0.002		0.001																						
	Н	0.006																									
	F																0.034	0.012	0.013	0.010	0.006	0.007					
Bifenthrin	1		0.003		0.005					0.003																	
	F	0.035	0.082	0.041	0.074	0.025	0.037	0.054	0.025	0.046	0.039	0.027	0.026	0.034	0.025	0.039	0.038	0.069	0.048	0.045	0.054	0.069	0.056	0.050	0.055	0.037	0.052
	Н	0.016				0.003						0.025			0.030		0.032	0.025		0.042						0.045	0.04
	F				0.005	0.007		0.009				0.002			0.009		0.002	0.006									
Chlorantraniliprole	ı		0.003	0.007			0.004								0.002			0.002									
	F	0.003				-												-									
	H									$\sim$	0.024		0.026		0.022	0.027			0.022								
	F										0.006		0.000	0.007	0.010		0.012	0.014	0.010								
Diazinon	i				0.088	0.007	0.007	0.009	0.003	0.036		0.002	0.003				0.003										
	H				0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.012		0.000	0.000										
	H	0.030	0.053	0.027	0.061	0.016	0.022	0.047	0.016	0.025	0.011	0.006	0.006		0.004	0.003	0.018	0.015	0.012	0.007	0.005	0.005	0.004	0.003	0.003	0.002	0.00
Dinotefuran	i i	0.000	0.000			0.073			0.010	0.020	0.011	0.000	0.000	0.000	0.004	0.000	0.010	0.010	0.012	0.001	0.000	0.000	0.004	0.000	0.000	0.002	0.00
	<u>.</u> Н			3.0.2	3.0.0	3.0.0	3.0.0	3.000								0.003	0.053	0.024	0.022	0.013	0.009	0.008	0.006	0.004	0.003	0.003	
	H							0.002	0.001							0.000	0.000	0.024	0.022	0.010	0.000	0.000	3.000	3.004	0.000	0.000	
Ethoprop	1	0.002						3.002	3.001																		
Fipronil	1	0.002	0.005			0.002				0.002										0.004							
	F	0.005	5.003			0.002					0.005	0.004	0.005	0.006	0 000	0.013	0.008	0.010	0.008	0.004	0.007	0.007	0.007	0.006	0.007	0.005	0.00
	<u>'</u> Н	0.003	0.005	0.007	0.000	0.002	0.005		0.004								0.004							0.000		0.005	
	<u>п</u>	0.024		0.007	0.008	0.002		0.036				0.004		0.004		0.004		0.065	0.005	0.005	0.005	0.008	0.006		0.006	0.005	0.00
Imidacloprid	<u>'</u> Н	0.034	0.060	0.030	0.040		0.024	0.030	0.008	0.013	0.009		0.006	0.029	0.009		0.017	0.005	0.014		<u> </u>	0.016			-	-	0.00
			0.000					0.450							0.002												
	H		0.029					0.153								0.040	0.000										-
	D					-									0.000		0.002	0.004	0.044	0.044		0.005			0.004		0.00
Malathion	<u> </u>		0.040	0.044	0.005	0.044		0.047						0.000	0.006	0.106	0.026	0.021	0.014	0.011		0.005			0.004		0.00
	<u>H</u>	0.050		0.011			0.000	0.047	0.047	0.004	0.004	0.040	0.050	0.023	0.054	0.055	0.000	0.000	0.057	0.054	0.054	0.050	0.050	0.054	0.000	0.050	0.05
motorary	<u>F</u>	0.050	0.085	0.069	0.342	0.051		0.069	0.047	0.064	0.061	0.048	0.058	0.058	0.054	0.055	0.060	0.069	0.057	0.051	0.051	0.059	0.056	0.051	0.062	0.052	0.05
Methiocarb	!						0.005																				
Methomyl	<u> </u>												0.005		0.103		0.065	0.018	0.013	0.006							
	D																0.026		0.014								
	<u>H</u>	0.007		0.024			0.020		0.005		0.006	0.005	0.005		0.006	0.009	0.003	0.008	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.00
	H F			0.005	0.010	0.003		0.003		0.005				0.003													
Wyciobatariii			0.005				0.004	0.012			0.005			0.006	0.004			0.005									
N,N-Diethyl-m-toluamide		0.004			0.004				0.002	0.002				0.004				0.010			0.002		0.002				
	<u>H</u>		0.006		0.010			0.004																			
	H							0.003		0.003					0.004	0.004	0.006	0.005	0.006	0.007	0.006	0.007	0.006	0.005	0.007	0.006	0.006
	Н			0.025																							
	Н	0.006				0.004									0.002												
Oxamyl	<u> </u>			0.034								0.055					0.094	0.064		0.080	0.076	0.087				0.070	
	D	0.044	0.010	0.059	0.022		0.063	0.071	0.095	0.127	0.157	0.152	0.149	0.249	0.272	0.173	0.221	0.192	0.235	0.294	0.282	0.393	0.300	0.314	0.379	0.313	0.30
	WP					0.617																					
	Н																	0.003		0.003					0.004	0.003	
	F		0.012	0.006	0.046	0.039	0.010	0.008																			
Pyrimethanil	F												0.009				0.007										
Simazine	Н	0.018	0.119	0.058	0.143	0.314	0.137	0.110	0.040	0.135	0.029	0.036	0.030	0.451	0.078	0.037	0.099	0.096	0.069	0.071	0.032	0.043	0.031	0.030	0.033	0.025	0.02
Simetryn	Н																			0.005		0.006					
Sulfentrazone	Н	0.020	0.011	0.027	0.028	0.005	0.018	0.029	0.033	0.034	0.036	0.040	0.056	0.036	0.035	0.034	0.042	0.031	0.042	0.039	0.032	0.038	0.043	0.043	0.051	0.044	0.05
	Н							0.004				0.004	0.006	0.004		0.003	0.003	0.004	0.004	0.004	0.003	0.004		0.003	0.005	0.004	0.00
	Н	0.019	0.019	0.019	0.015	0.005	0.013	0.025	0.012	0.012	0.009	0.010	0.007	0.022	0.005	0.004	0.003	0.059	0.008	0.004							
	D			0.015								0.012					0.012		0.013	0.008	0.007	0.008	0.009	0.010	0.017	0.007	0.01
Thiamethoxam	I	0.026	0.011	0.086	0.054	0.030				0.050				0.056	0.108				0.056	0.046		0.047		0.043		0.063	0.06
Triadimefon	F	,_,						,						,				0.003			1						
Triazine DEA degradate	D	0.002						0.002	0.002	0.001	0.002	0.002	0.002	0.003	0.002	0.002	0.003	0.003	0.003	0.001	0.002	0.002	0.002	0.002	0.002	0.002	
Triazine DIA degradate		0.302		0.004	0 000	0.019	0.007					0.002					0.054					0.002				0.30Z	
Triclopyr acid	<u>Н</u>			0.004	0.000	0.019	0.001	3.300	3.000	0.020	0.000	0.000	3.008	J.JJZ	0.020	0.010	0.004	0.049	0.009	0.020	0.010	0.014	0.010	0.000			<del>                                     </del>
	H	0.006	0.005	0.006		0.002										<b> </b>					<b>+</b>		0.021				1
	11	0.000									L				<b>—</b>	<del>                                     </del>	<b>—</b>	<b>—</b>	<b></b>	-	<del>                                     </del>					-	-
Trifluralin		2 ^	E0 0	2 0	7 ^	1E 0																					
Trifluralin Total suspended solids (		3.0	59.0	3.0	7.0	15.0	6.0	4.0	2.0	2.0	2.0	1.0	1.0	2.0	14.0	10.0	11.0	E 0	 6 F	6.2	 E 1	17	4.0	4.0	4.0	47	
Trifluralin	mg/L)	3.0 52.2 0.50	59.0  1.34	3.0 62.8 0.62	7.0  1.65	15.0	6.0 64.2 0.08	4.0 49.6 0.19	2.0 46.3	2.0 66.3 0.61	2.0 25.6 0	1.0 19.1 0	1.0 18.0 0.17	19.9 0.31	11.9 0.06	12.2 0.07	11.0	5.8 0.70	6.5 0.17	6.3 0.28	5.1 0.47	4.7 0	4.9 0.41	4.9 0.17	4.8 0.21	4.7 0.28	6.0



<sup>\* (</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent, WP: Wood preservative)

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

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet the state water quality standard many times at Upper and Lower Bertrand Creek sites. Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in Figure 6 are shown below.

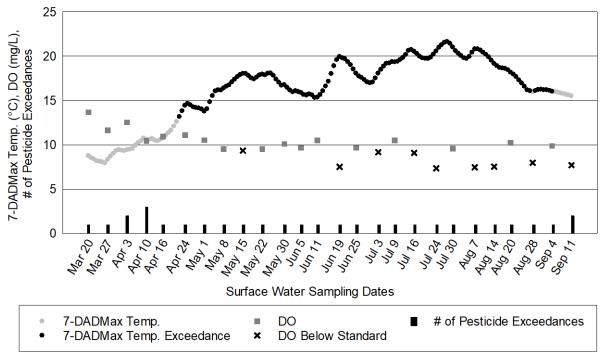


Figure 5 – Upper Bertrand Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

Pesticide exceedances in Upper Bertrand Creek coincided with failures to meet state water quality standards at 21 of the 26 site visits (81%). All pH measurements met the standard, ranging from 7.04 to 7.75 with an average of 7.42. The DO measurements ranged from 7.35 mg/L to 13.67 mg/L with an average of 9.73 mg/L. Less than half (35%) of these measurements fell below the standard with 9 measurements were less than 9.5 mg/L. All below standard DO measurements coincided with at least 1 pesticide exceedance and 7 of the measurements also overlapped with 7-DADMax temperature exceedances.

Upper Bertrand Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, 2 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 the beginning of the sampling season, March 20, through June 15, the 7-DADMax temperature exceeded the standard for 55 days from April 22 to June 15. From June 16 to the end of the sampling season, September 11, the 7-DADMax temperature exceeded the standard for 80 days from June 16 to September 4, excluding August 28.

There was at least 1 pesticide exceedance at every site visit with a 7-DADMax temperature exceedance.

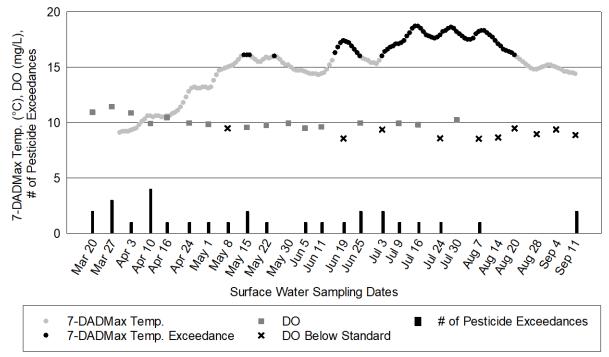


Figure 6 - Lower Bertrand Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

Pesticide exceedances in Lower Bertrand Creek coincided with failures to meet state water quality standards at 10 of the 26 site visits (38%). The pH measurements ranged from 7.08 to 7.75 with an average of 7.30. Similar to Upper Bertrand Creek, there were no pH measurements at Lower Bertrand Creek that exceeded state water quality standards. DO measurements ranged from 8.55 mg/L to 11.45 mg/L with an average of 9.69 mg/L. Less than half (38%) of the measurements fell below the DO standard with 10 measurements were less than 9.5 mg/L. Six of the below standard DO measurements coincided with at least 1 pesticide exceedance. The 7-DADMax temperature exceeded the standard of 16 °C for 63 days of the sampling season, primarily from June 16 through June 25 and from July 3 through August 20. Seven of the 7-DADMax temperature exceedances coincided with at least 1 pesticide exceedance. On June 19, July 3, July 24, and August 7, pesticide exceedances overlapped with both 7-DADMax temperature exceedances and DO failures.

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**

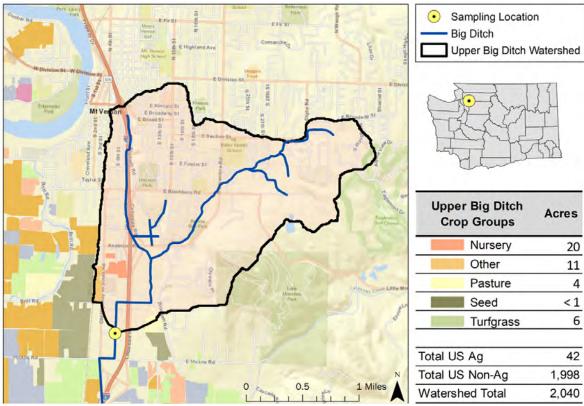


Figure 7 – Map of Upper Big Ditch and its drainage area with associated sampling location and crop groups identified

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 has consistently had 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).



Figure 8 – Upper Big Ditch upstream view

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

and coho salmon within the reach of ditch that encompasses the monitoring site (WDFW, 2019). A culvert upstream of the Upper Big Ditch monitoring site is scheduled to be replaced by 2022 to extend fish passage by over 2 miles upstream (WSDOT, 2019). Coho salmon currently spawn just below the culvert. Staff frequently observed juvenile fish of unknown species at the site (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 July 2 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 samples have primarily nursery or greenhouse crop groups as their main agricultural commodity. The 'Other' crop group category consists mostly of fallow fields (Figure 7).

Below is a brief overview of the pesticide findings in Upper Big Ditch in 2018.

- WSDA tested for 144 unique pesticides in Upper Big Ditch.
- There were 821 total pesticide detections from 8 different use categories: 28 types of herbicides, 15 fungicides, 11 insecticides, 9 degradates, 1 antimicrobial, 1 insect repellent, 1 synergist, and 1 wood preservative.
- Pesticides were detected at all 32 sampling events.
- Up to 44 pesticides were detected at the same time.
- Of the total pesticide detections, 32 were above WSDA's assessment criteria (Table 7).
  - o The 2 detections of 4,4'-DDD exceededNRWQC and WAC chronic criteria (both  $0.001 \mu g/L$ ).
  - Dichlorvos was detected once above the invertebrate NOAEC (0.0058 μg/L).
  - o Out of 19 pyraclostrobin detections, only 1 exceeded the WSDA Endangered Species Level of Concern (ESLOC), (0.155 µg/L).

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

- Every bifenthrin detection (6) was above the invertebrate NOAEC (0.0013 μg/L).
- All 20 detections of imidacloprid were approaching the invertebrate NOAEC (0.01 µg/L). Of those, 16 detections exceeded the invertebrate NOAEC (0.01 µg/L). Detections on May 7 and May 14 were approaching the invertebrate  $EC_{50}$  (0.77  $\mu g/L$ ).
- Only 2 of the 9 sulfometuron methyl detections were approaching the plant EC<sub>50</sub> (0.45
- The 13 detections of pyridaben and 26 detections of thiamethoxam did not exceed any assessment criteria in 2018, but the pesticides were still classified as watershed POCs because of detections in 2016 and 2017 that did exceed criteria.

The Upper Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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 7 – Upper Big Ditch pesticide calendar (μg/L)

Month		M	ar			Apr				М	ay			Ju	ın				Jul				Αι	ıa			S	ер			0	ct	
Day of the Month	Use*	19	26	2	9	16	23	30	7	14	21	29	4	12	18	26	2	10	17	23	31	6	13	21	27	5		17	24	1	8	15	22
2,4-D	H	19	20		_	0.077		0.180	_	0.034	21	23		0.111	10		0.312	10	-17	23	31		0.095		21	J		0.149	24	-	0	13	
		0.000	0.045	0.202							0.454	0.474			0.440			0.000	0.440	0.400	0.004				0.400	0.000			0.000	0.000	0.070	0.005	0.00
2,6-Dichlorobenzamide		0.230	0.215	0.302	0.378	0.357	0.309	0.329	0.204	0.220	0.151	0.171	0.158	0.132	0.119	0.151	0.130	0.098	0.110	0.103	0.064	0.101	0.100	0.101	0.100	0.099	0.155	0.137	0.089	0.083	0.078	0.095	0.08
4,4'-DDD	D																			-					0.002							0.002	
4-Nitrophenol	D											0.103													0.079								
Atrazine	Н												0.002				0.003		0.003					0.003									
Azoxystrobin	F	0.009	0.010	0.013		0.011	0.008		0.031	0.027		0.025	0.007	0.046	0.024	0.042	0.014	0.040	0.068	0.007	0.021	0.009	0.017	0.031	0.007	0.011	0.031	0.006		0.006	0.005	0.006	
Bifenthrin	ı	0.004	0.007				0.005		0.006	0.005	0.006																						
Boscalid	F	0.101	0.118	0.071	0.026	0.035	0.047	0.023	0.428	0.425	0.048	0.300	0.752	0.318	0.268	0.357	0.203	0.328	0.329	0.088	0.141	0.078	0.439	0.647	0.215	0.391	0.194	0.123	0.064	0.064	0.067	0.044	0.03
Bromacil	Н	0.006							0.004	0.004				0.004	0.005	0.006	0.005	0.004	0.006	0.005	0.007	0.007	0.008	0.007	0.007	0.006	0.006	0.005	0.006	0.005		0.006	0.00
Carbendazim	F		0.024	0.003	0.002	0.007	0.004	0.005			0.003	0.079	0.005								0.022										0.007		
Chlorothalonil	F			0.004					0.000	0.00									-									0.0.0					
Chlorpropham	H		0.005	0.004		_		0.002												+			_							<b>—</b>			
			0.003				0.000							0.000	0.000	0.007	0.000	0.000	0.040	0.000	0.004	0.000	0.000	0.004	0.000	0.004							
Chlorpyrifos						-	0.002		-					0.002	0.002	0.007	0.002	0.006	0.013	0.003	0.004	0.002	0.003	0.004	0.003	0.004	0.000						
Chlorsulfuron	H					_																					0.032						
Cyprodinil			0.036	0.176						0.030		0.017		0.007	0.007			0.028	0.050	)	0.015	0.008	0.011	0.019	0.009	0.006							
Dicamba acid	Н							0.012					0.102			0.042												0.016					
Dichlobenil	Н	0.009	0.057	0.064	0.122	0.087	0.033	0.053	0.011	0.011		0.008	0.014	0.035	0.009	0.012	0.008	0.006	0.004	0.003	0.002	0.003	0.004	0.003	0.002	0.002	0.013	0.007	0.004	0.003	0.004	0.004	0.00
Dichlorvos (DDVP)	1					0.009																											
Difenoconazole	F																	0.007															
Dinotefuran	ı	0.520	0.167	0.224	0.259	0.251	0.295	0.199	4.620	2.020	0.574	1.220	0.346	0.451	0.642	0.221	1.400		0.162	0.061	0.109	0.059	0.084	0.084	0.065	0.053	0.112	0.049	0.031	0.026	0.029	0.011	0.01
Dithiopyr	H		-	0.003		0.005														1										1	1		
Diuron	H	0.004	0.008		0.003		0.002			0.006	0.003	0.004	0.007	0.005	0.005	0.007		0.004	0.005	0.003	0.004	0.003	0.004	0.004	0.004	0.004	0.01E	0.007	0.005	0.004	0.004	0.004	0.00
	Н	0.004	0.008	0.003	0.003	0.004	0.004	0.008		0.006			0.007	0.003	0.005	0.007	0.000	0.004	0.005	0.003	0.004	0.003	0.004		0.004		0.015	0.007	0.005	0.004	0.004	0.004	0.00
Eptam		0.000	0.007	0.000	0.004	0.000	0.000	0.045					0.000	0.045		0.044			0.040	0.007				0.003	0.003	0.003	0.007	0.004			0.000		
Etridiazole	F	0.002	0.097	0.006	0.004	0.022	0.003	0.015			0.001	0.243	0.003	U.U15	0.009	0.011		0.002	U.U48	0.007							0.007	0.001		-	0.003		<u> </u>
Fenarimol	F								0.010								0.005				0.010											0.004	
Fipronil	1							0.004								0.004												0.005					
Fipronil disulfinyl	D							0.002								0.003											0.002						
Fipronil sulfide	D																0.001										0.003	0.003			0.003	0.003	0.00
Fipronil sulfone	D							0.003								0.004											0.004	0.005					
Fludioxonil	F	0 115	0 179	0.267	0.077	0.088	0.156			0.894	0 221	0 992	0.305	0.856	1.560	0.689	0.554	2 030	4 650	0.737	1.350	0.416	0 920	1 120	0.487	0.616			0 147	0 143	0.155	0.084	0.07
Flumioxazin	H	0.115	0.175	0.201	0.077	0.000	0.100	0.004	0.000	0.004	0.221	0.552	0.000	0.000	1.000	0.007	0.004	2.000	4.000	0.707	1.000	0.410	5.520	1.120	0.407	0.010	0.200	0.100	0.147	0.140	0.100	0.004	0.07
	H	0.003				1			_	0.004						0.007	0.004			_	0.004		$\sim$									0.005	
Hexazinone		0.003		0.005	0.007	0.005		0.000					0.005			0.000	0.004			-	0.004							-		-		0.005	
Imazapic	Н			0.005		0.005		0.008					0.005			0.008																	
Imazapyr	Н	0.020	0.010		0.014	0.010	0.012	0.029			0.020													0.841					0.075	0.040	0.050	0.015	
Imidacloprid	1			0.006			0.038		0.210	0.202		0.055	0.009	0.027	0.056	0.035		0.027	0.029		0.020	0.008	0.017	0.024		0.017	0.021						
Isoxaben	Н				0.010	0.002										0.003			0.010	0.004	0.012		800.0	0.020	0.003		0.060	0.008					
Malaoxon	D																	0.003															
Mecoprop (MCPP)	H							0.013					0.033			0.055	0.024																
Metalaxyl	F		0.045	0.016	0.009	0.014	0.036		0.090	0.173		0.137		0.051	0.093	0.114	0.026	0.088	0.315	5	0.038	0.019	0.054	0.055							0.032	0.074	0.01
Methiocarb	1		0.015																							0.183	0.021						
Metolachlor	H		0.0.0					0.005	0.002	0.003	0.002	0.002	0.012	0.004	0.002	0.012	0.008	0.002	0.002	,						0.100	0.021	0.002			0.003		
Myclobutanil	F					_		0.000	0.004	0.000	0.002	0.002		0.004				0.003					_					0.002			0.000		
N,N-Diethyl-m-toluamide		0.007		0.000	0.040	0.008	0.040			0.005				0.004	0.004		0.032				0.007		0.017		0.008		0.005	0.000	0.007	0.007	0.010	0.007	0.00
		0.007		0.008	0.013	0.008	0.013		0.003	0.005				0.011		0.059	0.032	0.011	0.009	,	0.007		0.017		0.008		0.005	0.020	0.007	0.007			0.00
Norflurazon	H					-		-	ļ																					-	0.005	0.005	
Oryzalin	Н															0.009																	
Pendimethalin	Н								0.003			0.003																					
Pentachlorophenol	WP		0.012			0.013										0.015											0.015	0.013					
Picloram	Н					$\geq \leq$	$\sim$	$\geq$	$\geq$	$>\!<$	0.068	0.095		0.032	0.032				0.043	3	0.059	0.082	0.094	0.084	0.082	0.093		0.065	0.076			0.061	0.06
Piperonyl butoxide	Sy		0.014							0.006						0.012	0.037	0.015	0.012	2			0.012		0.063	0.184	0.055	0.017	0.010	0.009			
Prodiamine	Н						0.025		0.066	0.066		0.037			0.021	0.024		0.018	0.045	0.016	0.016		0.019	0.023									
Prometon	H	0.010	0.009	0.010	0.015	0.010							0.005								0.008								0.007	0.007	0.007	0.008	0.00
Propiconazole	F		0.007			0.013		1		0.006			0.012				0.009		0.008									0.015					
	F		0.007	0.005		3.013			0.013			0.018			0.000		0.003	0.034			0.010		0.030	0.045	0.028	0.046					<del>                                     </del>		
Pyraclostrobin	-	<b>-</b>	0.007	0.005	<b>-</b>	<del>                                     </del>	-	<del>                                     </del>	0.013	0.008		บ.บไซ้	0.195	0.030	0.009	0.005		0.034												0.004	0.004	0.004	<del>                                     </del>
Pyridaben	1	<b>—</b>			-	-	1	<del>                                     </del>	<del>                                     </del>	1						-	0.004		0.005		0.005		0.005	0.006	0.005	0.004	0.006	0.004	0.004	0.004	0.004		-
D 1 (		1			<u> </u>	1				1									<u> </u>		0.004										0.004		-
Pyriproxyfen	I				ı	1	1	0.006		1							0.010			1	0.006		0.006				0.006	1	0.003	9	0.005	0.004	ı
Sulfentrazone	H				_	_											0.013		ı				_	_					0.000	_			
Sulfentrazone Sulfometuron methyl	Н							0.037					0.026												0.054			0.014					
Sulfentrazone	H	0.054		0.039	0.023	0.013	0.031			0.041	0.042	0.042	0.038	0.041	0.045	0.035	0.041		0.067	0.056	0.050	0.062	0.055				0.014					0.058	0.05
Sulfentrazone Sulfometuron methyl	Н	0.054		0.039	0.023	0.013	0.031			0.041	0.042	0.042		0.041	0.045		0.041	0.051	0.067	0.056	0.050	0.062	0.055									0.058	0.05
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide	H					0.013		0.022	0.027				0.038			0.035	0.041	0.002			0.050			0.064	0.073	0.064	0.014	0.033				0.058	0.05
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam	H							0.022	0.027		0.039		0.038			0.035	0.041	0.002						0.064	0.073	0.064	0.014 0.001	0.033				0.058	0.05
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate	H					0.020	0.023	0.022	0.027		0.039	0.136 0.003	0.038 0.005 0.057	0.097	0.170	0.035 0.001 0.061	0.041	0.002 0.023	0.048	0.023	0.023	0.011	0.024	0.064	0.073	0.064	0.014 0.001 0.043	0.033			0.077		0.05
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon	H H D I					0.020		0.022	0.027	0.115	0.039	0.136 0.003	0.038 0.005 0.057	0.097	0.170	0.035 0.001 0.061	0.041	0.002 0.023	0.048	0.023		0.011	0.024	0.064	0.073	0.064	0.014 0.001 0.043	0.033					0.05
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate	H H D I I				0.020	0.020	0.023	0.022	0.027	0.115	0.039	0.136 0.003	0.038 0.005 0.057 0.004	0.097	0.170	0.035 0.001 0.061 0.004	0.041 0.054 0.005	0.002 0.023	0.048	0.023	0.023	0.011	0.024	0.064	0.073	0.064	0.014 0.001 0.043 0.004	0.033			0.077	0.003	
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate Triclopyr acid	H H D I I F e D				0.020	0.020	0.023	0.022	0.027 0.134 0.026 0.039	0.115	0.039	0.136 0.003	0.038 0.005 0.057 0.004 0.894	0.097 0.019 0.086	0.170	0.035 0.001 0.061 0.004 0.361	0.041 0.054 0.005 0.200	0.002 0.023	0.048	0.023	0.023	0.011	0.024 0.002 0.127	0.064 0.019 0.002 0.025	0.073	0.064	0.014 0.001 0.043 0.004 0.794	0.033	0.059	0.056	0.077	0.003	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate Triclopyr acid Triclosan	H H D I I I F e D H	0.072	0.039	0.026	0.020	0.020	0.023	0.022	0.027	0.115	0.039	0.136 0.003	0.038 0.005 0.057 0.004 0.894	0.097	0.170	0.035 0.001 0.061 0.004 0.361 0.006	0.041 0.054 0.005 0.200 0.010	0.002 0.023 0.003	0.048	0.023	0.023	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025	0.073	0.064	0.014 0.001 0.043 0.004 0.794	0.033	0.059	0.056	0.077	0.003	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate Triclopyr acid	H H D I I I F e D H A	0.072		0.026	0.020	0.020	0.023	0.022	0.027 0.134 0.026 0.039	0.115 0.001 0.031	0.039	0.136 0.003	0.038 0.005 0.057 0.004 0.894	0.097 0.019 0.086	0.170	0.035 0.001 0.061 0.004 0.361 0.006	0.041 0.054 0.005 0.200 0.010 0.005	0.002 0.023 0.003	0.048	0.023	0.023	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025	0.073	0.064	0.014 0.001 0.043 0.004 0.794	0.033	0.059	0.056	0.077 0.003 0.031 0.010	0.003	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate Triclopyr acid Triclosan	H H D I I I F e D H	0.072	0.039	0.026	0.020	0.020	0.023	0.022	0.027 0.134 0.026 0.039	0.115 0.001 0.031 0.003	0.039	0.136 0.003	0.038 0.005 0.057 0.004 0.894	0.097 0.019 0.086	0.170	0.035 0.001 0.061 0.004 0.361 0.006	0.041 0.054 0.005 0.200 0.010	0.002 0.023 0.003	0.048	0.023	0.023	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025	0.073	0.064	0.014 0.001 0.043 0.004 0.794	0.033	0.059	0.056	0.077 0.003 0.031 0.010	0.003	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triazine DEA degradate Triclopyr acid Triclosan Trifloxystrobin Trifluralin	H H D I I F e D H A	0.072	0.039	0.026	0.020	0.003	0.023	0.022 0.014 0.756	0.027 0.134 0.026 0.039 0.017	0.115 0.001 0.031 0.003	0.039	0.136 0.003 0.006	0.038 0.005 0.057 0.004 0.894	0.097 0.019 0.086 0.004	0.170	0.035 0.001 0.061 0.004 0.361 0.006 0.007	0.041 0.054 0.005 0.200 0.010 0.005 0.003	0.002 0.023 0.003 0.006	0.048 0.015 0.003 0.013	0.003	0.023	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025 0.053	0.003	0.064 0.020 0.003	0.014 0.001 0.043 0.004 0.794 0.007	0.033 0.013 0.211 0.006	0.059	0.056	0.077 0.003 0.031 0.010	0.003 0.032 0.012	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triadimefon Triazine DEA degradate Triclopyr acid Triclosan Trifluvalini Trifluvalin Total suspended solids	H H D I I I F ee D H A F H B (mg/L)	0.072	0.039	0.026	0.020	0.020 0.003 0.353 0.003 13.0	0.023 0.004 0.108	0.022 0.014 0.756	0.027 0.134 0.026 0.039 0.017	0.001 0.001 0.003 0.003 12.0	0.039	0.136 0.003 0.006	0.038 0.005 0.057 0.004 0.894	0.097 0.019 0.086 0.004	0.170	0.035 0.001 0.061 0.004 0.361 0.006 0.007	0.041 0.054 0.005 0.200 0.010 0.005 0.003	0.002 0.023 0.003 0.006	0.048 0.015 0.003 0.013	3 0.023 5 0.007 8 0.003 3 3.0	0.023	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025 0.053	0.003	0.064 0.020 0.003	0.014 0.001 0.043 0.004 0.794 0.007	0.033 0.013 0.211 0.006	0.059	0.056	0.077 0.003 0.031 0.010 0.003 4.0	0.003 0.032 0.012	0.02
Sulfentrazone Sulfometuron methyl Tebuthiuron Tetrahydrophthalimide Thiamethoxam Total fluvalinate Triazine DEA degradate Triclopyr acid Triclosan Trifloxystrobin Trifluralin	H H D I I I F ee D H A F H G (mg/L)	0.072 0.011 12.0 1.95	0.039 0.026 16.0 5.90	0.026 0.007 5.0 4.02	0.020 0.036 7.0 7.47	0.003	0.023 0.004 0.108 4.0 3.79	0.022 0.014 0.756	0.027 0.134 0.026 0.039 0.017 9.0 1.81	0.001 0.001 0.003 0.003 12.0 1.58	0.039 0.003 46.0	0.136 0.003 0.006 11.0 0.87	0.038 0.005 0.057 0.004 0.894 5.0 0.98	0.097 0.019 0.086 0.004 9.0 0.68	0.170	0.035 0.001 0.061 0.004 0.361 0.006 0.007 4.0	0.041 0.054 0.005 0.200 0.010 0.005 0.003	0.002 0.023 0.003 0.006 3.0 0.84	0.048 0.015 0.003 0.013 5.0 0.63	0.003	0.023 0.003 0.010 2.0 0.51	0.011	0.024 0.002 0.127 0.006	0.064 0.019 0.002 0.025 0.053 1.0 0.38	0.003	0.064 0.020 0.003	0.014 0.001 0.043 0.004 0.794 0.007	0.033 0.013 0.211 0.006	0.059 0.005 7.0 0.48	0.056 0.005 0.005	0.003 0.003 0.003 0.003 4.0 1.02	0.003 0.032 0.012	0.02

Detection Current-use exceedance DDT/degradate exceedance

<sup>\* (</sup>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 fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 19 of the 32 site visits (59%). Water quality at the Upper Big Ditch site is shown below (Figure 9).

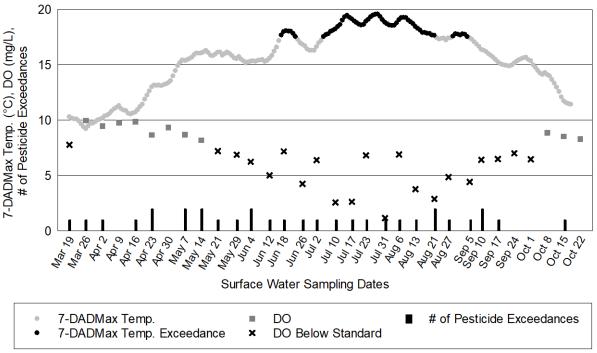


Figure 9 – Upper Big Ditch occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

All pH measurements met the state standard, ranging from 6.73 to 7.21 with an average of 6.94. The DO measurements ranged from 1.16 mg/L to 9.96 mg/L with an average of 6.66 mg/L. More than half (66%) of the DO measurements fell below the state standard in that 21 measurements were less than 8 mg/L. Most (90%) of the DO measurements that fell below the standard coincided with at least 1 pesticide exceedance. In addition, 8 of the DO measurements that fell below the standard also overlapped with a 7-DADMax temperature exceedance. Upper Big Ditch had the lowest DO measurement of any monitoring site in 2018. The 7-DADMax temperature standard of 17.5 °C was exceeded 62 days of the sampling season, from June 17 through June 23, July 5 through August 21, and August 29 through September 4. At every site visit with an exceeding 7-DADMax temperature, there was at least 1 pesticide exceedance.

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**

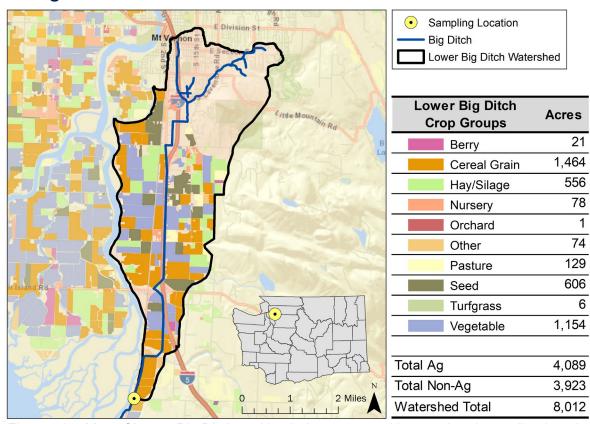


Figure 10 – Map of Lower Big Ditch and its drainage area with associated sampling location and crop groups identified

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 samples this site when the tide gate located downstream of the monitoring site is open and the water is flowing from Big Ditch into Puget Sound to avoid sample contamination with saltwater or pooling backwater. 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 influence the streamflow in the ditch. Big Ditch stretches north approximately 8 miles from the



Figure 11 – Lower Big Ditch upstream view

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 (Figure 10).

Below is a brief overview of the pesticide findings in Lower Big Ditch in 2018.

- WSDA tested for 144 unique pesticides in Lower Big Ditch.
- There were 398 total pesticide detections from 7 different use categories: 28 types of herbicides, 12 fungicides, 9 insecticides, 7 degradates, 1 antimicrobial, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 16 sampling events.
- Up to 43 pesticides were detected at the same time.
- Of the total pesticide detections, 35 were above WSDA's assessment criteria (Table 8).
  - The 9 detections of 4,4'-DDD, 9 detections of 4,4'-DDE, and 2 detections of 4,4'-DDT were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 μg/L).
  - Dichlorvos was detected once above the invertebrate NOAEC (0.0058 μg/L).
  - Out of 16 metolachlor detections, one on April 16 was approaching the invertebrate NOAEC (1 µg/L).
  - Out of 10 thiamethoxam detections, one on April 30 was approaching the invertebrate NOAEC (0.74 µg/L).

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

- Out of 10 fipronil detections, 4 were equal to or exceeded the invertebrate NOAEC (0.011
- All 8 detections of imidacloprid were approaching the invertebrate NOAEC (0.01 µg/L). Of those, 6 detections were equal to or exceeded the invertebrate NOAEC (0.01 µg/L).

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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 2018, WSDA primarily collected samples during the spring due to historically infrequent pesticide detections during the summer and fall.

Table 8 – Lower Big Ditch pesticide calendar (µg/L)

Month		M	ar			Apr				М	ay			Jı	ın		Jul
Day of the Month	Use*	19	26	2	9	16	23	30	7	14	21	29	4	12	18	26	2
2.4-D	Н			0.016	0.020	0.042			0.046	0.043				0.279			
2,6-Dichlorobenzamide	D	0.112	0.103	0.141	0.161						0.074	0.020	0.041	0.053	0.018		0.005
4,4'-DDD	D	0.003	0.003		0.003	0.002				0.001		0.001		0.001			
4,4'-DDE	D	0.002	0.002	0.003	0.003	0.004	0.002	0.002		0.001	0.002						
4,4'-DDT	I	0.003				0.003											
Atrazine	Н				0.020			0.004		0.003				0.005			
Azoxystrobin	F		0.031					0.019	0.010	0.015	0.015		0.006	0.063	0.028		
Boscalid	F		0.008	0.010	0.015		0.009		0.011	0.027	0.029	0.009	0.030	0.112	0.043	0.003	0.015
Bromacil	Н	0.009				0.004		0.006	0.004								
Carbendazim	F			0.002	0.004					0.003	0.003		0.004	0.004			
Chlorothalonil	F								0.003								
Chlorpropham	H	0.007	0.005	0.005				0.005	0.002		0.002						
Clothianidin	1					0.009				0.007							1
Dicamba acid	Н			0.086	0.080									0.019			
Dichlobenil	H	0.004	0.005	0.023	0.036		0.010	0.010	0.006	0.005	0.004	0.002	0.003	0.005	0.002		
Dichlorvos (DDVP)		0.040	0.005	0.005	0.000	0.006	0.047	0.040	0.000	0.000	0.000				0.007		₩
Difenoconazole	F	0.012	0.005	0.005	0.009	0.008	0.017	0.010			0.008			0.454	0.007		$\vdash$
Dimethoate	1	0.070	0.020	0.022	0.054	0.027	0.064	0.074	0.009		0.125	0.025	0.060	0.151	0.022		0.000
Dinotefuran Dithiopur	H	0.070	0.036	0.033	0.051	0.037	0.061		0.094	0.116	0.135	0.025	0.066	0.049	0.023		0.008
Dithiopyr	Н	0.046	0.005	0.000	0.040		0.040	0.002	0.044	0.040	0.044	0.005	0.007	0.000	0.000		<del>                                     </del>
Diuron Eptam	Н		0.025			0.028						0.005				0.000	0.005
Etridiazole	F	0.011	0.011		0.003			0.014	0.046	0.023	0.020	0.002	0.052	0.025	0.019	0.008	0.005
Fenarimol	F			0.000	0.003	0.004		0.004							0.002	0.002	
Fipronil	1		0.013	0.011	0.022	0.017	0.003	0.004	0.002	0.002				0.004	0.002	0.002	
Fipronil disulfinyl	D		0.013	0.011	0.022	0.002	0.003	0.004	0.002	0.002				0.004	0.003		
Fipronil sulfide	D	0.005	0.006	0.006	0.006		0.002		0.002	0.002				0.002			
Fipronil sulfone	D	0.000		0.010	0.000		0.003			0.003					0.004		
Fludioxonil	F	0.083	0.048		0.067		0.103				0 175	0.044	0.063			0.006	0.030
Hexazinone	H		0.004		0.00.	0.002	000	000	0.003	0.202	00	0.0	0.000	0.0.0	0.0.2	0.000	0.000
Imazapic	Н			0.011													
Imazapyr	Н	0.012	0.014		0.014	0.013	0.010	0.022	0.014	0.016	0.013		0.010	0.006			
Imidacloprid	ı			0.051		0.047		0.029		0.009							
MCPA	Н							0.020	0.020								
Malathion	I					0.008											
Mecoprop (MCPP)	Н					0.022											
Metalaxyl	F		0.013		0.036					0.016	0.024						0.021
Metolachlor	Н	0.019	0.028	0.081	0.102	0.128	0.044	0.041	0.033	0.655	0.245	0.018	0.031	0.139	0.027	0.002	0.003
Metribuzin	Н	0.005	0.014	0.014	0.012	0.010	0.004	0.008		0.003		0.003	0.004	0.004	0.011		0.003
Metsulfuron-methyl	Н				0.011	0.018											
N,N-Diethyl-m-toluamide							0.005		0.005	0.006	0.005			0.009			
Napropamide	Н	0.012	0.008	0.011	0.008	0.008		0.006									
Oryzalin	Н						0.011										
Pentachlorophenol	WP	0.017		0.012		0.026											
Prometon	Н	0.006	0.006	0.006	0.008	0.006	0.005	0.005	0.004	0.005	0.005	0.002	0.003				
Propiconazole	F														0.006		
Pyraclostrobin	F													0.011			
Simazine	Н			0.038	0.015	0.009											<b>—</b>
Sodium bentazon	H				0.040		0.048	0.000		0.040	0.041			0.005			$\vdash$
Sulfentrazone	H				0.013			0.008						0.005			_
	Н	0.004	0.000	0.005	0.000	0.040	0.000	0.058	0.000	0.007	0.004	0.000	0.045	0.009	0.005		
Tebuthiuron	Н		0.026	0.025	0.020	0.019						0.009	0.015	0.010	0.005		
Terbacil	Н	0.008	0.014	0.010	0.022	0.010	0.004	0.004	0.022	0.006	0.006			0.008			$\vdash$
Thiamethoxam Triadimefon	l F		0.014	0.010	0.023	0.012	0.252	0.594		0.005	0.045		0.000				
		0.001			0.006	0.002	0.002	0.002	0.002				0.003	0.003	0.002		
Triazine DEA degradate Triclopyr acid	Н	0.001			0.000		0.002		0.017				0.022	0.123			
Triclosan	А					0.134	0.054	0.200	0.017				0.032	0.123			
Trifluralin	Н					0.002			0.004	0.003				0.003			
Total suspended solids		26.0	25.0	25.0	62.0	25.0	73.0	21.0	17.0		17.0	7.0	6.0	6.0	5.0	17.0	3.0
Streamflow (cubic ft/sec		6.99		38.2		25.0			15.6			15.6	12.9	8.81	3.43		13.7
Precipitation (total in/wee		0.40			1.37	1.27	0.66		0.12		0	0	0.41	0.29	0.08	0.39	0.51
The "" signifies a samp											U		U. <del>T</del> I	0.23	0.00	0.03	0.01



<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent, WP: Wood Preservative)

<sup>†</sup> Washington State University AgWeatherNet station: Fir Island, (latitude: 48.36°, longitude: -122.42°)

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet the state water quality standards at 8 of the 16 site visits (50%). Water quality at the Lower Big Ditch site is shown below (Figure 12).

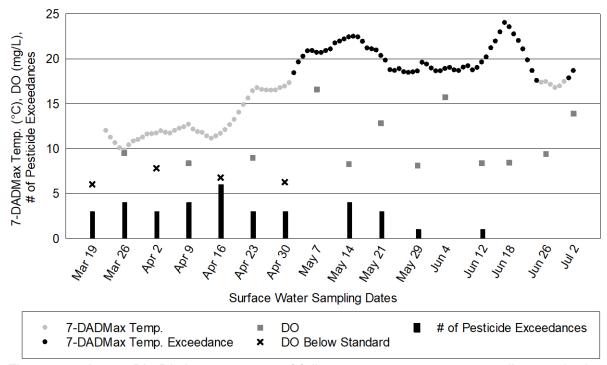


Figure 12 – Lower Big Ditch occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 6.67 to 8.94 with an average of 7.35. Of these measurements, 1 was greater than the pH standard of 8.5 on July 2. This pH exceedance coincided with a 7-DADMax temperature exceedance. DO measurements ranged from 6.02 mg/L to 16.59 mg/L with an average of 9.71 mg/L. One-quarter of these measurements fell below the DO standard with 4 measurements less than 8 mg/L. All of the below standard DO measurements coincided with at least 3 pesticide exceedances. The 7-DADMax temperatures were greater than the 17.5 °C standard for 56 days of the sampling season, primarily from May 2 through June 24. On May 14, May 21, May 29, and June 12, the 7-DADMax temperature exceedances coincided with pesticide 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 be monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

# **Burnt Bridge Creek**

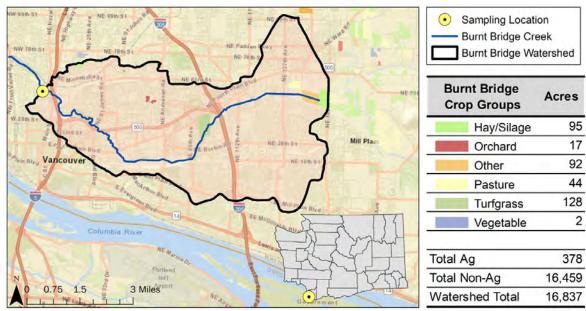


Figure 13 - Map of Burnt Bridge Creek and its drainage area with associated sampling location and crop groups identified

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°) (Figure 13). Roughly 10 miles of Burnt Bridge Creek flows through the center of Vancouver, Wash. making it the most urban site WSDA tests.

Burnt Bridge Creek flows into Vancouver Lake, draining 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 14).

The watershed is highly impacted by residential, commercial, industrial and agricultural development. The 'Other' crop group category includes mostly land used for conservation purposes (Figure 13).



Figure 14 – Burnt Bridge Creek upstream view

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 9 – Burnt Bridge Creek pesticide calendar (µg/L)

Month		Mar	Α	pr		ay	Jı	ın	J	ul		Aug		S	ер
Day of the Month	Use*	27	11	25	9	23	6	20	2	18	1	15	29	12	25
2.4-D	Н	0.039			0.025	20			_				0.143	0.412	
2,6-Dichlorobenzamide	D		0.263	0.268	0.219	0.231	0.239	0.216	0.215	0.237	0.225	0.223	0.232	0.189	0.187
4.4'-DDD	D	0.003	0.003	0.200	0.210	0.002	0.200	0.210	0.210	0.002	0.003	0.003	0.003	0.003	0.003
4,4'-DDE	D	0.002	0.002			0.001				0.001	0.000	0.000	0.000	0.000	0.000
Atrazine	Н		0.007	0.004		0.003			0.003	0.004	0.004	0.004	0.003		
Boscalid	F	0.002			0.002	0.002				0.003		0.005	0.004	0.003	0.005
Bromacil	Н					0.004	0.004	0.005	0.005	0.005		0.007		0.005	
Carbendazim	F					0.002									
Dicamba acid	Н												0.012	0.043	
Dichlobenil	Н	0.011	0.016	0.007	0.007		0.004	0.006	0.003	0.002	0.002	0.003	0.003	0.004	0.004
Dithiopyr	Н	0.005		0.003				0.003	0.002		0.002			0.002	
Diuron	Н	0.004	0.003		0.003			0.005						0.006	
Eptam	Н										0.003				
Ethoprop	I		0.003											0.002	
Fenarimol	F		0.006		0.003						0.006	0.006			
Fipronil	I							0.003							
Fipronil sulfide	D				0.001					0.003				0.003	
Fipronil sulfone	D				0.002			0.003			0.003	0.003			
Fludioxonil	F									0.006			0.004		0.004
Hexazinone	Н	0.004			0.002						0.004	0.005			0.005
Imazapyr	Н	0.010	0.010	0.009	0.018	0.013	0.012	0.015	0.017	0.041			0.009	0.009	
Mecoprop (MCPP)	Н												0.026	0.085	
Metolachlor	Н	0.003											0.002	0.003	0.002
N,N-Diethyl-m-toluamide (DEET)	IR				0.008						0.006	0.007	0.016	0.014	
Norflurazon	Н														0.005
Oryzalin	Н	0.042						0.012					0.005	0.011	0.006
Pendimethalin	Н		0.009	0.006	0.003	0.004	0.003	0.005	0.004	0.005	0.004		0.004	0.005	0.005
Prometon	Н	0.003					0.002			0.003			0.003		0.004
Propiconazole	F	0.011													
Pyridaben	I														0.004
Pyriproxyfen	I											0.004			0.004
Simazine	Н	0.019	0.011		0.008						0.004		0.008	0.020	0.007
Sulfentrazone	Н	0.005						0.005	0.004	0.003	0.005	0.009	0.004	0.004	0.009
Terbacil	Н	0.006				0.004	0.004								
Triadimefon	F				0.002		0.003				0.002				0.003
Triazine DEA degradate	D	0.003	0.003	0.003	0.004	0.005	0.004	0.007	0.006	0.008	0.005	0.005	0.005	0.003	0.004
Triazine DIA degradate	D							0.009		0.005					
Triclopyr acid	Н		0.029		0.020		0.065	0.028	0.015	0.035	0.016		0.068	0.188	
Triclosan	Α	0.012	0.015		0.008	0.003					0.008	0.008			0.013
Trifluralin	Н	0.006			0.002										$ldsymbol{ldsymbol{\sqcup}}$
cis-Permethrin	I														0.006
Total suspended solids (mg/L)		13.0	12.0	8.0	8.0	12.0	6.0		7.0	6.0	6.0	5.0	4.0	13.0	3.0
Streamflow (cubic ft/sec)		25.53	24.95	14.84	11.16	9.11	7.44	7.45	6.41	4.70	4.00	4.44	4.89	5.82	4.76
Precipitation (total in/week)†		1.53	1.25	0	0.01	0	0.09	0.16	0	0	0	0	0.07	0.12	0

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.



- WSDA tested for 144 unique pesticides in Burnt Bridge Creek.
- There were 218 total pesticide detections from 6 different use categories: 21 types of herbicides, 7 degradates, 6 fungicides, 5 insecticides, 1 antimicrobial, and 1 insect repellent.

<sup>(</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

<sup>†</sup> Washington State University AgWeatherNet station: WSU Vancouver RE, (latitude: 45.68°, longitude: -122.65°)

- Pesticides were detected at all 14 sampling events.
- Up to 21 pesticides were detected at the same time.
- Of the total pesticide detections, 14 were above WSDA's assessment criteria (Table 9).
  - The 9 detections of 4.4'-DDD and 4 detections of 4.4'-DDE were equal to or exceeding NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - The single detection of cis-permethrin was greater than the invertebrate NOAEC  $(0.0014 \mu g/L)$ .

Diuron was the only Burnt Bridge watershed POC. There were 5 detections of the herbicide throughout the 2018 monitoring season; none of which exceeded any assessment criteria. However, diuron is still classified as a watershed POC due to detections at the site in 2017 exceeding assessment criteria.

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 5 of the 14 site visits (36%). Water quality at the Burnt Bridge Creek site is shown below (Figure 15).

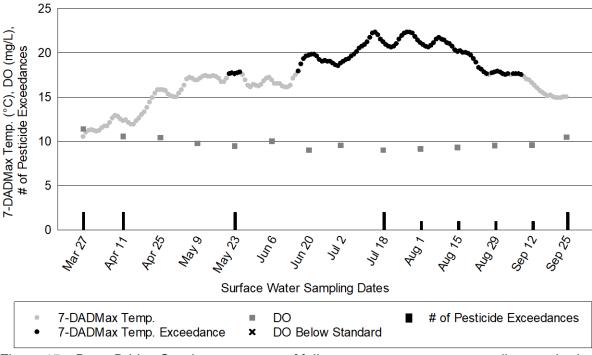


Figure 15 – Burnt Bridge Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

All pH measurements met the state water quality standard, ranging from 7.80 to 8.09 and averaging 7.97. Additionally, all DO measurements met the standard, ranging from 9.00 mg/L to 11.39 mg/L and averaging 9.80 mg/L. The 7-DADMax temperatures were greater than the 17.5 °C temperature standard for 88 days of the sampling season, primarily from June 16 through September 8. Pesticide exceedances coincided with 7-DADMax temperature exceedances on May 23 and at every site visit from July 18 through August 29.

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**

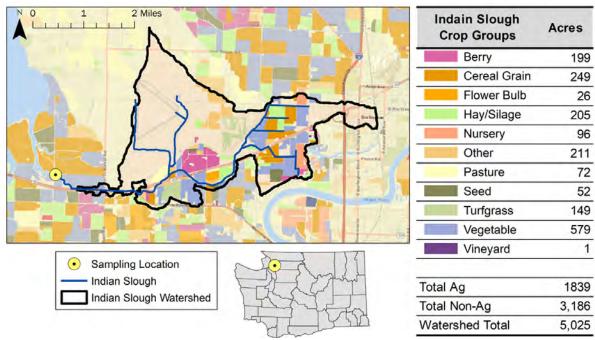


Figure 16 – Map of Indian Slough and its drainage area with associated sampling location and crop groups identified

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 16).

Indian Slough water drains directly into Puget Sound. Agricultural irrigation and precipitation events generally influence streamflow in the slough. The WDFW has documented winter steelhead and Chinook 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 17).

The Indian Slough watershed is a web of drainage ditches that pass through agricultural and industrial/residential areas. Indian Slough stretches



Figure 17 – Indian Slough upstream view

approximately 6 miles from its sources to the 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 of fallow fields (Figure 16). Indian Slough is another site where the presence of New Zealand mud snails has been confirmed.

Staff only sample this site when the tide gate is open and the water is flowing 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. In addition, in 2018, staff primarily collected samples during the spring and fall due to historically infrequent pesticide detections during the summer.

Below is a brief overview of the pesticide findings in Indian Slough in 2018.

- WSDA tested for 144 unique pesticides in Indian Slough.
- There were 232 total pesticide detections from 7 different use categories: 21 types of herbicides, 9 insecticides, 8 fungicides, 8 degradates, 1 antimicrobial, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 11 sampling events.
- Up to 31 pesticides were detected at the same time.
- Of the total pesticide detections, 20 were above WSDA's assessment criteria (Table 10).
  - o The 8 detections of 4,4'-DDD and 4 detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - Of the 3 clothianidin detections, one on April 9 was approaching the invertebrate NOAEC  $(0.05 \mu g/L)$ .

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

- The 3 detections of chlorpyrifos did not exceed any assessment criteria in 2018, but the pesticide was still classified as a watershed POC due to detections in 2016 that did exceed criteria.
- Diazinon was not detected at this site in 2018, but had been detected in 2016 exceeding
- Of the 4 fipronil detections, 3 were approaching the invertebrate NOAEC (0.011 μg/L).
- All 4 imidacloprid detections were approaching the invertebrate NOAEC (0.01 μg/L). Of those, 3 were also equal to 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 2018 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.

Table 10 – Indian Slough pesticide calendar (µg/L)

Month		M	ar		Apr			A	ug		Se	ер	
Day of the Month	Use*	19	26	2	9	16		21	27	5	10	18	24
2,4-D	H	.0		0.028		0.013						.0	
2,6-Dichlorobenzamide	D	0.210	0.162		0 175	0.204		0.042	0.057	0.059	0.041	0.004	0.002
4,4'-DDD	D	0.210		0.196	0.175	0.204	<		0.002			0.094	0.002
4,4'-DDE	D D			0.002	0.002	0.001		0.003	0.002	0.002	0.002		0.003
4-Nitrophenol	D D	0.002	0.002	0.002	0.002				0.092				
Atrazine	H	0.006	0.005	0.006		0.010			0.092				
	<del>п</del> F				0.012	0.010	<	0.007		0.007	0.000	0.010	0.000
Azoxystrobin Boscalid	F					0.011			0.007				
Bromacil	<u>г</u> Н	0.005		0.006	0.010	0.016	<	0.008				0.005	
Chlorantraniliprole	п		0.007	0.010		0.004			0.004	0.005	0.004	0.005	0.005
Chlorothalonil	F			0.010		0.021				0.003			
		0.000	0.004				$  \rangle$			0.003			0.004
Chlorpropham	Η	0.006	0.004				<				0.000	0.000	0.001
Chlorpyrifos				0.040	0.000	0.000					0.003	0.002	0.002
Clothianidin	<u> </u>	0.047		0.013	0.029	0.023							
Dacthal (DCPA)	H .:	0.017	0.000	0.040	0.040	0.004						0.000	0.000
Dichlobenil	H			0.013				0.004	0.000			0.002	
Diuron	H				0.017	0.016			0.003				0.004
Eptam	H	0.002	0.002	0.001				0.005	0.004	0.003	0.004	0.003	
Ethoprop			0.002										
Fenarimol	F								0.007				
Fipronil	I				0.009	0.007						0.005	
Fipronil disulfinyl	D			0.003									
Fipronil sulfide	D				0.005				0.003	0.003	0.003		
Fipronil sulfone	D				0.008							0.004	
Fludioxonil	F	0.022				0.003		0.006	0.005				
Hexazinone	Н					0.009			0.010	0.011	0.010	0.012	0.012
Imazapyr	Н	0.008	0.010			0.009							
Imidacloprid	I				0.018							0.009	
Methoxyfenozide	I			0.002		0.006		0.010			0.010		
Metolachlor	Н					0.046				0.002	0.002	0.003	0.003
Metribuzin	Н	0.006	0.005	0.007	0.013	0.008							
Metsulfuron-methyl	Н				0.022								
N,N-Diethyl-m-toluamide												0.005	
Oxadiazon	Н					0.003							
Pentachloronitrobenzene				0.002									
Pentachlorophenol	WP				0.012								
Prometon	Н	0.004	0.004	0.006	0.007	0.006				0.004			0.006
Propiconazole	F	0.015	0.026	0.028	0.035	0.040		0.005					
Pyriproxyfen										0.004			
Simazine	Н		0.011	0.014	0.024	0.011							
Sodium bentazon	Н								0.013				
Sulfentrazone	Н	0.011	0.013	0.020	0.019	0.017		0.007	0.008	0.009		0.006	0.010
Tebuthiuron	Н					0.042		0.045	0.045	0.051	0.045		
Terbacil	Н		0.005						0.011				
Tetrahydrophthalimide	D										0.004		
Thiamethoxam	I	0.010	0.014	0.021	0.031	0.039							
Triadimefon	F							0.002		0.003			
Triclosan	A								0.013				0.007
Trifluralin	H	0.006	0.006	0.006	0.006	0.003		0.003	3.313	3.307			3.501
Total suspended solids (						9.0	$\rightarrow$	4.0	3.0	4.0	8.0	5.0	12.0
Streamflow (cubic ft/sec)		31.7	50.2	63.1	60.2			4.05	5.86	3.71	4.73	6.78	6.81
Precipitation (total in/wee		0.39		1.16		1 49		0	0.02	0	0.33	0.78	0.20
The "" signifies a samp							or coul				0.00	0.00	0.20

Current-use exceedance DDT/degradate exceedance Detection

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent, WP: Wood Preservative)

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

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 8 of the 11 site visits (72%). Water quality at the Indian Slough site is shown below (Figure 18).

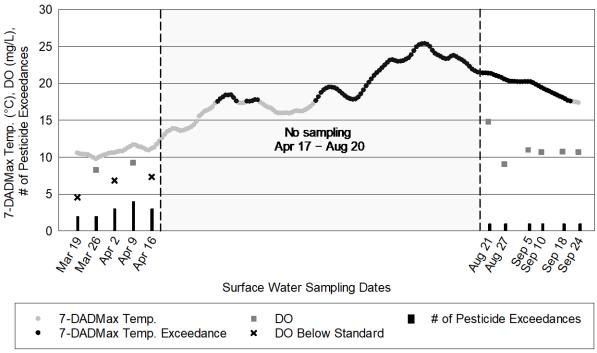


Figure 18 – Indian Slough occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria.

The pH measurements ranged from 6.58 to 8.62 and averaged 7.46. Of these measurements, 1 exceeded the state pH standard of 8.5 on August 21. DO measurements ranged from 4.54 mg/L to 14.80 mg/L with an average of 9.37 mg/L. Roughly a quarter (27%) of the measurements fell below the DO standard with 3 measurements less than 8 mg/L. All 3 of these DO measurements coincided with pesticide exceedances on March 19, April 2, and April 16. The 7-DADMax temperatures were greater than the 17.5 °C temperature standard for 110 days of the sampling season, primarily from May 11 through May 26 and from June 17 through September 21. Pesticide exceedances coincided with 7-DADMax temperature exceedances at every site visit from August 21 through September 18.

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**

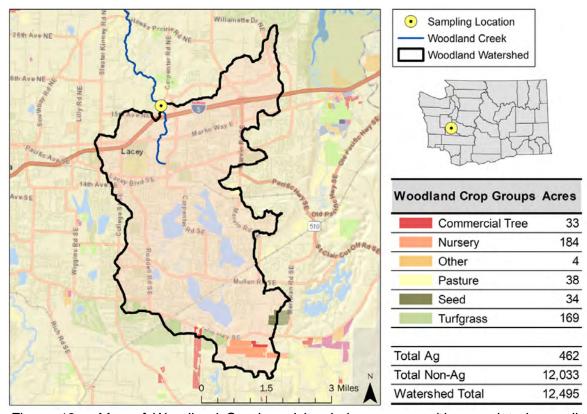


Figure 19 - Map of Woodland Creek and its drainage area with associated sampling location and crop groups identified

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 Woodland watershed is undergoing rapid urban development from prairie and wooded lands. Currently, 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 predominantly residential with a few ornamental nurseries, sod farms, golf courses, and pastures (Figure 19).



Figure 20 - 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 20).

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 campus that controls some of the streamflow upstream of the monitoring site.

The Woodland Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 11 – Woodland Creek pesticide calendar (µg/L)

Month		M	ar	Α	pr		May		Jı	ın	J	ul	Αı	ug	S	ер
Day of the Month	Use*	14	20	3	17	1	15	30	12	26	10	24	7	21	5	18
2,4-D	Н			0.013	$>\!<$		><	0.065	0.041	0.015						
2,6-Dichlorobenzamide	D	0.105	0.077	0.074	0.085	0.049	0.065					0.046	0.044	0.038	0.040	0.040
4,4'-DDD	D						0.001				0.001	0.001		0.002	0.002	
Atrazine	Н			0.004								0.003				
Boscalid	F					0.002				0.003	0.003		0.005	0.006		0.003
Dichlobenil	Н		0.003	0.002	0.006		0.003	0.002	0.002	0.001						
Difenoconazole	F							0.005			0.008					
Ethoprop	I			0.002												
Fenarimol	F		0.002	0.007						0.013	0.002	0.002		0.004		
Fenbuconazole	F							0.006								
Fipronil	I			0.002			0.002									
Fipronil sulfide	D										0.003					
Fludioxonil	F												0.004	0.005		
Hexazinone	Н		0.006	0.006	0.003				0.003	0.004	0.005	0.004			0.003	
Imazapyr	Н		0.004	0.003												
Isoxaben	Н							0.002								
Metolachlor	Н									0.001						
N,N-Diethyl-m-toluamide	IR	0.005	0.005		0.007		0.003		0.003							
Prometon	Н			0.003			0.002			0.003	0.003					
Prometryn	Н						0.002							0.005		
Pyridaben	I													0.004		
Pyriproxyfen	I										0.003	0.003		0.004		
Sulfentrazone	Н									0.006	0.002					
Triadimefon	F				0.002						0.004			0.002		
Triclosan	Α		0.010						0.004	0.015	0.003	0.003				
Trifluralin	Н				0.002											
Total suspended solids (	(mg/L)		4.0	3.0	7.0	6.0	5.0	5.0	4.0	4.0	5.0	3.0	3.0	3.0	3.0	2.0
Streamflow (cubic ft/sec)	)						25.00	19.03	17.07	14.91	13.56	10.14	8.81	8.62	8.00	8.27
Precipitation (total in/wee	_ , .		0.08		3.75	0.35	0.10	0	0.93	0.13	0.05	0	0	0	0	1.52

The "X" signifies data rejected by failing quality assurance performance measures.

Current-use exceedance DDT/degradate exceedance Detection No criteria

- WSDA tested for 144 unique pesticides in Woodland Creek.
- There were 93 total pesticide detections from 6 different use categories: 11 types of herbicides, 6 fungicides, 4 insecticides, 3 degradates, 1 antimicrobial, and 1 insect repellent.
- Pesticides were detected at all 15 sampling events.
- Up to 12 pesticides were detected at the same time.

<sup>(</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

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

- Of the total pesticide detections, 5 were above WSDA's assessment criteria (Table 11).
  - All 5 detections were of 4,4'-DDD, at concentrations equal to or exceeding NRWQC and WAC chronic criteria (both 0.001 µg/L).
- There were no watershed or statewide POCs detected in Woodland Creek.

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 3 of the 15 site visits (20%). Water quality at the Woodland Creek site is shown below (Figure 21).

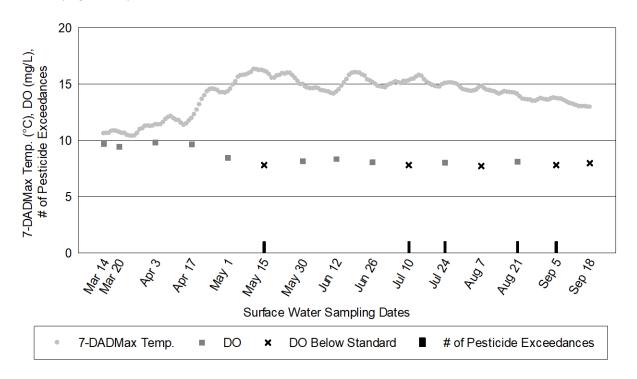


Figure 21 – Woodland Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

All pH measurements met the state water quality standard, ranging from 6.75 to 7.09 and averaging 6.95. DO measurements ranged from 7.75 mg/L to 9.82 mg/L and averaged 8.47 mg/L. Less than half (33%) of the DO measurements did not meet the standard with 5 measurements less than 8 mg/L. On May 15, July 10, and September 5, a below standard DO measurement coincided with a pesticide exceedance. None of the 7-DADMax temperatures exceeded the 17.5 °C standard throughout the sampling season.

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 continued to monitor the site through 2019 at which point it was dropped from the program due to lack of exceedances.

#### **Brender Creek**

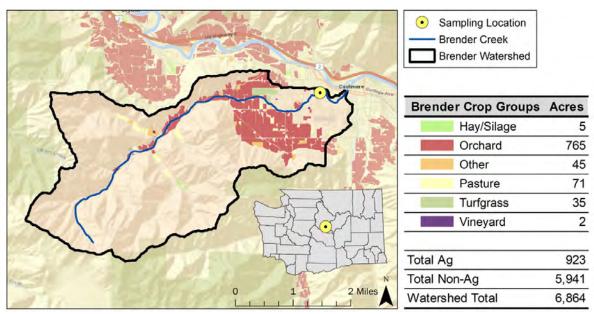


Figure 22 – Map of Brender Creek and its drainage area with associated sampling location and crop groups identified

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. DDT was widely used in orchard production until its banning in the U.S. in 1972. WSDA still detects the chemical in the Brender watershed due to the chemical's 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 22, Figure 23). Brender Creek is approximately 6.8 miles long and drains into the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence



Figure 23 - 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 in consists of fallow fields (Figure 22).

Below is a brief overview of the pesticide findings in Brender Creek in 2018.

- WSDA tested for 130 unique pesticides in Brender Creek.
- Pesticides were detected at all 24 sampling events.

- There were 267 total pesticide detections from 7 different use categories: 14 types of insecticides, 11 herbicides, 5 fungicides, 5 degradates, 1 antimicrobial, 1 insect repellent, and 1 synergist.
- Up to 20 pesticides were detected at the same time.
- Of the total pesticide detections, 89 were above WSDA's assessment criteria (Table 12).
  - o DDT and its degradates accounted for 69 of these exceedances. The 23 detections of 4,4'-DDD, 24 detections of 4,4'-DDE, and 22 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - Only 1 of the 7 etoxazole detections was approaching the invertebrate NOAEC  $(0.13 \mu g/L)$ .

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

- Only 8 of the 23 detections of chlorpyrifos exceeded assessment criteria.
  - Of these 8, 5 were greater than the NRWQC and state WAC chronic criteria (both  $0.041 \mu g/L$ ) and invertebrate NOAEC (0.04  $\mu g/L$ ).
  - o The detections on March 27, April 3, April 11, and May 1 also exceeded the NRWQC and state WAC acute criteria (0.083 µg/L) and invertebrate LC<sub>50</sub> criterion  $(0.1 \, \mu g/L)$ .
  - o On April 25, May 9, and May 15, the detections of chlorpyrifos were approaching the invertebrate NOAEC (0.04 µg/L).
- The single detection of imidacloprid was approaching the invertebrate NOAEC (0.01 µg/L).
- Of the 8 malathion detections, 3 exceeded criteria. The detections on March 27, April 3, and May 9 were above the invertebrate NOAEC (0.06 µg/L). The March 27 detection exceeded the invertebrate LC<sub>50</sub> (0.098 µg/L) and the NRWQC chronic criterion (0.1 µg/L).
- Pyridaben was detected 11 times. The detection May 22 exceeded the fish NOAEC (0.087 μg/L). Detections April 11, May 9, and May 22 exceeded the invertebrate NOAEC (0.044 µg/L). The remaining 7 detections were approaching the invertebrate NOAEC (0.044  $\mu g/L$ ).
- The 2 detections of pyriproxyfen in 2018 did not exceed any assessment criteria, but the pesticide was still classified as a watershed POC because of a 2016 detection that did exceed criteria.

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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. There were 11 herbicides, 2 herbicide degradates and a wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 12 – Brender Creek pesticide calendar (µg/L)

Month			Mar			A	pr				May				Jı	ın				Jul				Aug	
Day of the Month	Use*	13	20	27	3	11	17	25	1	9	15	22	30	5	12	19	26	2	11	17	24	31	6	14	21
2,6-Dichlorobenzamide	D	0.013	0.011	0.011	0.010	0.011	0.009	0.010	0.013	0.009	0.009	0.007	0.010	0.012	0.007	0.010	0.007	0.007	0.009	0.014	0.015	0.014	0.007	0.013	0.009
4,4'-DDD	D	0.004	0.006	0.007	0.008	0.009	0.004	0.004	0.009	0.007	0.004	0.007	0.003		0.005	0.003	0.004	0.004	0.003	0.003	0.003	0.004	0.005	0.004	0.007
4,4'-DDE	D	0.021	0.022	0.023	0.029	0.032	0.022	0.019	0.051	0.033	0.016	0.035	0.016	0.014	0.023	0.016	0.027	0.024	0.015	0.013	0.011	0.010	0.017	0.013	0.027
4,4'-DDT	1	0.007	0.007	0.004	0.006	0.006	0.004	0.002		0.011	0.004	0.005	0.004	0.003	0.004		0.009	0.008	0.006	0.005	0.005	0.004	0.006	0.005	0.008
Acetamiprid	I						0.006		0.014	0.024		0.008											0.016	0.006	
Bifenazate	I															0.022									
Boscalid	F							0.001	0.005	0.048		0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.004		0.005	0.005	0.005
Carbaryl	1									0.013															
Chlorpyrifos	ı		0.011	0.249	0.261	0.190	0.059	0.033	0.129	0.033	0.020	0.018	0.010	0.008	0.008	0.007	0.007	0.007	0.005	0.004	0.003	0.003	0.003	0.003	0.003
Diazinon	1						0.005		0.005	0.002									0.002	0.003					
	Н					0.001																			
Etoxazole	I											0.123			0.004	0.007	0.011	0.014	0.008	0.005					
	F																0.010								
Hexazinone	Н																0.003								
	Н				0.006	0.007	0.004																		
Imidacloprid	ı									0.006															
Malaoxon	D									0.011															
Malathion	ı	0.005	0.024	0.236	0.086	0.016	0.006			0.086	0.003														
Metolachlor	Н																0.001								
N,N-Diethyl-m-toluamide	IR										0.001								0.017			0.005	0.026	0.004	
		0.007		0.008	0.007		0.005	0.005	0.007	0.004	0.005	0.004	0.008	0.007	0.005	0.009	0.006	0.007	0.007	0.010	0.008	0.010	0.007	0.009	0.009
Oryzalin	Н																0.004								
Pendimethalin	Н								0.005	0.003							0.003								
Piperonyl butoxide	Sy																					0.007	0.005		
Prometon	Н										0.002						0.003			0.003	0.003				
Pyraclostrobin	F									0.005						0.010									
Pyridaben	I					0.069	0.029	0.033	0.029	0.065		0.101		0.031			0.004	0.005	0.004					0.005	
Pyriproxyfen	I																0.003				0.003				
Simazine	Н									0.007	0.006	0.040	0.058	0.010	0.010	0.011	0.005	0.009	0.006	0.007	0.005	0.006	0.005	0.006	0.005
Spirotetramat	1									0.017		0.526													
Sulfentrazone	Η			0.008	0.007	0.015	0.011	0.005	0.005	0.006	0.005		0.006	0.007			0.006	0.004	0.004	0.003		0.005		0.005	0.004
Tefluthrin	I																				0.001				
Thiamethoxam	1									0.036										0.018					
Triadimefon	F																0.002								
Triazine DIA degradate	D															0.005		0.005		0.005					
Triclosan	Α																0.012								
Trifloxystrobin	F					0.017									0.016										
Trifluralin	Н						0.002																		
Total suspended solids (	mg/L)	94.0	44.0	57.0	66.0	73.0	45.0	37.0	169.0	86.0	39.0	86.0	42.0	37.0	52.0	33.0	78.0	58.0	42.0	35.0	23.0	23.0	48.0	19.0	54.0
Streamflow (cubic ft/sec)		2.27	2.69	2.69	2.72	3.06	2.66	2.26	5.39	6.47	2.93	5.69	2.40	1.41	4.63	2.05	3.56	5.03	3.31	1.40	1.60	0.91	3.93		
Precipitation (total in/wee	k)+	0.07	0.12		0.00	0.65	0.72	0.00	0.22	0.17	0	0.76	0.00	0.00	0.14	0.09	0.01	0.01	0	0	0	0.00	0.00	0	0.00

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

DDT/degradate exceedance Detection Current-use exceedance

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

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

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 6 of the 24 site visits (25%). Water quality at the Brender site is shown below (Figure 24).

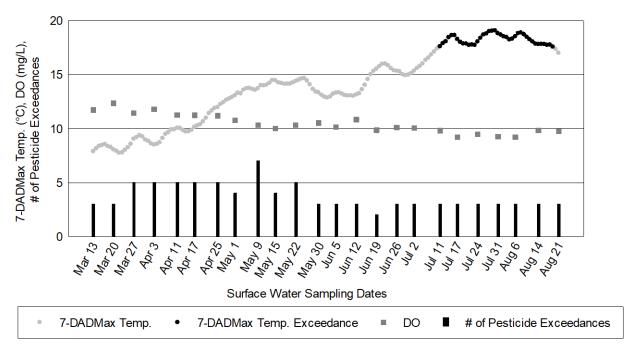


Figure 24 –Brender Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

All of the pH measurements met state standards, ranging from 7.98 to 8.34 with an average of 8.16. Also, all of DO measurements met state standards, ranging from 9.20 mg/L to 12.36 mg/L with an average of 10.44 mg/L. The 7-DADMax temperatures exceeded the 17.5 °C temperature standard for 40 days of the sampling season from July 11 through August 19. Pesticide exceedances coincided with 7-DADMax temperature exceedances at every site visit from July 11 through August 14.

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**

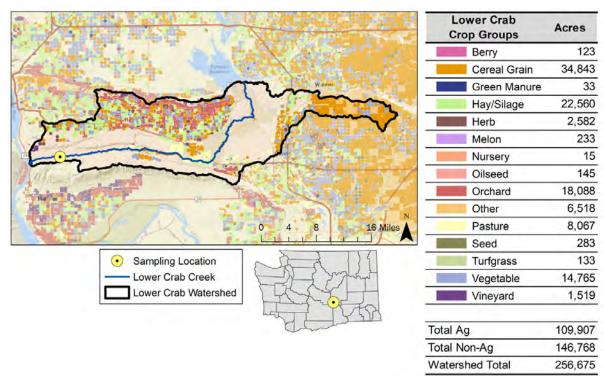


Figure 25 - Map of Lower Crab Creek and its drainage area with associated sampling location and crop groups identified

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 25).

The Columbia Basin Irrigation Project created a series of reservoirs and irrigation canals that provide Lower Crab Creek with consistent 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) (Figure 26). Data suggests the fall Chinook salmon in the



Figure 26 – Lower Crab Creek downstream view

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 includes fallow fields and land protected through conservation programs (Figure 25).

The Lower Crab Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 13 – Lower Crab Creek pesticide calendar (µg/L)

Month		Mar	Α	pr		May		Jı	ın	J	ul	Αι	ıa	Se	ер
Day of the Month	Use*	20	3	17	1	15	30	12	26	11	24	6	21	4	17
2.4-D	Н		0.017	0.023	0.038	0.128	0.263	0.218	0.130	0.305	0.223	0.158	0.227	0.059	0.065
2,6-Dichlorobenzamide	D	0.007	0.005	0.003	0.004	0.004	0.003	0.003	0.003	0.003	0.220	0.002	0.003	0.004	0.003
Atrazine	Н	0.011	0.008	0.012	0.011	0.008	0.008	0.011	0.000	0.000	0.011	0.009	0.008	0.008	0.007
Boscalid	F	0.004	0.010	0.005	0.006	0.000	0.014	0.006	0.009	0.013	0.011	0.014	0.014	0.011	0.010
Bromacil	Н	0.011	0.014	0.027	0.022	0.013	0.011	0.011	0.016	0.015	0.010	0.011	0.011	0.010	0.008
Carbaryl	ī			0.0				0.006							0.000
Carbendazim	F											0.011	0.010	0.009	0.003
Chlorantraniliprole	ı			0.003					0.002		0.002	0.003	0.002		
Chlorothalonil	F													0.006	
Chlorpyrifos	I	0.016	0.016	0.011	0.005	0.004	0.003	0.002	0.002			0.002			
Chlorsulfuron	Н							0.069					0.018		
Dacthal (DCPA)	Н	0.055	0.136	0.322	0.114	0.159	0.350	0.185	0.189	0.241	0.217	0.230	0.295	0.266	0.197
Dicamba acid	Н				0.027	0.060	0.035	0.027	0.014	0.020	0.016	0.012	0.038	0.021	0.010
Dichlobenil	Н		0.002				0.002								
Dimethoate	I											0.015	0.004	0.011	
Diuron	Н	0.030	0.208	0.090	0.048	0.024	0.027	0.019	0.015	0.011	0.007	0.006	0.005	0.004	0.010
Eptam	Н				0.005	0.018	0.013	0.015	0.008	0.006	0.002	0.004	0.003	0.005	0.003
Ethoprop	I			0.015	0.008	0.003									
Fenarimol	F								0.002						
Hexazinone	Н	0.011	0.009	0.008	0.012		0.007	0.007	0.006	0.007	0.007	0.008		0.008	0.008
Imazapyr	Н	0.041	0.044	0.034	0.037	0.020	0.023	0.012	0.018	0.019					
Isoxaben	Н							0.002							
Methomyl	1					0.013	0.006		0.004	0.005					
Metolachlor	Н		0.004		0.004	0.003	0.006	0.012	0.007	0.005	0.004	0.003	0.002	0.002	0.002
Metribuzin	Н			0.002	0.003	0.002			0.004	0.006			0.004	0.004	
Metsulfuron-methyl	Н					0.012		0.074							
N,N-Diethyl-m-toluamide	IR	0.007	0.006	0.004		0.003		0.005				0.007			0.003
Norflurazon	Н			0.004		0.002	0.002								
Oxamyl oxime	D									0.012					
Pendimethalin	Н	0.005		0.005	0.005	0.004	0.003		0.004	0.004				0.005	
Prometryn	Н								0.013						
Pyrimethanil	F									0.007					
Sodium bentazon	Н					0.017	0.053			0.018		0.032	0.033	0.027	0.028
Sulfentrazone	Н								0.004						
Terbacil	Н		0.039	0.010	0.013	0.012	0.042	0.022	0.013	0.008	0.009	0.009	0.005	0.005	0.006
Triadimefon	F								0.002						
Triazine DEA degradate	D	0.010	0.009	0.007	0.009	0.008	0.009	0.009	0.010	0.012	0.008	0.009	0.008	0.008	0.008
Triazine DIA degradate	D									0.005	0.006	0.006			
Trifluralin	Н					0.003									
Total suspended solids (r	mg/L)	23	28	30	53	40	44	47	72	28	41	71	48	12	9
Streamflow (cubic ft/sec)			232.00	276.00	187.00	204.00	172.00	184.00	168.00	132.00	107.00			239.00	
Precipitation (total in/weel	k)†	0.05	0	0.21	0.15	0.03	0	0.07	0	0	0	0	0	0	0.09

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



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

<sup>\* (</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

- WSDA tested for 144 unique pesticides in Lower Crab Creek.
- There were 254 total pesticide detections from 5 different use categories: 22 types of herbicides, 6 fungicides, 6 insecticides, 4 degradates, and 1 insect repellent.
- Pesticides were detected at all 14 sampling events.
- Up to 22 pesticides were detected at the same time.
- None of the pesticide detections exceeded WSDA's assessment criteria (Table 13).

Malathion was the only watershed POC at this site. It was not detected in 2018 but was detected in 2017 exceeding assessment criteria. There were 9 detections of chlorpyrifos, a statewide POC; none of which exceeded assessment criteria.

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. With no exceeding pesticide detections at Lower Crab Creek, this did not happen. Water quality at the Lower Crab Creek site is shown below (Figure 27).

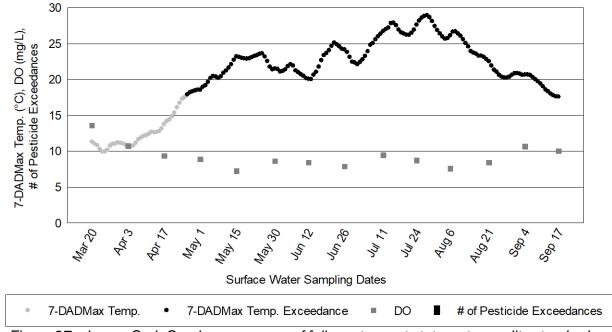


Figure 27 – Lower Crab Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 8.02 to 8.59 with an average of 8.31. Of these measurements, 1 exceeded the state standard of 8.5 on March 20. All of the DO measurements met the state standard, ranging from 7.23 mg/L to 13.58 mg/L with an average of 9.25 mg/L. The 7-DADMax temperatures exceeded the 17.5 °C standard for 145 days of the sampling season, from April 26 through September 17.

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 2019, at which point it will be evaluated for continued monitoring efforts.

### **Marion Drain**

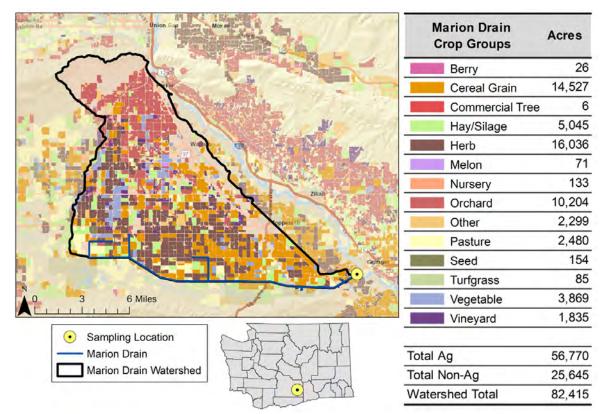


Figure 28 - Map of Marion Drain and its drainage area with associated sampling location and crop groups identified

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 28, Figure 29). 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 aquatic vegetation growing in the streambed in 2018. WDFW and the



Figure 29 – Marion Drain upstream view

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 tilled and idle fallow fields (Figure 28).

Samples were collected at this site in the spring and summer and again in the late fall because of historically 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 2018.

- WSDA tested for 144 unique pesticides in Marion Drain.
- There were 509 total pesticide detections from 6 different use categories: 20 types of herbicides, 12 insecticides, 8 fungicides, 5 degradates, 1 antimicrobial, and 1 insect repellent.
- Pesticides were detected at all 29 sampling events.
- Up to 26 pesticides were detected at the same time.
- Of the total pesticide detections, 17 were above WSDA's assessment criteria (Table 14).
  - o The 3 detections of 4,4'-DDD and 2 detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Only 1 chlorpyrifos detection out of 15 was approaching the invertebrate NOAEC (0.04
- Of the 29 detections of clothianidin, 9 were approaching the invertebrate NOAEC (0.05 μg/L).
- The 2 detections of imidacloprid were approaching the invertebrate NOAEC (0.01 µg/L).
- Malathion was detected 3 times below any assessment criteria at this site in 2018, but had been detected in 2016 exceeding criteria.
- Tefluthrin was not detected at this site in 2018, but the pesticide is still considered a watershed POC due to a 2017 detection that did exceed criteria.

The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 14 – Marion Drain pesticide calendar (μg/L)

Day of the Month  2,4-D  4,4-Dichlorobenzamide  4,4-DDD  A,4-DDE  D  Atrazine  H  Azoxystrobin  Bromacil  Bromacil  H  Bromoxynil  Carbaryl  I  Chlorantraniliprole  I  Chlorpyrifos  I  Clothianidin  I  Diazinon  I  Dicamba acid  H  Dicamba acid  H  Dimethoate  I  Diuron  H	0.1	0.011	.007	.010 (	0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.038	0.009 0.007 0.040 0.006 0.003	0.009 0.009 0.050 0.011	0.016 0.008 0.029	0.001 0.005 0.005 0.005	0.001 0.004 0.006	0.005	0.002 0.005 0.008	0.006		0.004	0.005	0.022	0.006	0.029	0.005	0.005	13 0.074 0.002 0.005	0.001	0.002 0.004 0.014	0.002 0.002 0.004 0.012			0.002 0.005 0.006	
2,4-D	0.1	0.011	.007	.010 (	0.002 0.001 0.007 0.004 0.045 0.007 0.007	0.002 0.006 0.005 0.058	0.004 0.005 0.004 0.005	0.015 0.011 0.009 0.007 0.040 0.006 0.003	0.031 0.009 0.009 0.050 0.011	0.016 0.008 0.029	0.001 0.005 0.005	0.037 0.001 0.004 0.006	0.034	0.002 0.005 0.008	0.002 0.006 0.012	0.036	0.019	0.005	0.068	0.079	0.029	0.026	0.005	0.074 0.002 0.005	0.043 0.001 0.005	0.002 0.004 0.014	0.002 0.002 0.004 0.012		0.005	0.002	
1,4 - DDD	0.1	0.	.005	.010 (	0.001 0.007 0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.005 0.038 0.004 0.005	0.011 0.009 0.007 0.040 0.006 0.003	0.009 0.009 0.050 0.011	0.016 0.008 0.029	0.001 0.005 0.005	0.001 0.004 0.006	0.005	0.002 0.005 0.008	0.002 0.006 0.012		0.004	0.005	0.022	0.006	0.005	0.005	0.005	0.002	0.001	0.002 0.004 0.014	0.002 0.002 0.004 0.012				
4,4'-DDD	0.1	0.	.005	.010 (	0.001 0.007 0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.005 0.038 0.004 0.005	0.009 0.007 0.040 0.006 0.003	0.009 0.050 0.011 0.005	0.008	0.005 0.005	0.004	0.006	0.005	0.006	0.016								0.005	0.005	0.004	0.002				
4,4'-DDE	0.1	0.	.005	.010 (	0.007 0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.005 0.038 0.004 0.005	0.009 0.007 0.040 0.006 0.003	0.009 0.050 0.011 0.005	0.008	0.005	0.004	0.006	0.008	0.012	0.016										0.014	0.012				
Atrazine H Azoxystrobin F Boscalid F Bromacil H Bromoxynil H Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate	0.	0.	.005	.010 (	0.007 0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.005 0.038 0.004 0.005	0.009 0.007 0.040 0.006 0.003	0.009 0.050 0.011 0.005	0.008	0.005	0.006	0.006	0.008	0.012	0.016										0.014	0.012	$\geq$			
Azoxystrobin F Boscalid F Bromacil H Bromoxynil H Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I	0.1	0.	.005	.010 (	0.004 0.045 0.007 0.007	0.005 0.058 0.005	0.005 0.038 0.004 0.005	0.009 0.007 0.040 0.006 0.003	0.009 0.050 0.011 0.005	0.008	0.005	0.006	0.006	0.008	0.012	0.016										0.014	0.012	$\leq$			
Boscalid F Bromacil H Bromoxynil H Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I	0.1		.005	.010 (	0.045	0.058	0.038 0.004 0.005	0.007 0.040 0.006 0.003	0.009 0.050 0.011 0.005	0.008						0.016	0.040					0.000	0.014	0.012	0.014			$\leq$	0.006	0.006	0.00
Bromacil H Bromoxynil H Carbaryl I Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I	0.		.005	.010 (	0.045	0.058	0.038 0.004 0.005	0.040 0.006 0.003	0.050 0.011 0.005	0.029	0.007						111117	0.012	0.003	0.010	0 010	11 (120						>	0.000	0.000	0.00
Bromoxynil H Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I	0.		.005	.010 (	0.007	0.005	0.004 0.005	0.006 0.003	0.011		0.007	0.000	0.004		0.006		0.004		0.003	0.003	0.013	0.023	0.011	0.005		0.003	0.004				
Carbaryl I Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I	0.		.005	.035	0.027		0.005	0.003	0.005	0.006				0.000	0.000	0.000	0.001	0.004		0.000				0.000	0.001	0.000	0.004	<			
Chlorantraniliprole I Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I			.005	.035	0.027		0.005	0.003		0.006												0.011		0.013	0.010			>			
Chlorpyrifos I Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I			.005	.035	0.027		0.005	0.003			0.004	0.005		0.004	0.009	0.007	0.006	0.007	0.012	0.007	0.007		0.006	0.004			0.008	<	0.015	0.012	0.01
Clothianidin I Diazinon I Dicamba acid H Dichlobenil H Dimethoate I				.035			0.000	0.000	10000	0.007	0.004		0.015		0.003		0.004			0.007	0.007	0.000	0.000	0.004	0.003		0.000	>	0.013	0.012	0.01
Diazinon I Dicamba acid H Dichlobenil H Dimethoate I		.014 0.	.030 0.		0.017	0.013		0.008							0.003	0.002			0.025		0.020	0.022	0.024	0.018	0.010	0.018	0.020	<	0.033	0.033	0.03
Dicamba acid H Dichlobenil H Dimethoate I								0.000	0.003	0.000	0.000	0.010	0.013	0.000	0.010	0.030	0.023	0.023	0.023	0.023	0.020	0.022	0.024	0.010	0.013	0.002		>	0.033	0.033	0.03
Dichlobenil H Dimethoate I									0.010	0.017			0.012		0.025		0.012	0.014	0.012	0.010	0.010			0.010		0.002		<			
Dimethoate I				(	0.001				0.016	0.017	0.002		0.012	0.002			0.012	0.014	0.013	0.019	0.010	0.005	0.001			0.005		>			
			I		0.001					0.002	0.003			0.002		0.005						0.005	0.001	0.009		0.003		<			
Ulululi			_	(	0.012	0.016	0.011	0.042	0.033	0.027	0.011	0.011	0.014	0.000	0.000		0.007	0.000	0.011	0.000	0.004	0.004	0.004	0.003	0.002		0.003	>			0.00
		-	_				0.002	0.042	0.033	0.027					0.021			0.009	0.011	0.008	0.004	0.004	0.004	0.003	0.003		0.003	<			0.00
		-				0.002	0.002			0.016	0.026	0.003	0.002	0.002	0.002	0.004	0.003											>		0.002	0.06
Ethoprop I Fenarimol F																												<		0.002	0.06
· onamino						0.000																						>		0.006	
Fipronil I	0	.004				0.002	0.000	0.040	0.011	0.000	0.000	0.005	0.004	0.044	0.015	0.000	0.006	0.000		0.008	0.007	0.040	0.007	0.007	0.000	0.000	0.000	<	0.040	0.000	0.00
Fludioxonil F			.003			0.015	0.022	0.013	0.011		0.008	0.005	0.004	0.011	0.015	0.008		0.008		0.008	0.007	0.010	0.007	0.007	0.006			>		0.006	
Hexazinone H		0.	.003					0.002		0.002					0.005			0.003		0.003						0.003		<	0.003	0.004	0.00
Imidacloprid I MCPA H								0.031							0.005												0.008	>			
Malathion I								0.031						0.005					0.005	0.000								<			
								0.000	0.002			0.001		0.005		0.001			0.005	0.003								>		$\longrightarrow$	
								0.002	0.002			0.001			0.004		0.004	0.004				0.005			0.004			<			
															0.004	0.004	0.004	0.004		0.004		0.005			0.004			>			
Myclobutanil F N,N-Diethyl-m-toluamide IR	,	-	_				0.003			0.003	0.002			0.006	0.006					0.004		0.005		0.006				<	0.002	0.000	
		005 0	000			0.000	0.003		0.000	0.003		0.000		0.006	0.006	0.004	0.004	0.004		0.004	0.004		0.004		0.004	0.005	0.005	>			0.00
		.005 0.	.006			0.006		0.007	0.003	0.050	0.003	0.003	0.040	0.040	0.045							0.004	0.004	0.004	0.004			<		0.007	0.00
		.004			800.0		0.015	0.007	0.041	0.052	0.024	0.046	0.018	0.018	0.015		0.006	0.005		0.007	0.006	0.005	0.005				0.005	>	0.004	0.004	0.00
Prometon H								0.040		0.044	0.040	0.000	0.000			0.003	0.000			0.003				0.004		0.004	0.004	<	0.004	0.004	0.004
Propiconazole F								0.016		0.014	0.010	0.008	0.009				0.006									0.000		>			
Pyridaben I Pyrimethanil F					0.000		0.007	0.005		0.005					0.000		0.000	0.000	0.000	0.007						0.003		<			
i yiiiiicaiaiii			244	(	800.0		0.007	0.005		0.005					0.008		0.008		0.006	0.007								>			0.00
Simazine H		.009 0.	.011					0.033	0.014	0.020				0.005	0.006		0.005		0.004		0.005		0.005		0.010		0.005	<		0.006	
Sodium bentazon H								0.007	0.007	0.000		0.000	0.047		0.016						0.028			0.027				$\rightarrow$	0.012		0.013
Sulfentrazone H									0.024		0.446		0.012		0.007		0.005				0.000	0.012		0.006				<		0.006	
Terbacil H				000				0.037	0.417	0.606	0.119	0.180				0.072	0.058				_	-		0.051			-	>		0.008	
Thiamethoxam I			0.	.009					-			<b>-</b>	<b> </b>	0.005	0.013	0.025	0.012	0.011	0.008	0.010	0.011	0.012	0.011	0.009	0.011	0.014	0.025	<		0.047	0.04
Triadimefon F				000					0.004										0.000				0.004	0.004			0.004	$\rightarrow$		0.003	
Triazine DEA degradate D		.002 0.	.009 0.0	.009 (	0.005	0.005		0.005	0.004	0.004	0.005	0.005	0.006	0.004	0.005		0.006	0.005			0.003	0.004		0.004	0.004	0.004	0.004	<	0.006	0.006	0.00
Triazine DIA degradate D																0.006			0.005	0.005			0.005				<b> </b>			0.000	
Triclosan A						0.071	0.000					0.53	0.00		0.0	0.00									0.071		1	<		0.009	
Trifluralin H							0.002		L_	0.009	0.006				0.004	0.004		0.003				0.003			0.003		<b>├</b>	$\rightarrow$			
Total suspended solids (mg					20.0		35.0	4.0	3.0	8.0	4.0	5.0	1.0	7.0	5.0	5	3.0	3.0	2.0	3.0	3.0	4.0	5.0	6.0	16.0	10.0			3.0		
Streamflow (cubic ft/sec)					234.8			35.54		31.47		51.44		25.91	37.28		26.61					30.22	41.73				41.3			17.08	
Precipitation (total in/week)					_	0.52		0	0			0.03	0.04	0.02	0.16	0.09	0.05	0	0.01	0.01	0.03	0.03	0.01	0.01	0.14	0	0.01		0	0.34	0.03
The "" signifies a sample	or mea	sureme	ent that wa	as not o	collecte	ed or c	ould no	ot be an	alyzed.				<u>ر</u>	rront		2400	edanc			Ъг	T/de	arodo	to co	,,,,,,	long	<u>,</u>		Do	tectio	an.	

<sup>\* (</sup>A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)
† Washington State University AgWeatherNet station: Toppenish, (latitude: 46.37°, longitude: -120.39°)

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet the state water quality standard at 7 of the 29 site visits (24%). Water quality at the Marion Drain site is shown below (Figure 30 and Figure 31).

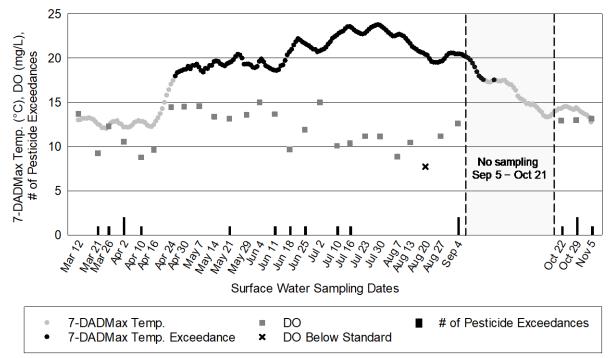


Figure 30 – Marion Drain occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

DO measurements ranged from 7.72 mg/L to 15.02 mg/L with an average of 11.92 mg/L. Of these measurements, 1 fell below the state standard of 8 mg/L on August 20. The 7-DADMax temperatures exceeded the 17.5 °C standard for 145 days of the sampling season, from April 26 through September 16 and on September 21. The temperature exceedance on August 20 coincided with the single DO measurement that fell below the state standard. Pesticide exceedances overlapped with temperature exceedances at 7 site visits: May 21, June 11, June 18, June 25, July 10, July 16, and September 4.

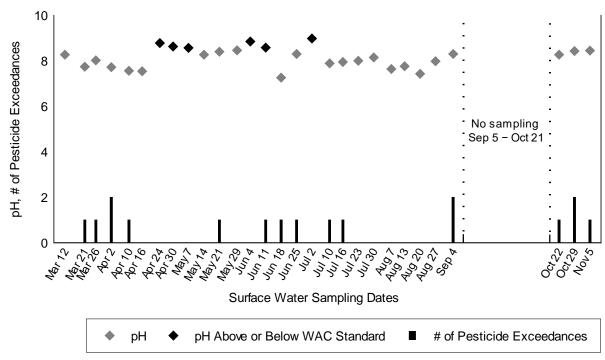


Figure 31 – Marion Drain occurrences of failures to meet state pH standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 7.26 to 8.98 with an average of 8.14. Less than a quarter (21%) of these measurements fell below the state water quality standard in that 6 measurements were above 8.5. These exceedances occurred primarily in the first half of the sampling season. On June 11, the pH exceedance coincided with both a pesticide exceedance and a 7-DADMax temperature exceedance. Four other pH exceedances on April 30, May 7, June 4, and July 2 also overlapped with 7-DADMax temperature exceedances.

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

### **Mission Creek**

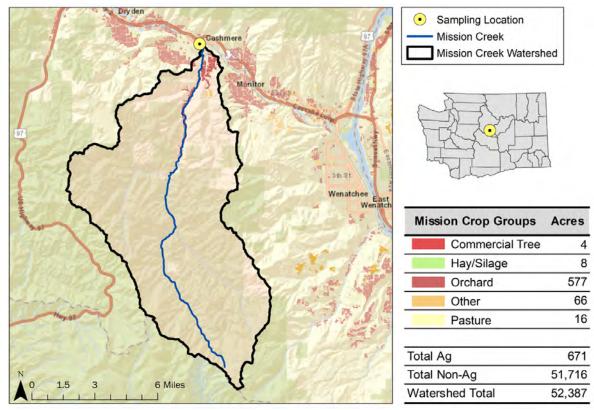


Figure 32 – Map of Mission Creek and its drainage area with associated sampling location and crop groups identified

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 Ecology manages a stream gauging station (latitude: 47.5212°, longitude: -120.4760°) (Figure 32).

Mission Creek Brender water joins Creek approximately 130 meters upstream of its confluence with the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. WDFW has documented summer spawning of steelhead at the headwaters of Mission Creek (WDFW, 2019). Staff at the site frequently observed juvenile fish of unknown species (Figure 33).



Figure 33 – Mission Creek downstream view

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. The 'Other' crop group category consists of fallow fields (Figure 32).

The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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. In addition, there were 19 herbicides, 4 herbicide degradates, 15 insecticides, 4 insecticide degradates, 11 fungicides, and a wood preservative removed from testing at the site as a result of uncommon historic detections.

Table 15 – Mission Creek pesticide calendar (µg/L)

Month			Mar			Α	pr		May
Day of the Month	Use*	13	20	27	3	11	17	25	1
2,6-Dichlorobenzamide	D		0.003		0.002				
4,4'-DDD	D					0.003			
4,4'-DDE	D		0.001	0.001	0.002	0.003			0.004
Boscalid	F								0.001
Chlorpyrifos	I		0.070	0.615	0.055	0.019	0.014	0.005	0.006
Dichlobenil	Н				0.001				
Hexazinone	Н	0.013	0.014	0.013	0.012	0.006	0.004	0.005	
Malathion	I	0.013	0.019	0.242	0.030		0.008		0.002
N,N-Diethyl-m-toluamide (DEET)	IR				0.003				
Norflurazon	Н	0.004	0.006	0.005					
Pendimethalin	Н						0.005		0.004
Piperonyl butoxide (PBO)	Sy			0.022					
Prometon	Н		0.003						
Pyridaben	I					0.048	0.029		
Total suspended solids (mg/L)		4.0	5.0	7.0	5.0	35.0	27.0	11.0	48.0
Streamflow (cubic ft/sec)		24.3	34.1	36.2	39.1	89.9	74.4	51.0	62.9
Precipitation (total in/week)†		0.07	0.12	0.44	0	0.65	0.72	0	0.22

- Current-use exceedance DDT/degradate exceedance Detection
- WSDA tested for 90 unique pesticides in Mission Creek.
- There were 40 total pesticide detections from 6 different use categories: 5 types of herbicides, 3 insecticides, 3 degradates, 1 fungicide, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 8 sampling events.
- Up to 7 pesticides were detected at the same time.
- Of the total pesticide detections, 13 were above WSDA's assessment criteria (Table 15).
  - The single detection of 4,4'-DDD and 5 detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - The pyridaben detection, April 17, was approaching the invertebrate NOAEC (0.044 µg/L). The April 11 detection exceeded the invertebrate NOAEC (0.044  $\mu$ g/L).

<sup>(</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent, Sy: Synergist)

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

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

- Of the 7 chlorpyrifos detections, 3 exceeded assessment criteria.
  - All 3 exceeding detections were greater than the NRWQC and state WAC chronic criteria (both 0.041 µg/L) and the invertebrate NOAEC (0.04 µg/L).
  - The March 27 detection was above the fish NOAEC (0.57 µg/L), NRWQC and state WAC acute criteria (both 0.083 µg/L), and invertebrate LC<sub>50</sub> criterion (0.1 μg/L).
- Only 2 of the 6 malathion detections exceeded criteria. The March 27 detection was greater than the invertebrate LC<sub>50</sub> (0.098  $\mu$ g/L), invertebrate NOAEC (0.06  $\mu$ g/L), and the NRWQC chronic criterion (0.1 µg/L). The April 3 detection was approaching the invertebrate NOAEC (0.06 µg/L).
- Imidacloprid was one of the pesticides not tested for at this site in 2018, but exceeded assessment criteria in 2017 and 2016.

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 2 of the 8 site visits (25%). Water quality at the Mission Creek site is shown below (Figure 34 and Figure 35).

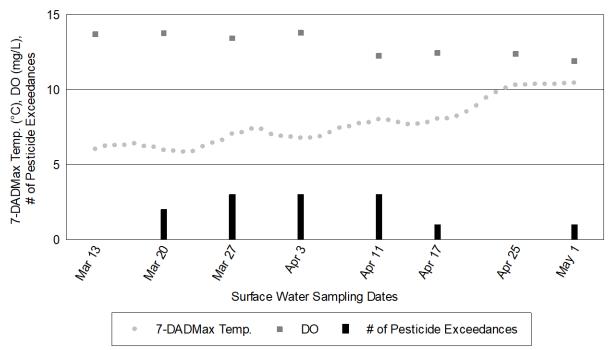


Figure 34 – Mission Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

All DO measurements met the state standard, ranging from 11.91 mg/L to 13.80 mg/L with an average of 12.97 mg/L. All 7-DADMax temperatures throughout the 2018 sampling season met the state standard by not exceeding 17.5 °C.

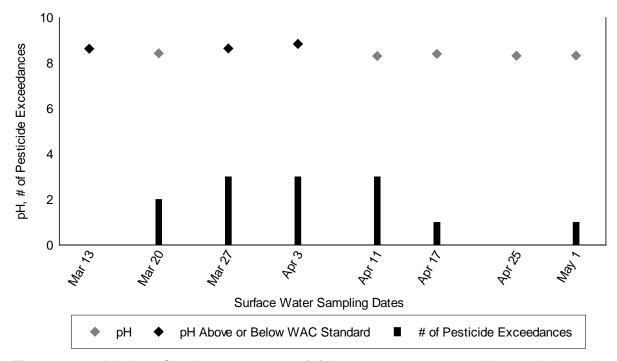


Figure 35 - Mission Creek occurrences of failures to meet state pH standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 8.31 to 8.84 with an average of 8.49. Less than half (38%) of these measurements fell below the state standard with 3 measurements exceeded 8.5. Two of these measurements coincided with 3 pesticide exceedances on March 27 and April 3.

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**

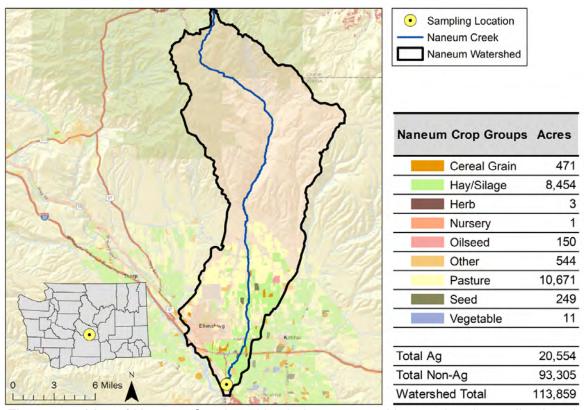


Figure 36 – Map of Naneum Creek and its drainage area with associated sampling location and crop groups identified

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



Figure 37 – Naneum Creek downstream view

agricultural 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 (Figure 36).

The Naneum Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 16 – Naneum Creek pesticide calendar (µg/L)

Month		M	ar	Ap	or	M	ay	Jı	ın		Jul		Α	ug	Se	ер	0	ct
Day of the Month	Use*	13	27	11	25	9	22	5	19	2	17	31	14	27	10	24	8	22
2,4-D	Н				0.259	0.324	0.153	0.111	0.076	0.163	0.421	0.143	0.119	0.059	0.276	0.077	0.142	
2,6-Dichlorobenzamide	D					0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.002	0.002		0.001	
4,4'-DDD	D										0.001			0.002				
Atrazine	Н				0.005	0.003	0.071	0.027	0.029	0.080	0.040	0.040	0.025	0.014	0.010	0.008	0.009	0.010
Boscalid	F					0.002	0.001	0.001		0.003	0.003	0.006	0.005	0.003	0.003	0.003		0.003
Bromacil	Н					0.005	0.004											
Bromoxynil	Н															0.022	0.071	
Clopyralid	Н				0.076	0.035	0.068			0.089	0.034	0.042			0.054		0.191	
Dicamba acid	Н				0.309	0.569	0.180	0.057	0.016	0.127	0.214	0.107	0.067	0.014	0.026	0.066	0.242	
Dichlobenil	Н					0.002												
Dimethoate	I					0.007				0.007								
Diuron	Н				0.021	0.010	0.008		0.003	0.005	0.009	0.004	0.015					
Eptam	Н					0.002	0.001		0.005	0.003								
Fipronil Disulfinyl	D													0.002				
Fipronil Sulfide	D													0.003				
Hexazinone	Н			0.003		0.002				0.003	0.004	0.004	0.004	0.003	0.003	0.004		0.003
Imazapyr	Н				0.011	0.006	0.012	0.005		0.006	0.009							
MCPA	Н				0.638	0.042	0.453	0.074										
Mecoprop (MCPP)	Н														0.058			
Metolachlor	Н					0.002				0.014	0.009	0.003	0.004	0.002	0.002	0.002		
Metribuzin	Н														0.012			
N,N-Diethyl-m-toluamide	IR					0.002		0.003				0.004	0.003				0.003	
Pendimethalin	Н				0.013	0.013	0.012	0.004	0.004	0.054	0.027	0.012	0.009	0.005	0.010	0.033	0.011	0.005
Prometon	Н										0.003						0.003	
Terbacil	Н									0.003								
Triazine DEA degradate	D		0.003		0.004	0.003	0.008	0.008	0.007	0.029	0.026	0.018	0.014	0.007	0.008	0.007	0.008	0.008
Triazine DIA degradate	D										0.007	0.007						
Triclopyr acid	Н				0.872	0.056	0.079	0.022	0.037	0.052	0.063	0.042			0.016		0.132	
Trifluralin	Н					0.002												
Total suspended solids (	(mg/L)	6.0	5.0	42.0	25.0	52.0	23.0	42.0	26.0	12.0	8.0	9.0	12.0	10.0	7.0	5.0	6.0	1.0
Streamflow (cubic ft/sec)	)	48.78	52.29	124.3	91.66		99.89	101.7	98.55	51.86	53.51	60.96		101.8	77.13	70.54	98.51	39.95
Precipitation (total in/wee	ek)†	0.01	0.15	0.33	0	0.37	0	0	0.16	0	0	0	0	0	0	0.01	0.18	0

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

Current-use exceedance DDT/degradate exceedance Detection

- WSDA tested for 144 unique pesticides in Naneum Creek.
- There were 173 total pesticide detections from 5 different use categories: 20 types of herbicides, 6 degradates, 1 fungicide, 1 insecticide, and 1 insect repellent.
- Pesticides were detected at 16 (94%) of the 17 sampling events.
- Up to 20 pesticides were detected at the same time.
- Of the total pesticide detections, 2 were above WSDA's assessment criteria (Table 16).
  - $_{\odot}$  Both detections were 4,4'-DDD and were equal to or exceeded the NRWQC and WAC chronic criteria (both 0.001  $\mu g/L).$
- There were no watershed or statewide POCs detected in Naneum Creek.

<sup>(</sup>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°)

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. A pesticide exceedance coincided with a failure to meet state water quality standards at 1 of the 17 site visits (6%). Water quality at the Naneum Creek site is shown below (Figure 38).

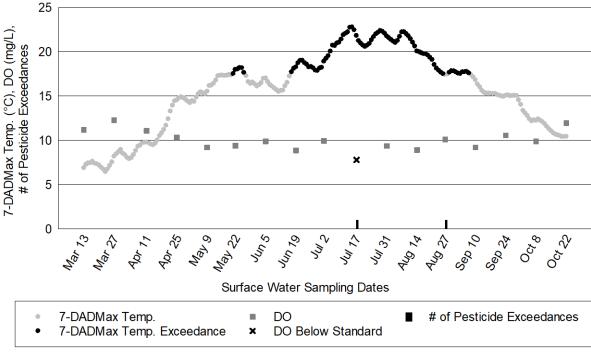


Figure 38 – Naneum Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria.

All pH measurements met the state water quality standard, ranging from 7.36 to 8.09 with an average of 7.69. DO measurements ranged from 7.79 mg/L to 12.27 mg/L with an average of 9.99 mg/L. Of these measurements, 1 fell below the standard of 8 mg/L on July 17. The 7-DADMax temperatures exceeded the 17.5 °C standard for 87 days of the sampling season, primarily from May 21 through May 26 and June 17 through September 7. On July 17, a pesticide exceedance coincided with both a DO failure and 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 continued to monitor the site through 2019 at which point it was dropped from the program due to lack of exceedances.

# **Snipes Creek**

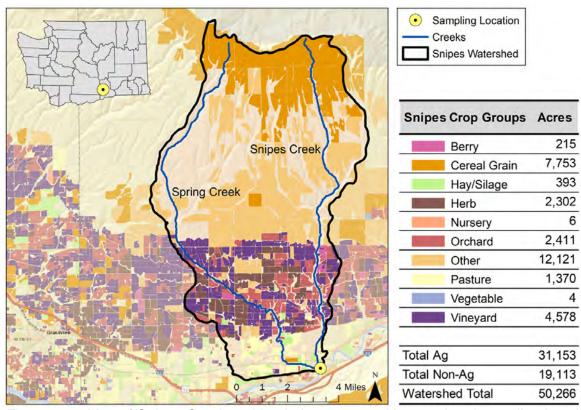


Figure 39 – Map of Snipes Creek and its drainage area with associated sampling location and crop groups identified

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 annually 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).



Figure 40 – Snipes Creek upstream view with average streamflow

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

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 fallow fields and Conservation Reserve Program lands (CRP) (Figure 39).

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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. Staff collected samples at Snipes Creek only during early spring, summer and fall due to historically few detections during the late spring, summer and fall.

Table 17 – Snipes Creek pesticide calendar (µg/L)

Month				lar				Apr			M	ay		Jun		Aı	ug
Day of the Month	Use*	7	12	21	26	2	10	16	24	30	21	29	4	11	18	7	13
	Н						0.374	0.066	0.447	0.059	0.059	0.097	0.057	0.141	0.100	0.071	0.046
2,6-Dichlorobenzamide	D	0.025	0.027	0.013		0.006	0.005	0.003	0.004	0.004	0.003	0.004	0.006	0.004	0.004	0.007	0.005
4,4'-DDD	D			0.002							0.001	0.001		0.001		0.003	0.002
4,4'-DDE	D			0.002	0.002	0.002	0.002			0.002	0.002	0.002	0.002	0.001		0.002	0.001
Atrazine	Н	0.018	0.019	0.013		0.005	0.006	0.003	0.004					0.004	0.004	0.005	0.004
Boscalid	F	0.005	0.006	0.009	0.007	0.006	0.006	0.004	0.011	0.010	0.005	0.007	0.015	0.010	0.017	0.025	0.012
Bromacil	Н							0.005	0.003	0.004	0.005		0.006		0.003		
Carbaryl	I									0.010							
Chlorantraniliprole	I	0.009			0.003		0.003		0.003	0.003	0.002	0.003	0.004		0.005		
Chlorpyrifos	I			0.070	0.099	0.110	0.147	0.066	0.020	0.015	0.007	0.003	0.887	0.024	0.017		0.002
Diazinon	I										0.001				0.004	0.002	0.005
Dicamba acid	Н									0.010							
Dichlobenil	Н			0.005	0.004	0.005	0.004	0.003	0.002			0.003	0.003	0.002		0.002	0.007
Dimethoate	I														0.006		
Diuron	Н	0.005		0.021	0.038	0.034	0.039	0.014	0.014	0.012	0.009	0.004	0.004	0.005	0.005		
Eptam	Н										0.001			0.002	0.004		
Fenarimol	F														0.001		
Fludioxonil	F		0.007			0.009	0.011	0.007	0.006	0.010	0.004	0.005	0.012	0.019	0.008	0.009	0.006
Hexazinone	Н			0.003	0.005			0.001	0.001						0.003		
Imidacloprid	I											0.007	0.228	0.046	0.029	0.011	0.007
Malathion	I														0.216		
Methoxyfenozide	I	0.005															
Metolachlor	Н									0.002			0.002	0.002	0.001		
Metribuzin	Н				0.007												
N,N-Diethyl-m-toluamide	IR					0.004		0.002					0.007	0.006			0.005
Norflurazon	Н	0.011	0.011	0.008	0.007	0.026	0.012	0.006	0.005	0.008	0.004	0.004	0.005	0.003	0.006	0.006	0.006
Pendimethalin	Н	0.003		0.008	0.011	0.013	0.022	0.011	0.009	0.010	0.005	0.006	0.004	0.003	0.005	0.004	0.004
Phosmet	I														0.005		
Prometon	Н			0.003													
Pyridaben	I															0.005	
Pyrimethanil	F													0.006			
Simazine	Н	0.008	0.009	0.010			0.012	0.007		0.015		0.008	0.005		0.004		0.006
Sulfentrazone	Н	0.026		0.007											0.004	0.005	
Terbacil	Н	0.005								0.003						0.004	
Thiamethoxam	I													0.071			
Triazine DEA degradate	D	0.023	0.013	0.009	0.003	0.004			0.003	0.003	0.003	0.003	0.004	0.004	0.005	0.003	0.004
Triclopyr acid	Н									0.015							
Trifluralin	Н			0.006	0.006			0.002									
Total suspended solids (	(mg/L)	9.0	6.0	31.0	30.0	41.0	21.0	22.0	19.0	28.0	47.0	54.0	102.0	28.0	17.0	14.0	15.0
Streamflow (cubic ft/sec)	)	2.61	2.71	14.07		60.7			54.29	83.99		74.67	50.9	78.69	51.8	44.00	
Precipitation (total in/wee	k)†	0.04	0.01	0.07	0.12	0	0.54	0.42	0	0.02	0	0.00	0	0.1	0.00	0	0

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



<sup>(</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

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

- WSDA tested for 144 unique pesticides in Snipes Creek.
- There were 240 total pesticide detections from 5 different use categories: 18 types of herbicides, 11 insecticides, 4 fungicides, 4 degradates, and 1 insect repellent.
- Pesticides were detected at all 16 sampling events.
- Up to 23 pesticides were detected at the same time.
- Of the total pesticide detections, 32 were above WSDA's assessment criteria (Table 17).
  - The 6 detections of 4,4'-DDD and 11 detections of 4,4'-DDE were equal to or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the 13 chlorpyrifos detections, 8 exceeded assessment criteria.
  - The detections on March 21, March 26, April 2, April 10, April 16, and June 4 were greater than the NRWQC and state WAC chronic criteria (both 0.041 µg/L) and the invertebrate NOAEC (0.04 µg/L).
  - o The detections on April 2, April 10, and June 4 also exceeded the NRWQC and state WAC acute criteria (0.083 µg/L) and the invertebrate LC<sub>50</sub> criterion (0.1 µg/L).
  - o The detection, June 4, was above the fish NOAEC (0.57 μg/L). This detection was also the highest chlorpyrifos concentration detected in 2018.
  - o On April 24 and June 11, the chlorpyrifos detections were approaching the invertebrate NOAEC (0.04 µg/L).
- There were 6 detections of imidacloprid. The detection, June 4, was approaching the invertebrate EC<sub>50</sub> (0.77 μg/L). Two detections were approaching the invertebrate NOAEC (0.01 µg/L) and the other 4 detections exceeded the invertebrate NOAEC (0.01 µg/L).
- Malathion was detected once at a concentration that exceeded the NRWQC chronic criterion (0.1  $\mu$ g/L), invertebrate EC<sub>50</sub> (0.098  $\mu$ g/L), and invertebrate NOAEC (0.06  $\mu$ g/L).

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 9 of the 16 site visits (56%). Water quality at the Snipes Creek site is shown below (Figure 41 and Figure 42).

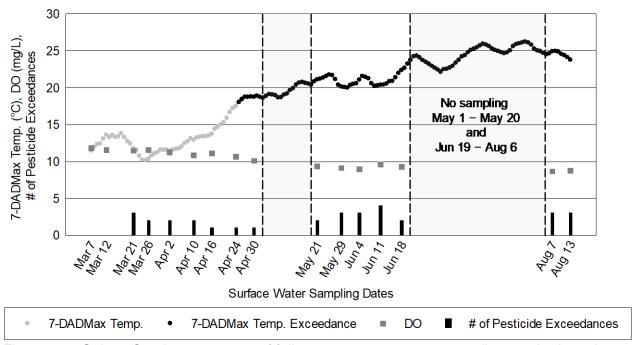


Figure 41 – Snipes Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

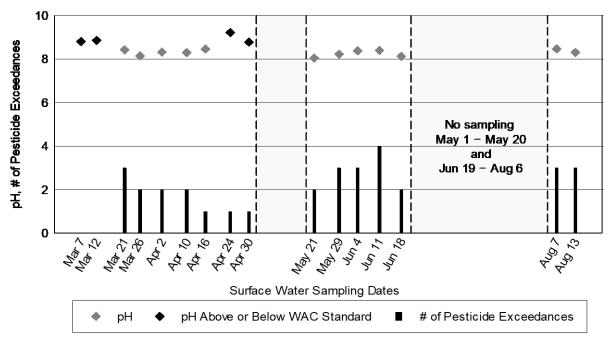


Figure 42 - Snipes Creek occurrences of failures to meet state pH standards and exceedances of WSDA assessment criteria

All DO measurements met state water quality standards, ranging from 8.66 mg/L to 11.81 mg/L with an average of 10.27 mg/L. The 7-DADMax temperatures exceeded the 17.5 °C standard for 111 days of the sampling season, from April 25 through August 13. Pesticide

exceedances coincided with 7-DADMax temperature exceedances at every site visit from April 30 through August 13.

The pH measurements ranged from 8.05 to 9.22 with an average of 8.46. One-quarter of these measurements fell above the state pH standard with 4 pH measurements greater than 8.5. On April 24, the pH exceedance coincided with a pesticide exceedance. Also, the pH exceedance on April 30 coincided with both a pesticide exceedance and a 7-DADMax temperature exceedance.

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**

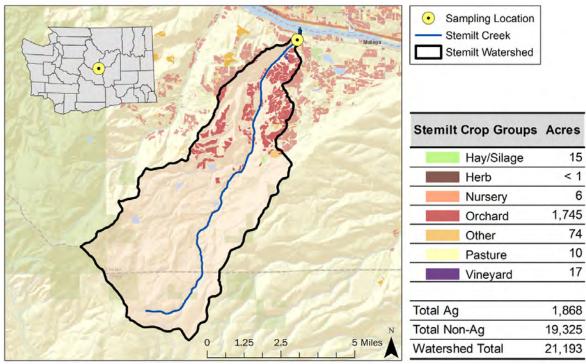


Figure 43 – Map of Stemilt Creek and its drainage area with associated sampling location and crop groups identified

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 influence streamflow in the creek. WDFW has documented spring Chinook salmon and summer steelhead within the reach of creek that encompasses the



Figure 44 – Stemilt Creek downstream view

monitoring site (WDFW, 2019). WDFW also notes 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: 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 2018 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. In addition, there were 19 herbicides, 4 herbicide degradates, 15 insecticides, 4 insecticide degradates, 11 fungicides, and a wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 18 – Stemilt Creek pesticide calendar (µg/L)

Month			Mar			Α	pr			May	
Day of the Month	Use*	13	20	27	3	11	17	25	1	9	15
2,6-Dichlorobenzamide	D	0.033	0.074	0.026	0.024	0.026	0.018	0.017	0.011	0.005	0.003
4,4'-DDD	D		0.003	0.003	0.003					0.001	0.001
4,4'-DDE	D				0.001					0.002	0.002
Boscalid	F	0.008	0.010	0.081	0.013	0.010	0.006	0.005	0.007	0.006	
Chlorpyrifos	I		0.045	0.052	0.049	0.027	0.011	0.011	0.006	0.004	0.003
Diazinon	I					0.005		0.005	0.007	0.003	0.002
Dichlobenil	Н	0.003	0.012	0.002	0.003	0.005		0.002			
Hexazinone	Н				0.003	0.004	0.002	0.002		0.002	
Malathion	I			0.026	0.010					0.003	
N,N-Diethyl-m-toluamide	IR				0.003						
Pendimethalin	Н						0.004				
Sulfentrazone	Н	0.018		0.010	0.013	0.014	0.013	0.009	0.010	0.007	0.004
Trifluralin	Н										0.003
Total suspended solids (r	mg/L)	5.0	3.0	7.0	4.0	9.0	7.0	7.0	22.0	103.0	41.0
Streamflow (cubic ft/sec)		5.36	4.89	6.98	7.18	13.17	7.81	6.19	17.71	47.09	
Precipitation (total in/week	k)†	0.05	0.14	0.34	0	0.61	0.49	0	0.15	0.14	0.11

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

Current-use exceedance DDT/degradate exceedance Detection

- WSDA tested for 90 unique pesticides in Stemilt Creek.
- There were 67 total pesticide detections from 5 different use categories: 5 types of herbicides, 3 insecticides, 3 degradates, 1 fungicide, and 1 insect repellent.
- Pesticides were detected at all 10 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).
  - o The 5 detections of 4,4'-DDD and 3 detections of 4,4'-DDE were equal to or exceeded the NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Only 4 of the 9 chlorpyrifos detections exceeded assessment criteria.
  - The detections on March 20, March 27, and April 3 were greater than the NRWQC and WAC chronic criteria (both 0.041 µg/L) and invertebrate NOAEC (0.04 µg/L).
  - On April 11, chlorpyrifos was approaching the invertebrate NOAEC (0.04 μg/L).

<sup>(</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

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

- The 5 detections of diazinon in 2018 did not exceed assessment criteria, but the pesticide was still classified as a watershed POC due to a 2017 detection that did exceed criteria.
- Imidacloprid was one of the pesticides not tested for at the site in 2018, but it did exceed assessment criteria in 2017.
- One out of 3 malathion detections was approaching the invertebrate  $EC_{50}$  (0.098 µg/L).

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. With all water quality parameters meeting state standards, that did not happen at this site. Water quality at the Stemilt Creek site is shown below (Figure 45).

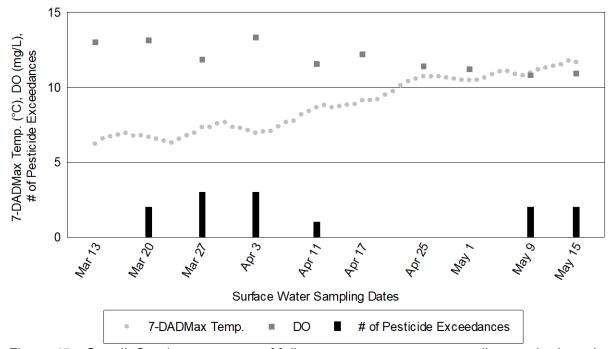


Figure 45 – Stemilt Creek occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria.

There were no pH or DO measurements that did not meet state water quality standards during the 10 site visits of the 2018 sampling season. The pH measurements ranged from 7.73 to 8.44 with an average of 8.20. DO measurements ranged from 10.80 mg/L to 13.33 mg/L with an average of 11.94 mg/L. All 7-DADMax temperatures were below the 17.5 °C standard throughout the short sampling season.

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**

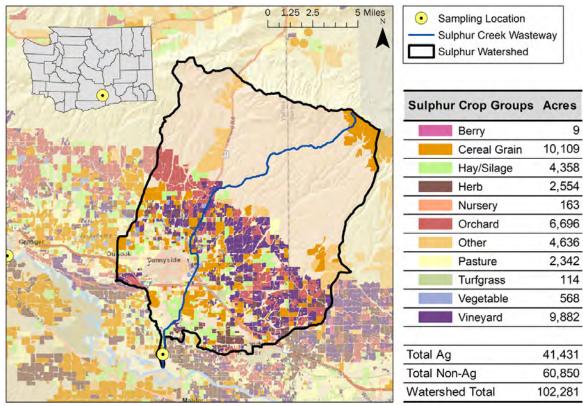


Figure 46 - Map of Sulphur Creek Wasteway and its drainage area with associated sampling location and crop groups identified

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 downstream of the monitoring site. Precipitation events, irrigation, and groundwater generally



Figure 47 – Sulphur Creek Wasteway downstream view

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 fallow fields and land protected through conservation programs (Figure 46).

Below is a brief overview of pesticide findings in Sulphur Creek Wasteway in 2018.

- WSDA tested for 144 unique pesticides in Sulphur Creek Wasteway.
- There were 371 total pesticide detections from 6 different use categories: 21 types of herbicides, 11 insecticides, 6 degradates, 3 fungicides, 1 antimicrobial, and 1 insect repellent.
- Pesticides were detected at all 17 sampling events.
- Up to 32 pesticides were detected at the same time.
- Of the total pesticide detections, 29 were above WSDA's assessment criteria (Table 19).
  - o The 6 detections of 4,4'-DDD and 17 detections of 4,4'-DDE were equal to or exceeded the NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Only 4 of the 9 detections of chlorpyrifos exceeded assessment criteria.
  - The detections on March 21, March 26, and April 2 were greater than the NRWQC and state WAC chronic criteria (both 0.041 µg/L) and invertebrate NOAEC (0.04 μg/L).
  - The detections on March 21 and March 26 also exceeded the NRWQC and state WAC acute criteria (0.083  $\mu$ g/L) and invertebrate LC<sub>50</sub> criterion (0.1  $\mu$ g/L).
  - The detection on March 26 was above the fish NOAEC (0.57 μg/L).
  - On April 10, the chlorpyrifos detection was approaching the invertebrate NOAEC  $(0.04 \mu g/L)$ .
- Both detections of imidacloprid were approaching the invertebrate NOAEC (0.01 µg/L).

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 19 – Sulphur Creek Wasteway pesticide calendar (µg/L)

Day of the Month   Use*   7   12   21   26   2   10   16   24   30   7	Month			N	lar				Apr			May		Jun			Jul			Aug
2.4-D	Day of the Month	Use*	7	12	21	26	2	10	16	24	30	7		25	2	10	16	23	30	7
2.6-Dichloroberzamide D 0.029 0.033 0.006 0.008		Н						0.211		0.076	0.066	0.047	$\overline{}$	0 129	0.330	0.152	0.198	0.139	0.115	2 710
4.4*DDD D D 0,003 0,002 0,005 0,003 0,007 0,007 0,007 0,004 0,003	,		0.029	0.033	0.006		0.011	_	0.007										-	
4.4-LDE	,	D	0.020	0.000																
Artzaire		D	0.003	0.002		0.003	0.002	0.003	0.002	0.002	0.004	0.003		0.001	0.002	0.002	0.002	0.002	0.002	0.002
Bosseald	Acetamiprid	I										0.006								
Bromacil	Atrazine	Н	0.012	0.013	0.006	0.006	0.007	0.007	0.004	0.005	0.005	0.005		0.008	0.007	0.007	0.007	0.006	0.007	0.006
Bromacil		F	0.006	0.010	0.006	0.004	0.005	0.007	0.003	0.004	0.008	0.004		0.025	0.016	0.014	0.024	0.011	0.014	0.017
Carbany		Н	0.037	0.046	0.010	0.016	0.021	0.025	0.011	0.014	0.012	0.014		0.013	0.008	0.012	0.013	0.012	0.014	0.014
Chlorywinds												0.020								
Clothiandin	Chlorantraniliprole	I			0.002			0.002				0.006		0.004		0.004		0.003	0.003	0.003
Dazina   D	Chlorpyrifos	I			0.112	0.605	0.051	0.024	0.013	0.007	0.004	0.003			0.002					
Diazinon   I	Clothianidin	I												0.007			0.010		0.008	0.010
Dichiobenil	Dacthal (DCPA)	Н	0.022	0.026			0.007													
Dichlobeni	Diazinon	I													0.004					0.003
Dimethoate   I	Dicamba acid	Η									0.043	0.029		0.025	0.021	0.018	0.021	0.010	0.017	
Ditron   H   0.008   0.035   0.037   0.085   0.032   0.072   0.026   0.017   0.021   0.014   0.014   0.009   0.005   0.006   0.005   0.005   0.006   0.005   0.006   0.005   0.006   0.005   0.008	Dichlobenil	I		0.002	0.002	0.001	0.002	0.003	0.002			0.002		0.002					0.005	0.001
Eptam	Dimethoate											0.008								
Etoxazole	Diuron	Н	0.008	0.035	0.037	0.085	0.032	0.072	0.026	0.017	0.021	0.014		0.018	0.009	0.011	0.014	0.005	0.006	0.005
Fludioxoni    F   0.008   0.014   0.017   0.012   0.020   0.007   0.008   0.010   0.009   0.009   0.008   0.009   0.009   0.009   0.005   0.006   0.006   0.003   0.003   0.003   0.003   0.008   0.004   0.005   0.006   0.	Eptam	I						0.001						0.004	0.003				0.003	0.003
Hexazinone	Etoxazole	l													0.008					
Imazapyr	Fludioxonil	F	0.008	0.014	0.017		0.012	0.020	0.007	0.008	0.010	0.009		0.013	0.008	0.012	0.013	0.008	0.011	0.008
Imidacloprid   I	Hexazinone	Η	0.008	0.009	0.009	0.005	0.006	0.006	0.003	0.003		0.003		0.005	0.004	0.005	0.006	0.006	0.006	0.006
Malathion         I         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         0.003         0.004         0.004         0.003         0.002         0.003         0.003         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.002         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         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         0.004         0.004 <th< td=""><td>Imazapyr</td><td>Н</td><td>0.024</td><td>0.005</td><td></td><td>0.007</td><td>0.008</td><td>0.010</td><td>0.006</td><td>0.007</td><td>0.005</td><td>0.006</td><td></td><td>0.008</td><td></td><td>0.008</td><td>0.011</td><td></td><td></td><td></td></th<>	Imazapyr	Н	0.024	0.005		0.007	0.008	0.010	0.006	0.007	0.005	0.006		0.008		0.008	0.011			
Metolachlor         H         0.013         0.004         0.004         0.004         0.003         0.004         0.003         0.002         0.003           N,N-Diethyl-m-toluamide IR         0.007         0.004         0.002         0.003         0.002         0.003         0.002         0.007         0.003         0.007         0.000         0.007         0.003         0.002         0.008         0.001         0.007         0.007         0.008         0.008         0.001         0.007         0.007         0.008         0.008         0.001         0.007         0.008         0.008         0.001         0.006         0.006         0.005         0.005         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.005         0.005         0.006         0.006         0.006         0.006         0.006         0.009         0.008         0.003         0.003         0.004         0.006         0.006         0.006         0.009         0.008         0.005         0.008         0.007         0.006         0.006         0.009         0.008         0.005         0.005         0.003         0.004         0.004         0.004         0.004         0.004         0.0	Imidacloprid	l												0.005			0.006			
Metribuzin	Malathion	I			0.004									0.012						
N.N-Diethyl-m-toluamide   IR   0.007   0.004   0.004   0.002   0.004   0.003   0.003   0.002   0.004   0.003   0.002   0.005   0.005   0.005   0.005   0.006	Metolachlor										0.004	0.004		0.004	0.003	0.004	0.004	0.003	0.002	0.003
Norflurazon	Metribuzin	Н						0.013	0.005	0.003										
Oryzalin	N,N-Diethyl-m-toluamide	IR		0.007	0.004		0.004		0.002	0.004		0.003		0.008			0.010		0.007	0.007
Pendimethalin	Norflurazon		0.005	0.007								0.002		0.005	0.005	0.005	0.006	0.006	0.006	0.006
Prometon	Oryzalin	Н									0.006									
Pyridaben   I	Pendimethalin		0.008	0.008	0.014	0.009	0.023	0.105	0.036	0.034	0.032	0.042			0.009				0.005	0.005
Pyrimethanil   F   0.038   0.059   0.011   0.019   0.031   0.026   0.013   0.023   0.019   0.011   0.007   0.007   0.007   0.003   0.005   0.005   0.003   0.006   0		Н			0.003			0.003		0.003						0.003	0.004	0.003		0.004
Simazine         H         0.007         0.009         0.005         0.003         0.004         0.003         0.005         0.005         0.005         0.005         0.006         0.006         0.004         0.003         0.004         0.003         0.005         0.007         0.006         0.007         0.006         0.007         0.006         0.007         0.008         0.007         0.008         0.006         0.006         0.006         0.004         0.004         0.004         0.005         0.007         0.008         0.007         0.008         0.006         0.006         0.006         0.006         0.004         0.004         0.004         0.004         0.004         0.004         0.005         0.007           Triazine DEA degradate D Triclosan A Triclosan A Triclosan B Tric	Pyridaben	1												0.004						
Sodium Bentazon   H   0.021   0.020   0.003   0.005   0.003   0.006   0.005   0.003   0.006	Pyrimethanil	•	0.038	0.059	0.011	0.019	0.031	0.026	0.013	0.023	0.019	0.011			0.007	0.007	0.013	0.005		
Sulfentrazone         H         0.021         0.020         0.005         0.003         0.003         0.006         0.004         0.004         0.005         0.007           Terbacil         H         0.010         0.014         0.004         0.004         0.004         0.004         0.005         0.007           Tetrahydrophthalimide         D         0.001         0.009         0.003         0.006         0.006         0.006         0.006         0.001         0.001         0.005         0.009         0.009           Triazine DIA degradate         D         0.008         0.008         0.004         0.004         0.001         0.006         0.006         0.006         0.001         0.006         0.009<	Simazine		0.007	0.009													0.004			
Terbacil H 0.010 0.014 0.004 0.008 0.041 0.091 0.025 0.011 0.017 0.022  Tetrahydrophthalimide D 0 0.017 0.009 0.003 0.006 0.007 0.006 0.006 0.006  Triazine DEA degradate D 0.017 0.009 0.003 0.006 0.007 0.006 0.006 0.006  Triclosan A 0.008 0.008 0.003 0.004 0.005  Trifluralin H 0.002 0.007 0.006 0.008 0.003 0.00																				
Tetrahydrophthalimide	Sulfentrazone		0.021	0.020						0.005	0.003			0.000						
Triazine DEA degradate D         0.017         0.009         0.003         0.006         0.007         0.006         0.006         0.006         0.006         0.006         0.006         0.009         0.009         0.009         0.009         0.009         0.009         0.009         0.009         0.009         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.006         0.004         0.003         0.003         0.003         0.003         0.003         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.0	Terbacil	Н	0.010	0.014	0.004	800.0	0.041	0.091	0.025	0.011	0.017	0.022		0.008	0.034	0.106	0.054	0.029	0.031	0.039
Triazine DIA degradate         D         0.006         0.006           Triclosan         A         0.008         0.008         0.004         0.004         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.007         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.007         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.004         0.003         0.004         0.003	Tetrahydrophthalimide	D							0.003											
Triclosan         A         0.008         0.008         0.004         0.004         0.003         0.003         0.003         0.003         0.004         0.005           Trifluralin         H         0.002         0.007         0.006         0.008         0.003         0.003         0.007         0.003         0.004         0.003         0.007         0.003         0.003         0.007         0.003         0.003         0.007         0.003         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.003         0.004         0.003         0.007         0.003         0.003         0.004         0.003         0			0.017	0.009	0.003	0.006	0.007	0.006		0.006	0.006	0.006			0.006	0.012		800.0	0.009	
Trifluralin         H         0.002         0.007         0.006         0.008         0.003         0.003         0.004         0.003         0.007         0.003           Total suspended solids (mg/L)         27.0         17.0         354.0         50.0         24.0         27.0         68.0         50.0         93.0         61.0         4.0         31.0         5.0         6.0         5.0         7.0           Streamflow (cubic ft/sec)         121.9         105.3         457         227.4         189         225         362         272.6         351.5         341         77.60         145.52         81.08         73.28         84.56         76.52         82.24           Precipitation (total in/week)†         0.04         0.49         0         0.48         0.29         0         0.02          0.02         0.04         0.08         0.05         0.31         0.17         0.29	Triazine DIA degradate	D																		
Total suspended solids (mg/L) 27.0 17.0 354.0 50.0 24.0 27.0 68.0 50.0 93.0 61.0 Streamflow (cubic ft/sec) 121.9 105.3 457 227.4 189 225 362 272.6 351.5 341 Precipitation (total in/week)† 0.04 0 0.04 0.49 0 0.48 0.29 0 0.02 4.0 31.0 5.0 6.0 5.0 5.0 7.0 0.29																	0.003	0.003		
Streamflow (cubic ft/sec)	Trifluralin	Н						0.008				0.003		0.004	0.003		0.007		0.003	
Precipitation (total in/week)† 0.04 0 0.04 0.49 0 0.48 0.29 0 0.02 0.02 0.04 0.08 0.05 0.31 0.17 0.29																				_
			121.9	105.3		227.4	189	225	362	272.6	351.5	341			145.52	81.08	73.28	84.56	76.52	82.24
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.							_												_	0.29

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.



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

<sup>†</sup> Washington State Univ. AgWeatherNet station: Port of Sunnyside, (latitude: 46.28°, longitude: -120.01°)

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 10 of the 17 site visits (59%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 48).

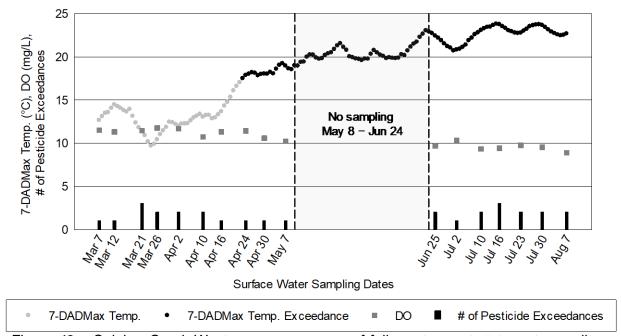


Figure 48 – Sulphur Creek Wasteway occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 8.04 to 8.75 with an average of 8.26. Less than a quarter (12%) of these measurements fell above the state standard with 2 measurements greater than 8.5. On April 24 and July 2, a pesticide exceedance coincided with both a pH exceedance and a 7-DADMax temperature exceedance. All DO measurements met the standard, ranging from 8.89 mg/L to 11.77 mg/L with an average of 10.53 mg/L. The 7-DADMax temperatures exceeded the 17.5 °C standard for 107 days of the sampling season, from April 23 to August 7. Pesticide exceedances coincided with 7-DADMax temperature exceedances at every site visit from April 24 through August 7.

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**

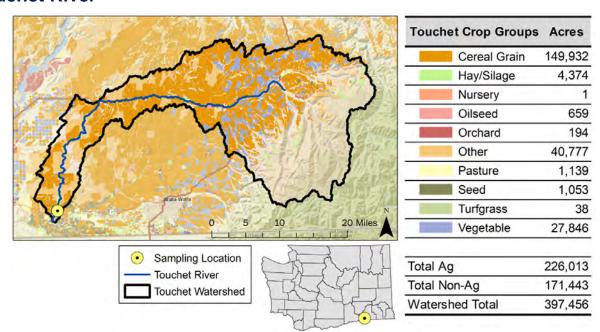


Figure 49 - Map of Touchet River and its drainage area with associated sampling location and crop groups identified

This was the first year WSDA sampled the Touchet River watershed in Walla Walla County. WSDA 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 fallow fields and land protected through conservation programs (Figure 49).

The Touchet River monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2018 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.

Table 20 – Touchet River pesticide calendar (µg/L)

Month		Mar		Apr		M	ay	Jı	ın	Jı	ul	Αι	ıg	Se	ep
Day of the Month	Use*	21	2	16	30	14	29	11	25	10	23	7	20	4	17
2,4-D	Н			> <		> <		0.045				0.032			
4,4'-DDD	D							0.001			0.001				
4-Nitrophenol	D												0.076		
Atrazine	Н									0.003	0.003	0.003	0.003		
Boscalid	F						0.001	0.002	0.003	0.003	0.003	0.005	0.005	0.003	0.004
Bromacil	Н		0.008	0.004	0.007	0.008	0.007	0.009	0.008	0.009	0.009	0.010	0.009	0.009	0.008
Chlorpyrifos	I	0.005													
Dichlobenil	Н		0.001												
Dichlorprop	Н						0.169								
Dichlorvos (DDVP)	I										0.003				
Dimethoate	I							0.006							
Diuron	Н			0.004		0.003									
Eptam	Н						0.004								
Hexazinone	Н	0.005	0.005	0.003					0.003	0.004	0.004			0.003	
MCPA	Н		0.013				0.970								
Metolachlor	Н				0.002	0.002		0.002	0.001						
Metribuzin	Н		0.005	0.007	0.004	0.007	0.003	0.003	0.006						
N,N-Diethyl-m-toluamide	IR		0.004	0.003		0.002	0.025	0.004							
Pendimethalin	Н			0.017	0.006	0.003	0.002	0.003		0.004					
Prometon	Н									0.003	0.003			0.003	
Propiconazole	F							0.006	0.012						
Sulfentrazone	Н			0.003									0.004		
Tebuthiuron	Н			0.004		0.005	0.004		0.003	0.003					
Triclopyr acid	Н						0.166								
Trifluralin	Н					0.003									
Total suspended solids	(mg/L)	72.0	43.0	261.0	43.0	10.0	8.0	7.0	3.0	2.0	1.0		1.0		
Streamflow (cubic ft/sec	)	521	390	965	378	239	117	99.2	60.6	22.8	12.4	6.5	9.4	16.1	17.1
Precipitation (total in/wee	_,.	0.13	0.01	0.69	0.23	0.73	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.01

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 DDT/degradate exceedance Detection

- WSDA tested for 144 unique pesticides in Touchet River.
- There were 84 total pesticide detections from 5 different use categories: 17 types of herbicides, 3 insecticides, 2 fungicides, 2 degradates, and 1 insect repellent.
- Pesticides were detected at all 14 sampling events.
- Up to 10 pesticides were detected at the same time.
- Of the total pesticide detections, 3 were above WSDA's assessment criteria (Table 20).
  - The 2 detections of 4,4'-DDD were equal to the NRWQC and WAC chronic criteria (both 0.001  $\mu$ g/L).
  - A single detection of dichlorvos was approaching the invertebrate NOAEC (0.0058)  $\mu g/L$ ).

<sup>(</sup>D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect Repellent)

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

There were no watershed POCs detected at the site. However, chlorpyrifos, a statewide POC, was detected once in the spring below assessment criteria.

When water quality parameters fail to meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with failures to meet state water quality standards at 2 of the 14 site visits (14%). Water quality at the Touchet River site is shown below (Figure 51).

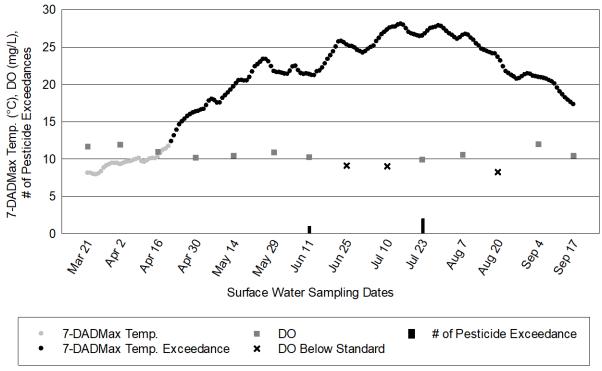


Figure 51- Touchet River occurrences of failures to meet state water quality standards and exceedances of WSDA assessment criteria

The pH measurements ranged from 7.70 to 9.06 with an average of 8.28. About 21% of these measurements fell above the state water quality standard with 3 measurements that exceeded 8.5 on May 14, May 29, and September 4. All 3 of these exceedances coincided with a 7-DADMax exceedance. DO measurements ranged from 8.22 mg/L to 11.96 mg/L with an average of 10.38 mg/L. Less than a quarter (21%) of these measurements did not meet the state standard with 3 measurements less than 9.5 mg/L. The 7-DADMax temperatures exceeded the 12 °C temperature standard for 150 days of the sampling season from April 21 through September 17.

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 (8 to 32 sampling events) and samples from several sites are tested for a subset of pesticides compared to the majority of sites (90 to 144 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.

Table 21 – Statewide pesticide detections summarized by general use category

Pesticide general use category	# of analytes tested for	# of analytes detected	# of analytes with detections above assessment criteria	# of individual detections
Antimicrobial	1	1		44
Degradate	13	11		576
DDT and degradate	3	3	3	191
Fungicide	20	18	1	888
Herbicide	54	42	2	2,326
Insect repellent	1	1		105
Insecticide	49	28	12	703
Synergist	2	1		16
Wood preservative	1	1	1	11
Total analytes	144	106	19	4,860

There were 106 different analytes detected in 2018 (Table 21). Across 16 monitoring sites, WSDA identified 4,860 detections. This is a 197% increase in total detections from 2017 (1,639 detections total). The substantial increase is largely due to new equipment at the lab and does not necessarily reflect an increase in pesticide usage. Every monitoring site had detections of at least 1 herbicide, fungicide, insecticide, and degradate. To determine if the concentration of the detections could negatively affect aquatic life, WSDA compared each detection to WSDA assessment criteria.

There were 364 instances where analytes exceeded the WSDA assessment criteria which are listed in Appendix A: Assessment Criteria for Pesticides. This represents an increase of 244 exceeding detections compared to 2017 exceedances. 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 364 individual exceedances, 173 (48%) were currently registered pesticides and the other 191 (52%) were detections of DDT or its degradates. Approximately half of the

exceedances, 198 (54%), occurred at monitoring sites in Eastern Washington including many of the statewide exceedances of DDT or its degradates (132). Imidacloprid, a neonicotinoid insecticide, accounted for 87 (24%) of the individual pesticide exceedances and was found at 9 of the 16 monitoring sites. Lower Crab Creek, in Eastern Washington, was the only monitoring site that did not have a pesticide detection found above any assessment criteria.

# **Pesticide Detection Summary**

Below, statewide detections are summarized by pesticide general use categories. This subsection only presents analytes detected in 2018. Appendix B: 2018 Quality Assurance Summary provides a list of all analytes tested.

#### **Herbicide Detections**

Herbicides were the most frequently detected group making up approximately 48% (2,326 detections) of the total pesticide detections. Of the 54 herbicides included in the laboratory analysis, 42 (78%) were detected in surface water samples. Table 22 provides a statewide summary of the detected herbicides.

Table 22 – Statewide summary of herbicides with 1 or more detections in 2018

Analyte	# of samples collected*	# of detection s (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Dichlobenil	289	164 (57%)	-	16	-	0.0006 - 0.153
Diuron	271	148 (55%)		12		0.003 - 0.208
Hexazinone	289	146 (51%)		16		0.001 - 0.018
Bromacil	289	137 (47%)		11		0.003 - 0.058
Metolachlor	289	133 (46%)	1	14	1	0.001 - 0.655
Sulfentrazone	289	125 (43%)		14		0.002 - 0.056
2,4-D	247	116 (47%)		13		0.012 - 2.710
Simazine	289	116 (40%)		9		0.003 - 0.950
Terbacil	289	113 (39%)		10		0.003 - 0.606
Atrazine	289	109 (38%)		12		0.002 - 0.080
Pendimethalin	289	103 (36%)		11		0.002 - 0.105
Norflurazon	289	94 (33%)		9		0.002 - 0.026
Prometon	289	93 (32%)		13		0.002 - 0.015
Imazapyr	271	88 (32%)		10		0.003 - 0.892
Tebuthiuron	289	76 (26%)		5		0.003 - 0.077
Eptam	289	73 (25%)		12		0.001 - 0.052
Dicamba acid	247	60 (24%)		10		0.009 - 0.569
Trifluralin	289	56 (19%)		15		0.002 - 0.009
Metribuzin	289	55 (19%)		10		0.002 - 0.014

Analyte	# of samples collected*	# of detection s (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Triclopyr acid	247	46 (19%)	<del>-</del>	7	-	0.015 - 0.894
Sodium bentazon	247	31 (13%)		5		0.012 - 0.069
Oxadiazon	289	29 (10%)		3		0.002 - 0.014
Isoxaben	271	22 (8%)		5		0.002 - 0.060
Mecoprop (MCPP)	247	20 (8%)		6		0.011 - 0.150
Dacthal (DCPA)	247	18 (7%)		3		0.007 - 0.350
MCPA	247	16 (6%)		6		0.013 - 0.970
Napropamide	289	16 (6%)		3		0.003 - 0.012
Chlorpropham	289	15 (5%)		3		0.001 - 0.013
Picloram	247	15 (6%)		1		0.032 - 0.095
Prodiamine	289	15 (5%)		1		0.016 - 0.066
Oryzalin	289	14 (5%)		6		0.004 - 0.042
Clopyralid	247	13 (5%)		2		0.022 - 0.191
Dithiopyr	289	13 (4%)		3		0.002 - 0.008
Sulfometuron methyl	271	11 (4%)	2	2	1	0.009 - 0.335
Imazapic	271	7 (3%)		2		0.005 - 0.011
Metsulfuron methyl	271	6 (2%)		3		0.006 - 0.074
Bromoxynil	247	3 (1%)		2		0.011 - 0.071
Chlorsulfuron	271	3 (1%)		2		0.018 - 0.069
Prometryn	289	3 (1%)		2		0.002 - 0.013
Flumioxazin	289	2 (1%)		1		0.004 - 0.007
Simetryn	289	2 (1%)		1		0.005 - 0.006
Dichlorprop	247	1 (0%)		1		0.169 - 0.169

<sup>\*</sup> The '# of samples collected' varies among analytes because Upper Brender Creek, Stemilt Creek, and Mission Creek samples had a shortened analyte list.

Dichlobenil, diuron, and hexazinone were the most frequently detected herbicides with 164, 148, and 146 detections, respectively. There were 18 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Only 2 herbicides, sulfometuron methyl and metolachlor, were detected above the WSDA assessment criteria, accounting for less than 1% of the total exceedances in 2018. Metolachlor is often used as a pre-emergent herbicide on crops. It has been found at many monitoring sites across the state annually. Sulfometuron methyl is used mostly as a preemergent or post-emergent application for weeds in non-agricultural locations such as road right-of-ways and outside of buildings. It has been found at various monitoring sites since 2015 when WSDA added it to the analyte testing list.

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.

- Dichlobenil → 2,6-dichlorobenzamide (detected at 15 monitoring sites),
- Atrazine → triazine DEA (detected at 10 monitoring sites) and triazine DIA (detected at 8 monitoring sites).

## **Fungicide Detections**

Fungicides were the second most frequently detected group of pesticides making up 888 detections, or 18%, of the total number of detections. In 2017, fungicides were also the second most frequently detected group of pesticides making up 22% of the total number of detections. Out of 20 fungicides included in the laboratory analysis, 18 (90%) were detected in surface water samples. Table 23 provides a statewide summary of the detected fungicides.

Table 23 – Statewide summary of fungicides with 1 or more detections in 2018

Analyte	# of samples collected*	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detection s	# of sites with exceeding detections	Concentration range (µg/L)
Boscalid	289	242 (84%)		16		0.0006 - 0.752
Fludioxonil	289	149 (52%)		10		0.003 - 4.650
Carbendazim	271	81 (30%)		6		0.002 - 0.079
Metalaxyl	289	72 (25%)		4		0.007 - 0.413
Azoxystrobin	271	61 (23%)		5		0.005 - 0.068
Propiconazole	271	43 (16%)		8		0.005 - 0.078
Triadimefon	289	43 (15%)		10		0.002 - 0.026
Myclobutanil	271	37 (14%)		4		0.003 - 0.021
Pyrimethanil	271	33 (12%)		6		0.005 - 0.059
Etridiazole	289	27 (9%)		2		0.001 - 0.243
Cyprodinil	271	24 (9%)		2		0.006 - 0.176
Pyraclostrobin	271	22 (8%)	1	3	1	0.005 - 0.195
Fenarimol	289	21 (7%)		9		0.001 - 0.013
Difenoconazole	271	14 (5%)		3		0.005 - 0.017
Trifloxystrobin	271	10 (4%)		2		0.005 - 0.053
Chlorothalonil	289	7 (2%)		6		0.003 - 0.006
Fenbuconazole	271	1 (0%)		1		0.006 - 0.006
PCNB	289	1 (0%)		1		0.002 - 0.002

<sup>\*</sup>The '# of samples collected' varies among analytes because Upper Brender Creek, Stemilt Creek, and Mission Creek samples had a shortened analyte list.

Boscalid, fludioxonil, and carbendazim were the most commonly detected fungicides with 242, 149, and 81 detections, respectively. Boscalid and fludioxonil were also the most

commonly detected fungicides each year since 2015. Boscalid was detected the most of any analyte tested for in 2018. Carbendazim, detected the third most commonly, is rarely used as a fungicide and is more often found in the environment as a degradate of another fungicide WSDA does not test for (Montague et al., 2014). Detections of fungicides occur primarily at Western Washington sampling sites (approximately 74% of 2018 detections). The wetter climate of Western Washington drives the usage of more fungicides than in Eastern Washington.

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

Boscalid

Triadimefon

Fludioxonil

Fenarimol

Propiconazole

Pyraclostrobin was the only fungicide in 2018 that exceeded any assessment criteria, accounting for less than 1% of the total exceedances. It can be used on many different crops in Washington including in greenhouses, grass, many vegetables, alfalfa, oat, and wheat. In comparison, there were a total of 5 exceedances of fungicides in 2015, none in 2016, and 2 in 2017.

#### **Insecticide Detections**

Current-use insecticides were the third most frequently detected group of pesticides representing approximately 14% (703 detections) of the total pesticide detections. Of the 49 current-use insecticides included in the laboratory analysis, 28 (57%) were detected in surface water samples. Table 24 provides a statewide summary of the detected insecticides.

Table 24 – Statewide summary of insecticides with 1 or more detections in 2018

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	271	104 (38%)	1	8	1	0.005 - 0.594
Chlorpyrifos	289	103 (36%)	28	10	6	0.002 - 0.887
Imidacloprid	271	87 (32%)	87	9	9	0.005 - 0.228
Chlorantraniliprole	271	58 (21%)		7		0.002 - 0.021
Dinotefuran	271	52 (19%)		3		0.008 - 4.620
Clothianidin	271	39 (14%)	10	4	2	0.007 - 0.036
Malathion	289	37 (13%)	9	9	5	0.002 - 0.242
Oxamyl	271	37 (14%)		2		0.001 - 0.103
Diazinon	289	33 (11%)	2	7	2	0.001 - 0.098
Pyridaben	289	31 (11%)	9	8	2	0.003 - 0.101
Fipronil	289	25 (9%)	7	7	2	0.002 - 0.022
Dimethoate	289	12 (4%)		7		0.004 - 0.151
Ethoprop	289	11 (4%)		7		0.002 - 0.066
Pyriproxyfen	289	11 (4%)		5		0.003 - 0.004
Bifenthrin	289	10 (3%)	10	3	3	0.003 - 0.007
Methomyl	271	10 (4%)		2		0.004 - 0.103
Etoxazole	289	8 (3%)	1	2	1	0.004 - 0.123
Acetamiprid	271	7 (3%)		2		0.006 - 0.024
Carbaryl	271	7 (3%)		5		0.006 - 0.020
Methoxyfenozide	271	7 (3%)		2		0.002 - 0.012
Methiocarb	271	4 (1%)		2		0.005 - 0.183
Dichlorvos (DDVP)	289	3 (1%)	3	3	3	0.003 - 0.009
Spirotetramat	271	2 (1%)		1		0.017 - 0.526
Bifenazate	289	1 (0%)		1		0.022 - 0.022
cis-Permethrin	289	1 (0%)	1	1	1	0.006 - 0.006
Phosmet	289	1 (0%)		1		0.005 - 0.005
Tefluthrin	289	1 (0%)		1		0.0009 - 0.0009
Total Fluvalinate	289	1 (0%)		1		0.003 - 0.003

<sup>\*</sup>The '# of samples collected' varies among analytes because Upper Brender Creek, Stemilt Creek, and Mission Creek samples had a shortened analyte list. WSDA classifies bolded analytes as statewide POCs.

Thiamethoxam, chlorpyrifos, and imidacloprid were the most commonly detected insecticides with 104, 103, and 87 detections, respectively. The insecticides thiamethoxam and imidacloprid have been the most commonly detected insecticides every year since 2015.

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

- Chlorpyrifos
- Imidacloprid
- Malathion

- Pyridaben
- Thiamethoxam

Current-use insecticides accounted for 46% (168 detections) of all exceedances in 2018. All detections of imidacloprid, bifenthrin, dichlorvos, and cis-permethrin were above WSDA assessment criteria. Of the 28 current-use insecticides that were detected, 43% (12 insecticides) were detected above WSDA assessment criteria at least once.

The 3 statewide POCs identified in 2018 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 2018 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. Every detection of imidacloprid exceeded WSDAs assessment criteria because it could not be reliably detected at concentrations below WSDA's assessment criteria. This insecticide can be applied to over 250 commercial crop types and also has residential uses; it was found ubiquitously across the state.

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.

- Malathion → malaoxon (detected at 3 monitoring sites),
- Fipronil → fipronil sulfide (detected at 6 monitoring site).
  - → fipronil sulfone (detected at 4 monitoring site),
  - → fipronil disulfinyl (detected at 4 monitoring site),
- Oxamyl → oxamyl oxime (detected at 3 monitoring sites),
- Methomyl → methomyl oxime (detected at 1 monitoring sites),
- Clothianidin → thiamethoxam. Although clothianidin degrades into thiamethoxam, both insecticides are registered independently in Washington.

## **Degradate and Other Pesticide Detections**

This group includes degradates of current-use pesticides as well as several other pesticide-related chemicals. They were the least frequently detected groups of pesticides with degradates representing 12% (576 detections) and pesticide-related chemicals representing 4% (176 detections) of total detections. Of the 13 current-use degradates included in the laboratory analysis, 11 (85%) were detected in surface water samples. Only 1 of the 2 synergists tested for was detected. Each antimicrobial, wood preservative, and insect repellent tested for had at least 1 detection. Table 25 provides a statewide summary of the detected degradates and other pesticide product ingredients.

Table 25 – Statewide summary of degradates and other pesticide products in 2018

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	289	238 (82%)		15		0.001 - 0.378
Triazine DEA	271	131 (48%)		10		0.001 - 0.029
Triazine DIA	271	60 (22%)		8		0.004 - 0.097
Tetrahydrophthalimide	289	44 (15%)		5		0.001 - 0.060
Oxamyl oxime	271	35 (13%)		3		0.010 - 0.393
Fipronil sulfide	289	29 (10%)		6		0.001 - 0.006
Fipronil sulfone	289	21 (7%)		4		0.002 - 0.010
Fipronil disulfinyl	289	8 (3%)		4		0.002 - 0.003
4-Nitrophenol	247	4 (2%)		3		0.076 - 0.103
Malaoxon	271	4 (1%)		3		0.002 - 0.011
Methomyl oxime	271	2 (1%)		1		0.014 - 0.026
Antimicrobial:						
Triclosan	289	44 (15%)		9		0.003 - 0.017
Insect repellent:						
DEET	289	105 (36%)		16		0.001 - 0.067
Synergist:						
Piperonyl butoxide	289	16 (6%)		3		0.005 - 0.184
Wood preservative:						
Pentachlorophenol	247	11 (4%)	1	5	1	0.012 - 0.617

<sup>\*</sup>The '# of samples collected' varies among analytes because Upper Brender Creek, Stemilt Creek, and Mission Creek samples had a shortened analyte list.

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 238 detections, followed by triazine DEA (degradate of atrazine) with 131 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 except Touchet River in Eastern Washington. There were no degradates from current-use pesticides that exceeded any assessment criteria. The degradates detected that did not have a parent compound detected at any of the monitoring sites were tetrahydrophthalimide and 4-nitrophenol. Tetrahydrophthalimide is the main breakdown product of captan, a fungicide and the chemical 4-nitrophenol is a breakdown product of several natural and synthetic products.

Other associated pesticide ingredients detected include pentachlorophenol, triclosan and piperonyl butoxide. Pentachlorophenol's main usage is for wood preservation. A single detection exceeded WSDA assessment criteria. Also, the insect repellent DEET (N,N-Diethyl-m-toluamide), detected 105 times, was the only analyte found at every monitoring

site at least once. The only federally registered uses of DEET are for application to horses, the human body, and clothing.

### **Legacy Insecticide DDT and Degradate Detections**

The U.S. EPA banned products containing DDT in 1972. DDT and its associated degradates may be detected in areas where DDT-containing products were historically used due to its persistence in soils. Contaminated soil can enter surface water as a result of runoff or when sediment is disturbed.

Detected DDT and its associated degradates accounted for 4% (191 detections) of the total pesticide detections. All 3 legacy chemicals included in the lab analysis were detected. A statewide summary of DDT and 2 of its degradates (4,4'-DDE and 4,4'-DDD) is shown below in Table 26.

Table 26 – Statewide summary of DDT and degradates with 1 or more detections in 2018

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'-DDD	289	84 (29%)	84	15	15	0.0009 - 0.009
4,4'-DDE	289	83 (29%)	83	11	11	0.001 - 0.051
4,4'-DDT	289	24 (8%)	24	2	2	0.002 - 0.011

There were detections of all 3 legacy analytes. DDT's degradate 4,4'-DDD was the most frequently detected legacy chemical with 84 detections closely followed by 4,4'-DDE with 83 detections. DDT or an associated degradate were found in all Western and all but 1 Eastern Washington monitoring sites.

The parent compound 4.4'-DDT and its degradates (4.4'-DDE and 4.4'-DDD) accounted for 52% of the total exceedances detected in 2018. Of the 191 combined DDT exceedances, 69 (36%) 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 use patterns.

# **Conclusions**

Staff collected surface water monitoring data at 16 locations across Eastern and Western Washington in 2018. Water samples were collected during the peak pesticide application season (March – November) a total of 289 times. Samples taken from 13 of the monitoring sites were tested in a lab for 144 pesticide and pesticide-related chemicals while 1 monitoring site was tested for a subset of 130 chemicals and 2 more monitoring sites were tested for a subset of 90 chemicals.

- Of 144 pesticides tested for, 106 unique pesticides were detected.
- WSDA detected pesticides in water samples a total of 4,860 times.
- Dichlobenil, diuron, and hexazinone were the most frequently detected herbicides (164, 148, and 146 times, respectively).
- Thiamethoxam, chlorpyrifos, and imidacloprid were the most frequently detected insecticides (104, 103, and 87 times, respectively).
- Boscalid, fludioxonil, and carbendazim were the most frequently detected fungicides (242, 149, and 81 times, respectively).
- Substantially more fungicides were detected at Western Washington sites (661 total detections) than Eastern Washington sites (227 total detections).
- Only 6 chemicals were detected in over 50% of the sampling events in which they were tested for. Boscalid and 2,6-dichlorobenzamide were each detected at more than 80% of sampling events.

In 2018, mixtures of pesticides were frequently present at monitoring sites. Of the 16 monitoring sites, 15 sites had 2 or more pesticide detections at every sampling event during the entire field season. Only the Naneum Creek monitoring site had 3 sampling events with less than 2 detections. The maximum number of detections (44) at a single sampling event occurred June 26 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 364 exceedances at 15 monitoring sites. Only 1 monitoring location, Lower Crab Creek in Eastern Washington, had no exceedances. Almost half of the total exceedances (173 exceedances) were from 16 current-use pesticides. Every detection of bifenthrin, dichlorvos, imidacloprid, and cis-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 27. Detections of DDT and associated degradates accounted for the remaining half (52%, 191 exceedances) of the total exceedances. DDT and/or one of its degradates tested for were detected at every Western Washington site, ranging from 2 detections at Upper Bertrand Creek and Lower Big Ditch to 20 detections at the Lower Big Ditch site. In Eastern Washington, DDT and/or one of its degradates were detected at all but one site (Lower Crab Creek). Eastern sites with DDT or degradate detections ranged from 2 detections at Naneum Creek and the Touchet River, to

a maximum of 69 exceedances at Upper Brender Creek alone. Every detection of DDT exceeded WSDA assessment criteria.

Table 27 – Summary of WSDA assessment criteria exceedances from current-use pesticides

Analyta	# of	# of detections above
Analyte	detections	assessment criteria
Imidacloprid	87	87 (100%)
Chlorpyrifos	103	28 (27%)
Clothianidin	39	10 (26%)
Bifenthrin	10	10 (100%)
Malathion	37	9 (24%)
Pyridaben	31	9 (29%)
Fipronil	25	7 (28%)
Dichlorvos (DDVP)	3	3 (100%)
Diazinon	33	2 (6%)
Sulfometuron methyl	11	2 (18%)
Metolachlor	133	1 (1%)
Thiamethoxam	104	1 (1%)
Pyraclostrobin	22	1 (5%)
Pentachlorophenol	11	1 (9%)
Etoxazole	8	1 (13%)
cis-Permethrin	1	1 (100%)

Exceedances by current-use pesticide types are as follows.

- Out of 2,326 total herbicide detections, 3 detections exceeded criteria (<1%).</li>
- Out of 888 total fungicide detections, 1 detection exceeded criteria (<1%).</li>
- Out of 703 total insecticide detections, 168 detections exceeded criteria (24%).

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, which was used retroactively on this 2018 data. 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 3. 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 US 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 2018 were tested for roughly 17% 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**

There were very few program changes between 2018 and 2019 sampling seasons. Between the 2018 and 2019, all 16 monitoring sites remained the same. The 144 analytes tested for in 2018 were retained for 2019 with the addition of 12 new analytes (Table 28).

Table 28 – Additional analytes for 2019

Analytes added	CAS number	General use
1-(3,4-Dichlorophenyl)-3-methylurea	3567-62-2	Degradate
Acephate	30560-19-1	Insecticide
Acetochlor ESA	187022-11-3	Degradate
Afidopyropen	915972-17-7	Insecticide
Bensulide	741-58-2	Herbicide
Fenbutatin oxide	13356-08-6	Insecticide
Hexythiazox	78587-05-0	Insecticide
Indaziflam	950782-86-2	Herbicide
Methamidophos	10265-92-6	Insecticide
Methidathion	950-37-8	Insecticide
Paclobutrazol	76738-62-0	Fungicide
Triazine HA	2163-68-0	Degradate

WSDA conducted a special herbicide project in 2019. Glyphosate, aminomethylphosphonic acid (a glyphosate breakdown product), and glufosinate-ammonium, were tested for at 14 of the 16 monitoring sites every 2 weeks for the duration of the sampling season.

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# **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, invertebrates, and aquatic plants. Various EPA derived risk assessments were reviewed 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 29a. 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:
  - AS-Atlantic salmon
  - BS-bluegill sunfish
  - BT-brook trout
  - BrT-brown trout
  - o CC-carp
  - CF-catfish

- FF-flagfish
- FM-fathead minnow
- JM-Japanese medaka
- LT-lake trout

- ND-not described
- o RT-rainbow trout
- SB-striped bass

- Invertebrate:
  - o ACR-acute to chronic ratio
  - AG-astacopsis gouldi (crayfish)
  - CG-chloroperia grammatical (stonefly)
  - o CR-chironomus riparius
  - CT-chironomus tentans (midge)

- o DM-daphnia magna
- o DP-daphnia pulex
- o GF-gammarus fasciatus (scud)
- o HA-hyalella azteca (amphipod)
- o ND-not described
- o PC-pteronarcys californica (stonefly)

- · Aquatic plant:
  - AF-anabaena flos-aquae (cyanobacteria)
  - EN-elodea nuttali (waterweed)
  - o LG- lemna gibba
  - o LM-Lemna minor
  - ND-not described
  - NP-navicula pelliculosa

- OL-oscillatoria lutea (blue-green algae)
- o SC-pseudokirchneriella subcapitata
- o 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 29a contains only chemicals detected in 2018. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2018 Quality Assurance Summary.

Table 29a – WSDA Freshwater assessment criteria (WSDA safety factors applied, μg/L)

	TWATER GOOD	<u>Fish</u>		<u>Invertebrate</u>			Aquatic Plant		WAC		NRWQC		
	Endangered Species												
Pesticide	Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
2,4-D <sup>1,b</sup>	2040	20400	11800	RT/FM	6250	8025	DM	149.6	LG				
2,6-Dichlorobenzamide <sup>2</sup>	3000	30000	5000	BS/RT	46000	160000	DM	50000	SP				
4,4'-DDD <sup>3,4</sup>										0.55a	0.0005a	0.55 <sup>a</sup>	0.0005 <sup>a</sup>
4,4'-DDE <sup>3,4</sup>										0.55a	0.0005a	0.55 <sup>a</sup>	0.0005a
4,4'-DDT <sup>3,4</sup>										0.55a	0.0005a	0.55a	0.0005a
4-Nitrophenol <sup>5</sup>	100	1000		RT	1250		DM						
Acetamiprid <sup>6</sup>	2500	25000	9600	RT/FM	5.25	1.05	CR/ACR	500	LG				
Atrazine <sup>7</sup>	132.5	1325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin <sup>8</sup>	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Bifenazate <sup>9</sup>	14.5	145	150	BS	125	75	DM	445	SC				
Bifenthrin <sup>10</sup>	0.00375	0.0375	0.02	RT/FM	0.4	0.00065	DM						
Boscalid <sup>11</sup>	67.5	675	58		1332.5	395		670					
Bromacil <sup>12</sup>	900	9000	1500	RT	30250	4100	DM	3.4	SC				
Bromoxynil <sup>13</sup>	52.5	525		RT	4805		DM						
Carbaryl <sup>4,14</sup>	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	330	NP			1.05	1.05
Carbendazim <sup>15</sup>	0.25	2.5	0.495		27.5	1.55							
Chlorantraniliprole <sup>16</sup>	345	3450	55	RT	2.9	2.235	DM	890	SC				
Chlorothalonil <sup>17</sup>	0.2625	2.625	1.5	RT/AG	0.9	0.3	DM	3.4	SC				
Chlorpropham <sup>18</sup>	75.25	752.5		RT	927.5		DM						
Chlorpyrifos <sup>3,4,19</sup>	0.045	0.45	0.285	RT/FM	0.025	0.02	DM	70		0.0415	0.0205	0.0415	0.0205
Chlorsulfuron <sup>20</sup>	7500	75000	16000	RT	92500	10000	DM	0.175	LG				
cis-Permethrin <sup>21</sup>	0.01975	0.1975	0.02575	BS/FM	0.00975	0.0007	DM	34	SC				
Clopyralid <sup>22</sup>	2587.5	25875		RT	58250		DM	3450	SC				
Clothianidin <sup>23</sup>	2537.5	25375	4850	RT/FM	5.5	0.025	CR	32000					
Cyprodinil <sup>24</sup>	60.25	602.5	115	RT/FM	8	4		1125					
Dacthal (DCPA) <sup>25</sup>	165	1650	•	RT	4505		DM						-

	<u>Fish</u> Endangered				<u>lr</u>	nvertebra	<u>te</u>	Aquatio	: Plant	WAC		NRWQC	
Pesticide	Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	СМС	ccc
Diazinon <sup>4,26</sup>	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1850	SC			0.085	0.085
Dicamba acid <sup>27</sup>	700	7000		RT	25000		DM	30.5	AF				
Dichlobenil <sup>2</sup>	123.25	1232.5	165	RT	1550	280	DM	15	LG				
Dichlorprop <sup>28</sup>	2287.5	22875		RT	139500	50000	DM	38.5	NP				
Dichlorvos (DDVP) <sup>29</sup>	4.575	45.75	2.6	LT/RT	0.0175	0.0029	DM	7000	ND				
Difenoconazole <sup>30</sup>	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP				
Dimethoate <sup>31</sup>	155	1550	215	RT	10.75	0.25	PC	10000	AF				
Dinotefuran <sup>32</sup>	2477.5	24775	3180	CC/RT	242075	47650	DM	48800	SC				
Dithiopyr <sup>33</sup>	11.75	117.5	28	BS/RT	425	40.5	DM	10	SC				
Diuron <sup>34</sup>	10	100	13.2	SB/FM	40	100	GF/DM	1.2	SC				
Eptam <sup>35</sup>	350	3500		BS	1625	400	DM	700	SC				
Ethoprop <sup>36</sup>	7.5	75	12	RT/FM	11	0.4	DM	4200					
Etoxazole <sup>37</sup>	9.25	92.5	7.5	RT	1.825	0.065	DM	25.95	NP				
Etridiazole <sup>38</sup>	30.25	302.5	60	RT	770	185	DM	36	SC				
Fenarimol <sup>39</sup>	22.5	225	90	RT	1700	56.5	DM	50	SC				
Fenbuconazole													
Fipronil <sup>40</sup>	2.075	20.75	3.3	BS	0.055	0.0055	DM/ACR	50					
Fipronil Disulfinyl <sup>40</sup>	0.5	5	0.295		50	5.155		38					
Fipronil Sulfide <sup>40</sup>	2.075	20.75	3.3		0.26625	0.055		50	ND				
Fipronil Sulfone <sup>40</sup>	0.625	6.25	0.335	RT/ND	0.18	0.0185	DM/ND	50	ND				
Fludioxonil <sup>41</sup>	11.75	117.5	9.5	RT/FM	225	9.5	DM	35					
Flumioxazin <sup>42</sup>	57.5	575	3.85	RT	1375	14	DP/DM	0.245	LG				
Hexazinone <sup>43</sup>	6850	68500	8500	RT/FM	37900	10000	DM	3.5	SC				
Imazapic <sup>44</sup>	2500	25000	48000	RT/FM	25000	48000	DM	3.11	LM				
Imazapyr <sup>45</sup>	2500	25000	21550	RT/FM	25000	48550	DM	9	LM				
Imidacloprid <sup>46</sup>	5725	57250	4500	RT	0.1925	0.005		5000	ND				
Isoxaben <sup>47</sup>	25	250	200	RT	325	345	DM	5	LG				

	F.,	<u>Fis</u>	<u>h</u>		<u>lı</u>	nvertebrat	<u>e</u>	Aquatio	: Plant	WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	СМС	ccc
Malaoxon <sup>4,48</sup>	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020	•				0.05
Malathion <sup>4,48</sup>	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020					0.05
MCPA <sup>49</sup>								85	SC				
Mecoprop (MCPP)50	2325	23250		RT	22750	25400	DM	7	SC				
Metalaxyl <sup>51</sup>	3250	32500	4550	RT/FM	7000	50	DM	46000	SC				
Methiocarb <sup>52</sup>	4.5	45	25	BS	1.375								
Methomyl <sup>53</sup>	8	80	6	CF	1.25	0.35	DM						
Methomyl Oxime													
Methoxyfenozide <sup>54</sup>	105	1050	265	RT/FM	12.5	3.15	CR	1700	SC				
Metolachlor <sup>55</sup>	95	950	15	RT	275	0.5	DM	4	SC				
Metribuzin <sup>56</sup>	1050	10500	1500	RT	1050	645	DM	4.05					
Metsulfuron-methyl57	3750	37500	2250	BS	37500		DM	0.18	LG				
Myclobutanil <sup>58</sup>	60	600	490	BS/FM	2750		DM	415	SC				
N,N-Diethyl-m-toluamide	1875	18750		RT	18750		DM						
Napropamide <sup>60</sup>	160	1600	550	RT	3575	550	DM	1700	SC				
Norflurazon <sup>61</sup>	202.5	2025	385	RT	3750	500	DM	4.85	SC				
Oryzalin <sup>62</sup>	72	720	110	BS/FM	375	179	DM	6.5	LG				
Oxadiazon <sup>63</sup>	30	300	16.5	RT/FM	545	16.5	DM	2.6	SC				
Oxamyl <sup>64</sup>	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Oxamyl oxime <sup>64</sup>	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Pendimethalin <sup>65</sup>	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC				
Pentachloronitrobenzene <sup>66</sup>	2.5	25	6.5		192.5	9							
Pentachlorophenol <sup>4,67</sup>	0.375	3.75	5.5	RT	23	2.05	DM	25	SC			9.5	7.5
Phosmet <sup>68</sup>	1.75	17.5	1.6	RT	0.5	0.4	DM						
Picloram <sup>69</sup>	137.5	1375	275	RT	8600	5900	DM	17450	SC				
Piperonyl butoxide <sup>70</sup>	47.5	475	20	RT	127.5	15	DM						

	<u>Fish</u> Endangered				<u>lı</u>	nvertebra	Aquatic Plant		WAC		NRWQC		
Pesticide	Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	СМС	ccc
Prodiamine <sup>71</sup>	0.325	3.25		BS	3.25	0.75	DM						
Prometon <sup>72</sup>	300	3000	9850	RT/FM	6425	1725	DM	49	SC				
Prometryn <sup>73</sup>	72.75	727.5	310	RT/FM	2425	500	DM	0.52	NP				
Propiconazole <sup>74</sup>	21.25	212.5	47.5	RT/FM	325	130	DM	10.5	ND				
Pyraclostrobin <sup>75</sup>	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP				
Pyridaben <sup>76</sup>	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG				
Pyrimethanil <sup>77</sup>	252.5	2525	10	RT	750	500	DM	900	ND				
Pyriproxyfen <sup>78</sup>	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG				
Simazine <sup>79</sup>	160	1600	30	FM	250	20	DM/ACR	3	SC				
Simetryn													
Sodium bentazon80	4750	47500	4915	RT/FM	15575	50600	CR/DM	2250	SC				
Spirotetramat <sup>81</sup>	35.25	352.5	267	RT/FM	165	50	СТ	2025	NP				
Sulfentrazone82	2345	23450	1475	BS/RT	15100	100	DM	14.4	SC				
Sulfometuron methyl <sup>83</sup>	3700	37000		RT	37500	48500	DM	0.225	LG				
Tebuthiuron <sup>84</sup>	2650	26500	4650	FM	74250	10900	DM	25	SC				
Tefluthrin <sup>85</sup>	0.0015	0.015	0.002	RT/FM	0.0175	0.004	DM						
Terbacil <sup>86</sup>	1155	11550	600	RT	16250	25	DM	5.5	NP				
Tetrahydrophthalimide 87	3000	30000		RT	28250		DM	90500					
Thiamethoxam88	2850	28500	10000	BS/RT	8.75	0.37	CR	45100	LM				
Total Fluvalinate89	0.00875	0.0875	0.032	CC/FM	0.235	0.05	DM						
Triadimefon <sup>90</sup>	102.5	1025	85	RT	400	26	DM	1000	SC				
Triazine DEA degradate <sup>7</sup>								500					
Triazine DIA degradate <sup>7</sup>	425	4250			31500			1250					
Triclopyr acid <sup>91</sup>	2925	29250	52000	RT/FM	33225	40350	DM	2950	SC				
Triclosan <sup>92</sup>	7.2	72		RT	97.5		DM	0.35	SS				
Trifloxystrobin <sup>93</sup>	0.3575	3.575	2.15	RT	6.325	1.38	DM	18.55	SC				
Trifluralin <sup>94</sup>	0.4625	4.625	0.95		62.75	1.2		10.95					

		<u>l</u>	<u>Invertebrate</u>			Aquatic Plant		WAC		/QC			
	Endangered												
	Species												
Pesticide	Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC

CMC: Criteria Maximum Concentration CCC: Criteria Continuous Concentration

<sup>&</sup>lt;sup>a</sup> Criteria is specific to total DDT but is used here for individual metabolites as well.

<sup>&</sup>lt;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.

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# **Appendix B: 2018 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 2018, QA/QC samples were 11% of all the samples collected in the field. There were 140 QC samples in total: 59 field replicates, 33 field blanks, 31 MS/MSD samples and 17 conductivity check samples. The lab contributed the remaining LCS/LCSD and method blank samples.

#### **Data Qualification**

Performance measures are 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 is used to assess bias in an analysis; a known amount of chemical is added to a sample before analysis and compared to the amount detected during analysis. Systematically low percent recoveries show analytical bias. The analytical method named GCMS-Pesticide in this report has percent recovery control limits that are analyte-specific. All other percent recovery limits are default limits specified by the EPA method. RPD is used to assess analytical precision; the difference between replicate pairs (matrix spike duplicates, laboratory control sample duplicates, and field replicates) is compared. When RPDs and percent recoveries are outside control limits, analytical results may be qualified.

The Manchester Environmental Laboratory (MEL) qualify all sample results based on the analysis of LCS/LCSDs, MS/MSDs, surrogates, and method blanks. LCS/LCSD are generated by adding analytes at known concentrations to purified water free of all organics. An LCS/LCSD pair is extracted and analyzed with every batch of field samples and other QC samples. They are 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 have added analytes 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. An MS/MSD sample was collected once during the season at each site for each analysis method, except in a few cases where budgetary restrictions were prohibitive. In 2018, all analytes tested for during the season were used to spike MS/MSDs and LCS/LCSDs, although the lab rotated between 2 spike mixtures for the GCMS-Pesticides analytical method to avoid coelution of analytes. Surrogates are analytes not normally found in environmental samples that are 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 are used to evaluate variability in analytical results. No field sample results were qualified due solely to field replicate results in 2018. Field blank results are used to examine bias caused by contamination in the field, during transport to the lab and during processing at the lab. No field samples or QC results were qualified due solely to field blank results or MS/MSD results.

MEL reports the method reporting limit (MRL) which is the lowest concentration used in the initial calibration for each analyte. The MRL is 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 MRL (calculated for each individual sample in 2018) and standard deviation are presented in Table 30b.

Table 30b – Mean performance of method reporting limits (MRL) in µg/L

Analyte	CAS number	Analytical method	Pesticide type	Mean MRL	Standard deviation
2,4-D	94-75-7	GCMS-Herbicides	Herbicide	6.05E-02	1.35E-02
2,6-Dichlorobenzamide	2008-58-4	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
3,5-Dichlorobenzoic Acid	51-36-5	GCMS-Herbicides	Degradate	5.96E-02	7.55E-04
4,4'-DDD	72-54-8	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
4,4'-DDE	72-55-9	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
4,4'-DDT	50-29-3	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
4-Nitrophenol	100-02-7	GCMS-Herbicides	Degradate	5.96E-02	7.55E-04
Acetamiprid	135410-20-7	LCMS-Pesticides	Insecticide	2.00E-02	2.87E-09
Acetochlor	34256-82-1	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Alachlor	15972-60-8	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Aldicarb Sulfoxide	1646-87-3	LCMS-Pesticides	Degradate	1.00E-02	1.44E-09
Atrazine	1912-24-9	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Azoxystrobin	131860-33-8	LCMS-Pesticides	Fungicide	2.00E-02	2.87E-09
Baygon	114-26-1	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Benefin	1861-40-1	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Bentazon	25057-89-0	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Bifenazate	149877-41-8	GCMS-Pesticides	Insecticide	5.00E-03	7.80E-10
Bifenthrin	82657-04-3	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Boscalid	188425-85-6	GCMS-Pesticides	Fungicide	5.16E-03	2.38E-03
Bromacil	314-40-9	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Bromoxynil	1689-84-5	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Captan	133-06-2	GCMS-Pesticides	Fungicide	6.77E-03	4.12E-03
Carbaryl	63-25-2	LCMS-Pesticides	Insecticide	2.00E-02	2.87E-09
Carbendazim	10605-21-7	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
Chlorantraniliprole	500008-45-7	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09

Analyte	CAS number	Analytical method	Pesticide type	Mean MRL	Standard deviation
Chlorethoxyfos	54593-83-8	GCMS-Pesticides	Insecticide	9.93E-03	6.00E-04
Chlorothalonil (Daconil)	1897-45-6	GCMS-Pesticides	Fungicide	5.00E-03	7.83E-10
Chlorpropham	101-21-3	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Chlorpyriphos	2921-88-2	GCMS-Pesticides	Insecticide	5.11E-03	2.18E-03
Chlorsulfuron	64902-72-3	LCMS-Pesticides	Herbicide	5.04E-02	2.89E-03
cis-Permethrin	54774-45-7	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Clopyralid	1702-17-6	GCMS-Herbicides	Herbicide	5.96E-02	7.35E-04
Clothianidin	210880-92-5	LCMS-Pesticides	Insecticide	1.00E-01	1.54E-08
Coumaphos	56-72-4	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Cycloate	1134-23-2	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Cyfluthrin	68359-37-5	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Cypermethrin	52315-07-8	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Cyprodinil	121552-61-2	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
Dacthal	1861-32-1	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Deisopropyl Atrazine	1007-28-9	LCMS-Pesticides	Degradate	1.00E-02	1.44E-09
Deltamethrin	52918-63-5	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Desethylatrazine	6190-65-4	LCMS-Pesticides	Degradate	1.00E-02	1.44E-09
Diazinon	333-41-5	GCMS-Pesticides	Insecticide	5.01E-03	1.97E-04
Dicamba	1918-00-9	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Dichlobenil	1194-65-6	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Dichlorprop	120-36-5	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Dichlorvos (DDVP)	62-73-7	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Difenoconazole	119446-68-3	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
Diflubenzuron	35367-38-5	LCMS-Pesticides	Insecticide	7.00E-02	8.36E-09
Dimethoate	60-51-5	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Dinotefuran	165252-70-0	LCMS-Pesticides	Insecticide	2.21E-02	1.89E-02
Dithiopyr	97886-45-8	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Diuron	330-54-1	LCMS-Pesticides	Herbicide	1.00E-02	1.44E-09
Eptam	759-94-4	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Ethalfluralin (Sonalan)	55283-68-6	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Ethoprop	13194-48-4	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Etoxazole	153233-91-1	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Etridiazole	2593-15-9	GCMS-Pesticides	Fungicide	5.00E-03	7.83E-10
Fenarimol	60168-88-9	GCMS-Pesticides	Fungicide	5.00E-03	9.87E-05
Fenbuconazole	114369-43-6	LCMS-Pesticides	Fungicide	2.00E-02	2.87E-09
Fenvalerate	51630-58-1	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Fipronil	120068-37-3	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Fipronil Desulfinyl	205650-65-3	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
Fipronil Sulfide	120067-83-6	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
Fipronil Sulfone	120068-36-2	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
Fludioxonil	131341-86-1	GCMS-Pesticides	Fungicide	6.52E-03	8.52E-03

Analyte	CAS number	Analytical method	Pesticide type	Mean MRL	Standard deviation
Flumiovazia	400004.00.	00140 D. W. I.			7.67E-10
Flumioxazin	103361-09-7	GCMS-Pesticides	Herbicide	5.00E-03 2.46E-02	2.42E-03
Fluroxypyr-meptyl Hexazinone	81406-37-3	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
	51235-04-2	GCMS-Pesticides	Herbicide		
Imazapic	104098-48-8	LCMS-Pesticides	Herbicide	1.00E-01	1.54E-08
Imazapyr	81334-34-1	LCMS-Pesticides	Herbicide	1.00E-01	1.54E-08
Imidacloprid	138261-41-3	LCMS-Pesticides	Insecticide	2.00E-02	2.87E-09
Imidan 	732-11-6	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Isoxaben	82558-50-7	LCMS-Pesticides	Herbicide	1.00E-02	1.44E-09
Kelthane	115-32-2	GCMS-Pesticides	Insecticide	2.46E-02	2.59E-03
Linuron	330-55-2	LCMS-Pesticides	Herbicide	7.00E-02	8.36E-09
Malaoxon	1634-78-2	LCMS-Pesticides	Degradate	1.00E-02	1.44E-09
Malathion	121-75-5	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
MCPA	94-74-6	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
MCPP	93-65-2	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Metalaxyl	57837-19-1	GCMS-Pesticides	Fungicide	5.00E-03	7.83E-10
Methiocarb	2032-65-7	LCMS-Pesticides	Insecticide	3.00E-02	3.84E-09
Methomyl	16752-77-5	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Methomyl oxime	13749-94-5	LCMS-Pesticides	Degradate	1.00E-01	1.54E-08
Methoxyfenozide	161050-58-4	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Methyl Chlorpyrifos	5598-13-0	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Metolachlor	51218-45-2	GCMS-Pesticides	Herbicide	5.05E-03	9.87E-04
Metribuzin	21087-64-9	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Metsulfuron-methyl	74223-64-6	LCMS-Pesticides	Herbicide	5.00E-02	7.69E-09
MGK264	113-48-4	GCMS-Pesticides	Synergist	5.00E-03	7.83E-10
Myclobutanil	88671-89-0	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
N,N-Diethyl-m-toluamide	134-62-3	GCMS-Pesticides	Insect Repellent	5.01E-03	1.97E-04
Naled	300-76-5	GCMS-Pesticides	Insecticide	5.00E-03	7.62E-10
Napropamide	15299-99-7	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Norflurazon	27314-13-2	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Oryzalin	19044-88-3	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Oxadiazon	19666-30-9	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Oxamyl		LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Oxamyl oxime	23135-22-0			1.60E-02	9.17E-03
Oxyfluorfen	30558-43-1	LCMS-Pesticides	Degradate	4.91E-02	5.42E-03
Pendimethalin	42874-03-3	GCMS-Pesticides	Herbicide	4.91E-02 5.00E-03	7.83E-10
Pendimethalin Pentachloronitrobenzene	40487-42-1	GCMS-Pesticides	Herbicide		
	82-68-8	GCMS-Pesticides	Fungicide Wood	5.00E-03	7.83E-10
Pentachlorophenol	87-86-5	GCMS-Herbicides	Preservative	5.96E-02	7.55E-04
Phenothrin	26002-80-2	GCMS-Pesticides	Insecticide	9.93E-03	6.00E-04
Phorate	298-02-2	GCMS-Pesticides	Insecticide	6.15E-03	2.10E-03

Analyte	CAS number	Analytical method	Pesticide type	Mean MRL	Standard deviation
Picloram	1918-02-1	GCMS-Herbicides	Herbicide	5.97E-02	7.51E-04
Piperonyl Butoxide (PBO)	51-03-6	GCMS-Pesticides	Synergist	5.00E-03	7.83E-10
Prallethrin	23031-36-9	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Prodiamine	29091-21-2	GCMS-Pesticides	Herbicide	2.46E-02	2.42E-03
Prometon	1610-18-0	GCMS-Pesticides	Herbicide	5.02E-03	3.48E-04
Prometryn	7287-19-6	GCMS-Pesticides	Herbicide	6.32E-03	2.20E-03
Pronamide (Kerb)	23950-58-5	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Propargite	2312-35-8	GCMS-Pesticides	Insecticide	9.93E-03	6.00E-04
Propiconazole	60207-90-1	LCMS-Pesticides	Fungicide	2.00E-02	2.87E-09
Pyraclostrobin	175013-18-0	LCMS-Pesticides	Fungicide	2.00E-02	2.87E-09
Pyraflufen-ethyl	129630-19-9	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Pyrethrins	121-21-1	GCMS-Pesticides	Insecticide	2.49E-02	3.89E-04
Pyridaben	96489-71-3	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Pyrimethanil	53112-28-0	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
Pyriproxyfen	95737-68-1	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Simazine	122-34-9	GCMS-Pesticides	Herbicide	5.11E-03	2.22E-03
Simetryn	1014-70-6	GCMS-Pesticides	Herbicide	6.34E-03	2.22E-03
Specific Conductivity	COND	COND	N/A	15 µS/cm	0.00E+00
Spirotetramat	203313-25-1	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Sulfentrazone	122836-35-5	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Sulfometuron methyl	74222-97-2	LCMS-Pesticides	Herbicide	2.00E-02	2.87E-09
Tau-fluvalinate	102851-06-9	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Tebuthiuron	34014-18-1	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Tefluthrin	79538-32-2	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Terbacil	5902-51-2	GCMS-Pesticides	Herbicide	5.05E-03	9.87E-04
Tetrachlorvinphos	961-11-5	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Tetrahydrophthalimide	27813-21-4	GCMS-Pesticides	Degradate	5.00E-03	7.83E-10
Tetramethrin	7696-12-0	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Thiacloprid	111988-49-9	LCMS-Pesticides	Insecticide	1.00E-02	1.44E-09
Thiamethoxam	153719-23-4	LCMS-Pesticides	Insecticide	2.00E-02	2.87E-09
Total Suspended Solids	TSS	TSS	N/A	3.19 mg/L	2.66E+00
Tralomethrin	66841-25-6	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
trans-Permethrin	61949-77-7	GCMS-Pesticides	Insecticide	5.00E-03	7.83E-10
Treflan (Trifluralin)	1582-09-8	GCMS-Pesticides	Herbicide	6.27E-03	2.18E-03
Triadimefon	43121-43-3	GCMS-Pesticides	Fungicide	5.00E-03	7.83E-10
Triallate	2303-17-5	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Triclopyr	55335-06-3	GCMS-Herbicides	Herbicide	5.96E-02	7.55E-04
Triclopyr-butoxyl	64700-56-7	GCMS-Pesticides	Herbicide	5.00E-03	7.83E-10
Triclosan	3380-34-5	GCMS-Pesticides	Antimicrobial	5.27E-03	5.56E-03
Trifloxystrobin	141517-21-7	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09
Zoxamide	156052-68-5	LCMS-Pesticides	Fungicide	1.00E-02	1.44E-09

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 31b that are used for sample analysis of pesticides, TSS, and specific conductivity (MEL, 2016).

Table 31b – Data qualification definitions

Qualifier	Definition
	The analyte was positively identified and was detected at the reported concentration.
E	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.
N	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.
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**

Field replicate samples were collected in order to assess the potential for variation in sample homogeneity and the entire process of sampling and analysis. Field replicate analysis for 2018 data was revised. Previously, sample and field replicate concentrations were averaged regardless if they were consistently or inconsistently paired. The qualifier of only the sample, not field replicate, was used to determine if the sample concentration should be considered a positive detection or not. Now, sample and field replicate concentrations are no longer averaged. The qualifier of both the sample and field replicate is taken into consideration. If the sample and replicate are consistently identified, then the higher concentration is chosen as the concentration of the confirmed detection. If the sample and replicate are inconsistently identified, then the sample or replicate with the unqualified, J or E qualification is chosen with its respective concentration as the positive detection.

During 2018, 5% of pesticide and TSS samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 243 consistently identified pairs for pesticide analysis and 14 consistently identified pairs for TSS analysis. Consistent identification refers to analytes identified in both the original sample and field replicate with unqualified or qualified J and E results. Conversely, inconsistently identified replicate pairs are those where the analyte was detected in only 1 of the 2 samples collected. Only 51 inconsistently identified pairs for pesticide analysis and 2 inconsistently identified pairs for TSS were found.

Of the 146 analytes tested for, 51% (74 pesticides) were not detected in any field replicates. Table 32b presents the variability of analyte detections in field replicates with at least 1 detection in a replicate set and average replicate RPDs. RPDs were only calculated for consistently identified replicate pairs. Variability of detection and RPDs could not be calculated for the 74 analytes without replicate detections and, therefore, are not found in Table 32b.

Table 32b – Variability of pesticide detections in field replicates and mean RPDs

Analyte	Analytical method	pairs (n) pairs (n) detect pairs		consistent	Inconsistent detects (n)	Identified pairs with inconsistent detects (%)	Uncertainty: 90% upper confidence bound (%)
Diazinon	GCMS-Pesticide	16	0		1	100	100
Dichlorprop	GCMS-Herbicide	11	0		1	100	100
Dithiopyr	GCMS-Pesticide	16	0		1	100	100
Fipronil Desulfinyl	GCMS-Pesticide	15	0		2	100	100
Fipronil Sulfide	GCMS-Pesticide	14	0		3	100	100
Fipronil Sulfone	GCMS-Pesticide	15	0		2	100	100
MCPA	GCMS-Herbicide	11	0		1	100	100
Pentachloronitrobenzene	GCMS-Pesticide	16	0		1	100	100
Pyridaben	GCMS-Pesticide	15	0		2	100	100
4,4'-DDE	GCMS-Pesticide	10	3	3	4	57	83
Bentazon	GCMS-Herbicide	10	1	5	1	50	95
Deisopropyl Atrazine	LCMS-Pesticide	12	1	29	1	50	95
Fenarimol	GCMS-Pesticide	15	1	86	1	50	95
Metribuzin	GCMS-Pesticide	15	1	0	1	50	95
Myclobutanil	LCMS-Pesticide	12	1	5	1	50	95
Triadimefon	GCMS-Pesticide	15	1	22	1	50	95
Treflan (Trifluralin)	GCMS-Pesticide	13	2	0	2	50	86
Chlorantraniliprole	LCMS-Pesticide	7	4	2	3	43	72
Simazine	GCMS-Pesticide	10	4	5	3	43	72
Triclosan	GCMS-Pesticide	14	2	67	1	33	80
4,4'-DDD	GCMS-Pesticide	11	4	0	2	33	67
Hexazinone	GCMS-Pesticide	5	8	2	4	33	56
Fludioxonil	GCMS-Pesticide	10	5	0	2	29	83
Norflurazon	GCMS-Pesticide	13	3	5	1	25	68
Sulfentrazone	GCMS-Pesticide	9	6	19	2	25	54
Propiconazole	LCMS-Pesticide	9	4	17	1	20	58

Analyte	method pairs (n		Consistent detect pairs (n)	Mean RPD (%) consistent detect pairs	Inconsistent detects (n)	Identified pairs with inconsistent detects (%)	Uncertainty: 90% upper confidence bound (%)
Eptam	GCMS-Pesticide	11	5	2	1	17	51
Pendimethalin	GCMS-Pesticide	11	5	0	1	17	51
Prometon	GCMS-Pesticide	11	5	8	1	17	51
Terbacil	GCMS-Pesticide	11	5	7	1	17	51
Total Suspended Solids	TSS	0	14	13	2	13	30
Atrazine	GCMS-Pesticide	8	8	7	1	11	37
Boscalid	GCMS-Pesticide	4	12	4	1	8	27
4,4'-DDT	GCMS-Pesticide	16	1	15	0	0	90
Chlorpropham	GCMS-Pesticide	16	1	0	0	0	90
Cyprodinil	LCMS-Pesticide	13	1	11	0	0	90
Dacthal	GCMS-Herbicide	11	1	50	0	0	90
Etridiazole	GCMS-Pesticide	16	1	0	0	0	90
Fipronil	GCMS-Pesticide	16	1	0	0	0	90
Methoxyfenozide	LCMS-Pesticide	13	1	0	0	0	90
Oxadiazon	GCMS-Pesticide	16	1	15	0	0	90
Oxamyl oxime	LCMS-Pesticide	13	1	31	0	0	90
Pyrimethanil	LCMS-Pesticide	13	1	4	0	0	90
Simetryn	GCMS-Pesticide	16	1	0	0	0	90
Sulfometuron methyl	LCMS-Pesticide	13	1	40	0	0	90
Clothianidin	LCMS-Pesticide	12	2	4	0	0	68
Oxamyl	LCMS-Pesticide	12	2	1	0	0	68
Pentachlorophenol	GCMS-Herbicide	10	2	94	0	0	68
Piperonyl Butoxide	GCMS-Pesticide	15	2	8	0	0	68
Pyraclostrobin	LCMS-Pesticide	12	2	4	0	0	68
Azoxystrobin	LCMS-Pesticide	11	3	5	0	0	54
Dinotefuran	LCMS-Pesticide	11	3	4	0	0	54
Tetrahydrophthalimide	GCMS-Pesticide	14	3	8	0	0	54

Analyte	Analytical method	Consistent nondetect pairs (n)	Consistent detect pairs (n)	Mean RPD (%) consistent detect pairs	Inconsistent detects (n)	Identified pairs with inconsistent detects (%)	Uncertainty: 90% upper confidence bound (%)
Carbendazim	LCMS-Pesticide	10	4	0	0	0	44
MCPP	GCMS-Herbicide	8	4	13	0	0	44
Metalaxyl	GCMS-Pesticide	13	4	3	0	0	44
Tebuthiuron	GCMS-Pesticide	13	4	13	0	0	44
Triclopyr	GCMS-Herbicide	8	4	46	0	0	44
Dicamba	GCMS-Herbicide	7	5	4	0	0	37
Imazapyr	LCMS-Pesticide	9	5	4	0	0	37
Imidacloprid	LCMS-Pesticide	9	5	8	0	0	37
Malathion	GCMS-Pesticide	12	5	3	0	0	37
Bromacil	GCMS-Pesticide	11	6	1	0	0	32
Desethylatrazine	LCMS-Pesticide	8	6	5	0	0	32
Diuron	LCMS-Pesticide	8	6	11	0	0	32
Thiamethoxam	LCMS-Pesticide	8	6	4	0	0	32
Chlorpyrifos	GCMS-Pesticide	10	7	7	0	0	28
N,N-Diethyl-m-toluamide	GCMS-Pesticide	10	7	6	0	0	28
Dichlobenil	GCMS-Pesticide	8	9	5	0	0	23
2,4-D	GCMS-Herbicide	2	10	15	0	0	21
Metolachlor	GCMS-Pesticide	7	10	4	0	0	21
2,6-Dichlorobenzamide	GCMS-Pesticide	3	14	7	0	0	15

Staff used 2 methods to estimate the uncertainty of replicate variability. The first was the percentage of inconsistently identified replicate pairs and the second is an evaluation of the upper confidence bound associated with the percentage of inconsistently identified replicate pairs. It is assumed that if the percentage of inconsistently identified replicate pairs out of the total count of consistently and inconsistently identified replicate pairs is 25% or less, it can indicate low variability of detection whereas 50% or greater can indicate high variability of detection (Martin, 2002, p. 33). Almost 34% of analytes (49 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 2018 using the second method indicate only 4 analytes have a low detection variability rather than the 49 analytes estimated through the first method. These 4 include 2,4-D, 2,6dichlorobenzamide, dichlobenil and metolachlor. All 4 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 1 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 9%. Only 12 of the 243 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 replicatepaired analyte was 13%. Only 1 of the 14 consistently identified replicate pairs for TSS had an RPD that was equal to or greater than the 40% 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 53 inconsistently identified pairs were detections between the MRL 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.

#### 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 2018, there were 13 detections in the 33 field blank samples collected for TSS and pesticide analysis (Table 33b). If a detection occurs in a field blank, all sample detections of the same analyte in the analytical batch is reviewed for qualification. No samples were qualified solely due to field blank detection results.

Table 33b – Analyte detections in field blanks

Sampling date	Monitoring Site	Analytical method	Analyte	Result (µg/L)	MRL (µg/L)	MDL (µg/L)	Qualifier
3/27	Lower Bertrand	GCMS-Pesticides	2,6-Dichlorobenzamide	0.002	0.005	0.001	J
3/27	Lower Bertrand	GCMS-Pesticides	Fludioxonil	0.004	0.005	0.003	J
3/27	Naneum	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.016	0.005	0.001	D
4/11	Stemilt	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.022	0.005	0.001	D
5/01	Brender	GCMS-Pesticides	Dichlobenil	0.002	0.005	0.001	J
5/01	Brender	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.019	0.005	0.001	J
5/01	Brender	GCMS-Pesticides	Treflan (Trifluralin)	0.003	0.005	0.001	J
5/21	Snipes	GCMS-Pesticides	Chlorpropham	0.001	0.005	0.001	J
5/21	Snipes	GCMS-Pesticides	Dichlobenil	0.002	0.005	0.001	J
5/21	Snipes	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.026	0.005	0.001	D
6/20	Burnt Bridge	TSS	Total Suspended Solids	2	1	N/A	D
7/24	Upper Bertrand	GCMS-Pesticides	2,6-Dichlorobenzamide	0.001	0.005	0.001	J
7/24	Upper Bertrand	GCMS-Pesticides	Acetochlor	0.028	0.005	0.003	D

### **Laboratory Duplicates**

MEL uses split sample duplicates to evaluate the precision of TSS and conductivity analyses. In 2018, there were 115 laboratory duplicate pairs for TSS and 7 duplicate pairs for conductivity (Table 34b). Of the TSS duplicate pairs, 2 were U-qualified, leaving 113 TSS pairs with RPD calculated. No field TSS or conductivity samples were qualified due solely to RPD exceedances. Overall, laboratory duplicate results were of acceptable data quality.

Table 34b – Laboratory duplicate results

Parameter	Results	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Specific conductivity	7	20	0	0
Total suspended solids	113	20	0	0

## Matrix Spike/Matrix Spike Duplicate Results

Summary MS/MSD results for each analyte are shown in Table 35b, 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 TSS and specific conductivity.

Table 35b – Summary statistics for MS/MSD recoveries and RPD

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 number of detections in 2018
2,4-D	16	10	150	79	41 - 120	0	0	8	6	0.6 - 18	116
2,6-Dichlorobenzamide	24	30	140	108	73 - 159	0	2	12	4	0.7 - 15	238
3,5-Dichlorobenzoic Acid	16	21	144	84	71 - 121	0	0	8	5	0.3 - 19	0
4,4'-DDD	24	49	143	119	97 - 158	0	2	12	3	0.1 - 14	84
4,4'-DDE	24	40	130	90	73 - 104	0	0	12	4	0.4 - 15	83
4,4'-DDT	24	42	120	64	45 - 82	0	0	12	5	0.2 - 14	24
4-Nitrophenol	16	10	172	96	40 - 145	0	0	8	14	0.1 - 49	4
Acetamiprid	22	70	122	116	96 - 148	0	6	11	1	0.3 - 3	7
Acetochlor	24	30	130	121	100 - 156	0	6	12	3	0.3 - 13	0
Alachlor	24	16	181	110	91 - 146	0	0	12	3	0.006 - 11	0
Aldicarb Sulfoxide	22	68	119	94	82 - 115	0	0	11	3	0.1 - 5	0
Atrazine	24	13	172	103	85 - 136	0	0	12	4	1 - 14	109
Azoxystrobin	22	63	130	91	78 - 114	0	0	11	2	0.7 - 6	61
Baygon	22	62	120	91	81 - 107	0	0	11	2	0.03 - 3	0
Benefin	24	50	151	104	90 - 139	0	0	12	4	0.1 - 14	0
Bentazon	16	25	159	93	81 - 113	0	0	8	6	0.3 - 23	31
Bifenazate	21	50	150	257	166 - 383	0	21	10	6	0.7 - 13	1
Bifenthrin	24	30	130	113	92 - 133	0	4	12	5	0.06 - 17	10
Boscalid	24	50	150	122	13 - 153	2	3	12	4	0.1 - 14	242

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 (%)	Range of	Total number of detections in 2018
Bromacil	24	55	181	134	117 - 162	0	0	12	3	0.3 - 10	137
Bromoxynil	16	28	138	94	84 - 118	0	0	8	6	0.6 - 23	3
Captan	24	10	219	60	24 - 100	0	0	12	9	4 - 16	0
Carbaryl	22	29	139	98	88 - 112	0	0	11	5	2 - 9	7
Carbendazim	22	40	130	91	80 - 110	0	0	11	2	1 - 5	81
Chlorantraniliprole	22	53	130	95	80 - 119	0	0	11	3	0.3 - 6	58
Chlorethoxyfos	24	30	130	100	84 - 130	0	0	12	5	0.2 - 11	0
Chlorothalonil (Daconil)	24	57	227	92	58 - 116	0	0	12	6	1 - 16	7
Chlorpropham	24	53	181	116	96 - 158	0	0	12	3	0.3 - 16	15
Chlorpyriphos	22	52	152	102	83 - 126	0	0	11	3	0.2 - 12	103
Chlorsulfuron	22	10	125	105	35 - 229	0	5	11	4	0.7 - 14	3
cis-Permethrin	24	17	201	125	105 - 155	0	0	12	4	0.8 - 17	1
Clopyralid	16	10	106	52	30 - 80	0	0	8	7	0.2 - 10	13
Clothianidin	22	29	148	119	93 - 172	0	4	11	2	0.4 - 4	39
Coumaphos	24	10	487	134	113 - 162	0	0	12	3	0.05 - 14	0
Cycloate	24	49	151	114	82 - 157	0	1	12	6	2 - 19	0
Cyfluthrin	24	50	150	137	118 - 177	0	4	12	5	0.2 - 20	0
Cypermethrin	24	30	130	144	123 - 182	0	14	12	4	0.2 - 19	0
Cyprodinil	22	72	130	94	81 - 106	0	0	11	2	0.4 - 6	24
Dacthal	16	38	173	102	79 - 129	0	0	8	5	0.2 - 17	18
Deisopropyl Atrazine	22	10	146	132	92 - 160	0	8	11	3	0.4 - 7	60
Deltamethrin	24	30	130	140	109 - 188	0	12	12	4	0.1 - 18	0
Desethylatrazine	22	21	131	104	93 - 114	0	0	11	2	0.3 - 4	131
Diazinon	24	59	168	108	92 - 149	0	0	12	3	0.9 - 12	33
Dicamba	16	10	146	86	74 - 118	0	0	8	4	0.2 - 17	60
Dichlobenil	24	34	153	100	78 - 124	Ō	0	12	7	0.6 - 18	164
Dichlorprop	16	22	160	92	77 - 124	Ö	Ö	8	5	0.8 - 19	1
Dichlorvos (DDVP)	24	27	169	127	87 - 168	Ö	Ö	12	6	0.7 - 21	3
Difenoconazole	22	44	153	76	61 - 104	Ö	Ö	11	5	0.7 - 25	14
Diflubenzuron	22	45	127	88	76 - 111	Ō	Ō	11	6	0.4 - 18	0

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 (%)	Range of	Total number of detections in 2018
Dimethoate	24	65	217	126	103 - 170	0	0	12	3	0.6 - 13	12
Dinotefuran	22	36	175	133	95 - 176	0	1	11	2	0.1 - 6	52
Dithiopyr	24	30	130	105	89 - 129	0	0	12	4	0.6 - 12	13
Diuron	22	75	115	92	84 - 106	0	0	11	3	0.2 - 6	148
Eptam	24	41	159	102	81 - 133	0	0	12	6	0.5 - 17	73
Ethalfluralin (Sonalan)	24	6	243	114	98 - 157	0	0	12	3	0.09 - 11	0
Ethoprop	24	10	263	118	95 - 157	0	0	12	4	0.4 - 17	11
Etoxazole	24	50	150	128	105 - 155	0	2	12	5	0.6 - 20	8
Etridiazole	24	50	150	82	71 - 101	0	0	12	7	0.7 - 16	27
Fenarimol	24	30	130	136	118 - 154	0	16	12	3	0.02 - 13	21
Fenbuconazole	22	34	152	85	75 - 110	0	0	11	3	0.2 - 9	1
Fenvalerate	24	30	130	128	104 - 167	0	6	12	5	0.8 - 20	0
Fipronil	24	30	130	131	112 - 161	0	9	12	4	0.3 - 12	25
Fipronil Desulfinyl	24	30	130	115	99 - 151	0	4	12	4	0.4 - 12	8
Fipronil Sulfide	24	30	130	111	97 - 142	0	3	12	3	0.04 - 11	29
Fipronil Sulfone	24	30	130	127	107 - 161	0	8	12	4	0.3 - 13	21
Fludioxonil	24	50	150	110	0 - 155	2	1	12	3	0.1 - 13	149
Flumioxazin	24	50	150	125	90 - 180	0	4	12	5	2 - 14	2
Fluroxypyr-meptyl	24	50	150	123	103 - 181	0	2	12	4	0.3 - 12	0
Hexazinone	24	41	183	120	96 - 137	0	0	12	3	0.4 - 13	146
Imazapic	22	45	141	109	91 - 151	0	2	11	2	0.2 - 3	7
Imazapyr	22	40	109	110	93 - 133	0	12	11	2	0.2 - 4	88
Imidacloprid	22	58	135	155	110 - 235	0	13	11	5	0.2 - 31	87
Imidan <sup>.</sup>	24	32	203	115	93 - 139	0	0	12	3	0.1 - 12	1
Isoxaben	22	59	138	90	79 - 106	0	0	11	2	0.2 - 4	22
Kelthane	12	10	265	141	91 - 206	0	0	6	18	0.6 - 43	0
Linuron	22	35	144	92	80 - 104	0	0	11	5	1 - 9	0
Malaoxon	22	10	145	93	85 - 106	0	0	11	1	0.007 - 3	4
Malathion	24	50	147	125	101 - 159	0	2	12	3	0.09 - 13	37
MCPA	16	14	148	88	72 - 123	0	0	8	6	0.6 - 18	16

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 (%)	_	Total number of detections in 2018
MCPP	16	23	162	92	80 - 125	0	0	8	6	0.03 - 18	20
Metalaxyl	24	56	149	113	86 - 170	0	2	12	4	1 - 12	72
Methiocarb	22	10	154	98	86 - 116	0	0	11	5	0.05 - 10	4
Methomyl	22	65	119	87	80 - 101	0	0	11	2	0.05 - 5	10
Methomyl oxime	22	13	164	82	72 - 116	0	0	11	5	0.3 - 12	2
Methoxyfenozide	22	62	134	90	78 - 109	0	0	11	3	0.1 - 5	7
Methyl Chlorpyrifos	24	50	144	105	84 - 143	0	0	12	4	0.8 - 13	0
Metolachlor	24	55	180	111	92 - 150	0	0	12	3	0.2 - 12	133
Metribuzin	24	30	130	107	85 - 144	0	2	12	4	0.1 - 18	55
Metsulfuron-methyl	22	10	119	147	31 - 302	0	10	11	4	0.7 - 8	6
MGK264	24	49	193	108	89 - 142	0	0	12	3	0.3 - 13	0
Myclobutanil	22	59	123	92	81 - 109	0	0	11	3	0.4 - 7	37
N,N-Diethyl-m-toluamide	24	50	150	112	91 - 149	0	0	12	4	0.3 - 15	105
Naled	24	10	220	60	38 - 82	0	0	12	8	0.4 - 23	0
Napropamide	24	70	180	118	102 - 149	0	0	12	4	0.4 - 12	16
Norflurazon	24	70	168	122	102 - 165	0	0	12	4	0.7 - 10	94
Oryzalin	24	10	230	97	65 - 137	0	0	12	7	0.3 - 17	14
Oxadiazon	24	50	150	109	91 - 151	0	1	12	3	0.4 - 11	29
Oxamyl	22	10	173	89	82 - 110	0	0	11	2	0.7 - 3	37
Oxamyl oxime	22	37	189	168	110 - 269	0	5	11	5	1 - 12	35
Oxyfluorfen	24	51	153	130	112 - 162	0	2	12	3	0.02 - 11	0
Pendimethalin	24	39	163	117	103 - 152	0	0	12	3	0.3 - 11	103
Pentachloronitrobenzene	24	50	150	98	81 - 123	0	0	12	4	0.8 - 11	1
Pentachlorophenol	16	32	136	91	82 - 121	0	0	8	7	2 - 21	11
Phenothrin	24	22	130	84	49 - 143	0	1	12	8	0.8 - 18	0
Phorate	24	12	130	117	106 - 156	0	4	12	4	0.04 - 14	0
Picloram	14	10	110	35	4 - 75	4	0	7	41	9 - 89	15
Piperonyl Butoxide	24	30	130	174	91 - 246	0	18	12	3	0.01 - 10	16
Prallethrin	24	30	130	126	10 - 168	2	15	12	12	0.8 - 65	0
Prodiamine	24	30	130	115	98 - 152	0	4	12	5	0.8 - 11	15

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 (%)	Range of	Total number of detections in 2018
Prometon	24	55	164	114	95 - 158	0	0	12	3	0.2 - 13	93
Prometryn	24	62	165	115	99 - 145	0	0	12	3	0.2 - 12	3
Pronamide (Kerb)	24	63	169	113	94 - 152	0	0	12	4	0.06 - 15	0
Propargite	24	30	130	150	74 - 227	0	18	12	4	0.4 - 10	0
Propiconazole	22	47	146	85	17 - 107	1	0	11	16	0.4 - 134	43
Pyraclostrobin	22	64	142	89	77 - 106	0	0	11	2	0.1 - 5	22
Pyraflufen-ethyl	24	50	150	127	100 - 169	0	2	12	3	0.1 - 9	0
Pyrethrins	6	30	150	92	13 - 245	4	2	3	6	0.4 - 16	0
Pyridaben	24	50	150	137	112 - 178	0	2	12	4	0.9 - 15	31
Pyrimethanil	22	78	122	88	77 - 106	1	0	11	4	0.9 - 10	33
Pyriproxyfen	24	30	130	120	94 - 151	0	4	12	3	0.4 - 14	11
Simazine	24	72	192	101	72 - 130	0	0	12	3	0.1 - 14	116
Simetryn	24	61	171	109	93 - 139	0	0	12	3	0.2 - 12	2
Spirotetramat	22	17	133	94	66 - 145	0	3	11	5	1 - 11	2
Sulfentrazone	24	50	150	144	113 - 187	0	9	12	5	0.02 - 13	125
Sulfometuron methyl	22	41	122	107	81 - 152	0	8	11	2	0.06 - 6	11
Tau-fluvalinate	24	50	150	141	113 - 193	0	6	12	5	0.2 - 21	1
Tebuthiuron	24	10	235	128	100 - 174	0	0	12	5	0.3 - 15	76
Tefluthrin	24	30	130	101	82 - 140	0	2	12	4	0.2 - 16	1
Terbacil	24	27	237	143	112 - 193	0	0	12	3	0.2 - 11	113
Tetrachlorvinphos	24	70	196	127	103 - 161	0	0	12	4	0.4 - 13	0
Tetrahydrophthalimide	24	50	150	129	78 - 194	0	8	12	6	1 - 17	44
Tetramethrin	24	30	130	125	99 - 158	0	8	12	5	0.1 - 13	0
Thiacloprid	22	64	121	112	92 - 143	0	6	11	2	0.09 - 8	0
Thiamethoxam	22	58	131	150	126 - 186	0	19	11	2	0.2 - 4	104
Tralomethrin	24	30	130	140	109 - 187	0	12	12	4	0.04 - 18	0
trans-Permethrin	24	30	130	122	102 - 156	0	6	12	5	2 - 17	0
Treflan (Trifluralin)	24	58	174	98	83 - 136	0	0	12	3	0.2 - 14	56
Triadimefon	24	61	178	116	98 - 162	0	0	12	3	0.04 - 11	43
Triallate	24	52	128	104	87 - 139	0	2	12	4	1 - 13	0

Analyte	MS/MSD recoveries (n)		Upper control limit (%)	•	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	_	Total number of ) detections in 2018
Triclopyr	16	10	190	97	85 - 134	0	0	8	4	0.6 - 15	46
Triclopyr-butoxyl	24	50	150	108	79 - 156	0	2	12	4	0.6 - 11	0
Triclosan	24	30	130	144	126 - 173	0	20	12	5	0.7 - 12	44
Trifloxystrobin	22	41	142	103	95 - 116	0	0	11	2	0.03 - 3	10
Zoxamide	22	56	111	93	85 - 111	0	0	11	3	0.5 - 6	0

<sup>\*</sup> RPD control limit for every analyte in this table is 40%.

There were a total of 3,227 spiked results (1,613 MS/MSD pairs) from MS and MSD recoveries that were unqualified or J qualified. The lab did not calculate a recovery for 1 MS sample. Overall, the mean recovery was 111% with a standard deviation of 32  $\mu$ g/L. RPDs calculated for 1,613 MS/MSD pairs were below the 40% RPD control limit 99% of the time; only 7 pairs had RPDs above the control limit. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 4% with a standard deviation of 4  $\mu$ g/L. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 71% with a standard deviation of 32  $\mu$ g/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) 12% of analyte recoveries (380 recoveries) fell below the control limits for MS/MSD samples,
- 2) 88% of analyte recoveries (2,831 recoveries) were within the control limits for MS/MSD samples,
- 3) < 1% of analyte recoveries (16 recoveries) were above the control limits for MS/MSD samples.

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 MRL may be increased, and detections may be qualified as estimates. Table 36b lists the analyte detections that occurred in the laboratory blanks (63 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.

Table 36b – Analyte detections in laboratory blanks

Analysis	Analytical	Analyte	Result	MRL	MDL	Qualifier
date	method	Allalyte	(µg/L)	(µg/L)	(µg/L)	Quanner
4/10	GCMS-Pesticides	Kelthane	0.002	0.025	0.016	J
5/11	GCMS-Pesticides	Fenarimol	0.002	0.005	0.001	J
5/23	GCMS-Pesticides	4,4'-DDD	0.001	0.005	0.0007	J
5/23	GCMS-Pesticides	4,4'-DDT	0.004	0.005	0.0008	J
5/23	GCMS-Pesticides	Fenarimol	0.003	0.005	0.001	J
5/23	GCMS-Pesticides	Hexazinone	0.002	0.005	0.001	J
5/23	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
5/23	GCMS-Pesticides	Pyridaben	0.001	0.005	0.001	J
5/23	GCMS-Pesticides	Pyriproxyfen	0.002	0.005	0.001	J
5/23	GCMS-Pesticides	Triadimefon	0.002	0.005	0.002	J
5/23	GCMS-Pesticides	Triclosan	0.007	0.005	0.002	
6/06	GCMS-Pesticides	Boscalid	0.001	0.005	0.0006	J
6/06	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
6/06	GCMS-Pesticides	Hexazinone	0.002	0.005	0.001	J
6/06	GCMS-Pesticides	Pyriproxyfen	0.002	0.005	0.001	J
6/06	GCMS-Pesticides	Triadimefon	0.002	0.005	0.002	J
6/06	GCMS-Pesticides	Triclosan	0.004	0.005	0.002	J
6/12	GCMS-Pesticides	Fenarimol	0.003	0.005	0.001	J
6/14	GCMS-Pesticides	Fenarimol	0.003	0.005	0.001	J
6/14	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
6/14	GCMS-Pesticides	Triclosan	0.006	0.005	0.002	
6/27	GCMS-Pesticides	4,4'-DDD	0.001	0.005	0.0007	J
6/27	GCMS-Pesticides	Ethoprop	0.002	0.005	0.001	J

Analysis date	Analytical method	Analyte	Result (µg/L)	MRL (µg/L)	MDL (µg/L)	Qualifier
6/27	GCMS-Pesticides	Fenarimol	0.003	0.005	0.001	J
6/25	LCMS-Pesticides	Spirotetramat	0.003	0.01	0.001	J
7/27	GCMS-Pesticides	4,4'-DDT	0.004	0.005	0.0008	J
7/27	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
7/25	GCMS-Pesticides	4,4'-DDT	0.004	0.005	0.0008	J
7/25	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
7/27	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
7/27	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
8/09	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
8/09	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
8/13	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.003	0.005	0.001	J
8/22	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
9/05	GCMS-Pesticides	Hexazinone	0.003	0.005	0.001	J
9/05	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.002	0.005	0.001	J
9/05	GCMS-Pesticides	Triclosan	0.004	0.005	0.002	J
9/25	GCMS-Pesticides	Dichlobenil	0.0003	0.005	0.001	J
9/25	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
9/27	GCMS-Pesticides	Dichlobenil	0.0004	0.005	0.001	J
9/27	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
9/27	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
9/27	GCMS-Pesticides	Dichlobenil	0.0004	0.005	0.001	J
9/27	GCMS-Pesticides	Fenarimol	0.0009	0.005	0.001	J
9/27	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J
10/04	GCMS-Pesticides	Dichlobenil	0.0003	0.005	0.001	J
10/04	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
10/10	GCMS-Pesticides	2,6-Dichlorobenzamide	0.0008	0.005	0.001	J
10/10	GCMS-Pesticides	Dichlobenil	0.0004	0.005	0.001	J
10/10	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
10/10	GCMS-Pesticides	N,N-Diethyl-m-toluamide	0.001	0.005	0.001	J

Analysis date	Analytical method	Analyte	Result (µg/L)	MRL (µg/L)	MDL (µg/L)	Qualifier
10/10	GCMS-Pesticides	Dichlobenil	0.0004	0.005	0.001	J
10/10	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
10/19	GCMS-Pesticides	4,4'-DDD	0.002	0.005	0.0007	J
10/19	GCMS-Pesticides	4,4'-DDT	0.004	0.005	0.0008	J
10/19	GCMS-Pesticides	Dichlobenil	0.0003	0.005	0.001	J
10/19	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
10/19	GCMS-Pesticides	Hexazinone	0.003	0.005	0.001	J
10/29	GCMS-Pesticides	Dichlobenil	0.0005	0.005	0.001	J
10/29	GCMS-Pesticides	Dichlobenil	0.0004	0.005	0.001	J
11/15	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J
11/15	GCMS-Pesticides	Fenarimol	0.001	0.005	0.001	J

# **Surrogates**

Surrogates are analytes used to assess recovery for a group of structurally related chemicals. Surrogates specific to the list of analytes are 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 37b presents summary statistics for surrogate recoveries.

Table 37b – Pesticide surrogates

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
Carbamate pesticides:						
Carbaryl C13	LCMS-Pesticides	416	104	100.0	67	132
Acid-derivitizable herbicides:						
2,4,6-Tribromophenol	GCMS-Herbicides	401	85	98.0	41	116
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	401	97	99.5	31	149
Nitrogen containing pesticides:						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	476	100	99.6	41	135

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	476	92	100.0	20	117
Decachlorobiphenyl (DCB)	GCMS-Pesticides	380	76	86.6	13	98
Organophosphate pesticides:						
Chlorpyrifos-D10	GCMS-Pesticides	476	107	100.0	30	178
Triphenyl phosphate	GCMS-Pesticides	380	116	95.5	45	137
Chlorine and nitrogen containing pesticides:						
Trifluralin-D14	GCMS-Pesticides	476	98	100.0	26	180
Atrazine-D5	GCMS-Pesticides	476	114	99.2	45	167

In 2018, the overall mean recovery for surrogates was 99% and 98% of surrogate recoveries were within control limits.

## **Laboratory Control Samples**

Summary LCS/LCSD results for each analyte are shown in Table 38b, 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.

Table 38b – Summary statistics for LCS/LCSD recoveries and RPD

Analyte	LCS/LCSD recoveries (n)			•	Range of recoveries (%)	recoveries	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
2,4-D	74	10	147	78	3 - 118	5	0	37	13	0.5 - 90
2,6-Dichlorobenzamide	73	30	140	97	73 - 133	0	0	36	4	0.6 - 16

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* (%)
3,5-Dichlorobenzoic Acid	74	14	135	84	55 - 124	0	0	37	5	0.2 - 17
4,4'-DDD	73	64	138	109	93 - 149	0	2	36	2	0.2 - 6
4,4'-DDE	73	43	140	96	86 - 115	0	0	36	2	0.3 - 6
4,4'-DDT	73	49	148	96	69 - 124	0	0	36	3	0.003 - 20
4-Nitrophenol	74	11	187	89	24 - 181	0	0	37	19	0.3 - 102
Acetamiprid	60	79	129	95	80 - 126	0	0	30	4	0.002 - 14
Acetochlor	73	30	130	113	96 - 142	0	8	36	3	0.1 - 8
Alachlor	73	13	184	103	90 - 130	0	0	36	2	0.3 - 7
Aldicarb Sulfoxide	60	55	145	97	76 - 125	0	0	30	4	0.03 - 14
Atrazine	73	14	178	99	86 - 127	0	0	36	3	0.005 - 8
Azoxystrobin	60	73	130	96	70 - 119	1	0	30	5	0.08 - 14
Baygon	60	72	127	99	81 - 117	0	0	30	4	0.2 - 12
Benefin	73	44	143	97	84 - 127	0	0	36	3	0.02 - 9
Bentazon	74	35	152	97	77 - 135	0	0	37	4	0.05 - 16
Bifenazate	73	50	150	121	27 - 276	3	21	36	9	0.4 - 57
Bifenthrin	73	30	130	109	81 - 135	0	2	36	3	0.01 - 11
Boscalid	73	50	150	113	88 - 136	0	0	36	3	0.05 - 10
Bromacil	73	58	170	117	92 - 139	0	0	36	3	0.05 - 8
Bromoxynil	74	32	128	92	77 - 115	Ö	Ö	37	5	0.6 - 18
Captan	73	36	168	75	2 - 139	5	Ö	36	14	0.2 - 174
Carbaryl	60	67	127	98	85 - 122	Ö	Ö	30	6	0.8 - 18
Carbendazim	60	40	130	92	73 - 117	Ö	Ö	30	4	0.03 - 12
Chlorantraniliprole	60	56	146	97	75 - 121	Ö	Ö	30	5	0.2 - 12
Chlorethoxyfos	73	30	130	95	72 - 118	Ö	Ö	36	5	0.1 - 24
Chlorothalonil (Daconil)	73	86	221	90	45 - 117	26	Ö	36	8	0.002 - 51
Chlorpropham	73	58	150	104	88 - 137	0	0	36	3	0.2 - 8
Chlorpyriphos	73	64	146	97	80 - 116	Ö	Ö	36	3	0.01 - 8
Chlorsulfuron	60	10	142	73	18 - 215	Ö	2	30	6	0.09 - 18
cis-Permethrin	73	48	178	119	90 - 149	Ö	0	36	3	0.03 10
Clopyralid	74	10	119	43	7 - 91	2	0	37	18	1 - 60

Clothianidin 60 52 146 94 68 - 134 0 Coumaphos 73 65 207 112 84 - 140 0 Cycloate 73 50 141 110 82 - 146 0 Cyfluthrin 73 30 130 118 89 - 143 0 Cypermethrin 73 30 130 126 93 - 302 0 19 Cyprodinil 60 66 133 95 76 - 112 0 Dacthal 74 40 154 95 57 - 135 0 Deisopropyl Atrazine 60 31 144 98 79 - 146 0 Deltamethrin 73 30 130 116 96 - 156 0 1 Desethylatrazine 60 31 151 98 80 - 161 0 Diazinon 73 70 142 103 85 - 129 0 Dicamba 74 12 138 82 44 - 119 0 Dichlobenil 73 44 139 99 68 - 123 0 Dichlorprop 74 16 153 88 51 - 129 0 Dichlorprop 74 16 153 88 51 - 129 0 Dichlorprop 74 16 153 88 51 - 129 0 Dichlorprop 74 16 153 88 51 - 129 0 Diffenoconazole 60 10 190 90 63 - 125 0 Diffubenzuron 60 42 139 93 74 - 126 0 Dimethoate 73 48 206 107 85 - 134 0 Dinotefuran 60 66 138 93 77 - 127 0 Dithiopyr 73 30 130 103 93 - 122 0 Dithopyr 74 149 96 80 - 114 0 Eptam 73 48 142 95 62 - 127 0 Ethalfluralin (Sonalan) 73 55 163 106 82 - 142 0 Ethoprop 73 55 163 106 82 - 142 0 Ethoprop 73 55 163 106 82 - 142 0 Etitodazole 73 30 130 91 64 - 128 0 Fenarimol 73 10 114 87 - 134 0	veries ove itrol	LCS/LCSD recoveries above control	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Coumaphos         73         65         207         112         84 - 140         0           Cycloate         73         50         141         110         82 - 146         0           Cyfluthrin         73         30         130         118         89 - 143         0           Cypermethrin         73         30         130         118         89 - 143         0           Cyprodinil         60         66         133         95         76 - 112         0           Cyprodinil         60         66         133         95         76 - 112         0           Dacthal         74         40         154         95         57 - 135         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         1           Diazinon         73		limits	00		0.000 44
Cycloate         73         50         141         110         82 - 146         0           Cyfluthrin         73         30         130         118         89 - 143         0         15           Cypermethrin         73         30         130         126         93 - 302         0         15           Cyprodinil         60         66         133         95         76 - 112         0         0           Dacthal         74         40         154         95         57 - 135         0         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         0           Ditazinon         73         70         142         103         85 - 129         0         0           Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123	0		30	4	0.003 - 14
Cyfluthrin         73         30         130         118         89 - 143         0         15           Cypermethrin         73         30         130         126         93 - 302         0         15           Cyprodinil         60         66         133         95         76 - 112         0         0           Deisopropyl Atrazine         60         31         154         95         57 - 135         0         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         1           Diesamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         0           Diflubenzuron         60         42	0		36	4	0.02 - 19
Cypermethrin         73         30         130         126         93 - 302         0         18           Cyprodinil         60         66         133         95         76 - 112         0         0           Dacthal         74         40         154         95         57 - 135         0         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         1           Diesethylatrazine         60         31         151         98         80 - 161         0         1           Diesethylatrazine         60         31         151         98         80 - 161         0         1           Diesethylatrazine         60         31         151         98         80 - 161         0           Diizainon         73         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139	1	· · · · · · · · · · · · · · · · · · ·	36	4	0.05 - 27
Cyprodinil         60         66         133         95         76 - 112         0         0           Dacthal         74         40         154         95         57 - 135         0         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         1           Disazinon         73         70         142         103         85 - 129         0         0           Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         0           Diflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107	9		36	4	0.1 - 21
Dacthal         74         40         154         95         57 - 135         0           Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         2           Diazinon         73         70         142         103         85 - 129         0         0           Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichlorprop         74         16         153         88         51 - 129         0         0           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         0           Difflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107         85 -		15	36	4	0.2 - 19
Deisopropyl Atrazine         60         31         144         98         79 - 146         0           Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         2           Diazinon         73         70         142         103         85 - 129         0         6           Dicamba         74         12         138         82         44 - 119         0         6           Dichlobenil         73         44         139         99         68 - 123         0         6           Dichlorprop         74         16         153         88         51 - 129         0         6           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         6           Diffenoconazole         60         10         190         90         63 - 125         0         6           Difflubenzuron         60         42         139         93         74 - 126         0         6           Dimethoate         73         48         206 <td< td=""><td>0</td><td></td><td>30</td><td>5</td><td>0.05 - 14</td></td<>	0		30	5	0.05 - 14
Deltamethrin         73         30         130         116         96 - 156         0         1           Desethylatrazine         60         31         151         98         80 - 161         0         3           Diazinon         73         70         142         103         85 - 129         0         6           Dicamba         74         12         138         82         44 - 119         0         6           Dichlobenil         73         44         139         99         68 - 123         0         6           Dichlorprop         74         16         153         88         51 - 129         0         6           Dichlorvos (DDVP)         73         39         145         103         62 - 158         0         6           Diffenoconazole         60         10         190         90         63 - 125         0         6           Difflubenzuron         60         42         139         93         74 - 126         0         6           Dimethoate         73         48         206         107         85 - 134         0         6           Dinotefuran         60         66         138	0		37	5	0.1 - 17
Desethylatrazine         60         31         151         98         80 - 161         0           Diazinon         73         70         142         103         85 - 129         0         0           Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         0           Difenoconazole         60         10         190         90         63 - 125         0         0           Diflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         30         130         103         93 - 122         0         0           Dithiopyr         73         30         130         103	1	· · · · · · · · · · · · · · · · · · ·	30	4	0.01 - 11
Diazinon         73         70         142         103         85 - 129         0         0           Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichloryorop         74         16         153         88         51 - 129         0         0           Dichloryos (DDVP)         73         39         145         103         62 - 158         0         0           Direnconazole         60         10         190         90         63 - 125         0         0           Diflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         30         130         103         93 - 122         0         0           Dithiopyr         73         30         130 <td< td=""><td>1</td><td>11</td><td>36</td><td>4</td><td>0.03 - 13</td></td<>	1	11	36	4	0.03 - 13
Dicamba         74         12         138         82         44 - 119         0         0           Dichlobenil         73         44         139         99         68 - 123         0         0           Dichloryor         74         16         153         88         51 - 129         0         0           Dichloryors (DDVP)         73         39         145         103         62 - 158         0         0           Diffenoconazole         60         10         190         90         63 - 125         0         0           Difflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         30         130         103         93 - 72 - 127         0         0           Dithiopyr         73         30         130         103         93 - 122         0         0           Diuron         60         76         124	2	2	30	3	0.04 - 13
Dichlobenil         73         44         139         99         68 - 123         0         0           Dichlorprop         74         16         153         88         51 - 129         0         0           Dichlorvos (DDVP)         73         39         145         103         62 - 158         0         0           Difenoconazole         60         10         190         90         63 - 125         0         0           Diflubenzuron         60         42         139         93         74 - 126         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         30         130         103         93 - 122         0         0           Dithiopyr         73         30         130         103         93 - 122         0         0           Ethaffluralin (Sonalan)         73         31         1	0	0	36	2	0.1 - 8
Dichlorprop         74         16         153         88         51 - 129         0           Dichlorvos (DDVP)         73         39         145         103         62 - 158         0           Difenoconazole         60         10         190         90         63 - 125         0           Diflubenzuron         60         42         139         93         74 - 126         0           Dimethoate         73         48         206         107         85 - 134         0           Dimethoate         73         48         206         107         85 - 134         0           Dinotefuran         60         66         138         93         77 - 127         0           Dithiopyr         73         30         130         103         93 - 122         0           Diuron         60         76         124         96         80 - 114         0           Eptam         73         48         142         95         62 - 127         0           Ethalfluralin (Sonalan)         73         31         167         103         87 - 139         0           Etoxazole         73         50         150         120	0	0	37	6	0.07 - 19
Dichlorvos (DDVP)         73         39         145         103         62 - 158         0           Difenoconazole         60         10         190         90         63 - 125         0           Diflubenzuron         60         42         139         93         74 - 126         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dimethoate         73         48         206         107         85 - 134         0         0           Dinotefuran         60         66         138         93         77 - 127         0         0           Dithiopyr         73         30         130         103         93 - 122         0         0           Diuron         60         76         124         96         80 - 114         0         0           Eptam         73         48         142         95         62 - 127         0         0           Ethalfluralin (Sonalan)         73         31         167         103         87 - 139         0         0           Etoxazole         73         50         150         120         94 - 144         0<	0	0	36	4	0.1 - 26
Dichlorvos (DDVP)         73         39         145         103         62 - 158         0           Difenoconazole         60         10         190         90         63 - 125         0           Diflubenzuron         60         42         139         93         74 - 126         0           Dimethoate         73         48         206         107         85 - 134         0           Dinotefuran         60         66         138         93         77 - 127         0           Dithiopyr         73         30         130         103         93 - 122         0           Diuron         60         76         124         96         80 - 114         0           Eptam         73         48         142         95         62 - 127         0           Ethalfluralin (Sonalan)         73         31         167         103         87 - 139         0           Ethoprop         73         55         163         106         82 - 142         0           Etoxazole         73         30         130         91         64 - 128         0           Fenarimol         73         30         130         114	0	0	37	5	0.05 - 19
Difenoconazole         60         10         190         90         63 - 125         0           Diflubenzuron         60         42         139         93         74 - 126         0           Dimethoate         73         48         206         107         85 - 134         0           Dinotefuran         60         66         138         93         77 - 127         0           Dithiopyr         73         30         130         103         93 - 122         0           Diuron         60         76         124         96         80 - 114         0           Eptam         73         48         142         95         62 - 127         0           Ethalfluralin (Sonalan)         73         31         167         103         87 - 139         0           Ethoprop         73         55         163         106         82 - 142         0           Etoxazole         73         50         150         120         94 - 144         0           Etridiazole         73         30         130         91         64 - 128         0           Fenarimol         73         30         130         114         <	4		36	5	0.3 - 29
Diflubenzuron       60       42       139       93       74 - 126       0         Dimethoate       73       48       206       107       85 - 134       0         Dinotefuran       60       66       138       93       77 - 127       0         Dithiopyr       73       30       130       103       93 - 122       0         Diuron       60       76       124       96       80 - 114       0         Eptam       73       48       142       95       62 - 127       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0         Ethoprop       73       55       163       106       82 - 142       0         Etoxazole       73       50       150       120       94 - 144       0         Etridiazole       73       30       130       91       64 - 128       0         Fenarimol       73       30       130       114       87 - 134       0	0		30	4	0.05 - 9
Dimethoate       73       48       206       107       85 - 134       0         Dinotefuran       60       66       138       93       77 - 127       0         Dithiopyr       73       30       130       103       93 - 122       0         Diuron       60       76       124       96       80 - 114       0         Eptam       73       48       142       95       62 - 127       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0         Ethoprop       73       55       163       106       82 - 142       0         Etoxazole       73       50       150       120       94 - 144       0         Etridiazole       73       30       130       91       64 - 128       0         Fenarimol       73       30       130       114       87 - 134       0	0		30	7	0.4 - 17
Dinotefuran       60       66       138       93       77 - 127       0       0         Dithiopyr       73       30       130       103       93 - 122       0       0         Diuron       60       76       124       96       80 - 114       0       0         Eptam       73       48       142       95       62 - 127       0       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0       0         Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       0	0		36	3	0.03 - 8
Dithiopyr       73       30       130       103       93 - 122       0       0         Diuron       60       76       124       96       80 - 114       0       0         Eptam       73       48       142       95       62 - 127       0       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0       0         Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		30	4	0.01 - 10
Diuron       60       76       124       96       80 - 114       0       0         Eptam       73       48       142       95       62 - 127       0       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0       0         Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		36	2	0.009 - 9
Eptam       73       48       142       95       62 - 127       0       0         Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0       0         Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		30	5	0.3 - 13
Ethalfluralin (Sonalan)       73       31       167       103       87 - 139       0       0         Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		36	5	0.4 - 29
Ethoprop       73       55       163       106       82 - 142       0       0         Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		36	4	0.1 - 14
Etoxazole       73       50       150       120       94 - 144       0       0         Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		36	4	0.6 - 17
Etridiazole       73       30       130       91       64 - 128       0       0         Fenarimol       73       30       130       114       87 - 134       0       2	0		36	3	0.04 - 16
Fenarimol 73 30 130 114 87 - 134 0	0		36	5	0.04 - 10
	2		36	3	0.2 - 20
Early 200 20 162 04 70 140 0 $\theta$	0		30	ა 5	0.2 - 12
	3	10	36 36	3 3	0.03 - 11 0.3 - 9

Analyte	LCS/LCSD recoveries (n)	control limit (%)	limit (%)	(%)	recoveries (%)	recoveries below control limits	above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Fipronil Desulfinyl	73	30	130	107	90 - 128	0	0	36	2	0.07 - 6
Fipronil Sulfide	73	30	130	104	93 - 124	0	0	36	3	0.3 - 8
Fipronil Sulfone	73	30	130	112	95 - 126	0	0	36	4	0.09 - 12
Fludioxonil	73	30	130	107	93 - 130	0	0	36	3	0.07 - 9
Flumioxazin	73	30	130	90	10 - 137	1	2	36	8	0.0005 - 12
Fluroxypyr-meptyl	73	30	130	113	87 - 149	0	11	36	4	0.6 - 9
Hexazinone	73	69	150	107	83 - 131	0	0	36	3	0.004 - 11
Imazapic	60	57	133	95	75 - 141	0	2	30	3	0.08 - 13
Imazapyr	60	35	153	97	68 - 157	0	2	30	4	0.4 - 25
Imidacloprid	60	66	134	100	61 - 155	2	2	30	6	0.6 - 35
Imidan	73	44	190	93	31 - 120	1	0	36	6	0.3 - 68
Isoxaben	60	67	137	95	74 - 112	0	0	30	4	0.3 - 12
Kelthane	32	31	179	165	69 - 372	0	11	16	13	0.8 - 45
Linuron	60	35	154	95	79 - 125	0	0	30	6	0.08 - 17
Malaoxon	60	67	124	94	76 - 106	0	0	30	4	0.003 - 13
Malathion	73	61	138	111	89 - 135	0	0	36	3	0.02 - 8
MCPA	74	13	139	82	27 - 125	0	0	37	7	0.06 - 33
MCPP	74	23	148	88	61 - 126	0	0	37	5	0.1 - 18
Metalaxyl	73	59	153	105	85 - 139	0	0	36	3	0.4 - 6
Methiocarb	60	58	131	98	80 - 140	0	1	30	5	0.05 - 14
Methomyl	60	71	128	94	78 - 116	0	0	30	4	0.06 - 13
Methomyl oxime	60	14	160	99	83 - 120	0	0	30	5	0.2 - 10
Methoxyfenozide	60	69	140	94	76 - 114	0	0	30	5	0.02 - 12
Methyl Chlorpyrifos	73	58	135	99	79 - 133	0	0	36	2	0.09 - 7
Metolachlor	73	68	158	103	88 - 130	0	0	36	2	0.09 - 5
Metribuzin	73	30	130	96	69 - 125	0	0	36	3	0.1 - 33
Metsulfuron-methyl	60	10	141	77	15 - 269	0	2	30	6	0.2 - 18
MGK264	73	71	169	99	78 - 127	0	0	36	3	0.1 - 10
Myclobutanil	60	50	143	99	78 - 129	0	0	30	5	0.07 - 20
N,N-Diethyl-m-toluamide	73	30	130	104	87 - 135	0	4	36	3	0.04 - 14

Analyte	LCS/LCSD recoveries (n)	control	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control	LCS/LCSD recoveries above control	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
		` ´	` ,		` '	limits	limits		,	
Naled	73	22	159	86	41 - 168	0	1	36	7	0.2 - 52
Napropamide	73	82	176	107	86 - 130	0	0	36	2	0.02 - 14
Norflurazon	73	85	143	106	88 - 134	0	0	36	3	0.2 - 8
Oryzalin	73	10	277	82	58 - 118	0	0	36	5	0.2 - 19
Oxadiazon	73	30	130	106	91 - 133	0	2	36	2	0.05 - 7
Oxamyl	60	64	135	96	81 - 121	0	0	30	4	0.01 - 12
Oxamyl oxime	60	61	149	107	73 - 151	0	1	30	4	0.04 - 16
Oxyfluorfen	73	42	154	113	98 - 133	0	0	36	3	0.2 - 12
Pendimethalin	73	49	159	106	94 - 129	0	0	36	3	0.07 - 8
Pentachloronitrobenzene	73	30	130	97	74 - 125	0	0	36	3	0.04 - 18
Pentachlorophenol	74	32	125	84	62 - 116	0	0	37	5	0.1 - 17
Phenothrin	73	20	95	74	39 - 123	0	9	36	8	0.2 - 41
Phorate	73	13	114	109	82 - 153	0	20	36	4	0.2 - 14
Picloram	69	10	110	23	5 - 75	9	0	34	34	0.9 - 114
Piperonyl Butoxide	73	30	130	139	77 - 212	0	45	36	3	0.07 - 10
Prallethrin	73	30	130	112	54 - 174	0	8	36	5	0.06 - 29
Prodiamine	73	30	130	106	90 - 126	0	0	36	5	0.06 - 26
Prometon	73	59	161	107	88 - 135	0	0	36	2	0.1 - 8
Prometryn	73	60	160	107	88 - 135	Ō	Ö	36	2	0.03 - 6
Pronamide (Kerb)	73	74	150	106	93 - 135	0	0	36	2	0.01 - 9
Propargite	73	30	130	125	70 - 193	0	41	36	3	0.02 - 8
Propiconazole	60	29	175	96	72 - 124	0	0	30	5	1 - 11
Pyraclostrobin	60	55	156	93	64 - 120	Ö	Ö	30	4	0.2 - 9
Pyraflufen-ethyl	73	30	130	116	83 - 140	Ö	12	36	3	0.008 - 7
Pyrethrins	73	30	130	68	31 - 144	Ö	2	36	10	0.5 - 48
Pyridaben	73	30	130	123	89 - 151	Ö	17	36	3	0.2 - 17
Pyrimethanil	60	68	138	95	80 - 131	Ö	0	30	5	0.05 - 14
Pyriproxyfen	73	30	130	112	83 - 141	Ö	5	36	3	0.05 - 10
Simazine	73	80	184	98	83 - 123	Ö	Ö	36	3	0.009 - 9
Simetryn	73	44	168	103	83 - 125	Ö	Ö	36	2	0.02 - 9

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* (%)
Specific Conductivity	6	95	105	100	100 - 100	0	0	0		
Spirotetramat	60	39	152	91	57 - 139	0	0	30	6	0.07 - 23
Sulfentrazone	73	30	130	95	24 - 132	2	1	36	9	0.09 - 61
Sulfometuron methyl	60	42	134	86	58 - 104	0	0	30	4	0.1 - 12
Tau-fluvalinate	73	30	130	116	92 - 157	0	8	36	4	0.08 - 12
Tebuthiuron	73	10	94	111	88 - 151	0	70	36	3	0.09 - 9
Tefluthrin	73	30	130	99	85 - 127	0	0	36	3	0.07 - 9
Terbacil	73	57	183	109	85 - 142	0	0	36	3	0.06 - 7
Tetrachlorvinphos	73	84	176	108	77 - 138	4	0	36	4	0.2 - 13
Tetrahydrophthalimide	73	50	150	84	55 - 138	0	0	36	4	0.09 - 20
Tetramethrin	73	30	130	100	41 - 126	0	0	36	6	0.2 - 64
Thiacloprid	60	71	131	97	79 - 118	0	0	30	4	0.3 - 13
Thiamethoxam	60	61	144	97	63 - 141	0	0	30	3	0.08 - 12
Total Suspended Solids	63	80	120	96	86 - 103	0	0	0		
Tralomethrin	73	30	130	116	96 - 156	0	11	36	4	0.03 - 13
trans-Permethrin	73	30	130	114	88 - 146	0	8	36	3	0.06 - 12
Treflan (Trifluralin)	73	41	173	94	81 - 121	0	0	36	3	0.04 - 8
Triadimefon	73	74	166	102	83 - 133	0	0	36	3	0.1 - 10
Triallate	73	58	126	101	84 - 124	0	0	36	2	0.04 - 8
Triclopyr	74	10	183	87	40 - 130	0	0	37	6	0.07 - 27
Triclopyr-butoxyl	73	30	130	108	88 - 136	0	6	36	3	0.3 - 7
Triclosan	73	30	130	111	96 - 146	0	1	36	6	0.2 - 21
Trifloxystrobin	60	46	165	102	86 - 128	0	0	30	4	0.3 - 10
Zoxamide	60	49	136	95	74 - 115	0	0	30	4	0.1 - 14

<sup>\*</sup>RPD control limit for all pesticide analytes is 40% and RPD control limits for TSS and conductivity is 20%.

There were a total of 10,029 spiked results from LCS and LCSD recoveries that were unqualified or J qualified. The lab did not calculate a recovery for every LCS or LCSD sample. Overall, the mean recovery was 100% with a standard deviation of 21 µg/L. RPDs calculated for 4,936 LCS/LCSD pairs were below the 40% RPD control limit 99% of the time; only 41 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 4% with

a standard deviation of 4 µg/L. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 65% with a standard deviation of 27 µg/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) < 1% of analyte recoveries (61 recoveries) fell below the control limits for LCS/LCSD samples,
- 2) 95% of analyte recoveries (9,570 recoveries) were within the control limits for LCS/LCSD samples,
- 3) 4% of analyte recoveries (398 recoveries) were above the control limits for LCS/LCSD samples.

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, 2014). 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 (NRAS, 2018). The airsaturated (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, 2015). 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 Anderson and Sargeant (2009). Data that did not meet MQOs were qualified.

#### **Field Data Collection Performance**

Quality control results for several conventional water quality parameter replicates are shown below in Table 39b.

Table 39b – Quality control results for conventional water qualiter parameter replicates

Replicate meter parameter	MQO	Western \	Washington	Eastern Washington		
Replicate meter parameter	IVIQU	Mean		Mean	Maximum	
Conductivity (field meter vs. laboratory)	10% RSD	3% RSD	15% RSD	1% RSD	2% RSD	
Streamflow	10% RSD	2% RSD	8% RSD	2% RSD	11% RSD	

The field meters met MQOs for laboratory conductivity comparisons for all Eastern Washington monitoring locations. There was 1 conductivity MQO exceedance that occurred at Indian Slough in Western Washington on March 19 with a laboratory conductivity result of 700  $\mu$ S/cm compared to the field meter reading of 940  $\mu$ S/cm (RSD of 15%). Field notes indicate a stratified water column due to tidal influence and thick aquatic vegetation. The data were qualified as estimates but are not found in this report.

The 2018 streamflow replicate results for both the Eastern and Western Washington sites met MQO (Table 39b) except for the following site visits:

- Upper Brender Creek, 11.1% RSD, May 15 (3.25 cfs and 2.60 cfs)
- Upper Brender Creek, 10.3% RSD, July 24 (1.43 cfs and 1.76 cfs)

The 2 Upper Brender Creek replicates not meeting the MQO occurred during low-flow conditions when the percent RSD statistic producers higher variability (Mathieu, 2006). Streamflow results for the sampling events were acceptable. Streamflow replicate results for the dates listed above were averaged and reported as an estimate based on higher statistical variability coupled with difficulty measuring consistent streamflow during periods of low flow.

Table 40b describes data quality objectives for field meter post-checks as described in the Quality Assurance Project Plan Addendum 3 (Anderson and Sargeant, 2009).

Table 40b – Data quality objectives for YSI ProDSS or other field meter post-checks

Parameter	Units	Accept	Qualify	Reject
pН	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%

 $^1$ Criteria expressed as a percentage of readings; for example, buffer = 100.2 µmhos/cm and YSI = 98.7 µmhos/cm; [(100.2-98.7)/100.2]\*100 = 1.49% variation, which would fall into the acceptable data criteria of less than 5%.

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

 Westside YSI meter pH 4.0 calibration, August 6 (calibration = pH 4.0 and post-check = pH 4.36)

The 4 field pH readings taken by the Westside YSI meter between the calibration and postcheck were qualified as estimates. None of the 4 readings exceeded a statewide water quality standard so they were recorded in the Monitoring Site Summary section of this report.

#### 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 surface water monitoring site. 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 August 23, staff conducted a field audit at Woodland Creek in Lacey. Both teams met to perform the field audit simultaneously. Results are displayed in Table 41b.

Table 41b – Conventional water quality parameter and flow data from field audit

Equipment and location	Temperature (°C)	рН	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Field meter – West	11.80	6.49	165.2	7.88	72.6	
Field meter – East	12.10	7.04	165.5	7.79	72.4	
Flow – West						8.31
Flow – East						9.07
RSD (%)	1.26	4.07	0.09	0.57	0.14	4.35

All meter results were acceptable based on the Measurement Quality Objectives described in Anderson and Sargeant (2009). Table 39b shows some of the MQOs for conventional field parameters.

The teams calibrated their YSI ProDSS Multi-Meters on August 22 in Olympia at the Natural Resources Building in the storage room. The Westside YSI ProDSS was post-checked on August 23 in Olympia, while the Eastside YSI ProDSS was post-checked on August 23 at the WSDA Yakima office in the NRAS lab. Both meter post-checks passed Data Quality Objectives found in Table 40b.

# **Quality Assurance Summary References**

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

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

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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.

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OTT. 2015. OTT MF Pro Basic User Manual, Edition 6. Document #026.53.80211.

YSI. 2014. ProDSS User Manual, Revision B. Document #626973-01REF.