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Agriculture

Ambient Monitoring for Pesticides in Washington State Surface Water

2020 Technical Report

August 2022

Washington State Department of Agriculture
Natural Resources Assessment Section

Derek I. Sandison, Director

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Contact Information

Central Washington Program Lead	Abigail Nickelson 509-895-9338 Natural Resources Assessment Section Washington State Department of Agriculture Yakima, WA ANickelson@agr.wa.gov
Western Washington Program Lead	Katie Noland 360-819-3690 Natural Resources Assessment Section Washington State Department of Agriculture Olympia, WA KNoland@agr.wa.gov
Acting Communications Director	Karla Salp 360-480-5397 Washington State Department of Agriculture Olympia, WA KSalp@agr.wa.gov

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

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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 concentration 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 2020, WSDA's Natural Resources Assessment Section (NRAS) collected surface water samples once or twice in March and then weekly or biweekly from June into December at 16 monitoring sites. We halted sampling from mid-March to mid-June due to the COVID-19 pandemic. Staff selected sites 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, King, Skagit, Walla Walla, Whatcom, Whitman and Yakima counties with watershed areas ranging from 2,000 acres to over 200,000 acres. Land use within each watershed varied from commercial, residential, and urban to agricultural uses like tree fruit, berry, wheat, corn, grass hay, and potato production. The Manchester Environmental Laboratory (MEL) in Port Orchard, Washington provided the sample analysis.

The United States Endangered Species Act lists several species of endangered salmonids found in Washington State's waterways including some in the waterways NRAS monitors (ESA 1973). Salmonids are valuable in the Pacific Northwest due to their cultural significance, contribution to the economy, and function in the ecosystem. All of the watersheds sampled in 2020 either have historically supported salmonid populations, contain habitat, or flow into habitat conducive to salmonid use. To assess potential biological effects and to be protective of endangered and non-endangered species, NRAS 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. NRAS 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, deltamethrin, diazinon, diuron, fipronil, metolachlor, permethrin, pyridaben, pyriproxyfen, sulfometuron-methyl, tefluthrin, and thiamethoxam.

This report summarizes activities and data from the 16 separate sites selected for the 2020 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 294 surface water sampling events between March 10 and December 7.
- Out of 169 pesticide active ingredients and breakdown products tested for, there were 112 unique pesticides detected.
- There were 5,010 positively identified pesticide detections.
- Out of 294 sampling events, mixtures of two or more pesticides were detected at 293 of them.
- Sulfentrazone was the most frequently detected herbicide (187 times), boscalid was the most frequently detected fungicide (218 times), and thiamethoxam was the most frequently detected insecticide (130 times) of the pesticides WSDA tested for.
- 2,6-dichlorobenzamide, a breakdown product of the herbicide dichlobenil or fungicide fluopicolide, had the most total detections with 223, followed by boscalid, with 218 detections. Detections of these analytes occurred at over 70% of sampling events.

- There were 193 unique pesticide detections with concentrations exceeding WSDA assessment criteria (3.9% of total detections), approaching levels that could adversely affect aquatic life.
 - Legacy pesticides and their breakdown products accounted for 73 of the exceedances (~38% of total exceedances). The chemicals include:
 - 4,4'-DDE (37 exceedances),
 - 4,4'-DDD (33 exceedances),
 - 4,4'-DDT (2 exceedances),
 - tralomethrin (1 exceedance).
 - Current-use pesticides accounted for 120 of the exceedances (~62% of total exceedances). The chemicals include:
 - bifenthrin (2 exceedances),
 - chlorpyrifos (1 exceedance),
 - clothianidin (14 exceedances),
 - deltamethrin (1 exceedance),
 - dichlorvos (2 exceedances),
 - dimethoate (2 exceedances),
 - fipronil (3 exceedances),
 - imidacloprid (89 exceedances),
 - linuron (2 exceedances),
 - malathion (4 exceedances).

Of the 193 detections that exceeded WSDA assessment criteria, many (72% or 138 detections) also exceeded state, national, or toxicity study criteria. Current-use pesticides accounted for 53% (73 detections) of those exceedances without the WSDA safety factor. Both detections of bifenthrin exceeded both the WSDA assessment criteria and its chronic invertebrate toxicity study criterion. Imidacloprid, found at 13 of the 16 monitoring sites, exceeded the chronic invertebrate toxicity study criterion 59 times out of a total 92 detections. Two reasons imidacloprid is detected so often exceeding this criterion is that it has very low laboratory method detection levels and a low chronic toxicity criterion. Other pesticides detected less often that still exceeded state, national, or toxicity study criteria included clothianidin, deltamethrin, dichlorvos, dimethoate, linuron, malathion, and tralomethrin (a legacy insecticide). Legacy insecticide DDT and its associated degradates accounted for the remaining 46% (64 detections) of the total detected exceedances of state or national standards.

NRAS collected samples for total suspended solids analysis and measured dissolved oxygen, pH, conductivity, water temperature, and streamflow in the field at sampling events. We also collected continuous air and water temperature measurements during the entire monitoring season in situ. Dissolved oxygen, pH, and water temperature measurements were compared to Water Quality Standards for Surface Waters of the State of Washington (WAC 2020). At least one conventional water quality parameter did not meet state water quality standards on one or more occasions at 14 of the 16 monitoring sites. For the program's first time, nutrient samples were collected at four monitoring sites. There was at least one exceedance of an Environmental Protection Agency (EPA) Ambient Water Quality Criteria Recommendation for nutrients at each sampling event at these four 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. NRAS 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 EPA (EPA 2017). Appendix B 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 & Cowles 2009). The program also forms the groundwork for additional studies focusing on particular scientific questions of interest regarding pesticide fate and transport. WSDA shares the data generated by this program with the agricultural community, regulatory and scientific community, and the public through WSDA's website, reports, watershed-specific fact sheets, and numerous public presentations.

Introduction

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

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

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

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

The technical report:

- Summarizes results, data quality, and monitoring activities conducted in 2020.
- Provides data for the pesticides that are listed for agency Endangered Species Act consultations.
- Determines if any pesticides in surface waters may be present at concentrations that could adversely affect aquatic life.
- Provides a basis for potential modifications to the program in upcoming years.
- Provides data to support implementation decisions under the agency's Pesticide Management Strategy (Cook and Cowles 2009).

NRAS conducted ambient surface water monitoring for pesticides in 2020 in March and June to December throughout the state. We suspended sampling from mid-March through mid-June due to travel and work restrictions in place during the early months of the COVID-19 pandemic. During the first year of monitoring (2003), NRAS sampled at nine monitoring sites in agricultural and urban areas. By 2020, the program has expanded to 16 monitoring sites, including two of the nine original sites. WSDA has monitored surface water in 22 unique watersheds since the start of the program. For the 2020 monitoring season, the Woodland Creek site in Thurston County was discontinued and replaced with the Juanita Creek site in King County; and the Naneum Creek site in Kittitas County was replaced with the Dry Creek site in Whitman County.

NRAS sent water samples to the Manchester Environmental Lab for analysis of pesticide and pesticide-related chemicals such as insecticides, herbicides, fungicides, degradates, an antimicrobial, a wood preservative, an insect repellent, and synergists. In 2020, NRAS tested for 169 chemicals, with 112 confirmed chemicals detected in surface water samples. Between the 2019 and 2020 monitoring seasons, 10 chemicals were added to the testing list. In addition, samples were collected for nutrient analysis for the first time during the 2020 monitoring season. The list of chemicals analyzed for every year may change because of new use restrictions, changes in pesticide registration, analytical cost, or lack of detections in surface water.

We compare 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 to be protective of aquatic life. Persistent contamination of surface waters with pesticides or pesticide-related chemicals can trigger the implementation of adaptive management techniques described in WSDA's EPA-approved Pesticide Management Strategy (Cook and Cowles 2009). These techniques can include voluntary best management practices, voluntary use prohibition, technical assistance, stakeholder outreach, and intensive monitoring. In addition, NRAS 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. We use 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 2020). Figure 1 shows the boundaries of the 10 subbasins that NRAS sampled in 2020, identified by their WRIA codes and corresponding subbasin names.

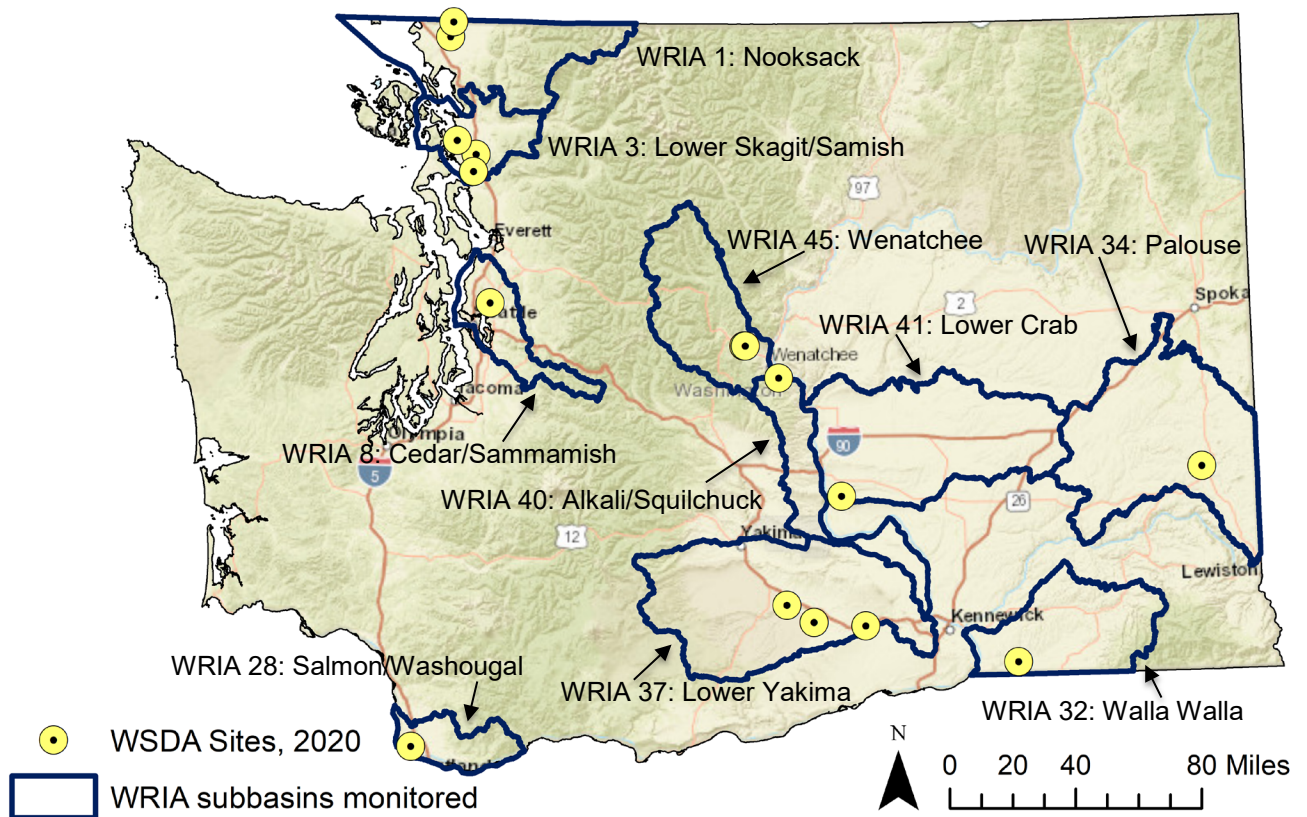


Figure 1 – Subbasins monitored in Washington State in 2020

All 10 subbasins are in the greater Pacific Northwest Region. Two of the subbasins represent mixed urban and residential landscapes and were selected due to land-use characteristics, history of pesticide detections, and the habitat provided for aquatic threatened and endangered species. The other eight subbasins represent a variety of agricultural landscapes and commodities in close proximity to streams. The proportion of watershed area in agricultural production varies widely, and all affect or provide habitat for endangered or threatened 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 October. However, unforeseen circumstances prevented staff from sampling for several months during the typical field season. The sampling schedule was pushed well into the fall and winter months with the last of the sampling completed the first week of December. Staff collected surface water samples at 16 monitoring sites across the state, which MEL analyzed for total suspended solids (TSS) and 166 pesticide active ingredients and pesticide-related products, with additional nutrient sampling at four of the sites. The sampling schedule and analytes tested was determined individually for each site.

Conventional water quality parameters such as pH, conductivity, continuous air and water temperature data (collected at 30-minute intervals), dissolved oxygen (DO), and streamflow were monitored at the monitoring sites. Additionally, the 2020 sampling season was the first time NRAS sampled for nutrients in Upper Big Ditch, Marion Drain, Sulphur Creek Wasteway, and Dry Creek. The nutrients sampled for were total phosphorus, ortho-phosphate, ammonia as N, and nitrate-nitrite as N. All these parameters were measured to assess overall stream health in relation to Washington State water quality standards in addition to the pesticide monitoring.

Detailed information on study design and quality assurance/quality control methods are described in the Quality Assurance Project Plan (Bischof et al. 2020).

Field Procedures

Surface water samples were collected using a 1-liter glass jar by hand grab or pole grab as described in the NRAS Standard Operating Procedure (SOP): Water Quality and Pesticides Monitoring (Bischof 2020a). Before delivery to MEL, staff labeled and preserved all samples according to the Quality Assurance Project Plan (Bischof et al. 2020). 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 NRAS SOP: YSI ProDSS (Bischof 2020b) and YSI ProDSS User Manual (YSI 2018). NRAS followed Ecology's SOP for Continuous Temperature Monitoring of Fresh Water Rivers and Streams for continuous, 30-minute-interval temperature data collection at 12 monitoring sites (Ward 2018). Mission Creek, Lower Bertrand Creek, and Touchet River temperature data was obtained from Ecology gauging stations present at those monitoring sites. Juanita Creek temperature data was obtained from a King County gauging station 20 feet downstream from the monitoring site.

Streamflow data in cubic feet per second was measured at 10 of the monitoring sites using an OTT MF Pro flow meter and top-setting wading rod, as described in Ecology SOP EAP024 (Mathieu 2019). We obtained streamflow data for the remaining five sites from gauging stations managed by other agencies. The gauging stations provided 15-minute streamflow measurements throughout the sampling season. NRAS used the recorded streamflow closest to the actual sampling start time. Details of those gauging stations are listed below.

- Juanita Creek – King County gauging station located at NE 120th St., Kirkland (Station ID: 27a)
- 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 2020 field data quality results are summarized in Appendix B of this report.

Laboratory Analyses

MEL analyzed the surface water grab samples for pesticides, TSS, nutrients, 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 ¹	Analytical method reference ¹	Instrument
GCMS-Pesticides	3535A	SW8270E	GC/MS/MS
GCMS-Herbicides (Derivatizable acid herbicides)	3535A	SW8270E	GC/MS
LCMS-Glyphos	3535A	SW8321B	LC/MS/MS
LCMS-Pesticides	n/a	SW8321B	LC/MS/MS
TSS	n/a	SM2540D	Gravimetric
Specific Conductivity	n/a	SM2510B	Electrode
Nitrate+Nitrite-N	n/a	SM4500NO3I	Lachat
Ammonia-N (NH3)	n/a	SM4500NH3H	Lachat
Phosphorus, Ortho- (OP)	n/a	SM4500PG	Lachat
Phosphorus, Total	n/a	SM4500PH	Lachat

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

GC/MS: gas chromatography/mass spectrometry

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

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

Data Quality, Quality Assurance, and Quality Control Measures

The quality assurance (QA) and quality control (QC) protocol for this program employs blanks, replicates, and surrogate recoveries. As a laboratory component of QA/QC, MEL analyzed surrogate recoveries, laboratory blanks, laboratory control samples, and laboratory control sample duplicates. Field blanks, field replicates, matrix spikes, and matrix spike duplicates integrate field and laboratory components. In 2020, 11% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2020 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 *UU*) were not used for comparison to pesticide assessment criteria or water quality standards. Appendix B describes all qualifiers.

Field Replicates

We collected field replicate samples to determine total sampling and analytical method variance. Identified replicate pairs can be considered consistently or inconsistently detected. Consistently identified replicate pairs are those where the pesticide or TSS was positively detected in both the sample and field replicate. Conversely, inconsistently identified replicate pairs are those where the

pesticide or TSS was detected in only one of the two samples collected. Replicate pairs where no identified detections were found in both sample and field replicate were not used in the NRAS analysis. The highest concentration of the positively detected sample or field replicate was selected for comparison to WSDA assessment criteria, regardless if the replicate pair was consistently or inconsistently identified. This procedure ensures a conservative approach to assessment criteria comparison.

Precision between identified replicate pairs was evaluated using relative percent difference (RPD). Only 5 of the 282 consistently identified replicate pairs detected for pesticide, nutrient, and TSS analysis exceeded an RPD criterion (40% RPD for pesticides, 20% RPD for TSS and nutrients). The results were not qualified for the five 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, NRAS 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 imazapyr, bromacil, fludioxonil, boscalid, 2,6-dichlorobenzamide, and TSS had low replicate variability among the 84 analytes detected in replicate pairs. There was not a high reproducibility of detections between replicate pairs for analytes detected in 2020. The analytes, in part, had high variability because of the small number of replicate pairs with at least one identified detection. Even so, all pesticide and TSS data for replicates were of acceptable data quality for this program's purpose. There were no sample or field replicate detections qualified due to inconsistently identified replicate pair results.

Replicate streamflow measurements and conductivity samples were collected for precision analysis. A streamflow measurement was replicated once a week for each OTT MF Pro flow meter used by Central and Westside sampling teams. A conductivity sample was collected once at each monitoring site, except Dry Creek, for comparison to a YSI ProDSS meter. In 2020, all relative standard deviations between the measurements and replicate measurements/samples but one were below the measurement quality objective of 10%.

Blanks

Field and laboratory blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were 19 detections in field blanks and 325 detections in laboratory blanks. Detections in field blanks included analytes such as DEET and 2,6-dichlorobenzamide, while detections in lab blanks included analytes such as DDT, fenarimol, dichlobenil, triclosan, and DEET. The origin of these detections was unknown. Regular field sample detections corresponding to the field or lab blank samples in the same batch were qualified as non-detects if the regular sample concentration was less than five times the blank concentration.

Surrogates, Matrix Spikes, and Laboratory Control Samples

MEL spikes surrogates into all samples to evaluate recoveries for structurally similar groups of organic compounds. The majority (99%) of surrogate recoveries fell within the control limits established by MEL in 2020. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

Matrix spikes (MS) and matrix spike duplicates (MSD) provide an indication of bias due to interferences from components of the sample matrix. We 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 98% of the time and the RPDs of

the paired recoveries fell below the 40% RPD upper control limit 99% of the time. If a MS/MSD sample exceeded MEL QC criteria, sample results were not qualified unless other QC criteria for that analyte was exceeded in the laboratory batch.

Laboratory control samples (LCS) are deionized water spiked with analytes at known concentrations and subjected to analysis. LCS help to evaluate precision and bias of pesticide residue recovery for a specific analyte. For most compounds, percent recovery and RPDs of LCS and LCS duplicates (LCSD) showed acceptable performance and were within limits for the project. Analyte recoveries from LCS and LCSD samples fell between both the upper and lower control limits 96% of the time and the RPDs of the paired recoveries fell below the 40% RPD upper control limit 97% of the time. Sample results were qualified as estimates if the LCS/LCSD recoveries did not meet MEL QC criteria.

Assessment Criteria for Pesticides

To evaluate potential effects of pesticide exposure to aquatic life and endangered species, NRAS 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 2020b), and Washington State regulations (WAC 2020). We apply a 0.5x safety factor to all of these reference values before comparison to detected pesticide concentrations to ensure that the criteria are protective of aquatic life and to detect potential water quality issues early on.

Several factors limit our 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. NRAS collects weekly or biweekly discrete grab samples that cannot be used to determine the exposure duration that would be needed to determine whether the time threshold has been exceeded. However, this comparison is consistent with Ecology practices; for Clean Water Act section 303(d) listing purposes instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards and assessment criteria for acute and chronic criteria (Ecology 2020). Appendix A 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 2020a).

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 LC₅₀ (concentration causing death to 50% of the organisms, in the case of fish) or EC₅₀ (concentration causing immobility or growth reduction to 50% of the organisms, in the case of invertebrates or plants) is calculated. The test duration is 96 hours for fish and aquatic plants and 48 hours for invertebrates.

Chronic toxicity tests normally use either reproductive effects or effects to offspring as the measured effect. Researchers use chronic toxicity study values to derive a pesticide's No Observable Adverse Effects Concentration (NOAEC). The concentration signifies the highest concentration in the toxicity test not showing a statistically significant difference from the control. The chronic toxicity test is longer than the 96-hour acute test (28 days for fish, 21 days for invertebrates) to simulate the type of exposure that would result from a persistent chemical or the effect of repeated applications.

NRAS uses an increased safety factor to provide an additional level of protection for endangered species. Researchers commonly use rainbow trout as a surrogate fish species to assess the potential risk of a pesticide to salmonids. As a result, the WSDA assessment criteria for endangered species (in this case, typically salmonids) is 1/20th of the most sensitive LC₅₀ 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 2020b). Acute and chronic toxicity data from pesticide registration toxicity studies provide the pesticide criteria in the NRWQC. NRAS used the 2020 NRWQC to develop some of the WSDA assessment criteria in this report.

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 2020). 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.

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

Relationship between WSDA Assessment Criteria and Sources

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

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

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 ₅₀ for fish or invertebrates
Endangered Species Acute	LC ₅₀	0.05	0.5	0.025	≥ 2.5% of the most protective LC ₅₀ 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 ₅₀	1	0.5	0.5	≥ 50% of the most protective EC ₅₀ 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

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

Pesticide of Concern Decision Matrix

Annually, NRAS identifies Pesticides of Concern and Pesticides of Interest (POIs) using the most recent surface water data. Washington and the other EPA Region 10 states (Oregon, Idaho, and Alaska) adopted the same method to identify statewide and watershed-specific POCs in 2019. For current-use pesticides detected in 2020, we used the past three years of data for each pesticide to sort each pesticide into a decision matrix by detection frequency and number of detections exceeding WSDA assessment criteria (Table 3).

Although there were two watersheds that contained multiple sites, staff chose to analyze the sites separately. Upper and Lower Big Ditch were separated because of their extreme difference in watershed land-use characteristics. Upper and Lower Bertrand were analyzed separately because the land and pesticide use of the upper watershed, located in Canada, is not fully known to us.

Statewide POCs/POIs are current-use pesticides that were POCs/POIs in more than 30% of monitored watersheds. In 2020, three watershed POCs were found in 5 or more of the 16 monitored watersheds, making them statewide POCs. Having a smaller number of identified POCs enables us to educate and outreach to pesticide applicators with focus on the highest priority pesticides. It also allows us 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 - NRAS 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 2020), waterbodies are required to meet numeric water quality standards based on the beneficial uses of the waterbody. Table 4 shows the beneficial aquatic life uses for each of the segments of stream that include the monitoring sites. Every site staff monitored in 2020 was fresh water and was only compared to WAC fresh water criteria.

Staff measured and compared conventional parameters including water temperature, dissolved oxygen, 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	pH
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). Two NRAS monitoring sites in 2020 had an additional temperature standard within the reaches of creek that encompassed the sites. The Upper Bertrand site had a 7-DADMax temperature standard of less than 13°C between February 15 and June 15 and the Juanita site had a 7-DADMax standard of less than 13°C between September 15 and May 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.

Numeric Water Quality Standards for Nutrients

EPA has recommended ambient water quality criteria for nutrients in surface waters. Table 5 shows the criteria nutrients were compared to. Nutrients such as nitrate-nitrite (NO₂ + NO₃) and total phosphorus (TP) detections were compared to EPA’s Ambient Water Quality Criteria Recommendations (EPA 2000a, EPA 2000b). The criteria are specific to nutrient ecoregions and sub-ecoregions across the U.S. for surface water from rivers and streams. The empirically derived criteria represent environmental conditions within waters that have been minimally impacted by human activities; specifically reference conditions based on the upper 25th percentiles of all nutrient data in a sub-ecoregion collected from 1990 through 1999.

Table 5 – Water quality standards for nitrate-nitrite as N and total phosphorus as P by Nutrient Ecoregion ID

EPA Ecoregion	Level 3, Nutrient Ecoregion ID	Monitoring sites	Criteria type	Criteria (mg/L)
II, Western Forested Mountains	2	Upper Big Ditch	NO ₂ + NO ₃	0.26
			TP	0.0195
III, Xeric West	10	Dry Creek, Marion Drain, Sulfur Creek Wasteway	NO ₂ + NO ₃	0.072
			TP	0.030

The ammonia detections were compared to the Water Quality Standards for Surface Waters of The State of Washington (WAC 2020). Acute criteria were derived for each detection of ammonia as N using the pH water quality parameter measured during the sampling event and the equations below. All sites monitored for nutrients in 2020 were considered salmonid present waterway as per the State Water Quality Standards.

$$\text{For salmonids present: } = \left(\frac{0.275}{1+10^{7.204-pH}} + \frac{39}{1+10^{pH-7.204}} \right)$$

$$\text{For salmonids absent: } = \left(\frac{0.411}{1+10^{7.204-pH}} + \frac{58.4}{1+10^{pH-7.204}} \right)$$

There were no known criteria to compare orthophosphate as P concentrations to.

Monitoring Site Results

In 2020, NRAS 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 2020 monitoring season and a visual comparison to the WSDA assessment criteria. For specific values and information on the assessment criteria development, please refer to Appendix A: Assessment Criteria for Pesticides.

In the calendars, the number below the months indicates the day of the month the sampling event occurred and each column below the sampling event date indicates the data associated with that event. The blank cells in the calendars often indicate no chemical detection but can also mean a chemical was detected below reportable sample quantitation limits. Concentrations are presented in $\mu\text{g/L}$, rounded to the thousandths place. The addition of a "<" identifies concentrations of imidacloprid less than $0.005 \mu\text{g/L}$ to show that those detections did not exceed WSDA assessment criterion of $0.005 \mu\text{g/L}$.

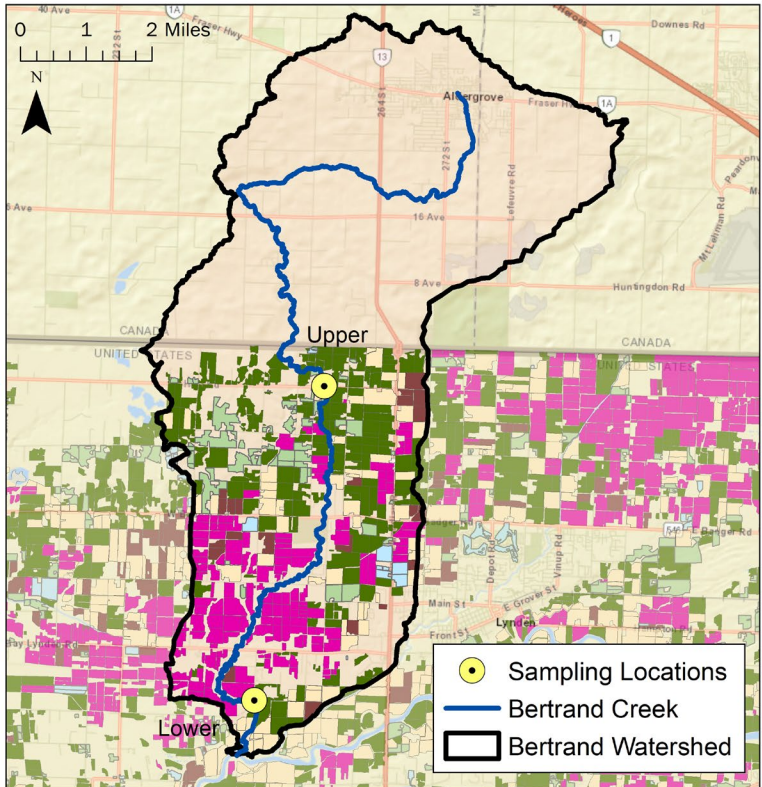
Detection of a pesticide concentration above the WSDA assessment criteria does not necessarily indicate an exceedance has occurred because the temporal component of the criteria must also be exceeded. For WSDA assessment criteria, measurements of instantaneous concentrations are assumed to represent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

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

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

Western Region

Bertrand Creek



Bertrand Creek Crop Groups	Acres
Other	156
Berry	2,337
Cereal Grain	1,264
Hay/Silage	3,162
Pasture	702
Vegetable	478
<hr/>	
Total U.S. Ag	8,099
Total U.S. Non-Ag	4,731
Watershed Total	26,893

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

In 2013, NRAS started sampling the Bertrand watershed in Whatcom County. Monitoring takes place at two locations along this stream to provide an opportunity to compare potential pesticide inputs from Canada to pesticide detections downstream in the United States. The headwaters of Bertrand Creek are located in Canada and it flows approximately 11 miles before crossing the border. Currently, the Upper Bertrand Creek site is located approximately a quarter mile south of the Canadian border at the upstream side of H Street Road (latitude: 48.9935°, longitude: -122.5094°) (Figure 2, Figure 3). The Lower Bertrand Creek site is located about 7.8 miles downstream from the upper monitoring site and just upstream of the bridge crossing on Rathbone Road (latitude: 48.9241°, longitude: -122.5300°) (Figure 2, Figure 4). From the Lower Bertrand Creek site, the creek flows approximately one more mile south to where it enters the Nooksack River.



Figure 3 – Upper Bertrand Creek site upstream view

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 the presence of winter steelhead and coho, chum, and sockeye salmon within the reaches of the creek that encompass both Bertrand sites (WDFW, 2021). Staff have frequently observed juvenile fish of unknown species and freshwater lamprey at the Upper Bertrand Creek monitoring site.



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 and a few nurseries (Figure 2). About 14,000 acres of the watershed is in Canada where the main crops and management practices are outside the scope of NRAS'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 2020.

- NRAS tested for 166 unique pesticides in Upper and Lower Bertrand Creek.
- Pesticides were detected at all 24 sampling events at each monitoring site.
- Up to 32 pesticides were detected at the same time in Upper Bertrand Creek and up to 37 in Lower Bertrand Creek.
- There were 45 pesticides that were detected at least once in both the Upper and Lower Bertrand Creek sites throughout the sampling season. Conversely, there were four pesticides that were found only at the upper site and 26 pesticides that were found only at the lower site.
- There were 483 total pesticide detections in Upper Bertrand Creek from six different use categories: 24 types of herbicides, 8 insecticides, 8 fungicides, 7 degradates, 1 antimicrobial, and 1 insect repellent.
- Of the total pesticide detections in Upper Bertrand Creek, 24 were above WSDA's assessment criteria (Table 6).
- There were 610 total pesticide detections in Lower Bertrand Creek from six different use categories: 27 types of herbicides, 18 insecticides, 12 fungicides, 12 degradates, 1 insect repellent, and 1 synergist.
- Of the total pesticide detections in Lower Bertrand Creek, 27 were above WSDA's assessment criteria (Table 7).
 - The 4,4'-DDE detection, a legacy degradate, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - The fipronil detection approached the invertebrate NOAEC (0.011 µg/L).

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

- All 24 detections of imidacloprid approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- There were no detections of diazinon and one detection of malathion that did not exceed any assessment criteria in 2020, but these pesticides were still classified as watershed POCs because of 2018 detections that did exceed criteria.

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

- The bifenthrin detection exceeded the invertebrate NOAEC (0.0013 µg/L).

Table 7 – Lower Bertrand pesticide calendar, µg/L

Month	Mar	Jun	Jul	Aug	Sep	Oct	Nov	
Day of the Month	Use* 17	15 22 29	6 13 21 28	3 11 17 25 31	9 14 21 28	5 12 20 26	2 9 16	
1-(3,4-Dichlorophenyl)-3-methylurea	D					0.010		
2,4-D	H	0.044	0.037			0.027 0.161	0.291 0.058 0.296 0.021	
2,6-Dichlorobenzamide	D 0.091	0.158 0.131 0.133 0.220	0.248 0.189 0.161 0.177	0.143 0.143 0.118 0.129	0.132 0.123 0.106 0.159	0.106 0.198 0.253 0.178	0.157 0.157 0.101	
4,4'-DDE	D						0.002	
Acephate	I	0.004 0.005	0.014		0.029		0.013 0.017 0.004 0.007	
Acetochlor ESA	D	0.031	0.042 0.033	0.074 0.037	0.116 0.054	0.067	0.034 0.057	
Atrazine	H			0.003			0.023	
Azoxystrobin	F	0.002 0.003			0.003		0.006	
Bifenthrin	I						0.002	
Boscalid	F 0.025	0.142 0.075 0.046 0.081	0.076 0.040 0.036 0.026	0.039 0.029 0.026 0.021	0.023 0.020 0.018 0.040	0.019 0.074 0.124 0.083	0.043 0.083 0.071	
Bromacil	H 0.008	0.011 0.013 0.018 0.014	0.027 0.030 0.031 0.035	0.023 0.031 0.024 0.028	0.028 0.028 0.028 0.028	0.018 0.021 0.008 0.009	0.01 0.017 0.013 0.005	
Carbendazim	F		0.001 0.001 0.003			0.004	0.014 0.008 0.002	
Chlorothalonil	F						0.002	
Chlorpyrifos	I					0.002 0.002 0.001	0.002 0.002	
Clopyralid	H			0.045				
Clothianidin	I			0.003			0.004	
Cyantranilprole	I					0.015		
Cyprodinil	F	0.005	0.006 0.006 0.006					
Diazinon	I	0.003					0.001	
Dicamba acid	H	0.016	0.010			0.054	0.029 0.020 0.024	
Dichlobenil	H 0.030	0.149 0.092 0.045 0.209	0.073 0.033 0.015 0.009	0.011 0.006 0.005	0.006 0.005	0.004 0.035 0.007	0.136 0.134 0.077 0.030	0.057 0.072
Dimethoate	I					0.012 0.006		
Dinotefuran	I 0.031						0.005	
Diuron	H	0.015 0.011 0.008	0.004 0.004 0.005		0.004 0.004	0.053 0.006 0.031 0.016	0.006 0.004 0.004	
Eptam	H						0.001	
Ethoprop	I				0.002		0.002	
Etoxazole	I				0.006			
Fipronil	I					0.002	0.007	
Fipronil sulfide	D						0.001	
Fipronil sulfone	D						0.002	
Fludioxonil	F	0.006 0.004 0.007 0.007	0.010 0.008 0.013 0.009	0.014 0.009 0.005 0.005	0.005 0.005 0.004 0.004		0.003 0.002 0.002 0.002	
Hexazinone	H 0.003	0.003 0.002 0.003 0.002	0.003 0.003 0.003 0.004	0.004 0.004 0.003 0.007	0.007 0.006 0.005 0.006		0.003 0.002 0.003 0.002	
Imazapyr	H						0.004 0.002 0.003 0.003	
Imidacloprid	I 0.019	0.038 0.029 0.020 0.045	0.038 0.021 0.016 0.011	0.013 0.014 0.009 0.008	0.009 0.009 0.007 0.011	0.022 0.011 0.048 0.073	0.070 0.037 0.040 0.037	
Isoxaben	H					0.003		
Malathion	I	0.004 0.009	0.010 0.005 0.012 0.020		0.004		0.006 0.005 0.003 0.010	
Mecoprop (MCP)	H	0.070	0.057			0.219	0.167 0.080 0.089 0.062 0.081	
Methamidophos	D	0.002 0.002	0.006 0.002		0.008	0.002	0.002 0.003 0.001 0.002	
Methomyl	I	0.004 0.002						
Methoxyfenozide	I				0.004			
Metolachlor	H 0.003	0.007 0.004 0.004 0.005	0.006 0.004 0.004	0.005 0.004	0.004 0.004 0.004 0.004	0.004 0.003 0.005	0.005 0.005 0.006 0.017	
Metribuzin	H	0.002					0.003 0.005	
Myclobutanil	F	0.006	0.012 0.005				0.024 0.011 0.014	
N,N-Diethyl-m-toluamide (DEET)	IR	0.007	0.015				0.018 0.011 0.011	
Napropamide	H 0.007					0.008	0.008 0.008 0.005 0.004 0.005 0.003	
Norflurazon	H 0.002	0.003 0.002	0.002 0.003 0.003 0.003	0.003 0.002 0.003 0.003	0.003 0.003 0.003 0.004	0.003 0.002 0.002	0.002 0.002 0.003 0.003	
Oxadiazon	H	0.003					0.004 0.005 0.004 0.003 0.005 0.003	
Oxamyl	I 0.031	0.018 0.021 0.025 0.019	0.022 0.030 0.037 0.035	0.040 0.036 0.028 0.032	0.032 0.032 0.035 0.031	0.016 0.025 0.004 0.004	0.022 0.016 0.029 0.046 0.038	
Oxamyl oxime	D 0.032	0.048 0.059 0.056 0.048	0.039 0.059 0.080 0.067	0.057 0.034 0.058 0.056	0.072 0.046 0.068 0.040	0.076 0.022 0.016 0.029 0.046 0.038		
Paclbutrazol	F		0.003					
Pendimethalin	H					0.003	0.003	
Pentachloronitrobenzene (PCNB)	F						0.005	
Piperonyl butoxide (PBO)	SY		0.005					
Prometon	H				0.003	0.002 0.010		
Prometryn	H					0.013		
Propiconazole	F	0.008 0.011	0.019 0.005	0.004			0.008 0.009 0.007	
Pyrimethanil	F	0.015 0.004 0.003 0.005	0.005 0.005 0.003 0.004	0.002		0.002	0.002	
Pyriproxyfen	I				0.002			
Simazine	H 0.008	0.149 0.141 0.049 0.075	0.070 0.025 0.019 0.012	0.024 0.043 0.030 0.034	0.020 0.013 0.010 0.119	0.020 1.190 0.095 0.134 0.052 0.025 0.040		
Sulfentrazone	H 0.025	0.030 0.028 0.036 0.039	0.038 0.039 0.041 0.043	0.036 0.042 0.033 0.040	0.041 0.048 0.044 0.032	0.038 0.086 0.060 0.038 0.049 0.031 0.015		
Sulfometuron methyl	H					0.009		
Tebuthiuron	H		0.004 0.004 0.005 0.005 0.005	0.005 0.006 0.005 0.005	0.007 0.006 0.005 0.005	0.005 0.005 0.005	0.004 0.004 0.004 0.004	
Terbacil	H 0.012	0.015 0.011 0.007 0.079	0.043 0.013 0.006 0.003	0.008 0.005 0.003 0.008	0.006 0.006 0.005 0.061	0.016 0.104 0.054 0.294 0.032 0.018 0.009		
Tetrahydrophthalimide (THPI)	D 0.004	0.457 0.014 0.006 0.025	0.010 0.012 0.019 0.017	0.028 0.034 0.039 0.040	0.030 0.030 0.018 0.013	0.011 0.032 0.012 0.015 0.009 0.014 0.013		
Thiamethoxam	I 0.014	0.013 0.017 0.017 0.016	0.017 0.020 0.018 0.019	0.031 0.021 0.019 0.022	0.024 0.023 0.026 0.013	0.022 0.009 0.012 0.009 0.015 0.010 0.017		
Triadimefon	F		0.002			0.002	0.002	
Triazine DEA degradate	D		0.003				0.003	
Triazine DIA degradate	D	0.031 0.014 0.010 0.021	0.011 0.006 0.003 0.005	0.004 0.007 0.005	0.002 0.002 0.003 0.002	0.002 0.015 0.005 0.033 0.017 0.010 0.005 0.010		
Triazine HA degradate	D 0.003	0.004 0.004 0.003 0.004	0.004 0.003 0.002 0.002	0.002 0.002 0.003 0.002	0.002 0.002 0.002 0.003	0.002 0.003 0.002 0.006 0.005 0.004 0.003 0.004 0.010		
Triclopyr acid	H						0.024	
Trifluralin	H					0.004		
Total suspended solids (mg/L)	4	2 1 1 2	1 5 1 1	5	1 1	1 1 3 2	2 13	
Streamflow (cubic ft/sec)	76.8	38.3 31.2 19.7 24.9	16.6 11.0 6.6 6.1	7.9 8.0 9.1 10.0	12.3 9.6 7.4 18.8	10.1 139.0 62.8 41.3	26.6 59.6 272.0	
Precipitation (total in/week)†	0.18	1.32 0.62 0.11 0.94	0.56 0.02 0.00 0.00	0.61 0.00 0.71 0.07	0.00 0.00 0.10 0.07	0.00 0.10 1.58 0.02	2.29 1.04 0.51 0.12 2.02 3.28	

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

Current-use exceedance
DDT/degradate exceedance
Detection
No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, SY: Synergist)
 † Washington State University AgWeatherNet station: Lynden.N, (latitude: 48.89°, longitude: -122.43°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet state standards at 17 site visits at Upper Bertrand and 18 site visits at Lower Bertrand. Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in Figure 6 are shown below.

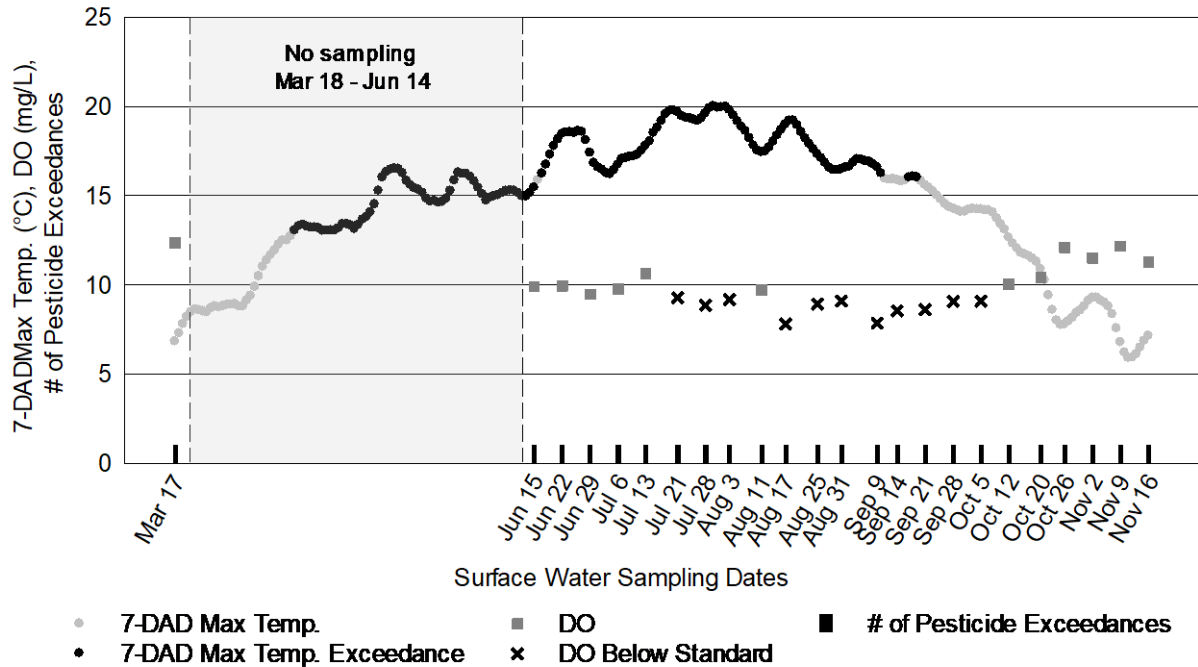


Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria

Pesticide exceedances in Upper Bertrand Creek coincided with water quality measurements that did not meet state standards at 17 of the 24 site visits (71%). All pH measurements met the state standard, ranging from 7.16 to 7.79 with an average of 7.54. The pH measurement on July 13 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). Dissolved oxygen (DO) measurements ranged from 7.81 mg/L to 12.35 mg/L with an average of 9.81 mg/L. Almost half (46%) of these measurements did not meet the state standard; 11 measurements were less than 9.5 mg/L. All DO measurements that did not meet standards coincided with one pesticide exceedance. At seven site visits (29%), a pesticide exceedance occurred with both a DO measurement below the standard and a 7-DADMax temperature above the standard.

Upper Bertrand Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods 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 2021). The 7-DADMax temperature exceeded the standard on 150 days, primarily from April 16 through September 19. There was one pesticide exceedance at every site visit with a 7-DADMax temperature exceedance.

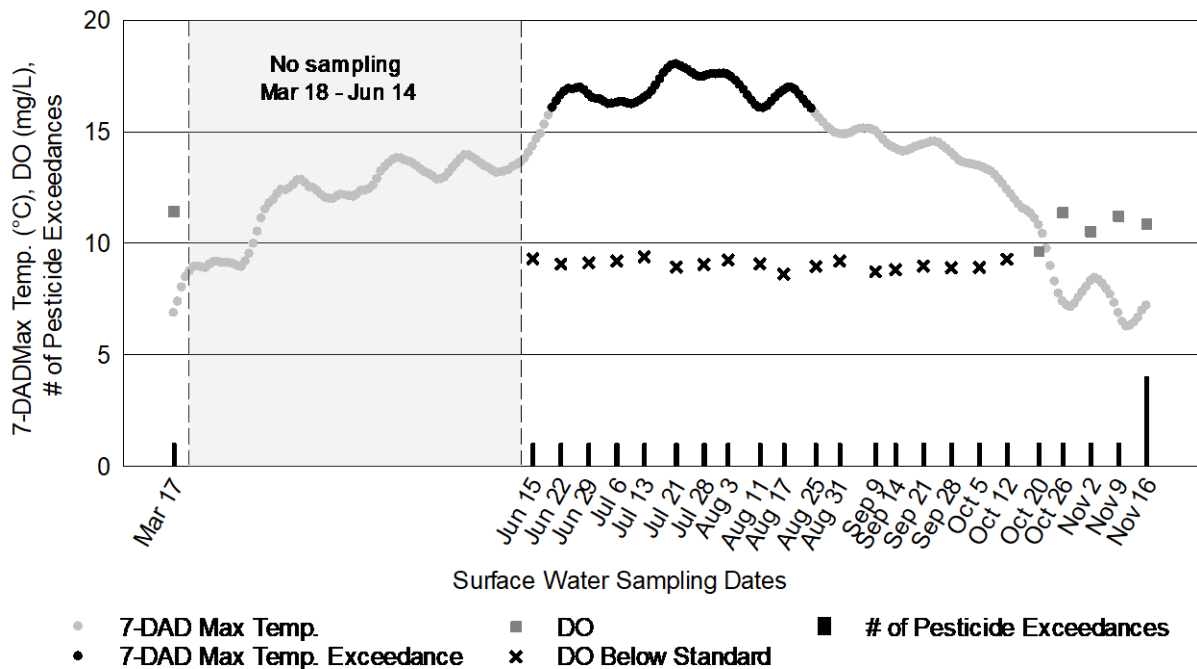


Figure 6 – Lower Bertrand Creek water quality measurements and exceedances of assessment criteria

Pesticide exceedances in Lower Bertrand Creek coincided with water quality measurements that did not meet state standards at 18 of the 24 site visits (75%). All pH measurements met the state standard, ranging from 7.11 to 7.46 with an average of 7.31. The pH measurement on July 13 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). DO measurements ranged from 8.62 mg/L to 11.43 mg/L with an average of 9.49 mg/L. Three-quarters (75%) of the measurements did not meet the standard; 18 measurements were less than 9.5 mg/L. The 7-DADMax temperature exceeded the standard of 16 °C for 66 days of the sampling season, from June 20 through August 24. Pesticide exceedances overlapped with both 7-DADMax temperature exceedances and DO measurements that did not meet the standard at nine site visits.

Bertrand Creek has been designated as a freshwater body that provides core summer habitat for salmonids by the WAC (WAC 2021). For several seasons, there has been a steelhead spawning nest at the Upper Bertrand Creek monitoring site. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Upper Big Ditch

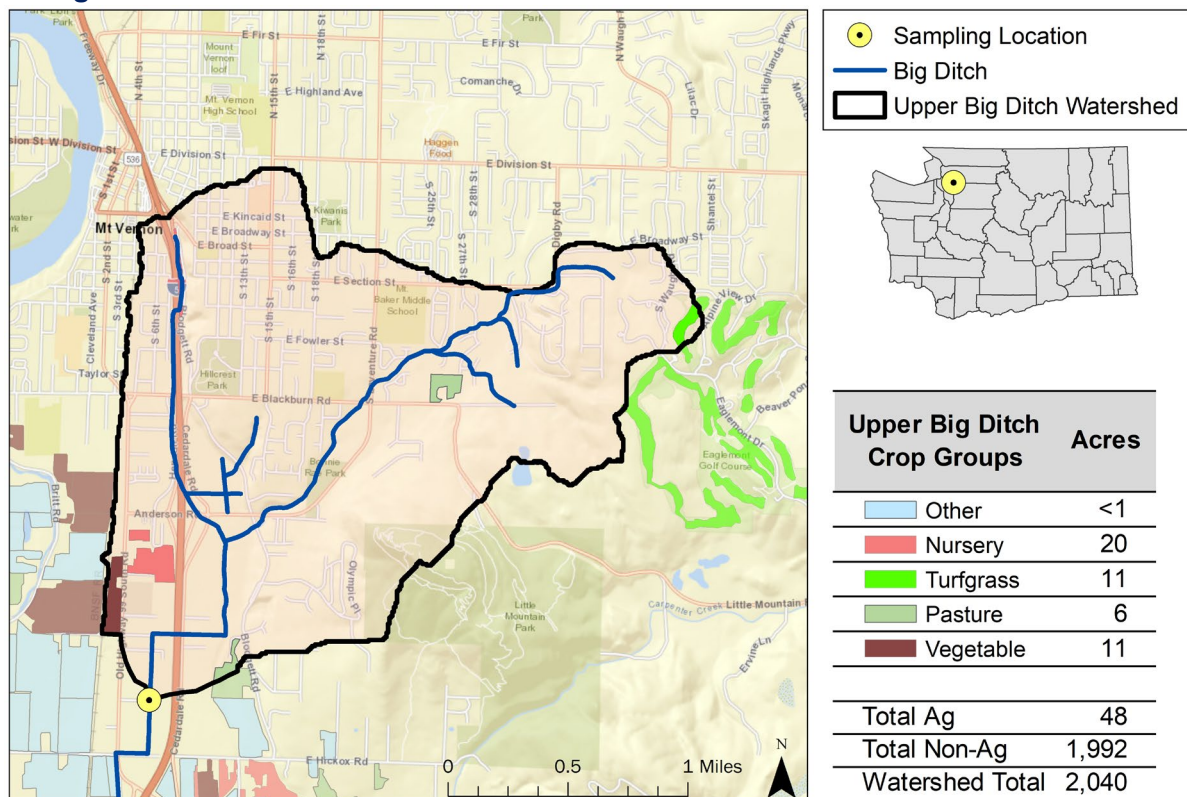


Figure 7 – Map of Upper Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2007, NRAS started monitoring the Upper Big Ditch in Skagit County. The entire Big Ditch watershed drains a mixture of non-agricultural and agricultural land. The Upper Big Ditch site consistently had the most pesticide detections each year compared to any other site NRAS 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).

Water from Big Ditch drains into Puget Sound. WDFW has documented the presence of winter steelhead and chum, fall Chinook, pink, and coho salmon within the reach of ditch that encompasses the monitoring site (WDFW 2021). A culvert that impeded fish passage upstream of the Upper Big Ditch monitoring site was removed in the fall of 2020. Coho were observed swimming through the reconstructed channel in late November (Skagit Conservation District 2021). Staff frequently observed juvenile fish of unknown species at the site and identified one coho fry.

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 double or single point sampling where the highest velocity water was flowing in the ditch for 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



Figure 8 – Upper Big Ditch upstream view

watersheds NRAS monitors have nursery or greenhouse crop groups as their main agricultural commodity. The 'Other' crop group category was a seed crop in 2020 (Figure 7).

Below is a brief overview of the pesticide findings in Upper Big Ditch in 2020.

- NRAS tested for 166 unique pesticides in Upper Big Ditch.
- There were 499 total pesticide detections from eight different use categories: 28 types of herbicides, 11 insecticides, 8 fungicides, 8 degradates, 1 antimicrobial, 1 insect repellent, 1 synergist, and 1 wood preservative.
- Pesticides were detected at all 26 sampling events.
- Up to 39 pesticides were detected at the same time.
- Of the total pesticide detections, five were above WSDA's assessment criteria (Table 8).
 - The single detections of 4,4'-DDE and 4,4'-DDD, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- The bifenthrin detection exceeded the invertebrate NOAEC (0.0013 µg/L).
- Out of three detections of imidacloprid, two detections approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- The two detections of sulfometuron-methyl and seven detections of thiamethoxam did not exceed any assessment criteria in 2020, but these pesticides were still considered watershed POCs because of detections that did exceed criteria in recent years. Similarly, fluvalinate was not detected but was considered a watershed POC because of the same logic.

The Upper Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet state standards at 2 of the 26 site visits (8%). Water quality at the Upper Big Ditch site is shown below (Figure 9).

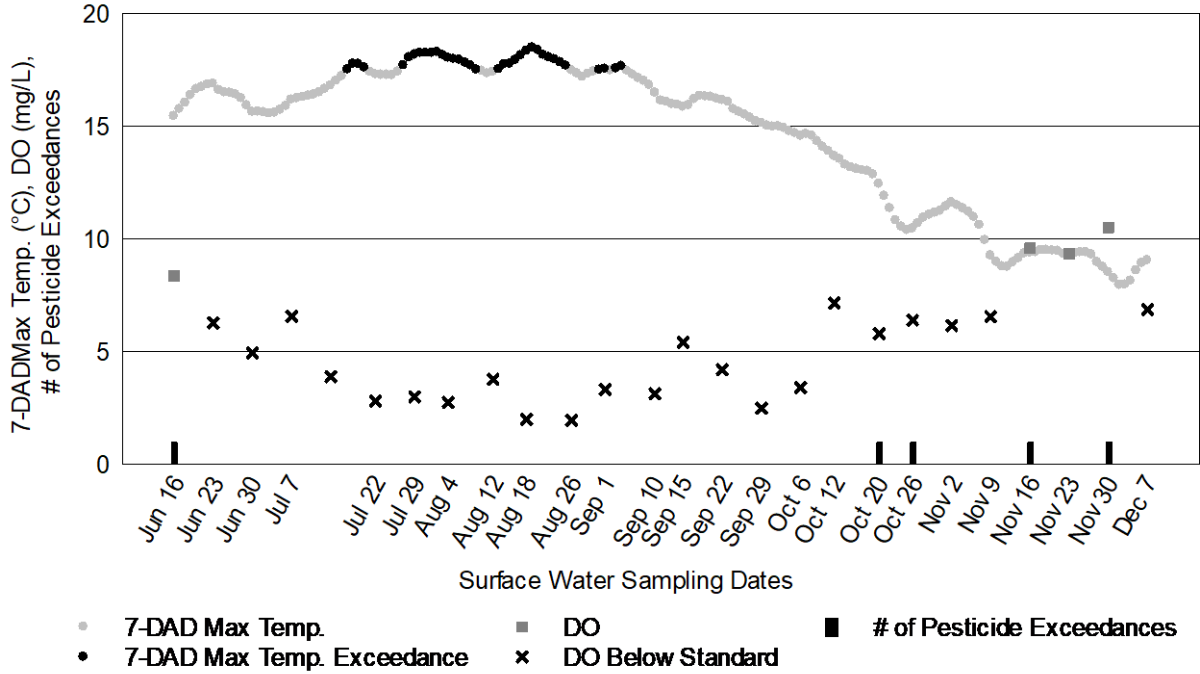


Figure 9 – Upper Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 6.88 to 7.24 with an average of 7.01. The pH measurement on July 14 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). DO measurements ranged from 1.97 mg/L to 10.52 mg/L with an average of 5.27 mg/L. More than three-quarters (85%) of the DO measurements did not meet the state standard; 22 measurements were less than 8 mg/L. Two of the DO measurements that did not meet the standard coincided with one pesticide exceedance. Upper Big Ditch had the lowest DO measurement compared to all other monitoring sites, which is consistent with the last three years of monitoring. The 7-DADMax temperature standard of 17.5°C was exceeded 35 days of the sampling season, intermittently from July 17 through September 4.

Upper Big Ditch has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC 2021). Flow in the ditch towards the end of summer was slowed substantially due to constriction from aquatic vegetation. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs.

Lower Big Ditch

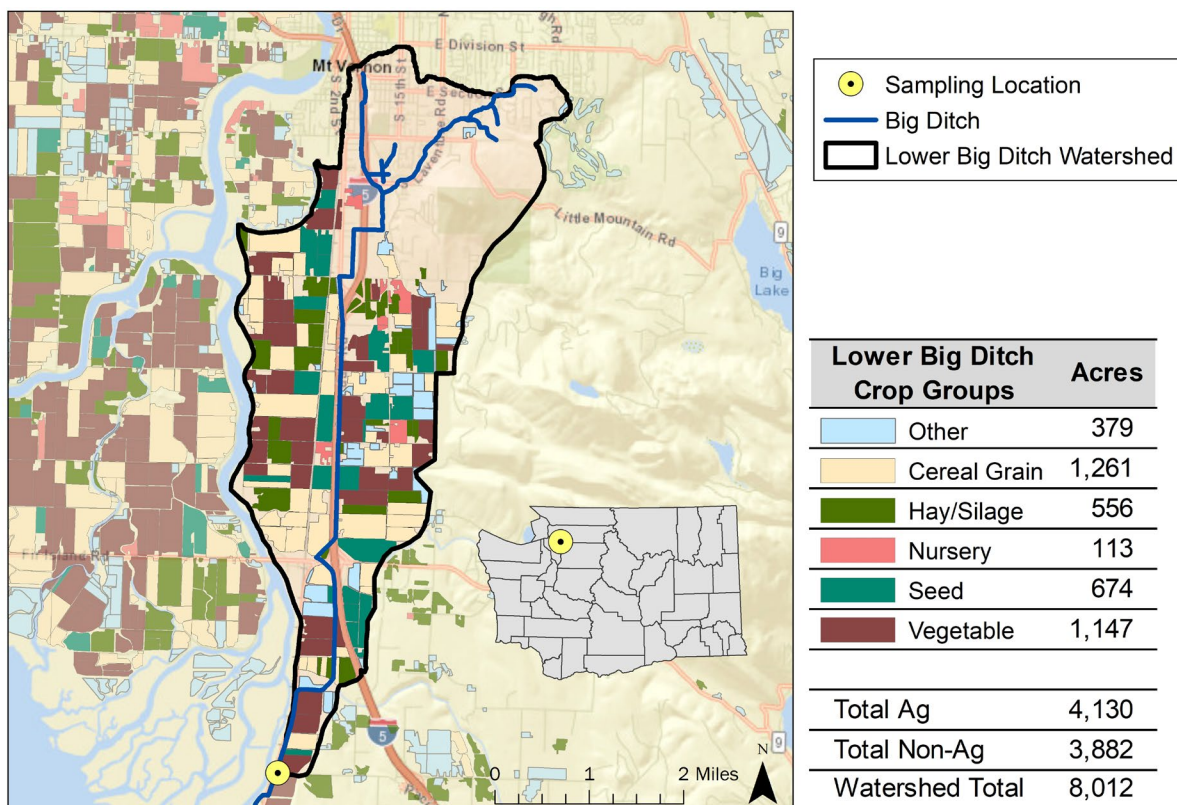


Figure 10 – Map of Lower Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2006, NRAS 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, Figure 11).

We only sampled this site when the tide gate located downstream of the monitoring site was open and the water was flowing from Big Ditch into Puget Sound to avoid sample contamination with saltwater or pooling backwater. Staff occasionally observed small fish and tadpoles. WDFW has documented the presence of winter steelhead and fall Chinook, coho, kokanee, pink, and chum salmon within the reach of ditch that encompasses the monitoring site (WDFW 2021).

Precipitation events and agricultural irrigation influence the streamflow in the ditch. Big Ditch stretches north approximately 8 miles from the monitoring site to its headwaters. Within the Lower Big Ditch drainage area, the agricultural land use is predominantly potatoes, field corn, barley, grass hay, and ryegrass seed. The ‘Other’ crop group category consists mostly of fallow fields and wildlife feed (Figure 10).



Figure 11 – Lower Big Ditch upstream view

Below is a brief overview of the pesticide findings in Lower Big Ditch in 2020.

- NRAS tested for 166 unique pesticides in Lower Big Ditch.
- There were 347 total pesticide detections from five different use categories: 27 types of herbicides, 9 insecticides, 10 fungicides, 11 degradates, and 1 insect repellent.
- Pesticides were detected at all 17 sampling events.
- Up to 38 pesticides were detected at the same time.
- Of the total pesticide detections, 14 were above WSDA's assessment criteria (Table 9).
 - Three detections of 4,4'-DDD and two detection of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L). An additional 4,4'-DDD detection August 18 approached the chronic criteria.

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

- Out of six fipronil detections, two approached the invertebrate NOAEC (0.011 µg/L).
- Of the six imidacloprid detections, two detections approached the invertebrate NOAEC and the other four detections exceeded the invertebrate NOAEC (0.01 µg/L).
- The 14 detections of metolachlor did not exceed any assessment criteria in 2020, but this herbicide was still considered a watershed POC because of detections that did exceed criteria in recent years at this site.

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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 – Lower Big Ditch pesticide calendar, µg/L

Month	Mar	Jun	Jul	Aug	Sep	
Day of the Month	Use* 16	16 23 30	7 14 22 29	4 12 18 26	1 10 15 22 29	
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.040	0.038 0.023 0.008 0.005			
2,4-D	H	0.203	0.395 0.041 0.059 0.119 0.443 0.014 0.017 0.234	0.050	0.036 0.046 0.034 0.143	
2,6-Dichlorobenzamide	D	0.071	0.114 0.104 0.035 0.038 0.101 0.020 0.003 0.009 0.053		0.012 0.019 0.042 0.034 0.060	
4,4'-DDD	D			0.001 0.001	0.002 0.001	
4,4'-DDE	D	0.004			0.003	
Acetochlor ESA	D		0.034			
Aminocyclopyrachlor	H		0.026		0.018	
Atrazine	H	0.005			0.004	
Azoxystrobin	F	0.322	0.041 0.032 0.017 0.015 0.010 0.004 0.002 0.002 0.005		0.003 0.002 0.004 0.004	
Boscalid	F		0.022 0.011 0.004 0.006 0.005 0.003	X	0.004 0.002 0.003 0.003 0.003 0.004 0.009	
Carbendazim	F		0.002 0.003	0.010	0.002	0.001 0.001 0.004
Chlorothalonil	F			0.002 0.002	0.002	
Chlorpropham	H	0.009				
Chlorpyrifos	I				0.002	
Chlorsulfuron	H		0.061			
Clothianidin	I		0.003			
Cyantraniliprole	I		0.053			
Cyprodinil	F		0.004			
Diazinon	I		0.005			
Dicamba acid	H		0.023 0.015		0.023	
Dichlobenil	H	0.004	0.013 0.013 0.002 0.003 0.002	0.003	0.005	
Difenoconazole	F	0.027		0.006		
Dinotefuran	I	0.066	0.069 0.037 0.043 0.048 0.024 0.011	0.028	0.004 0.012 0.011 0.008 0.014	
Diuron	H	0.009	0.307 0.068 0.039 0.010 0.009 0.004	0.005	0.005 0.007	
Eplam	H	0.012	0.008 0.005 0.009 0.003 0.002 0.002	0.001	0.001 0.001 0.001 0.003	
Fipronil	I	0.002	0.004 0.011 0.008 0.003		0.002	
Fipronil Disulfanyl	D		0.003	0.002 0.002		
Fipronil Sulfide	D	0.008	0.004 0.004 0.003 0.003 0.006 0.003 0.002 0.002 0.002 0.001	0.002 0.001	0.002 0.002 0.002 0.003 0.002	
Fipronil Sulfone	D	0.003	0.003 0.005 0.004 0.003 0.007 0.003		0.002 0.003 0.003 0.002	
Fludioxonil	F	0.350	0.052 0.049 0.028 0.026 0.052 0.027 0.026 0.025 0.041 0.029 0.019 0.028 0.031 0.028 0.037 0.036			
Fluopicolide	F			0.005		
Hexazinone	H	0.003	0.003 0.002	0.002 0.001	0.002	0.004 0.005 0.004
Imazapic	H		0.006 0.007			0.007
Imazapyr	H	0.018	0.089 0.113 0.031 0.033 0.024 0.314 0.049 0.700 1.070 0.042 0.039 0.135 0.198 0.520 7.640 1.670			
Imidacloprid	I	0.006	0.150 0.026 0.012 0.011 0.007			
Indaziflam	H		0.004 0.004			0.003
MCPA	H		0.101			
Mecoprop (MCP)	H		0.057			
Methamidophos	D			0.003 0.003		
Metolachlor	H	0.015	0.233 0.175 0.020 0.016 0.014 0.007	X	0.004 0.002 0.002 0.002 0.002 0.003 0.004	
Metribuzin	H	0.004	0.027 0.022 0.003 0.003		0.007	
Metsulfuron-methyl	H		0.014			
N,N-Diethyl-m-toluamide (DEET)	IR	0.003	0.017 0.016	0.014 0.027 0.024	X	0.018 0.022 X 0.008 X
Paclbutrazol	F			0.003		
Phosmet	I		0.063			
Picloram	H		0.092 0.088 0.121 0.094	0.072 0.191	0.072 0.120 0.223 0.241 0.152	
Prometon	H	0.004	0.005 0.004 0.002 0.002 0.004 0.003	0.005	0.003 0.003 0.006 0.005 0.005	
Propiconazole	F		0.017 0.009			
Sodium Bentazon	H			0.111		
Sulfentrazone	H		0.005 0.005	0.003 0.008		
Sulfometuron methyl	H		0.007 0.016	0.005 0.007		
Tebuthiuron	H	0.014	0.013 0.016 0.010 0.010 0.014 0.006	0.003 0.017	0.004 0.007 0.009 0.023 0.018 0.016	
Terbacil	H	0.003				
Tetrahydrophthalimide (THPI)	D		0.071 0.002			
Thiamethoxam	I		0.005	0.003 0.003		
Triazine HA Degradate	D	0.026	0.041 0.041 0.024 0.027 0.024 0.014 0.005 0.006 0.014 0.004 0.005 0.008 0.012 0.019 0.017 0.018			
Triclopyr acid	H		0.139 0.173	0.057 0.056 0.181	0.097	0.035 0.003
Trifluralin	H					0.003
Total suspended solids (mg/L)		87	19 8 6 3 7 5 8 6 9 4 14 5 39 23 28 7			
Streamflow (cubic ft/sec)		20.4	18.9 3.1 18.9 8.6 13.0 7.9 9.1 6.9 4.3 6.3 5.6 2.8 2.1 1.2 1.5 2.7			
Precipitation (total in/week)†		--	-- -- -- -- -- 0.00 0.00 0.00 0.26 0.00 0.28 0.10 0.00 0.08 0.02 0.97			

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  No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

† Washington State University AgWeatherNet station: Mt. Vernon, (latitude: 48.44°, longitude: -122.39°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 10 of the 17 site visits (59%). Water quality at the Lower Big Ditch site is shown below (Figure 12).

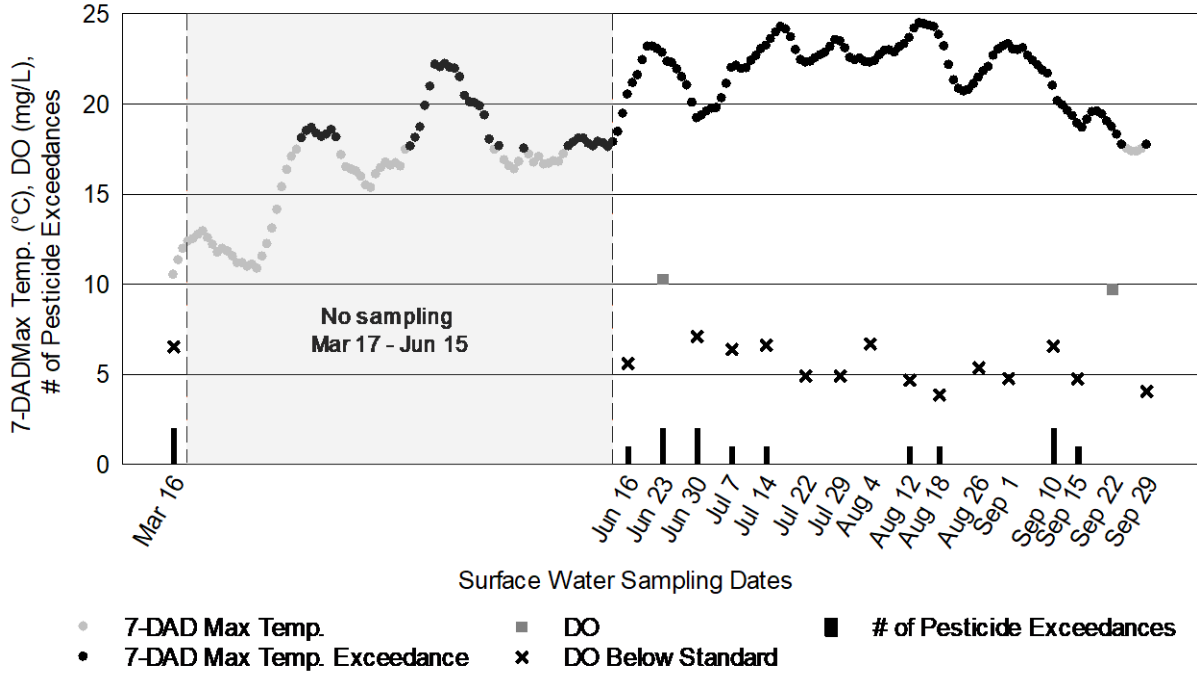


Figure 12 – Lower Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 6.90 to 8.22 with an average of 7.35. The pH measurement on July 14 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). DO measurements ranged from 3.86 mg/L to 10.28 mg/L with an average of 6.05 mg/L. More than half (88%) of these measurements did not meet the DO standard; 15 measurements were less than 8 mg/L. DO variability could have been due to the effects of tidal fluctuations. The 7-DADMax temperatures were greater than the 17.5°C standard on 141 days of the sampling season, primarily from May 3 through September 24. A 7-DADMax temperature exceedance coincided with at least one pesticide exceedance at nine site visits. At least one pesticide exceedance overlapped with both a 7-DADMax temperature exceedance and a DO measurement that did not meet the standard at seven site visits.

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 2021). WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

Burnt Bridge Creek

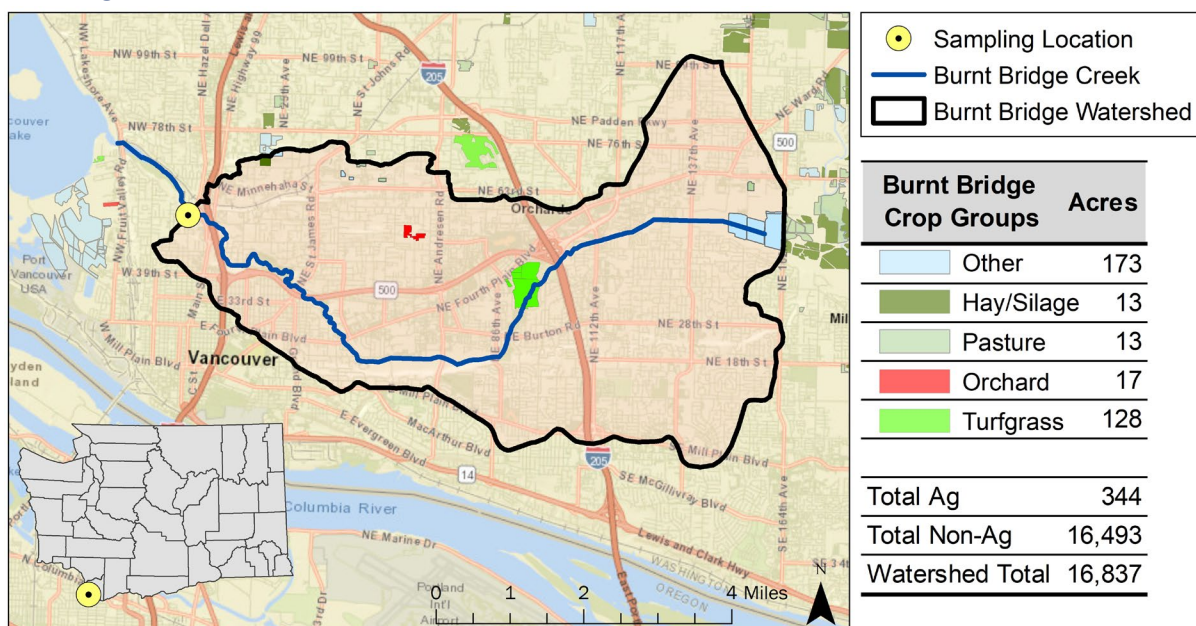


Figure 13 – Map of Burnt Bridge Creek and its drainage area with associated sampling location and crop groups identified

In 2017, NRAS 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, Figure 14). Roughly 10 miles of Burnt Bridge Creek flows through the center of Vancouver, Washington. The watershed is highly impacted by residential, commercial, and industrial development as shown in Figure 13. The ‘Other’ crop group category includes mostly land used for conservation purposes. This site was one of two urban sites we monitored in 2020.

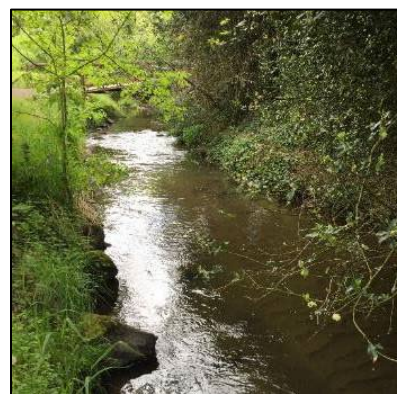


Figure 14 – Burnt Bridge Creek upstream view

Burnt Bridge Creek flows into Vancouver Lake, which drains into the Columbia River. Precipitation events generally influence streamflow in this creek. In summer, inflow from groundwater, residential irrigation, and industrial discharge from a manufacturing facility near the headwaters maintain the creek’s base flow. WDFW has documented the presence of winter steelhead and coho salmon within the Burnt Bridge watershed (WDFW 2021). Staff frequently observe fish of unknown species at the site.

Below is a brief overview of the pesticide findings in Burnt Bridge Creek in 2020.

- NRAS tested for 166 unique pesticides in Burnt Bridge Creek.
- There were 221 total pesticide detections from six different use categories: 20 types of herbicides, 5 insecticides, 3 fungicides, 12 degradates, 1 insect repellent and 1 wood preservative.
- Pesticides were detected at all 16 sampling events.
- Up to 25 pesticides were detected at the same time.
- Of the total pesticide detections, seven were above WSDA's assessment criteria (Table 10).
 - The three detections of 4,4'-DDD exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the four imidacloprid detections, three detections approached the invertebrate NOAEC and the other detection exceeded the invertebrate NOAEC (0.01 µg/L).
- There were five diuron detections throughout the 2020 monitoring season; none of which exceeded assessment criteria. However, diuron was still considered a watershed POC because it had been detected at this site exceeding assessment criteria in recent years.

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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 – Burnt Bridge Creek pesticide calendar, µg/L

Month	Use*	Jun			Jul				Aug				Sep					
		17	24	29	8	15	22	27	5	10	19	25	2	8	16	23	30	
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.004											0.007		
2,4-D	H	0.158		0.023		0.037										0.125		
2,6-Dichlorobenzamide	D	0.110	0.132	0.143	0.161	0.274	0.249	0.239	0.280	0.218	0.220	0.223	0.215	0.226	0.212	0.155	0.173	
3,5-Dichlorobenzoic Acid	D							0.019										
4,4'-DDD	D									0.001	0.001				0.001			
4-Nitrophenol	D															0.448		
Atrazine	H		0.003	0.003	0.004		0.004			0.004	0.003	0.003	0.003	0.003	0.004		0.004	
Boscalid	F		0.002	0.001	0.002						0.001					0.002	0.002	
Bromacil	H		0.003	0.004	0.003	0.007	0.006	0.005	0.006	0.004	0.004	0.004	0.007	0.006	0.005		0.004	
Carbendazim	F	0.003	0.003	0.002						0.001						0.003	0.002	
Chlorpyrifos	I																0.001	
Dicamba acid	H	0.028																
Dichlobenil	H	0.027	0.008	0.005	0.004	0.003	0.003	0.003	0.002	0.003	X	0.002				0.009	0.005	
Dinotefuran	I				0.005													
Dithiopyr	H	0.004		0.002		0.002	0.002	0.002		0.002	0.002				0.002	0.005	0.002	
Diuron	H	0.016	0.004	0.004												0.022	0.004	
Eptam	H	0.001														0.004	0.003	
Ethoprop	I															0.005		
Fipronil	I	0.003														0.003		
Fipronil Disulfanyl	D																0.002	
Fipronil Sulfide	D																0.002	
Fipronil Sulfone	D					0.003									0.002	0.003	0.003	
Hexazinone	H														0.004			
Imazapyr	H	0.112	0.058	0.056	0.043	0.045	0.043	0.033	0.042	0.025	0.028	0.037	0.040	0.048	0.040	0.026	0.034	
Imidacloprid	I	0.092	0.010	0.006	0.005													
Methamidophos	D						0.002	0.002										
Metolachlor	H	0.002														0.053	0.006	
Metribuzin	H															0.007	0.004	
N,N-Diethyl-m-toluamide (DEET)	IR	0.015	0.007		0.016				0.018	0.014	X			0.012		0.052	X	
Pendimethalin	H	0.004	0.003			0.004		0.002		0.002						0.011	0.003	
Pentachlorophenol	WP	0.013														0.027		
Prometon	H					0.002				0.003					0.003			
Propiconazole	F	0.059	0.030	0.015		0.010		0.012		0.011	0.006	0.013			0.009		0.011	
Simazine	H	0.018								0.009					0.005	0.015	0.025	0.008
Sulfentrazone	H	0.004		0.004		0.003	0.003		0.004	0.004				0.004		0.006	0.004	
Sulfometuron methyl	H	0.007																
Tebuthiuron	H	0.004										0.004	0.004			0.018		
Triazine DEA degradate	D		0.004	0.004	0.004	0.003	0.004	0.003	0.003	0.003	0.002	0.004	0.004	0.005	0.004		0.004	
Triazine DIA degradate	D															0.009	0.002	
Triazine HA Degradate	D	0.001						0.001			0.001			0.001			0.001	
Triclopyr acid	H	0.210	0.037		0.086	0.041	0.028		0.025	0.050	0.033	0.025	0.151	0.069	0.029	0.190	0.066	
Trifluralin	H	0.002								0.002						0.004		
Total suspended solids (mg/L)		15	7	6	7	15	4	10	7	7	8	4	9	3	4	33	3	
Streamflow (cubic ft/sec)		18.8	5.9	5.0	4.8	3.9	3.1	3.5	3.1	4.0	3.3	3.2	3.0	2.4	--	6.8	4.5	
Precipitation (total in/week)†		1.91	0.18	0.01	0.12	0.14	0.48	0.04	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.30	1.34	

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 No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, WP: Wood preservative)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 5 of the 16 site visits (31%). Water quality at the Burnt Bridge Creek site is shown below (Figure 15).

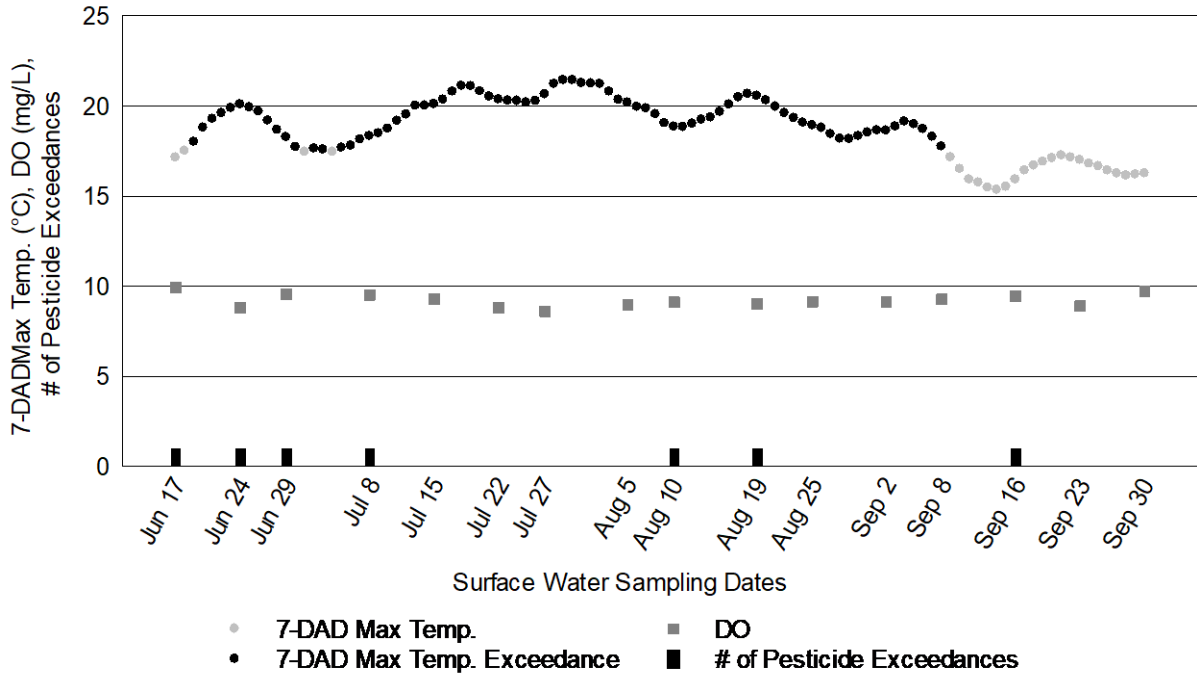


Figure 15– Burnt Bridge Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.63 to 8.16 with an average of 7.94. The pH measurement on July 14 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). All DO measurements also met the standard, ranging from 8.61 mg/L to 9.94 mg/L with an average of 9.20 mg/L. The 7-DADMax temperature was greater than the 17.5°C standard on 80 days of the sampling season, primarily from June 19 to September 8. Pesticide exceedances coincided with 7-DADMax temperature exceedances at five site visits.

Burnt Bridge Creek has been designated as a freshwater habitat for salmonid spawning, rearing, and migration (WAC 2021). 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

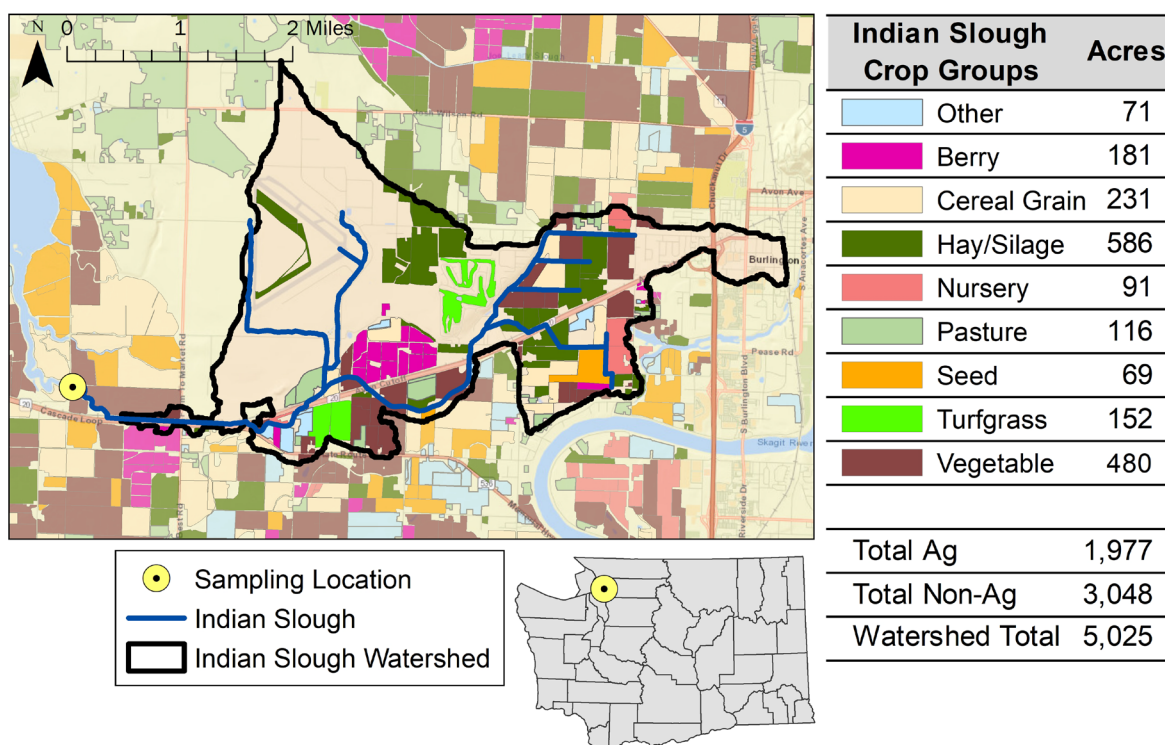


Figure 16 – Map of Indian Slough and its drainage area with associated sampling location and crop groups identified

In 2006, NRAS 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, Figure 17).

Indian Slough water drains directly into Puget Sound. Agricultural irrigation and precipitation events generally influence streamflow in the slough. WDFW has documented the presence of winter steelhead, Chinook salmon, chum salmon, and coho salmon within the reach of slough that encompasses the Indian Slough site (WDFW 2021). Staff frequently observe juvenile fish of unknown species at the site. In the late fall of 2021, adult salmon of unknown species were observed by staff.

The Indian Slough watershed is a web of drainage ditches that pass through agricultural and industrial/residential areas. Indian Slough stretches approximately 6 miles from its sources to the monitoring site. Within the watershed, the agricultural land use is predominantly potatoes, grass hay, field corn, blueberries and cucumber. The 'Other' crop group category consists mostly of fallow fields and assorted small acreage crops (Figure 16). Indian Slough is another site where the presence of invasive New Zealand mud snails has been confirmed.



Figure 17 – Indian Slough upstream view

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

Below is a brief overview of the pesticide findings in Indian Slough in 2020.

- NRAS tested for 166 unique pesticides in Indian Slough.
- There were 452 total pesticide detections from 5 different use categories: 30 types of herbicides, 10 insecticides, 8 fungicides, 10 degradates, and 1 insect repellent.
- Pesticides were detected at all 18 sampling events.
- Up to 42 pesticides were detected at the same time.
- Of the total pesticide detections, 10 were above WSDA's assessment criteria (Table 11).
 - The three detections of 4,4'-DDD approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the five detections of imidacloprid, two detections approached the invertebrate NOAEC and the other three detections exceeded the invertebrate NOAEC (0.01 µg/L).
- Out of three malathion detections, the July 14 detection approached the invertebrate NOAEC and the June 30 detection exceeded the invertebrate NOAEC (0.06 µg/L).
- Diuron was detected every sampling event (18); none of which exceeded assessment criteria. The three fipronil detections did not exceed any assessment criteria in 2020 either. Diuron and fipronil were still considered watershed POCs because they have been detected at this site exceeding assessment criteria in recent years.

The Indian Slough monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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 – Indian Slough pesticide calendar, µg/L

Month		Mar	Jun				Jul				Aug				Sep				Oct	
Day of the Month	Use*	16	16	23	30	7	14	22	29	4	12	18	26	1	10	15	22	29	6	
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.004	0.114	0.074	0.034	0.028	0.015	0.006	0.004										0.007	
2,4-D	H	0.036	0.213	0.650	0.034					0.024									0.180	0.045
2,6-Dichlorobenzamide	D	0.097	0.166	0.192	0.166	0.155	0.188	0.102	0.093	0.079	0.067	0.051	0.062	0.056	0.051	0.039	0.149	0.170	0.178	
4,4'-DDD	D										0.001	0.001				0.001				
Acetamiprid	I													0.002						
Acetochlor ESA	D									0.045										
Aminocyclopyrachlor	H	0.013	0.021	0.052	0.042	0.035	0.022	0.013	0.018											
Atrazine	H																		0.003	
Azoxystrobin	F	0.011	0.076	0.057	0.020	0.011	0.006	0.007	0.009	0.004	0.005	0.002	0.002	0.002	0.002			0.003	0.003	0.003
Boscalid	F	0.016	0.014	0.017	0.017	0.010	0.013	0.011	0.008	0.010	0.009	0.007	0.006	0.006	0.007	0.006	0.009	0.008	0.009	
Bromacil	H	0.004	0.012	0.059	0.004	0.005	0.010								0.004			0.019	0.005	
Bromoxynil	H	0.030																		
Carbaryl	I							0.009											0.003	
Carbendazim	F		0.003	0.004	0.002	0.003				0.001	0.002							0.003		
Chlorpropham	H																		0.001	
Chlorsulfuron	H		0.018	0.060																
Clothianidin	I		0.004	0.004	0.003															
Cyantraniliprole	I				0.009															
Cyprodinil	F			0.013	0.019															
Dacthal (DCPA)	H	0.050				0.033	0.018													
Dicamba acid	H	0.011	0.028	0.050															0.036	
Dichlobenil	H	0.004	0.013	0.025	0.005	0.005	0.003	0.002											0.017	0.012
Dithiopyr	H		0.006	0.005	0.002															
Diuron	H	0.013	0.469	0.326	0.110	0.069	0.042	0.021	0.014	0.010	0.009	0.010	0.008	0.006	0.006	0.005	0.011	0.017	0.013	
Eptam	H	0.002	0.005	0.005	0.002	0.002	0.002	0.002	0.001					0.001	0.001	0.001		0.003	0.002	
Fipronil	I		0.003	0.002															0.002	
Fipronil Sulfide	D		0.001			0.004	0.001	0.001						0.002	0.002			0.002		
Fipronil Sulfone	D		0.002			0.004														
Fludioxonil	F	0.007	0.009	0.013	0.017	0.006	0.007	0.005	0.006	0.007	0.006	0.005	0.007	0.005	0.007	0.007	0.008	0.005	0.010	
Hexazinone	H	0.037	0.105	0.115	0.145	0.047	0.054	0.022	0.020	0.021	0.016	0.020	0.016	0.021	0.019		0.058	0.044	0.051	
Imazapic	H			0.018															0.006	
Imazapyr	H	0.005	0.113	0.120	0.053	0.051	0.032	0.025	0.017	0.018	0.009	0.011	0.017	0.033	0.016	0.015	0.011	0.042	0.027	
Imidacloprid	I		0.011	0.068	0.018	0.008	0.006													
Indaziflam	H		0.010	0.036	0.008	0.006	0.004	0.002											0.005	
Isoxaben	H		0.006	0.005		0.003														
MCPA	H			0.231																
Malathion	I				0.088		0.028					0.006								
Mecoprop (MCP)	H		0.038																	
Methamidophos	D						0.002	0.002												
Methoxyfenozide	I	0.003	0.007	0.008	0.006	0.008	0.003		0.004		0.004							0.007	0.004	0.005
Metolachlor	H	0.005	0.048	0.150	0.016	0.008	0.007	0.004	0.008	0.009	0.017	0.004		0.004	0.002	0.002	0.002	0.004	0.003	
Metribuzin	H		0.008	0.021	0.003					0.003	0.005									
Metsulfuron-methyl	H		0.011	0.013															0.007	
Myclobutanil	F				0.016	0.007														
N,N-Diethyl-m-toluamide (DEET)	IR		0.004	0.006															X	
Phosmet	I			0.072	0.008	0.005														
Prometon	H		0.004	0.004	0.002		0.003												0.003	
Propiconazole	F	0.011	0.139	0.148	0.046	0.051	0.035	0.059	0.059	0.034		0.006	0.017	0.164	0.043	0.014	0.019	0.122	0.039	
Pyrimethanil	F					0.466	0.131	0.016	0.010	0.004	0.004	0.021	0.005	0.002	0.002		0.005	0.003	0.002	
Simazine	H		0.036	0.033	0.020	0.006	0.007										0.008		0.006	
Sulfentrazone	H	0.008	0.079	0.116	0.127	0.017	0.018	0.012	0.013	0.009	0.012	0.022	0.017	0.012	0.011	0.010	0.023	0.014	0.016	
Sulfometuron methyl	H	0.003	0.034	0.025	0.005	0.004	0.007	0.006	0.007											
Tebuthiuron	H	0.036	0.033	0.034	0.062	0.054	0.071	0.045	0.042	0.053	0.048	0.050	0.047	0.053	0.046	0.047	0.036	0.030	0.037	
Terbacil	H	0.007			0.007	0.006	0.009	0.010	0.009	0.009	0.007	0.015	0.013	0.016	0.015	0.016	0.015	0.013	0.012	
Tetrahydrophthalimide (THPI)	D		0.025	0.988	0.015	0.014	0.007					0.002	0.009		0.002	0.002	0.013			
Thiamethoxam	I	0.010	0.025	0.038	0.044	0.021	0.013	0.008	0.008	0.005	0.007	0.005	0.006	0.005	0.005	0.003	0.021	0.011	0.015	
Triazine DIA degradate	D		0.009	0.015	0.011	0.005						0.003							0.007	
Triazine HA Degradate	D	0.008	0.015	0.017	0.018	0.018	0.015	0.014	0.009	0.014	0.009	0.006	0.007	0.009	0.009	0.009	0.008	0.008	0.011	
Triclopyr acid	H		0.266	0.391	0.048	0.067													0.159	
Total suspended solids (mg/L)		14	5	6	5	7	8	5	7	13	9	5	5	10	5	25	7	9	6	
Streamflow (cubic ft/sec)		43.8	--	--	21.0	12.6	15.8	11.0	7.6	3.3	--	4.9	12.6	10.9	15.9	7.3	11.8	16.3	17.1	
Precipitation (total in/week)†		--	--	--	--	--	--	0.00	0.00	0.00	0.26	0.00	0.28	0.10	0.00	0.08	0.02	0.97	0.03	

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 No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 7 of the 18 site visits (39%). Water quality at the Indian Slough site is shown below (Figure 18).

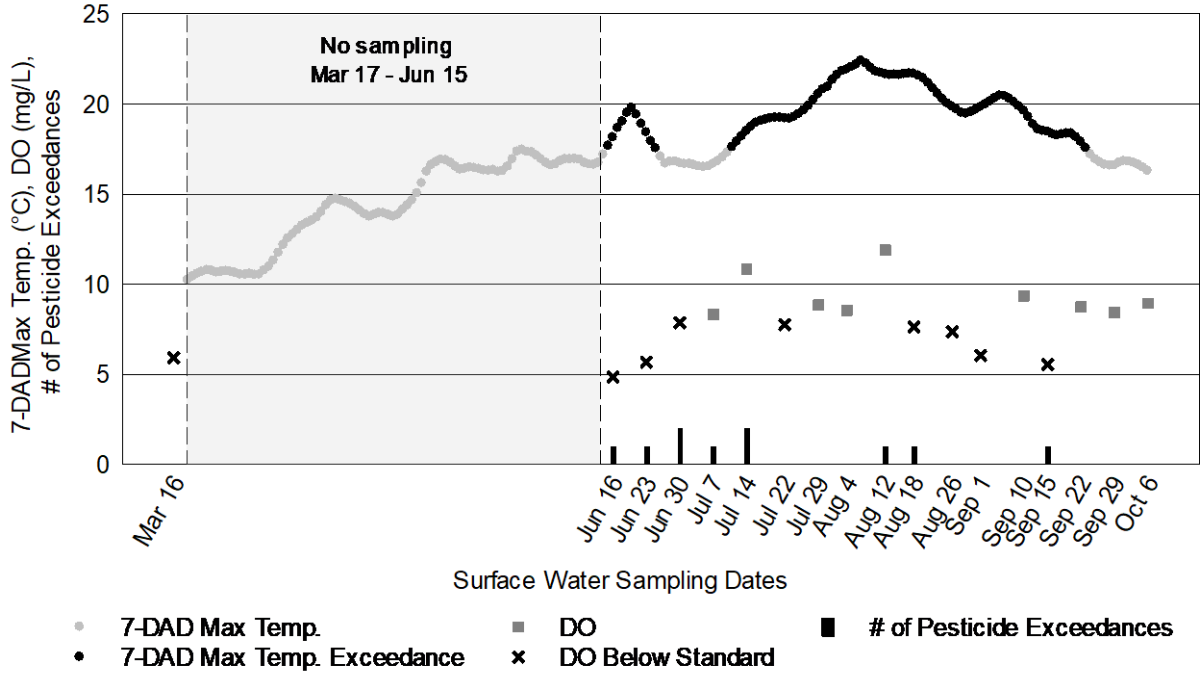


Figure 18 – Indian Slough water quality measurements and exceedances of assessment criteria

All pH measurements were within the state standard, ranging from 6.76 to 8.38 with an average of 7.16. The pH measurement on July 14 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). DO measurements ranged from 4.85 mg/L to 11.90 mg/L with an average of 7.93 mg/L. Half of the measurements did not meet the state DO standard; nine measurements were less than 8 mg/L. There were five instances when the DO measurement coincided with one or two pesticide exceedances. The 7-DADMax temperatures were greater than the 17.5°C temperature standard on 86 days of the sampling season, specifically from June 15 through June 25 and then July 11 through September 23. Pesticide exceedances overlapped with 7-DADMax temperature exceedances at six site visits.

Indian Slough is tidally influenced and grows extensive aquatic vegetation throughout the summer. These conditions mean the water sometimes is not well mixed at the monitoring site, so water quality measurements such as temperature and specific conductance are not uniform throughout the water column. This was evident when watching the real-time temperature and specific conductance measurements substantially change as staff lowered the water quality probe from the surface to the stream bottom. Indian Slough is not only considered habitat for salmonid spawning, rearing, and migration; but is also used as a corridor by migrating waterfowl (WAC 2021). NRAS will continue to monitor this drainage because of its representative regional land use.

Juanita Creek

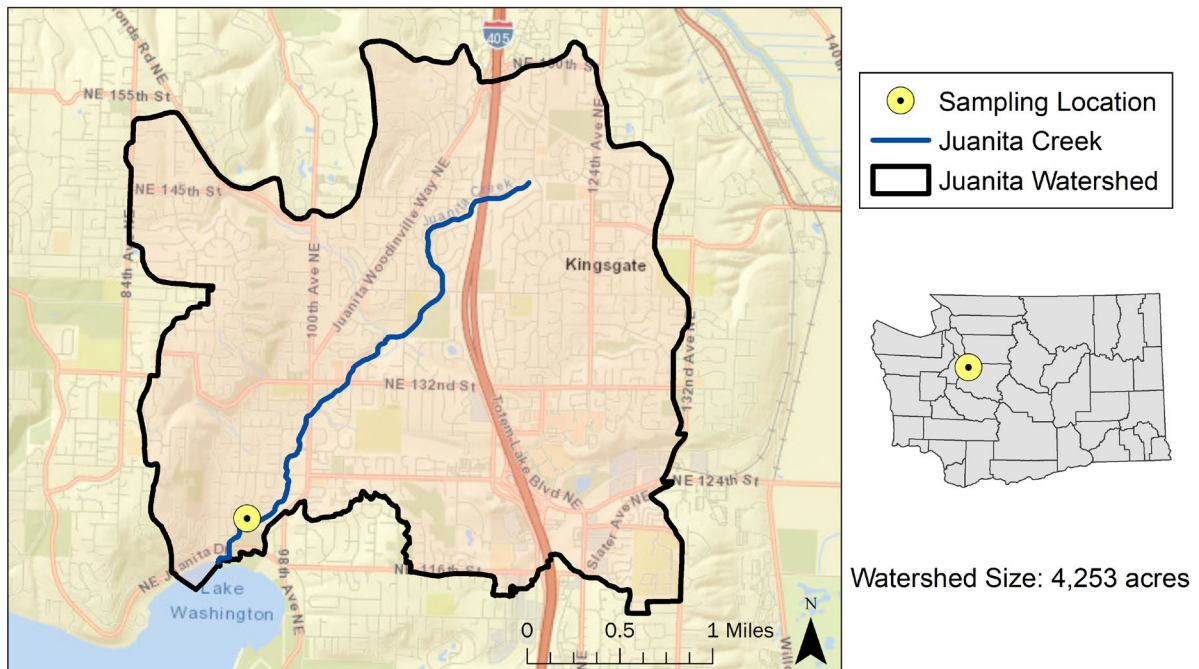


Figure 19 – Map of Juanita Creek and its drainage area with associated sampling location and crop groups identified

In 2020, NRAS started monitoring the Juanita watershed in King County. Juanita Creek flows roughly 5 miles through Kirkland, Washington. The Juanita monitoring site is located just downstream of an open-bottom culvert where an ephemeral tributary also drains alongside NE 120th Street (latitude: 47.7077°, longitude: -122.2148°). Within the Juanita drainage area, the land use is predominantly residential (Figure 19, Figure 20). This site was one of two urban sites NRAS monitored in 2020.

Juanita Creek drains into Lake Washington, which is known for its sport fishing. The water quality in Juanita is highly impacted by stormwater and irrigation runoff from impervious surfaces. King County and the City of Kirkland staff also monitor water quality in the Juanita Watershed with parameters such as benthic macroinvertebrates, streamflow, dissolved oxygen, and temperature. WDFW has documented winter steelhead, fall Chinook salmon, coho salmon, and sockeye salmon within the reach of creek that encompasses the monitoring site (WDFW 2021). City of Kirkland staff observed adult coho salmon in the creek during spawning season in 2021.

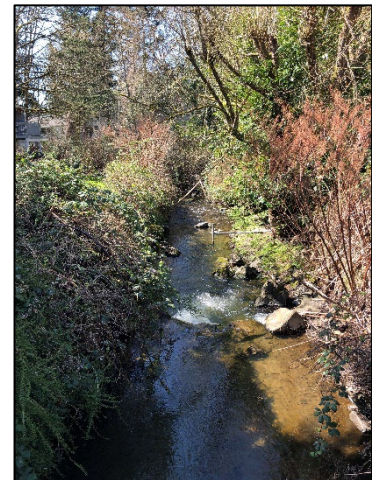


Figure 20 – Juanita Creek downstream view

Below is a brief overview of pesticide findings in Juanita Creek in 2020.

- NRAS tested for 166 unique pesticides in Juanita Creek.
- There were 194 total pesticide detections from five different use categories: 18 types of herbicides, 9 insecticides, 4 fungicides, 6 degradates, and 1 insect repellent.
- Pesticides were detected at all 15 sampling events.
- Up to 25 pesticides were detected at the same time.
- Of the total pesticide detections, four were above WSDA's assessment criteria (Table 12).
 - The imidacloprid detection approached the invertebrate NOAEC (0.01 µg/L).
 - The dichlorvos detection approached the invertebrate NOAEC (0.0058 µg/L).

The Juanita watershed POCs were tralomethrin and deltamethrin. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Tralomethrin was detected only in Juanita Creek in 2020. This insecticide was voluntarily cancelled by the pesticide registrants in 2012.
 - Persons may use existing stock of the pesticide until it is used up. The detection is likely from use of the pesticide beyond the product cancellation date.
 - The detection August 3 exceeded the invertebrate NOAEC (0.0044 µg/L).
 - Tralomethrin breaks down quickly in the environment into deltamethrin.
- Deltamethrin, a currently-registered pesticide, was detected only in Juanita Creek in 2020.
 - It is unknown whether the detection came from an insecticide product containing deltamethrin or tralomethrin.
 - Deltamethrin is even more toxic to aquatic life than tralomethrin. The detection August 3 exceeded the invertebrate NOAEC (0.0041 µg/L), exceeded the WSDA Endangered Species Level of Concern (0.0145 µg/L), and approached the fish NOAEC (0.017 µg/L).

The Juanita Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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.

Table 12 – Juanita Creek pesticide calendar, µg/L

Month		Mar	Jun			Jul				Aug					Sep	
Day of the Month	Use*	16	15	22	29	6	13	21	28	3	11	17	25	31	9	14
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.005											
2,4-D	H		0.048		0.040		0.024									0.154
2,6-Dichlorobenzamide	D	0.248	0.231	0.248	0.228	0.240	0.341	0.277	0.309	0.323	0.289	0.262	0.260	0.261	0.251	0.241
Atrazine	H								0.003				0.002		0.002	
Boscalid	F			0.002	0.002	0.001		0.001				0.001				
Bromacil	H	0.005	0.006	0.004	0.003		0.005			0.004	0.004	0.004	0.004		0.004	
Carbendazim	F	0.002	0.007	0.002	0.005	0.002				0.003	0.002	0.002	0.002			0.001
Deltamethrin	I									0.015						
Dichlobenil	H	0.011	0.032	0.010	0.020	0.005	0.005	0.008	0.004	0.003	0.004	X	0.004	0.003	0.006	
Dichlorvos (DDVP)	I		0.004													
Dinotefuran	I		0.004													
Dithiopyr	H		0.002								0.002	0.002				
Diuron	H	0.004	0.018	0.007	0.011	0.004	0.006	0.011	0.004	0.006	0.006	0.004	0.005	0.004		
Ethoprop	I														0.002	
Fipronil	I		0.002										0.002			
Fipronil Disulfinyl	D							0.002								
Fipronil Sulfide	D		0.001				0.004	0.002	0.001						0.002	
Fipronil Sulfone	D						0.003								0.002	0.002
Hexazinone	H	0.002	0.002	0.002												0.004
Imazapyr	H	0.009	0.030	0.017	0.020	0.010	0.010	0.028	0.008	0.008	0.010	0.021	0.030	0.019	0.011	0.023
Imidacloprid	I	0.005														
Metolachlor	H	0.001	0.001													
N,N-Diethyl-m-toluamide (DEET)	IR	0.003	0.013	0.006			0.028	0.015		0.008	0.015	X	0.036	0.011		
Norflurazon	H	0.001														
Pendimethalin	H		0.002													
Phosmet	I		0.005													
Prometon	H	0.004	0.006	0.005	0.004	0.004	0.007	0.005	0.005	0.006	0.006	0.005	0.005	0.004	0.005	0.004
Prometryn	H		0.002													
Propiconazole	F				0.006		0.005			0.005						
Pyriproxyfen	I		0.002													
Sulfentrazone	H		0.007		0.005	0.003	0.005	0.003	0.004		0.004		0.006			
Tebuthiuron	H	0.004	0.006	0.004	0.006	0.004	0.006	0.014	0.006	0.005	0.008	0.007	0.008	0.006		0.005
Tralomethrin	I									0.015						
Triadimefon	F			0.002								0.003		0.002	0.002	
Triazine HA Degradate	D	0.002	0.004	0.004	0.005	0.004	0.003	0.010	0.004	0.005	0.004	0.004	0.004	0.004	0.003	0.004
Triclopyr acid	H		0.082		0.041								0.045		0.022	
Triclopyr butoxyethyl ester	H	0.002														
Trifluralin	H		0.001													
Total suspended solids (mg/L)		3	9	3	7	1	2	4	1	2	4	1	1	1	1	2
Streamflow (cubic ft/sec)		6.4	13.9	4.3	5.1	2.8	2.7	4.5	2.5	2.4	2.7	2.3	2.3	2.0	1.7	2.1
Precipitation (total in/week)†		0.28	1.37	1.24	0.39	0.06	0.13	0.00	0.05	0.00	0.36	0.00	0.15	0.01	0.00	0.00

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

 Current-use exceedance  Detection  No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

† Washington State University AgWeatherNet station: Woodinville, (latitude: 47.75°, longitude: -122.15°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 1 of the 15 site visits (7%). Water quality at the Juanita Creek site is shown below (Figure 21).

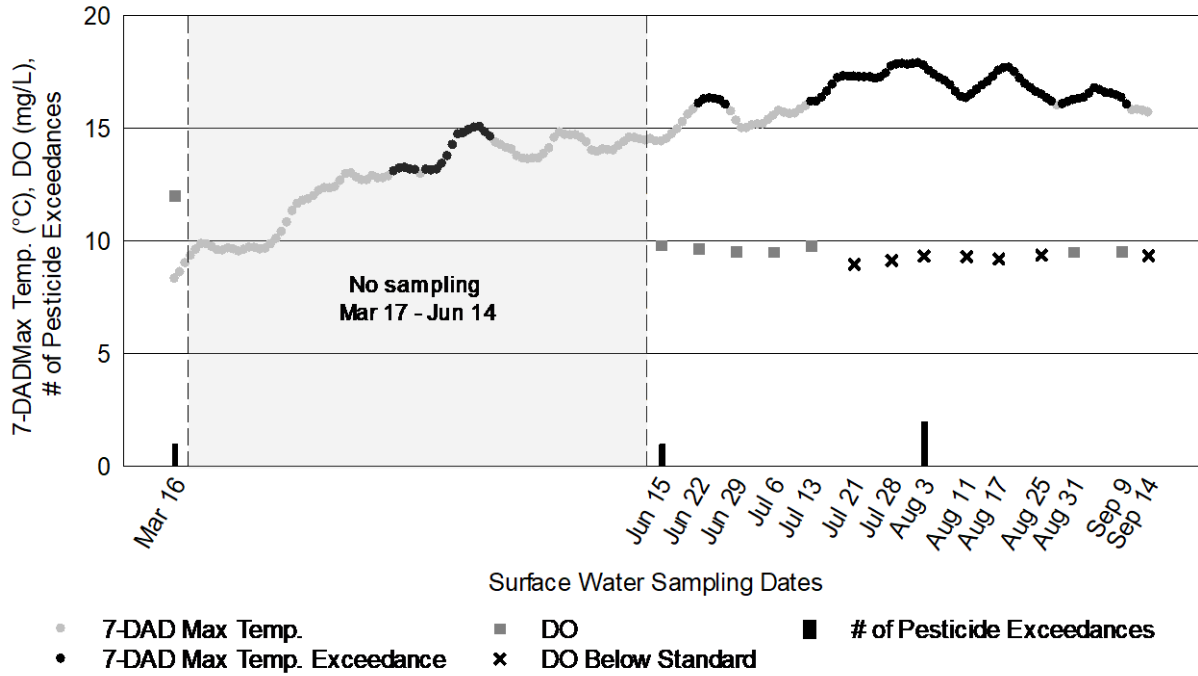


Figure 21 – Juanita Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.40 to 7.65 with an average of 7.52. The pH measurement on July 13 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). DO measurements ranged from 8.99 mg/L to 12.00 mg/L with an average of 9.60 mg/L. Half of the DO measurements did not meet the standard; eight measurements were less than 9.5 mg/L. On August 3, two pesticide exceedances coincided with both a DO measurement below the standard and a 7-DADMax temperature above the standard.

Juanita Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods of the sampling season. From September 15 through May 15, the 7-DADMax temperature should remain below 13°C. From May 16 through September 14, the 7-DADMax temperature should remain below 16°C (WAC 2021). The 7-DADMax temperature exceeded the standard on 83 days, primarily from April 26 through May 14 and July 13 through September 10.

Juanita Creek has been designated as a freshwater body that provides core summer habitat for salmonids by the WAC (WAC 2021). NRAS will continue to monitor this drainage because of its representative regional urban land use and exceeding detections of pesticides.

Central Region

Brender Creek

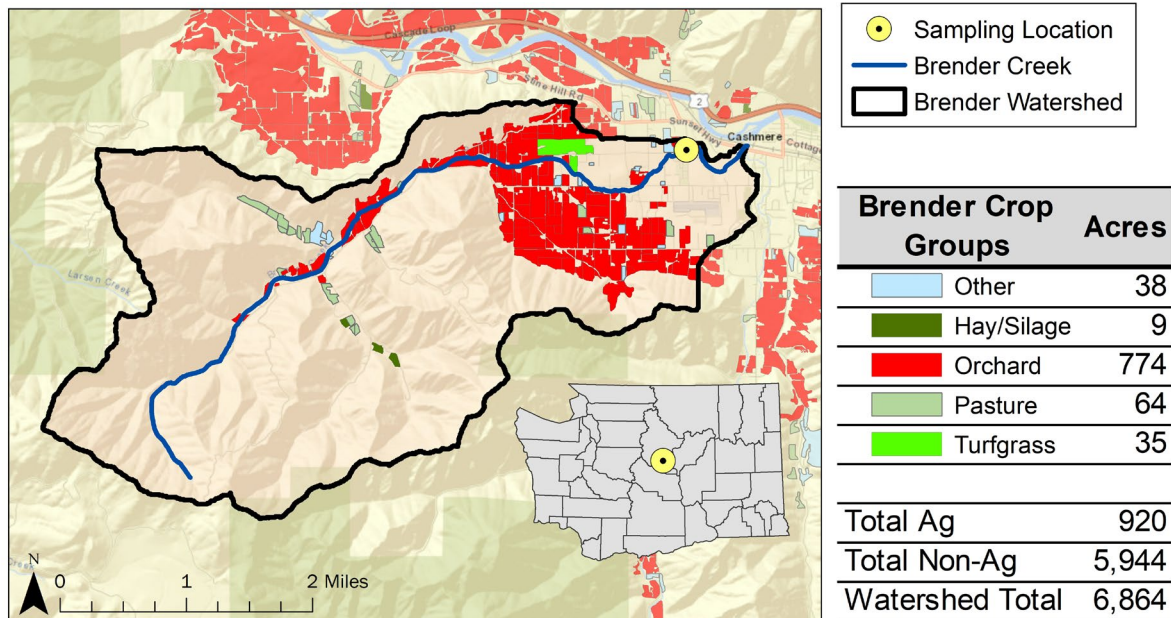


Figure 22 – Map of Brender Creek and its drainage area with associated sampling location and crop groups identified

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

The Brender site is located in Cashmere, on the upstream side of the culvert at Evergreen Drive (latitude: 47.5211°, longitude: -120.4863°) (Figure 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 streamflow in the creek. WDFW has documented the presence of spring Chinook salmon and summer steelhead within the lower reaches of the creek (WDFW 2021).



Figure 23 – Brender Creek upstream view

The watershed terrain in the upper three-quarters is mountainous with a transition into low-lying, flat terrain in the bottom quarter where tree fruit crops are plentiful. The agricultural land use is predominately pears, apples, pasture, and cherries. The 'Other' crop group category mostly consists of fallow fields (Figure 22).

Below is a brief overview of the pesticide findings in Brender Creek in 2020.

- NRAS tested for 152 unique pesticides in Brender Creek.
- Pesticides were detected at all 18 sampling events.
- There were 123 total pesticide detections from five different use categories: 7 types of herbicides, 9 insecticides, 2 fungicides, 3 degradates, and 1 insect repellent.
- Up to 11 pesticides were detected at the same time.
- Of the total pesticide detections, 29 were above WSDA's assessment criteria (Table 13).
 - DDT and its degradates account for 26 of these exceedances. The 8 detections of 4,4'-DDD, 16 detections of 4,4'-DDE, and 2 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the three imidacloprid detections, one detection approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.01 µg/L).
- The malathion detection on March 17 exceeded the invertebrate NOAEC (0.06 µg/L) and approached the invertebrate LC₅₀ (0.098 µg/L).
- The 10 chlorpyrifos detections did not exceed any assessment criteria in 2020, but this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years. Similarly, pyridaben was not detected but was considered a watershed POC because of the same logic.

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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. There were 11 herbicides, 2 herbicide degradates, and 1 wood preservative removed from testing at this site as a result of uncommon historic detections. On July 22, the GCMS-Pesticides analytical method sample made it to the laboratory outside of the temperature range requirements of the laboratory's standard operating procedure, so it was not analyzed.

Table 13 – Brender Creek pesticide calendar, µg/L

Month	Use*	Mar 17	Jun			Jul				Aug				Sep					Oct
			16	23	30	7	14	22	28	4	11	18	26	1	8	15	22	29	6
2,6-Dichlorobenzamide	D	0.007	0.004	0.004	0.004	0.003	0.009	--	0.005	0.012	0.008	0.005		0.007	0.004	0.005	0.005		0.006
4,4'-DDD	D		0.002	0.003	0.001	0.006		--			0.002	0.003			0.004	0.004			
4,4'-DDE	D		0.018	0.022	0.015	0.051	0.017	--	0.021	0.006	0.009	0.015	0.018	0.020	0.028	0.017	0.022	0.017	0.006
4,4'-DDT	I					0.015		--							0.008				
Acetamiprid	I			0.039	0.003		0.089				0.003	0.003		0.006		0.002			
Boscalid	F			0.002	0.001	0.001		--	0.001		0.001	0.001		0.006	0.004	0.002	0.002	0.002	
Carbendazim	F										0.001		0.012	0.008	0.003	0.007	0.002		
Chlorpyrifos	I	0.017	0.002	0.002	0.002		0.003	--	0.002			0.002	0.002	0.002	0.001				
Clothianidin	I						0.003												0.004
Etoxazole	I		0.003					--											
Hexazinone	H							--							0.004				
Hexythiazox	I			0.006															
Imidacloprid	I							<0.005	0.027		0.005								
Malathion	I	0.076						--											
N,N-Diethyl-m-toluamide (DEET)	IR							--	0.001						0.015				
Norflurazon	H	0.007	0.004	0.005	0.004	0.005	0.008	--	0.005	0.009	0.006	0.004	0.006	0.007	0.007	0.005	0.005	0.004	0.009
Pendimethalin	H		0.002	0.003	0.003	0.008	0.004	--					0.002	0.003	0.003	0.002	0.003	0.002	
Prometon	H							--		0.003	0.003								
Simazine	H						0.009	--	0.004						0.004				
Sulfentrazone	H		0.003					--		0.003	0.003			0.003					
Thiamethoxam	I			0.004	0.004		0.004												
Trifluralin	H							--											0.003
Total suspended solids (mg/L)		3	28	28	23	63	25	--	31	4	22	17	32	27	50	25	30	21	6
Streamflow (cubic ft/sec)		0.4	3.9	3.0	2.5	2.5	1.1	1.4	1.8	0.5	0.5	2.2	1.5	2.4	5.3	--	6.0	5.2	0.6
Precipitation (total in/week)†		0.34	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.55	0.00

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

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 3 of the 18 site visits (17%). Water quality at the Brender site is shown below (Figure 24).

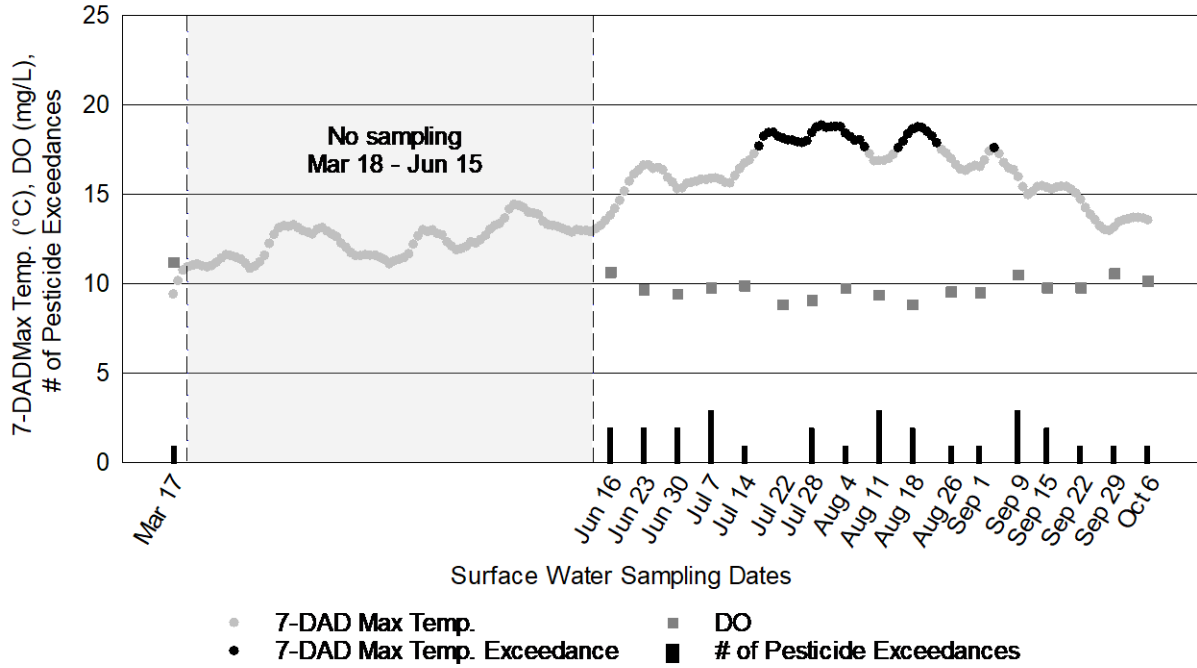


Figure 24– Brender Creek water quality measurements and exceedances of assessment criteria

All pH measurements met state standards, ranging from 7.66 to 8.50 with an average of 8.04. All DO measurements also met state standards, ranging from 8.83 mg/L to 11.19 mg/L with an average of 9.79 mg/L. The 7-DADMax temperatures exceeded the 17.5°C temperature standard on 33 days of the sampling season, primarily from July 17 through August 23. Pesticide exceedances coincided with 7-DADMax temperature exceedances on July 28, August 4, and August 18.

The lower portion of Brender Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2021). Staff observed juvenile fish of unknown species. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Lower Crab Creek

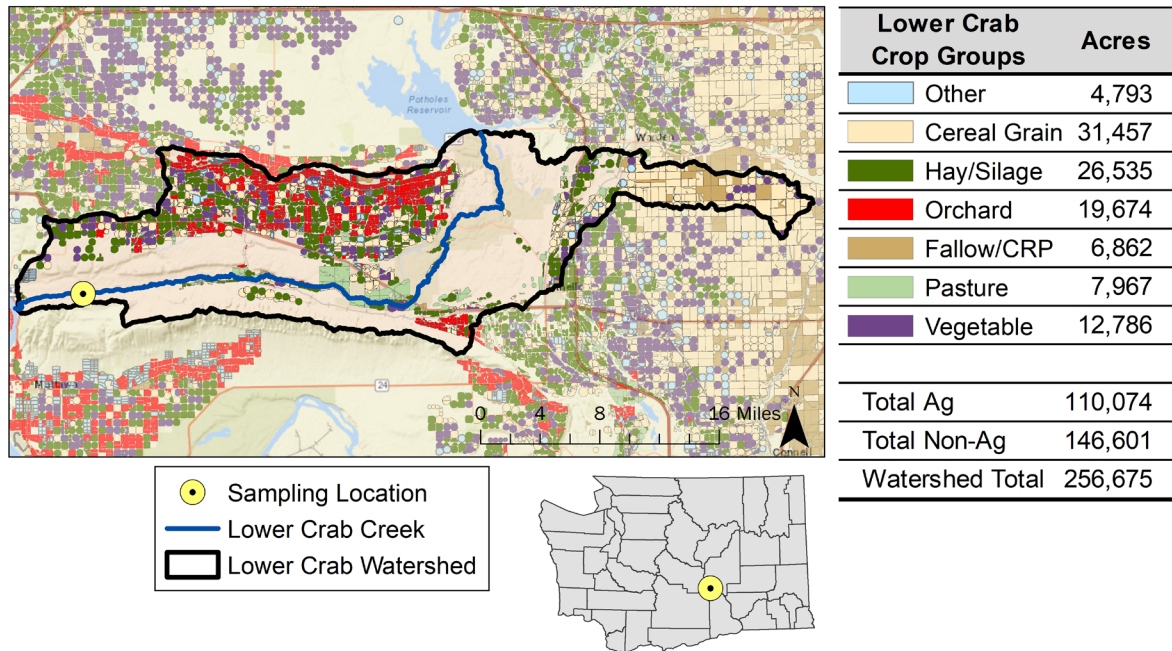


Figure 25 – Map of Lower Crab Creek and its drainage area with associated sampling location and crop groups identified

In 2017, NRAS started monitoring the Lower Crab watershed in Grant County. We 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, Figure 26).

The Columbia Basin Irrigation Project created a series of reservoirs and irrigation canals that provide Lower Crab Creek with perennial sources of water. Lower Crab Creek streamflow 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 2021). Data suggests the fall Chinook salmon in the creek are genetically diverse from hatchery salmon in the area (Small et al. 2011).



Figure 26 – Lower Crab Creek downstream view

The watershed that contains the approximately 48-mile-long Lower Crab Creek has desert-like 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 consists of sweet corn, mint, vineyards, seed crops and other assorted small acreage crops (Figure 25).

Below is a brief overview of pesticide findings in Lower Crab Creek in 2020.



- NRAS tested for 166 unique pesticides in Lower Crab Creek.
- There were 252 total pesticide detections from five different use categories: 18 types of herbicides, 11 insecticides, 5 fungicides, 8 degradates, and 1 insect repellent.
- Pesticides were detected at all 13 sampling events.
- Up to 28 pesticides were detected at the same time.
- Of the total pesticide detections, none were above WSDA's assessment criteria (Table 14).
- Malathion was the only 2020 watershed-specific POC at this site. The detection of malathion did not exceed any assessment criteria in 2020, but this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years at this site.

The Lower Crab Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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 – Lower Crab Creek pesticide calendar, µg/L

Month		Mar	Jun			Jul				Aug				Sep
Day of the Month	Use*	17	16	23	30	7	14	22	28	4	11	18	26	1
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.019	0.014	0.015	0.018	0.017	0.010	0.009	0.007		0.009	0.004		0.005
2,4-D	H		0.171	0.229	0.337	0.206	0.226	0.231	0.247	0.282	0.254	0.185	0.095	0.148
2,6-Dichlorobenzamide	D	0.003	0.002	0.002	0.002	0.005			0.003	0.005	0.003			0.004
Acephate	I									0.005				
Acetochlor ESA	D	0.043				0.057				0.056			0.054	0.049
Atrazine	H	0.008	0.010	0.008	0.012	0.010	0.014	0.010	0.011	0.013	0.010	0.009	0.008	0.012
Azoxystrobin	F													0.003
Boscalid	F		0.008	0.005	0.006	0.007	0.008	0.008	0.007	0.008	0.007	0.007	0.007	0.010
Bromacil	H	0.007	0.009	0.009	0.008	0.010	0.012	0.011	0.009	0.011	0.009	0.009	0.007	0.010
Carbendazim	F									0.004	0.018	0.013	0.009	0.012
Chlorpyrifos	I		0.007	0.004	0.003		0.003	0.002	0.002	0.002		0.002	0.002	
Dacthal (DCPA)	H	0.247	0.156	0.278	0.292	0.229	0.228	0.057	0.210	0.044	0.241	0.204	0.171	0.043
Diazinon	I			0.001	0.006	0.003	0.004	0.003						
Dicamba acid	H		0.037	0.032	0.091	0.026	0.018	0.009	0.017	0.018	0.021	0.010	0.013	0.082
Dimethoate	I								0.004	0.012			0.006	
Diuron	H	0.144	0.020	0.024	0.025	0.021	0.016	0.013	0.009	0.011	0.010	0.009	0.007	0.009
Eptam	H		0.022	0.014	0.008	0.004	0.004	0.003	0.002	0.010	0.004	0.003	0.002	0.002
Hexazinone	H	0.009	0.008	0.007	0.008	0.007	0.008	0.008		0.009	0.007		0.006	
Imazapyr	H	0.030	0.020	0.017	0.020	0.016	0.016	0.012	0.013	0.015	0.013	0.012	0.021	0.022
Malathion	I		0.003											
Methamidophos	D							0.003	0.004					
Methomyl	I								0.002	0.002	0.003			
Methoxyfenozide	I		0.002	0.002							0.002			
Metolachlor	H	0.001	0.006	0.006	0.007	0.007	0.007	0.005	X		0.004	0.003		0.002
Metribuzin	H		0.009							0.003				
Metsulfuron-methyl	H		0.012											0.005
N,N-Diethyl-m-toluamide (DEET)	IR	0.002	0.004						X	0.021	0.011			
Norflurazon	H	0.001												0.002
Oxamyl	I					0.001								0.003
Oxamyl oxime	D		0.039	0.035	0.030	0.033			0.025					0.032
Pendimethalin	H				0.002		0.004							
Pyridaben	I									0.002				
Pyrimethanil	F		0.002	0.004	0.003				0.002					
Pyriproxyfen	I									0.002				
Tebuthiuron	H									0.005				
Tefluthrin	I									0.001				
Terbacil	H						0.004	0.003		0.004	0.004	0.004		0.006
Triadimefon	F									0.004				
Triazine DEA degradate	D	0.007	0.007	0.007	0.007	0.008	0.007	0.008	0.009	0.007	0.007	0.005	0.008	0.010
Triazine DIA degradate	D					0.005								
Triazine HA Degradate	D		0.001	0.001	0.002	0.002			0.002	0.001		0.001	0.001	0.002
Triclopyr acid	H								0.016					
Trifluralin	H									0.002				
Total suspended solids (mg/L)		14	32	36	42	39	31	24	22	56	23	45	35	25
Streamflow (cubic ft/sec)		118	217	129	142	136	124	68	96	124	145	141	178	184
Precipitation (total in/week)†		0.29	0.40	0.01	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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

 Detection  No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

† Washington State University AgWeatherNet station: Royal City W, (latitude: 46.97°, longitude: -119.83°)

Water quality at the Lower Crab Creek site is shown below (Figure 27).

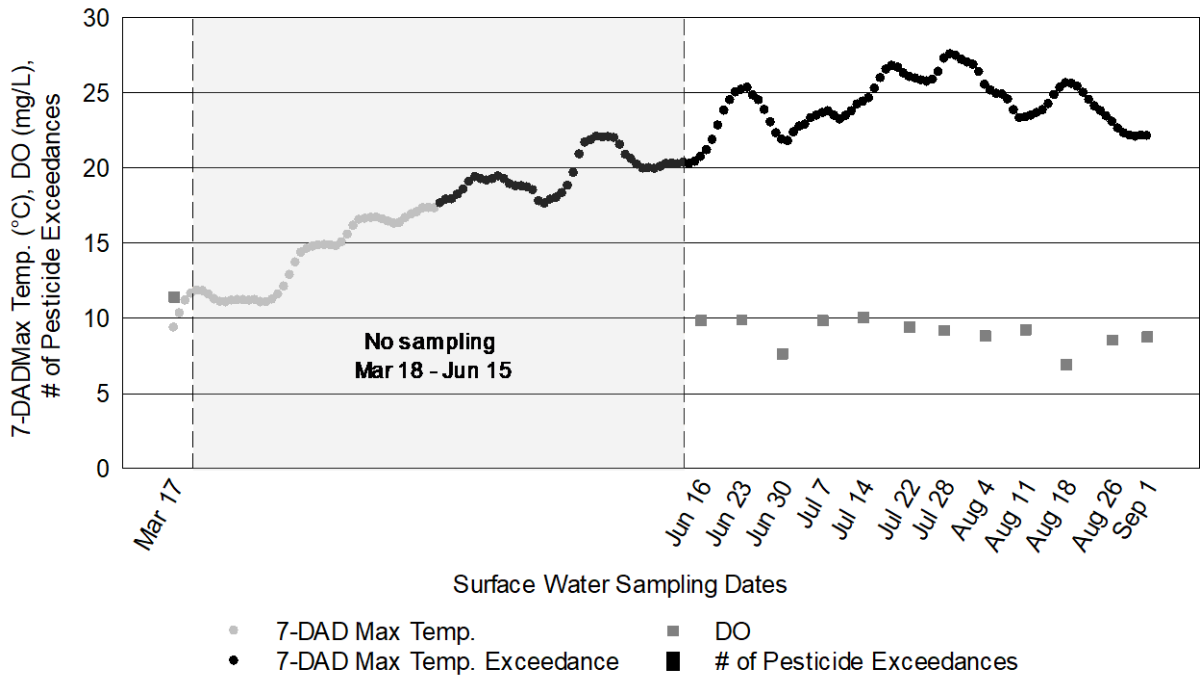


Figure 27 – Lower Crab Creek water quality measurements and exceedances of assessment criteria

The pH measurements met the state standard, ranging from 8.09 to 8.52, with an average of 8.34. The pH measurement of 8.52 was not considered an exceedance of the state standard due to being within the measurement’s uncertainty range. All DO measurements also met the state standard, ranging from 6.90 mg/L to 11.43 mg/L with an average of 9.20 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 123 days of the sampling season from May 2 through September 1.

Lower Crab Creek has been designated as a freshwater body that provides habitat for salmonid rearing and migration by the WAC (WAC 2021). Staff frequently observed juvenile fish of unknown species at the site. NRAS monitored the site through 2020, at which point it was dropped from the program due to lack of exceedances.

Marion Drain

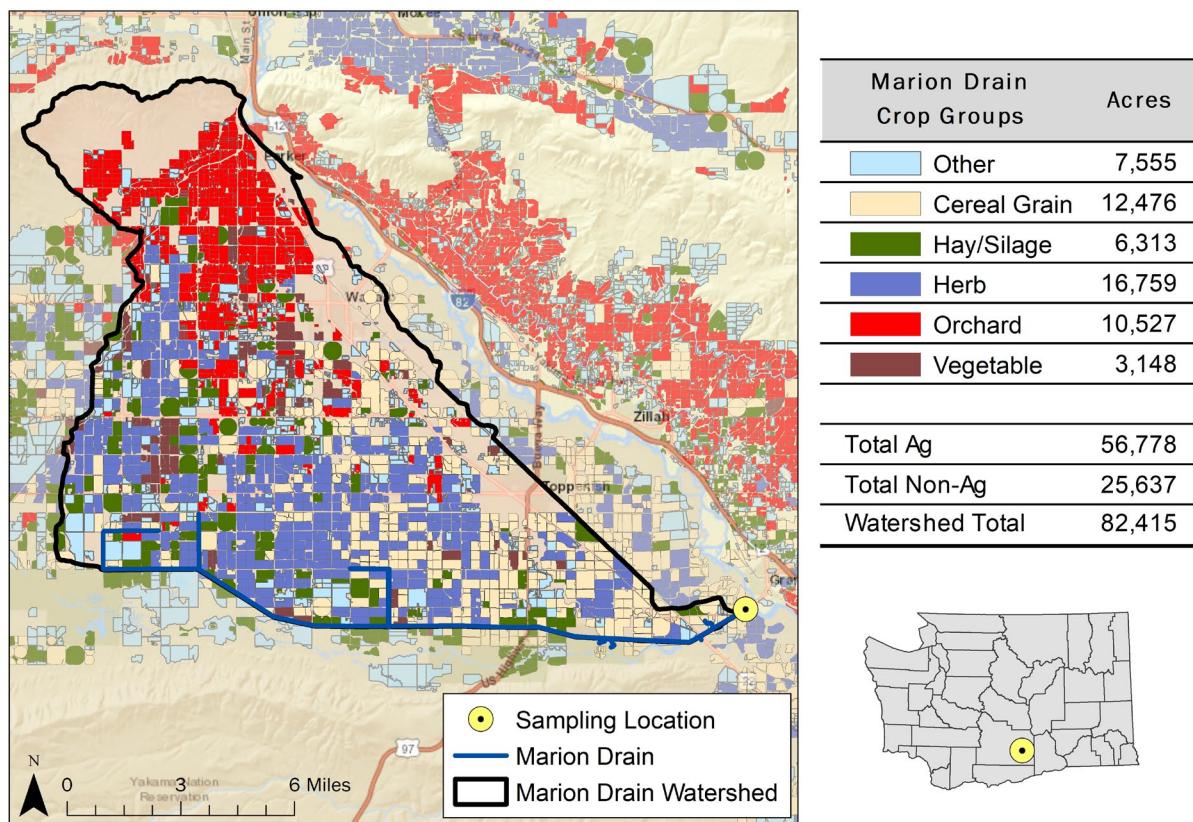


Figure 28 – Map of Marion Drain and its drainage area with associated sampling location and crop groups identified

In 2003, NRAS started monitoring 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 Central 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 lot of aquatic vegetation growing in the streambed in 2020. WDFW and the Yakama Nation have documented fall Chinook salmon, coho salmon, and summer steelhead within the Marion Drain watershed (WDFW 2021).



Figure 29 – Marion Drain upstream view

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 (considered an herb), field corn, apples, mint and wheat. The 'Other' crop group category consists of nurseries, melons, berries and other assorted small acreage crops (Figure 28).

Sampling events extended into December 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 2020.

- NRAS tested for 166 unique pesticides in Marion Drain.
- There were 484 total pesticide detections from six different use categories: 16 types of herbicides, 11 insecticides, 8 fungicides, 8 degradates, and 1 insect repellent.
- Pesticides were detected at all 28 sampling events.
- Up to 24 pesticides were detected at the same time.
- Of the total pesticide detections, 22 were above WSDA's assessment criteria (Table 15).
 - The three detections of 4,4'-DDD and two detections of 4,4'-DDE approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the 28 detections of clothianidin, eight approached the invertebrate NOAEC and six exceeded the invertebrate NOAEC (0.05 µg/L).
- Out of three imidacloprid detections, two detections approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.01 µg/L).
- The detection of chlorpyrifos did not exceed any assessment criteria in 2020, but this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years.

The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 4 of the 28 site visits (14%). Water quality at the Marion Drain site is shown below (Figure 30 and Figure 31).

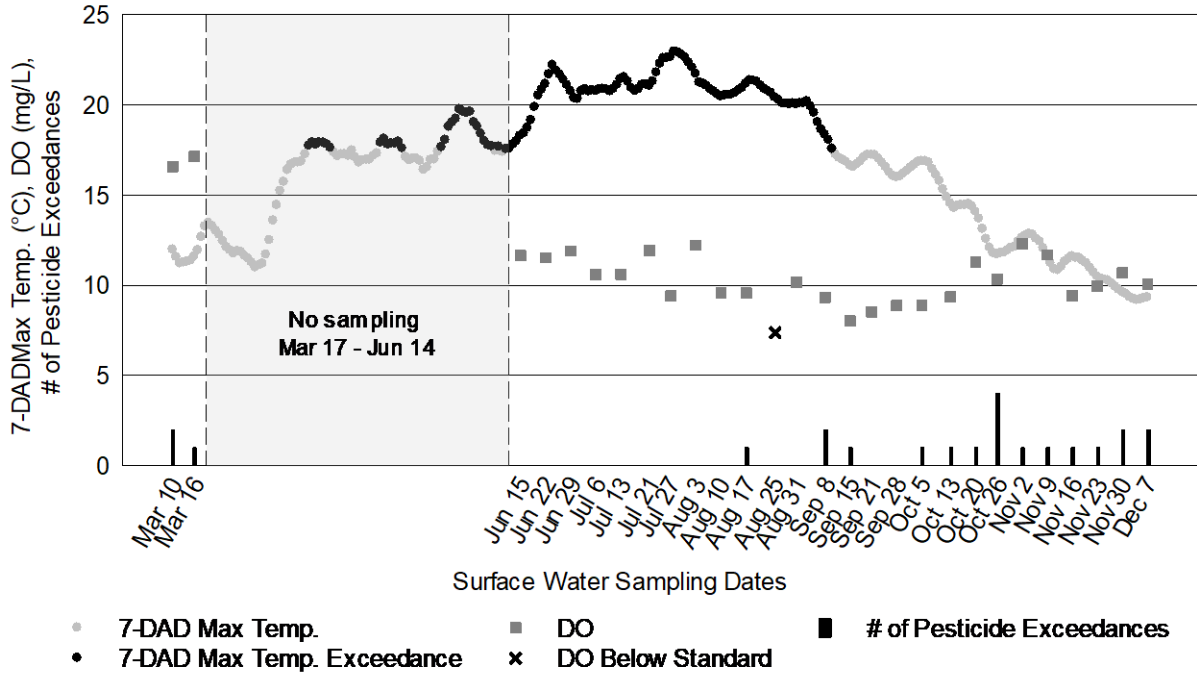


Figure 30 – Marion Drain water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

All DO measurements met the state standard, ranging from 7.37 mg/L to 17.15 mg/L with an average of 10.68 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 122 days of the sampling season, primarily from May 24 through September 10. Pesticide exceedances coincided with 7-DADMax temperature exceedances at on August 17 and September 8.

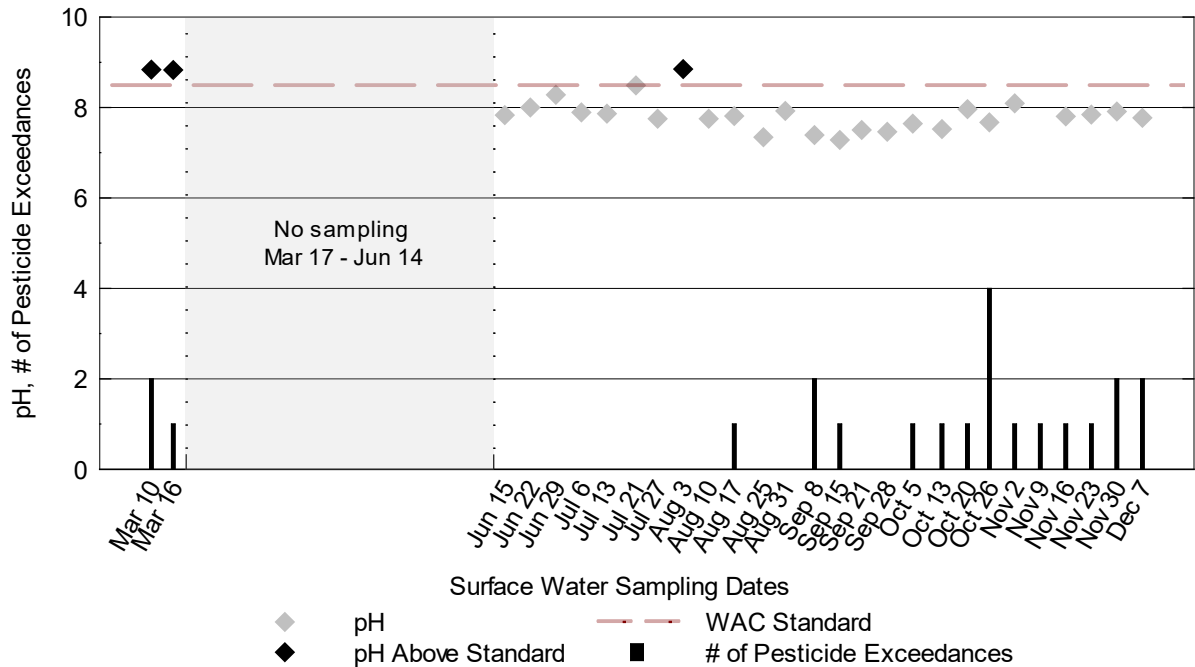


Figure 31 – Marion Drain pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.28 to 8.85 with an average of 7.90. The pH measurement on November 9 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). Less than half (11%) of these measurements exceeded the state standard; three measurements were above 8.50. Out of the three pH exceedances, two coincided with at least one pesticide exceedance on March 10 and March 16.

Marion Drain has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC 2021). Staff at the site frequently observed juvenile fish of an unknown species. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Mission Creek

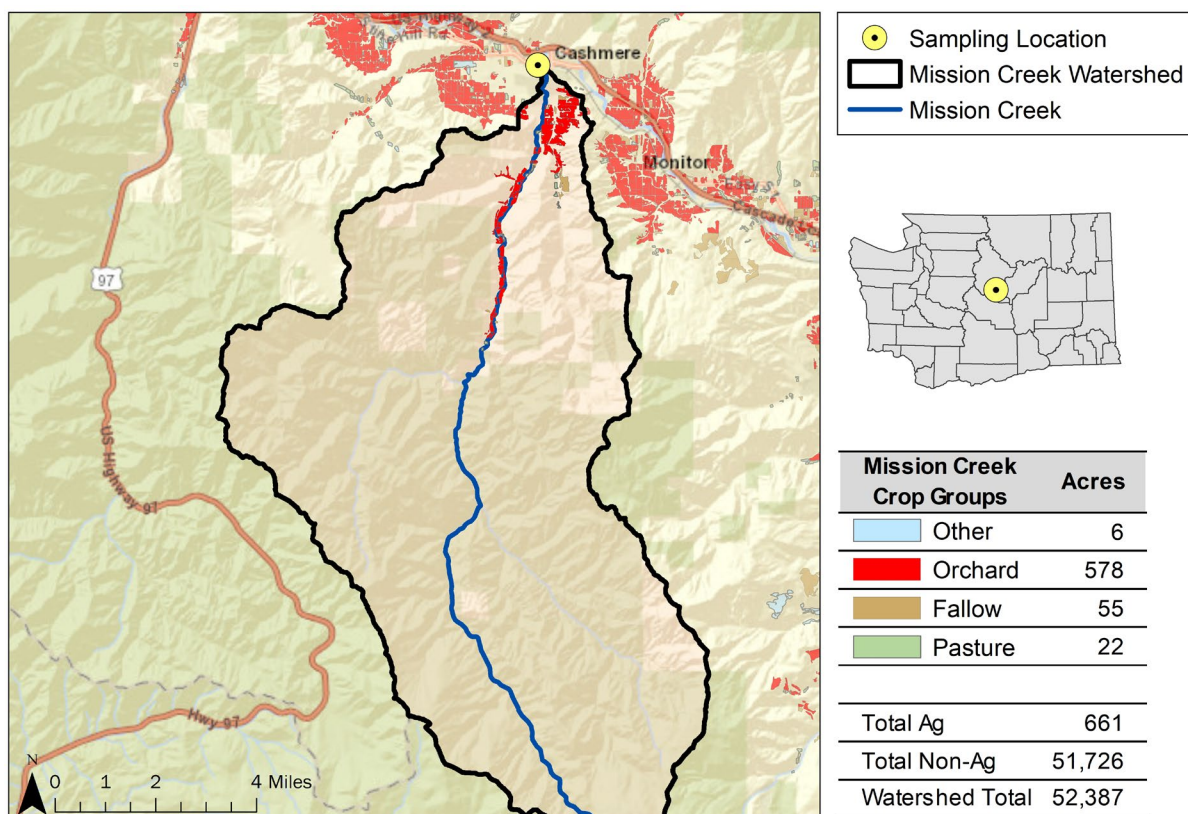


Figure 32 – Map of Mission Creek and its drainage area with associated sampling location and crop groups identified

In 2007, NRAS started monitoring the Mission Creek watershed in Chelan County. The site is located in Cashmere, approximately 10 meters downstream from the bridge crossing of Sunset Highway where the Department of Ecology manages a stream gauging station (latitude: 47.5212°, longitude: -120.4760°) (Figure 32, Figure 33). The watershed that contains the 18.5-mile-long Mission Creek has mountainous terrain. The agricultural land use is predominately tree fruit production of pears, cherries, and apples.

Mission Creek joins Brender Creek approximately 130 meters upstream of its confluence with the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. At the headwaters of Mission Creek, WDFW has documented the presence of spring Chinook and summer spawning of steelhead (WDFW 2021). Staff at the site frequently observed juvenile fish of unknown species.

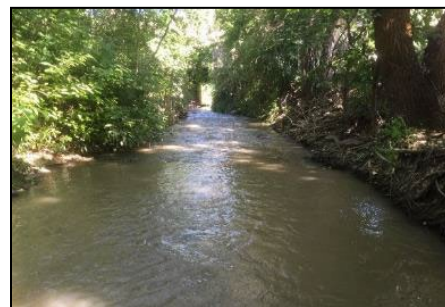


Figure 33 – Mission Creek downstream view

The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 monitoring season and a visual comparison to the WSDA assessment criteria (Figure 32). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. In addition, there were 24 herbicides, 25 insecticides, 14 fungicides, 12 degradates, and a wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 16 – Mission Creek pesticide calendar, µg/L

Month		Mar	Jun			Jul			Aug	Sep	
Day of the Month	Use*	17	16	23	30	7	14	28	11	8	22
2,6-Dichlorobenzamide	D						0.001	0.002	0.003	0.002	0.004
4,4'-DDD	D								0.001	0.002	
4,4'-DDE	D			0.002	0.007	0.003			0.001	0.003	
Boscalid	F			0.001	0.001	0.001		0.002	0.001	0.008	0.007
Chlorpyrifos	I	0.023	0.001	0.001	0.001		0.002	0.002		0.001	0.001
Dichlobenil	H										0.005
Hexazinone	H	0.044	0.007	0.006	0.006	0.004	0.006		0.003	0.004	0.004
Malathion	I	0.040									
N,N-Diethyl-m-toluamide (DEET)	IR				0.017				0.016	0.011	
Norflurazon	H		0.002	0.002	0.002		0.003	0.005	0.006	0.004	0.006
Pendimethalin	H		0.004	0.008	0.008	0.005	0.009	0.004	0.003	0.002	0.003
Prometon	H								0.003		
Total suspended solids (mg/L)		5	11	10	18	13	7	2	2	3	10
Streamflow (cubic ft/sec)		23.0	14.6	10.7	10.4	8.0	5.6	1.8	0.4	0.9	1.2
Precipitation (total in/week)†		0.34	0.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02

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

Current-use exceedance DDT/degradate exceedance Detection

Below is a brief overview of the pesticide findings in Mission Creek in 2020.

- NRAS tested for 90 unique pesticides.
- There were 57 total pesticide detections from five different use categories: five types of herbicides, two insecticides, one fungicide, three degradates, and one insect repellent.
- Pesticides were detected at all 10 sampling events.
- Up to nine pesticides were detected at the same time.
- Of the total pesticide detections, nine were above WSDA's assessment criteria (Table 16).
 - The two detections of 4,4'-DDD and five detections of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the eight chlorpyrifos detections, one exceeded assessment criteria.
 - The detection on March 17 approached the NRWQC and state WAC chronic criteria (both 0.041 µg/L) and the invertebrate NOAEC (0.04 µg/L).
- The malathion detection on March 17 approached the invertebrate NOAEC (0.06 µg/L).
- There were no detections of pyridaben or pyriproxyfen, but the insecticides were still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 4 of the 10 site visits (40%). Water quality at the Mission Creek site is shown below (Figure 34).

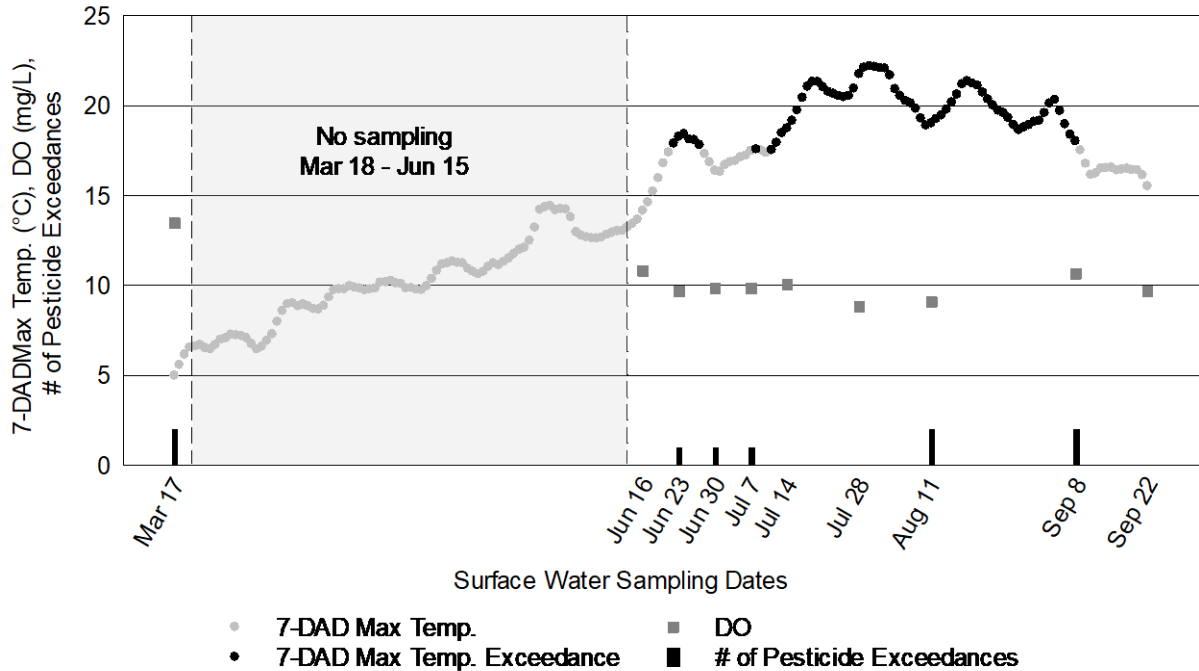


Figure 34 – Mission Creek water quality measurements and exceedances of assessment criteria

The pH measurements ranged from 7.91 to 8.55 with an average of 8.19. On March 17, the pH exceeded the state standard of 8.50 and coincided with two pesticide exceedances. All DO measurements met the state standard, ranging from 8.83 mg/L to 13.46 mg/L with an average of 10.19 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 67 days of the sampling season, primarily from July 8 through September 8. Pesticide exceedances coincided with 7-DADMax temperature exceedances on June 23, July 28, August 11, and September 8.

Mission Creek provides habitat for salmonid spawning, rearing and migration (WAC 2021). Dense riparian vegetation for most of the creek’s length helps prevent pesticide contamination from runoff and application drift. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as chlorpyrifos and malathion.

Snipes Creek

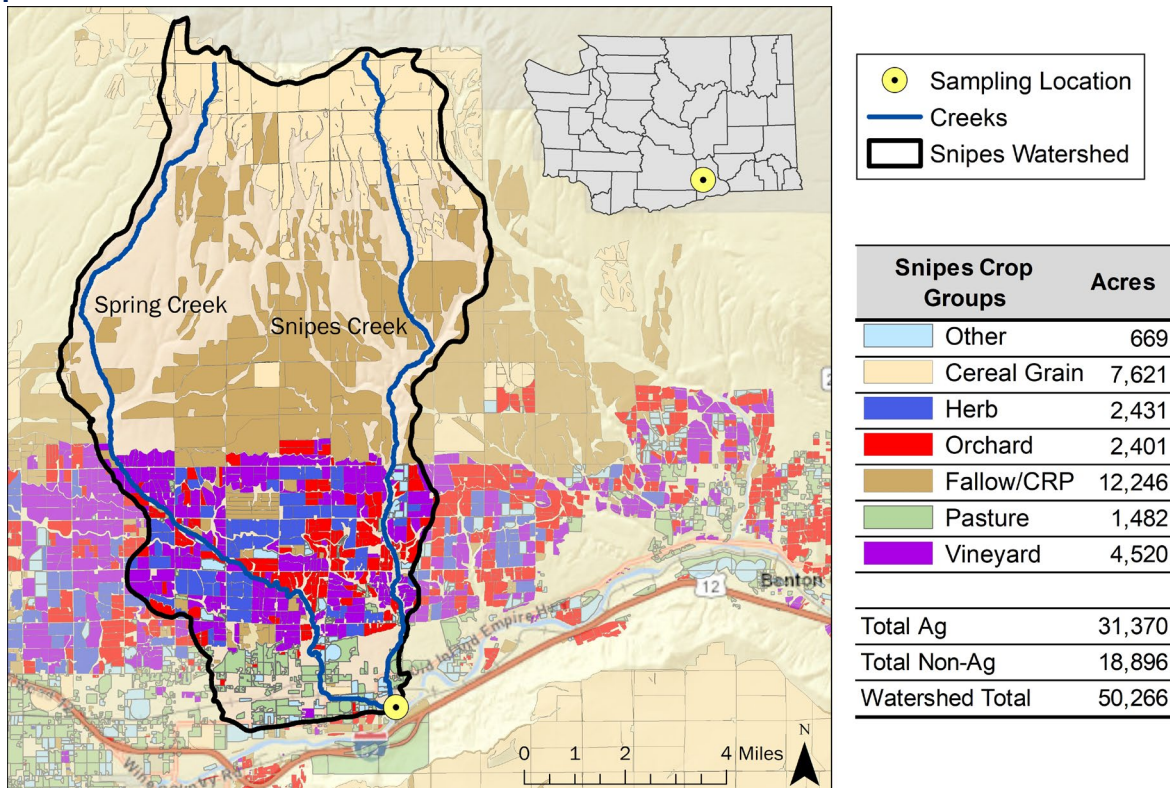


Figure 35 – Map of Snipes Creek and its drainage area with associated sampling location and crop groups identified

In 2016, NRAS started monitoring the Snipes Creek watershed in Benton County. A monitoring site within the Snipes Creek watershed on Spring Creek was sampled from 2003 to 2015. NRAS 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 35, Figure 36).



Figure 36 – 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 summer steelhead within the reach of creek that encompasses the monitoring site (WDFW 2021). In 2021, staff saw fall Chinook salmon actively spawning at the monitoring site.

The watershed has hilly terrain in the upper half that is protected through conservation programs or used for growing cereal grains. The lower half transitions into low-lying, flat terrain where crop diversity increases substantially. The agricultural land use in Snipes Creek watershed is predominantly wheat, wine and juice grapes, hops, and apples. The 'Other' crop group category consists of berries, hay/silage and other assorted small acreage crops (Figure 35).

Below is a brief overview of pesticide findings in Snipes Creek in 2020.

- NRAS tested for 166 unique pesticides in Snipes Creek.
- There were 380 total pesticide detections from five different use categories: 19 types of herbicides, 13 insecticides, 6 fungicides, 8 degradates, and 1 insect repellent.
- Pesticides were detected at all 24 sampling events.
- Up to 30 pesticides were detected at the same time.
- Of the total pesticide detections, 15 were above WSDA's assessment criteria (Table 17).
 - The four detections of 4,4'-DDD and two detections of 4,4'-DDE approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- There were 10 detections of imidacloprid; eight of which approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.01 µg/L).
- The two detections of chlorpyrifos and two detections of malathion did not exceed any assessment criteria in 2020, but these pesticides were still considered watershed POCs because of detections that did exceed criteria in recent years at the site.

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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.

Table 17 – Snipes Creek pesticide calendar, µg/L

Month	Use*	Mar		Jun			Jul				Aug					Sep				Oct				Nov		
		10	16	15	22	29	6	13	21	27	3	10	17	25	31	8	15	21	28	5	13	20	26	2	9	
1-(3,4-Dichlorophenyl)-3-methylurea	D			0.004		0.005								0.003	0.052											
2,4-D	H	0.032	0.028	-	0.037	0.053		0.047	0.036	0.031	0.035	0.063		0.016	0.045	0.379	0.045	0.043	0.168	0.034	0.039					
2,6-Dichlorobenzamide	D		0.010	0.003	0.004	0.004	0.008	0.006	0.008	0.007	0.006	0.013	0.018	0.009	0.007	0.006	0.007	0.007	0.010	0.008	0.009	0.022	0.023	0.032		
4,4'-DDD	D	0.001				0.001									0.001							0.001				
4,4'-DDE	D					0.001									0.002											
Acetamiprid	I														0.003											
Atrazine	H	0.008	0.007	0.002		0.005		0.004	0.003	0.004	0.004	0.005	0.003	0.003	0.006	0.003	0.003	0.004	0.004	0.003	0.003	0.008	0.009	0.010		
Boscalid	F	0.017	X	0.008	0.006	0.006	0.006	0.005	X		0.006	0.005	0.010	0.005	0.026	0.005	0.006	0.004	0.005	0.005	0.005	0.005	0.004	0.004		
Bromacil	H	0.008													0.070		0.003			0.004				0.005		
Carbaryl	I														0.003											
Carbendazim	F									0.003	0.002	0.015			0.003	0.002	0.003			0.004	0.004					
Chlorantraniliprole	I							0.021	0.013						0.015			0.012	0.011				0.013	0.018		
Chlorpyrifos	I	0.004	0.002																							
Clopyralid	H																0.080	0.149								
Clothianidin	I																					0.004	0.004	0.004		
Diazinon	I					0.002	0.003			0.002			0.003							0.002						
Dicamba acid	H					0.010	0.009	0.015							0.011			0.082								
Dichlobenil	H	0.002											X													
Dimethoate	I			0.004	0.004																					
Diuron	H		0.005	0.013	0.009	0.006	0.004				0.006	0.005		0.006	0.152	0.004	0.004	0.006		0.007	0.004					
Eptam	H	0.001		0.002	0.002		0.002			0.003								0.003	0.001	0.002	0.001			0.005		
Etiozazole	I					0.007																				
Fludioxonil	F	0.008		0.012	0.017	0.015	0.016	0.013	0.008	0.011	0.012	0.015	0.013	0.008	0.005	0.008	0.006	0.009	0.008	0.008	0.015	0.009				
Hexazinone	H	0.013								0.002	0.002				0.004			0.004			0.002	0.002	0.002	0.002		
Imazapyr	H														0.009			0.004				0.004				
Imidacloprid	I			0.021	0.007	0.010		0.008	0.009		0.005	<0.005	0.008		0.009					0.005						
Malathion	I				0.004	0.010																				
Methoxyfenozide	H	0.003	0.003												0.002			0.002				0.004	0.004	0.006		
Metolachlor	I					0.001			X		0.002				0.003	0.001										
Myclobutanil	F												0.005		0.005											
N,N-Diethyl-m-toluamide (DEET)	IR									0.011				0.010	0.012	0.009	0.007									
Norflurazon	H	0.007	0.004	0.002	0.003	0.003	0.003	0.004	0.005	0.003	0.004	0.004	0.005	0.003	0.003	0.012	0.003	0.003	0.003	0.004	0.004	0.004	0.009	0.009	0.010	
Pendimethalin	H	0.005		0.002	0.002		0.005	0.004	0.003	0.003	0.003	0.003	0.002	0.002	0.003	0.020	0.003	0.003	0.003	0.002	0.003	0.003	0.002	0.003		
Prometon	H																	0.002								
Propiconazole	F					0.004																				
Pyrimethanil	F			0.005	0.006	0.007	0.008	0.004		0.005		0.005	0.005	0.009	0.006	0.008	0.017	0.014	0.023	0.018	0.018	0.025	0.004	0.002		
Pyriproxyfen	I					0.002																				
Simazine	H														0.009								0.004	0.004	0.005	
Sulfentrazone	H	0.020						0.003		0.003		0.004	0.003		0.004	0.004		0.005	0.004	0.004	0.003	0.009	0.008	0.009		
Terbacil	H	0.016	0.004				0.015	0.003	0.004	0.005	0.004	0.004		0.012	0.030	0.029	0.031	0.041	0.014	0.021	0.011					
Tetrahydrophthalimide (THPI)	D			0.002	0.002																	0.002				
Thiamethoxam	I					0.002				0.005	0.005	0.007	0.005					0.023	0.006	0.004		0.009	0.007	0.007		
Triazine DEA degradate	D	0.011	0.010	0.003	0.002	0.003	0.002	0.003			0.003	0.004	0.003	0.003	0.003	0.003	0.002	0.003	0.004	0.004	0.003	0.004	0.013	0.014	0.018	
Triazine DIA degradate	D														0.005								0.003			
Triazine HA Degradate	D			0.001	0.001	0.001	0.002	0.001	0.002	0.001		0.001	0.002	0.002	0.002	0.006		0.002	0.003	0.002	0.001	0.002	0.001	0.001		
Triclopyr acid	H																	0.042								
Trifluralin	H	0.005																								
Total suspended solids (mg/L)		8	10	18	15	23	13	17	11	17	22	10	5	11	15	59	20	18	11	18	8	20	6	3	2	
Streamflow (cubic ft/sec)		4.2	4.5	69.2	74.3	54.0	62.0	82.4	30.2	83.3	-	42.2	13.2	60.4	81.0	-	-	85.4	70.6	45.8	69.6	76.2	9.7	7.0	5.3	
Precipitation (total in/week)†		0.22	0.05	0.18	0.08	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.39	0.00	0.00	0.00	0.30		

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

Current-use exceedance DDT/degradate exceedance Detection No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

† Washington State University AgWeatherNet station: Prosser.NE, (latitude: 46.25°, longitude: -119.74°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 10 of the 24 site visits (42%). Water quality at the Snipes Creek site is shown below (Figure 37 and Figure 38).

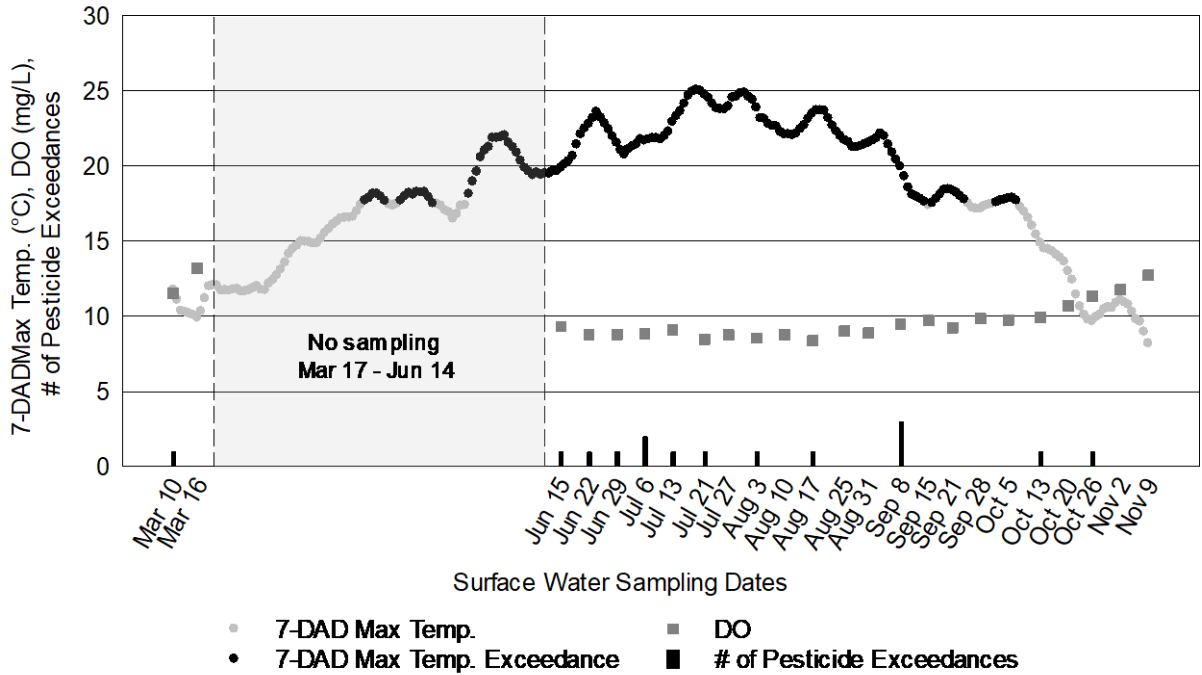


Figure 37 – Snipes Creek water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

All DO measurements met state water quality standards, ranging from 8.38 mg/L to 13.19 mg/L with an average of 9.79 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 145 days of the sampling season, primarily from May 23 through September 24. Pesticide exceedances coincided with 7-DADMax temperature exceedances at nine site visits.

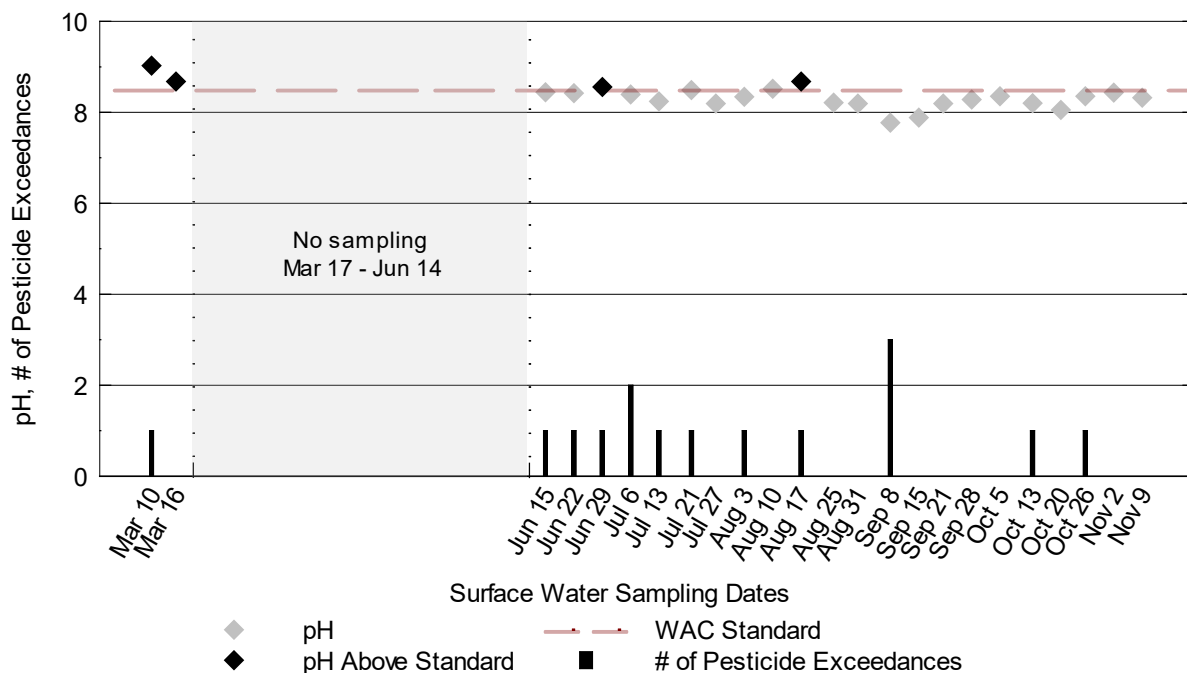


Figure 38 – Snipes Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.77 to 9.03 with an average of 8.34. The pH measurement on November 9 was excluded because the field meter that measures pH failed the post-check (described in the Field Data Quality Control Measures section). The pH measurement of 8.52 on August 10 was not considered an exceedance of the state standard due to being within the measurements uncertainty range. Roughly 17% (4) of the pH measurements exceeded the state standard. Three of the four pH exceedances coincided with one pesticide exceedance (Figure 38). Pesticide exceedances overlapped with both pH and 7-DADMax temperature exceedances on June 29 and August 17.

Snipes Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC 2021). 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. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

Stemilt Creek

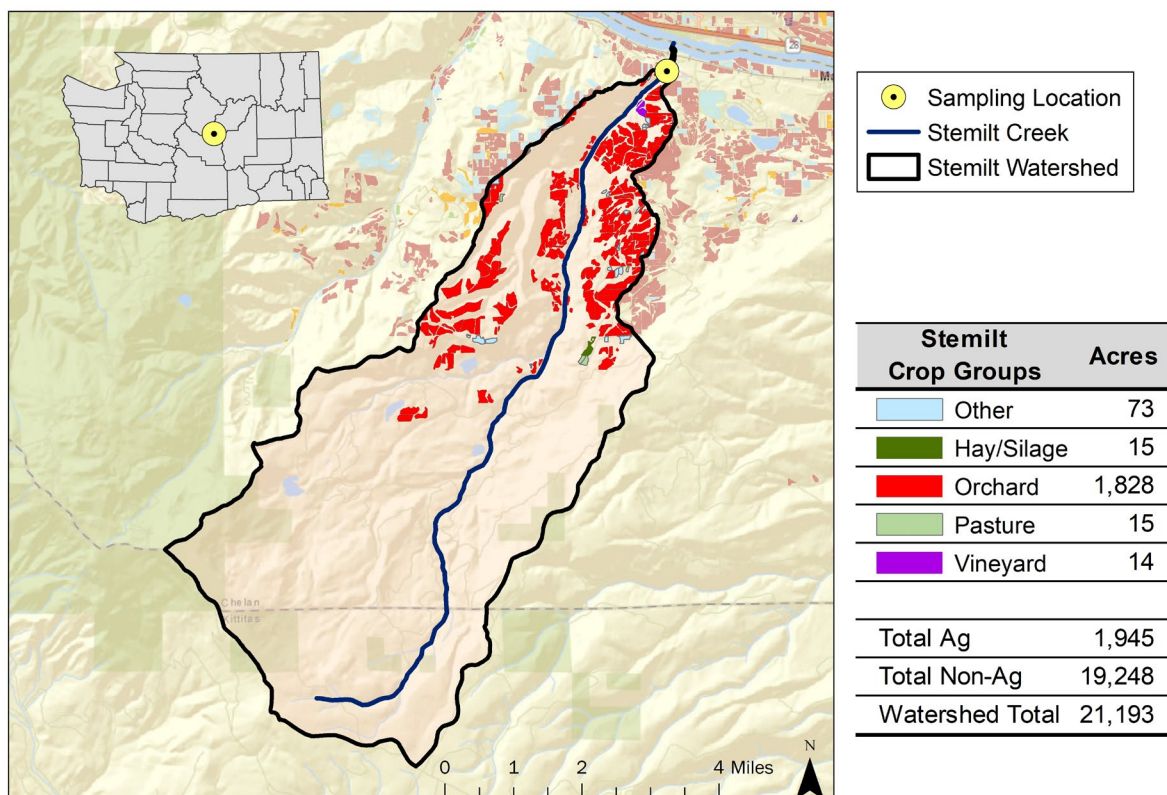


Figure 39 – Map of Stemilt Creek and its drainage area with associated sampling location and crop groups identified

In 2013, NRAS started monitoring 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 39, Figure 40). Stemilt Creek water drains directly into the Columbia River. Melting snowpack, precipitation events, and irrigation generally influenced streamflow in the creek. Within the reach of the creek that encompasses the monitoring site, WDFW has documented spring Chinook salmon and summer steelhead (WDFW 2021). In 2019, a WDFW fish biologist identified a salmonid fry as a Chinook salmon at the monitoring site. WDFW also noted that the inlet of Stemilt Creek provides rearing habitat for salmon.

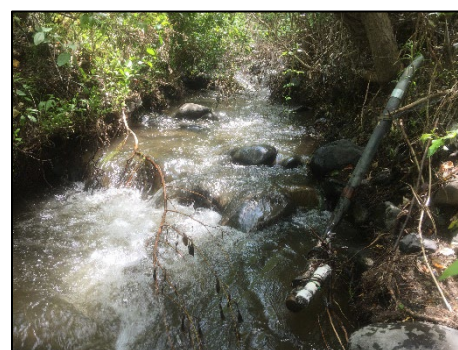


Figure 40 – Stemilt Creek upstream view

The watershed that contains the 12-mile-long Stemilt Creek has mountainous terrain. We selected the watershed to be representative of agricultural practices used in tree fruit cultivation in Central Washington. The agricultural land use is predominately tree fruit production of cherries, apples, and pears. The 'Other' crop group category consists of fallow fields and nursery acreage (Figure 39).

The Stemilt Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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. In addition, there were 24 herbicides, 25 insecticides,

14 fungicides, 12 degradates, 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	Jun			Jul			
Day of the Month	Use*	17	16	23	30	7	14	22	28
2,6-Dichlorobenzamide	D	0.015	0.011	0.029	0.023	0.021	0.051	0.035	0.070
Boscalid	F			0.008	0.007	0.007	0.009	0.009	0.012
Chlorpyrifos	I	0.003					0.001		
Diazinon	I		0.003						
Ethoprop	I							0.001	
Fenarimol	F							0.006	
Fipronil Sulfide	D							0.001	
Hexazinone	H			0.001				0.003	
Malathion	I		0.003	0.014	0.020	0.015	0.016	0.009	0.004
Metolachlor	H							0.001	
Norflurazon	H							0.002	
Prometon	H							0.003	
Pyridaben	I							0.002	
Simazine	H				0.066	0.021	0.014	0.006	0.008
Sulfentrazone	H		0.006	0.009	0.010	0.006	0.005	0.004	0.008
Triadimefon	F							0.002	
Total suspended solids (mg/L)		2	18	6	4	3	3	2	3
Streamflow (cubic ft/sec)		3.1	3.9	0.1	0.3	0.1	0.2	0.1	0.1
Precipitation (total in/week)†		0.37	0.16	0.00	0.07	0.00	0.00	0.00	0.00

 Detection

Below is a brief overview of pesticide findings in Stemilt Creek in 2020.

- NRAS tested for 90 unique pesticides in Stemilt Creek.
- There were 46 total pesticide detections from four different use categories: six types of herbicides, five insecticides, three fungicides, and two degradates.
- Pesticides were detected at all eight sampling events.
- Up to 14 pesticides were detected at the same time.
- Of the total pesticide detections, none were above WSDA's assessment criteria (Table 18).

The Stemilt Creek watershed-specific POCs were chlorpyrifos and malathion. The two detections of chlorpyrifos and seven detections of malathion did not exceed any assessment criteria in 2020, but these insecticides were still considered watershed POCs because of detections that did exceed criteria in recent years at this site.

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

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

Water quality at the Stemilt Creek site is shown below (Figure 41).

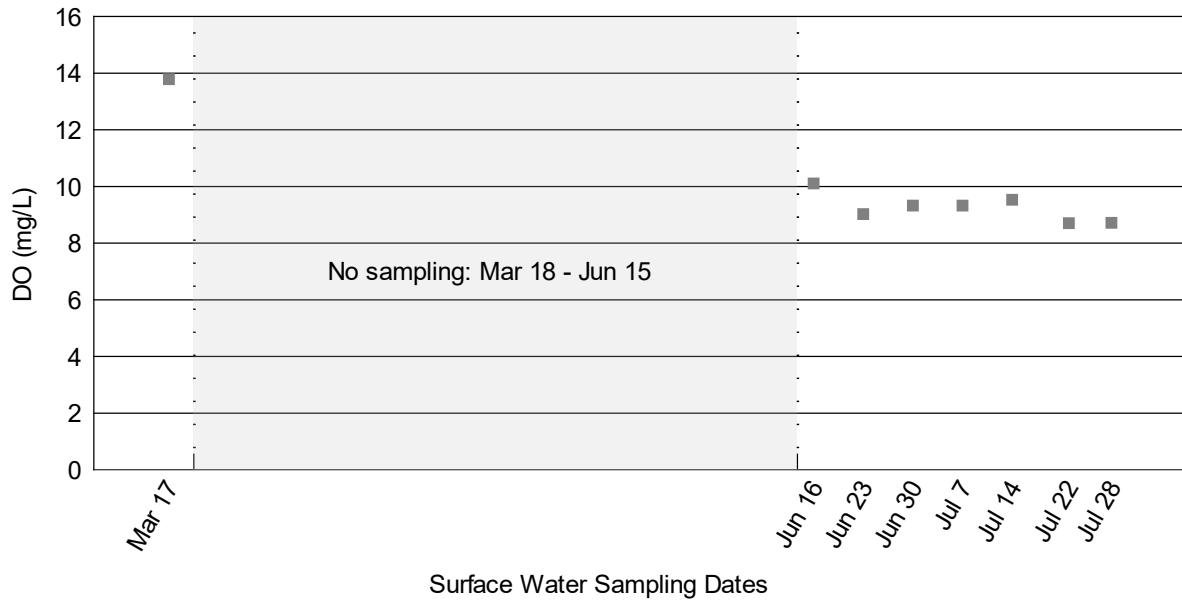


Figure 41 – Stemilt Creek dissolved oxygen measurements

All pH measurements met the state standard, ranging from 8.14 to 8.36 with an average of 8.24. All DO measurements also met the state standard, ranging from 8.71 mg/L to 13.79 mg/L with an average of 9.82 mg/L.

Extremely high streamflow in the spring dislodged and carried the temperature data logger away in 2019. Staff decided to not reinstall the data logger in 2020. Therefore, stream temperatures were not measured and 7-DADMax temperatures were not calculated.

Stemilt Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing and migration by the WAC (WAC 2021). Staff observed fish believed to be juvenile salmonids frequently during site visits. NRAS 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

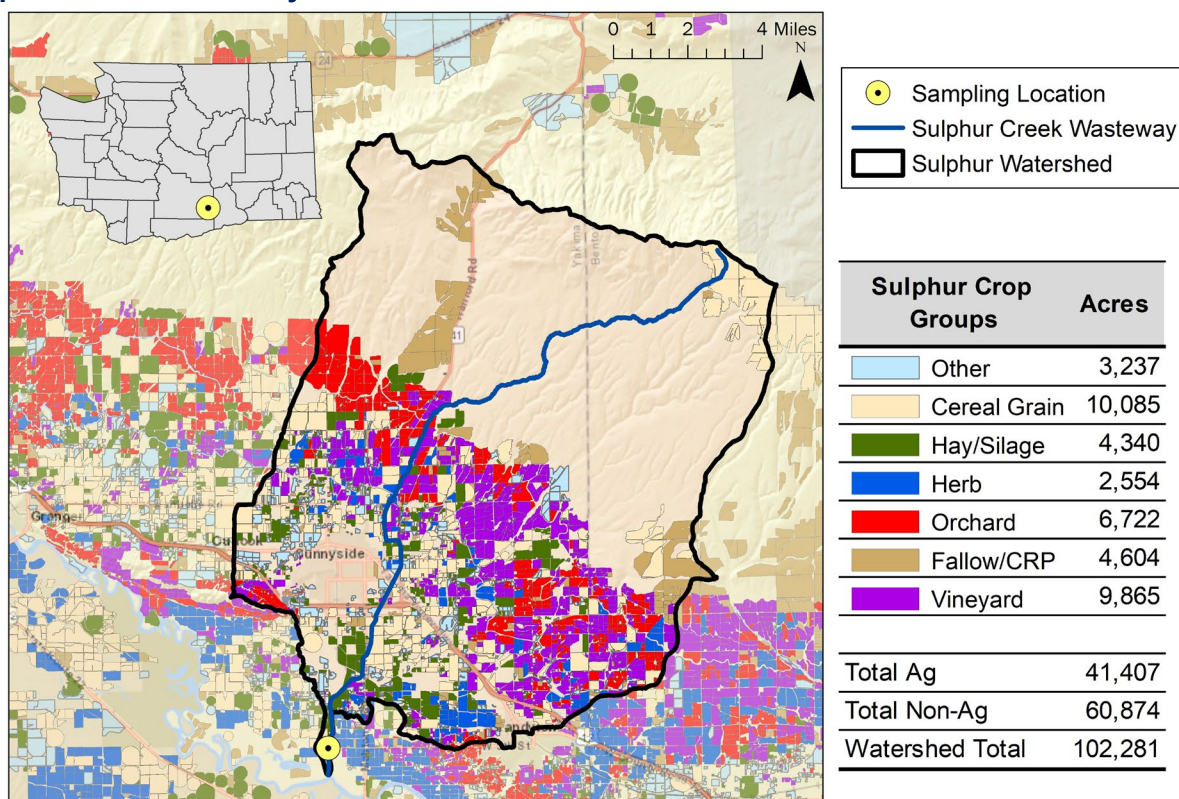


Figure 42 – Map of Sulphur Creek Wasteway and its drainage area with associated sampling location and crop groups identified

In 2003, NRAS started monitoring 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 42, Figure 43).

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 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 2021). 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.



Figure 43 – Sulphur Creek Wasteway downstream view

The watershed that contains the 23-mile-long Sulphur Creek Wasteway has flat, low-lying terrain. The agricultural land use is predominately field corn, juice grapes, apples, wine grapes, and alfalfa hay. The 'Other' crop group category consists of vegetables, turf grass, nurseries and other assorted small acreage crops (Figure 42).

Below is a brief overview of pesticide findings in Sulphur Creek Wasteway in 2020.

- NRAS tested for 166 unique pesticides in Sulphur Creek Wasteway.
- There were 474 total pesticide detections from six different use categories: 25 types of herbicides, 11 insecticides, 8 degradates, 7 fungicides, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 20 sampling events.
- Up to 31 pesticides were detected at the same time.
- Of the total pesticide detections, 14 were above WSDA's assessment criteria (Table 19).
 - The five detections of 4,4'-DDD and seven detections of 4,4'-DDE approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the two detections of imidacloprid, one detection approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.01 µg/L).
- The six detections of chlorpyrifos did not exceed any assessment criteria in 2020, but this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years at the site.

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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.

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 8 of the 20 site visits (40%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 44 and Figure 45).

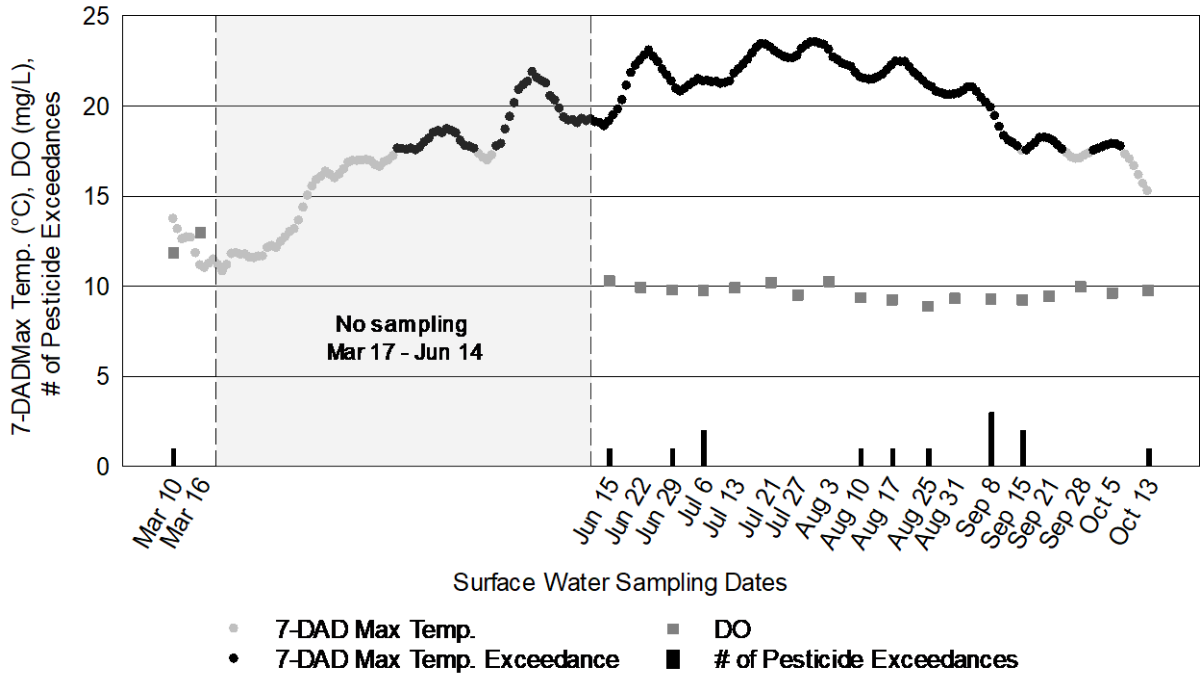


Figure 44 – Sulphur Creek Wasteway water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

All DO measurements met the state standard, ranging from 8.89 mg/L to 12.96 mg/L with an average of 9.93 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 151 days of the sampling season, primarily from April 29 through October 7. Pesticide exceedances coincided with 7-DADMax temperature exceedances at eight site visits.

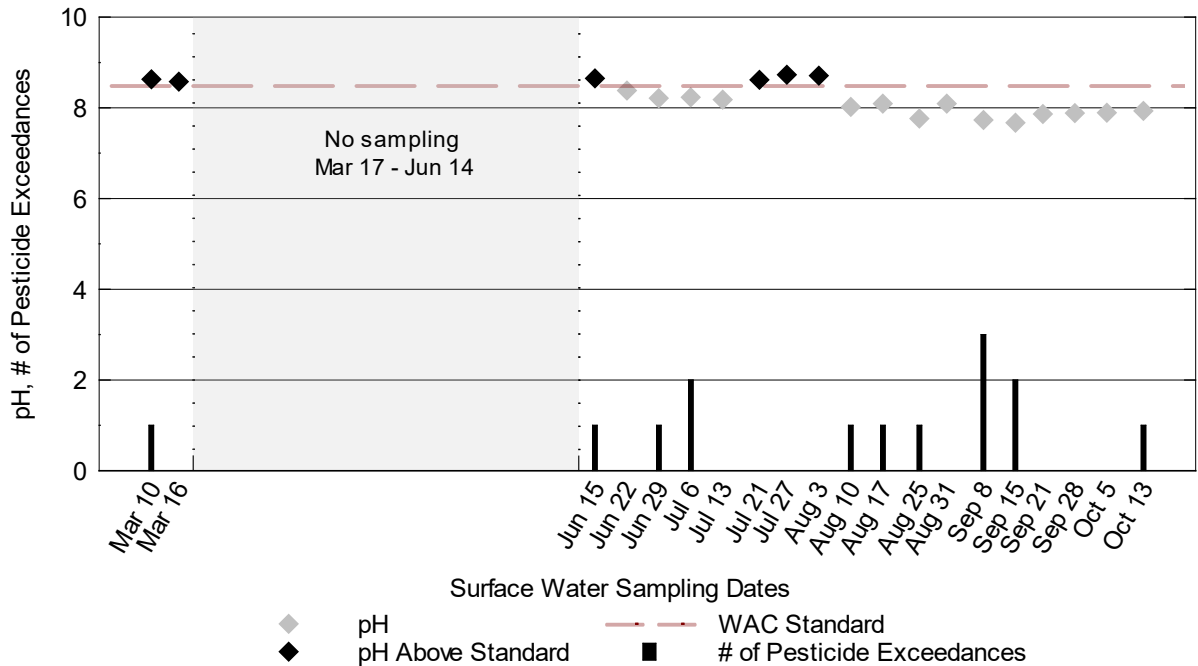


Figure 45 – Sulphur Creek Wasteway pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.67 to 8.73 with an average of 8.19. Less than half (30%) of these measurements exceeded the state standard; six measurements were greater than 8.50. The pH exceedances on March 10 coincided with one pesticide exceedance. On June 15, a pesticide exceedance overlapped with both a pH exceedance and a 7-DADMax temperature exceedance.

Sulphur Creek Wasteway provides habitat for salmonid rearing and migration (WAC 2021). 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. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, occurrences of watershed POCs.

Touchet River

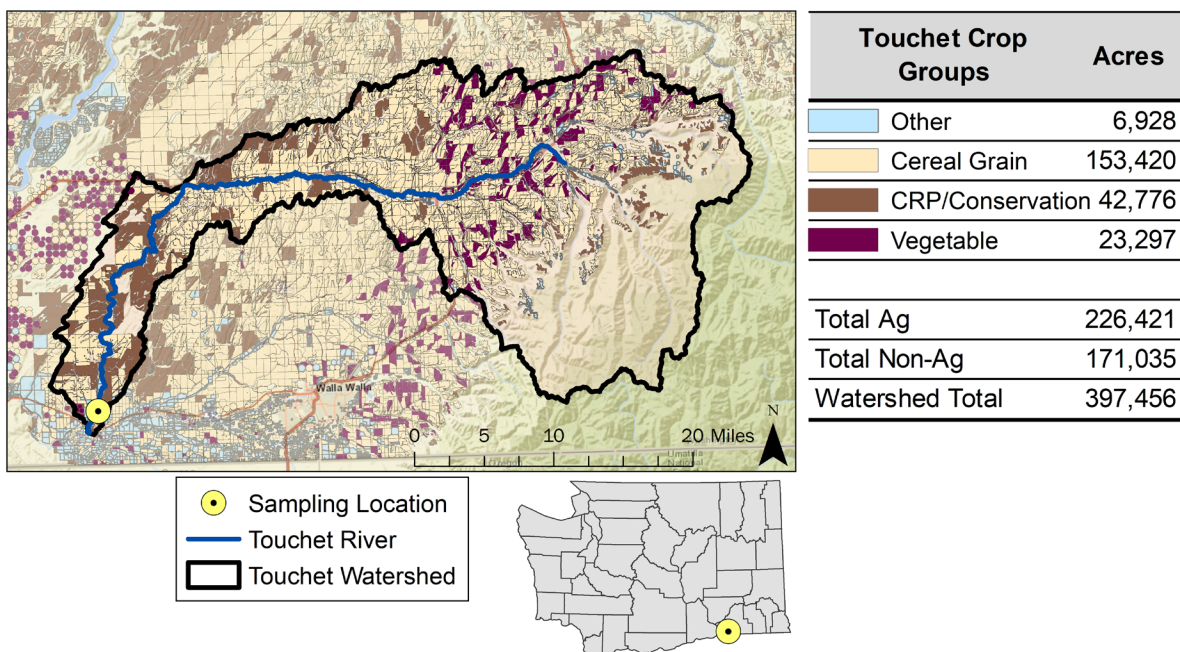


Figure 46 – Map of Touchet River and its drainage area with associated sampling location and crop groups identified

In 2018, NRAS started monitoring the Touchet River watershed in Walla Walla County. Staff selected the watershed to represent typical Eastern Washington dryland agricultural practices and to expand the monitoring further east where our 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 46, Figure 47).



Figure 47 - 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 the presence of spring Chinook salmon and summer steelhead throughout the main stem of Touchet River (WDFW 2021).

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 pasture, grass hay, oilseed, seed crops, nurseries and other assorted small acreage crops (Figure 46).

The Touchet River monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 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	Use*	Mar	Jun			Jul				Aug				Sep		Oct	
		10	15	22	29	6	13	21	27	3	10	17	31	8	21	5	20
2,4-D	H													0.032			
2,6-Dichlorobenzamide	D											0.002	0.002	0.002			
Boscalid	F			0.001	0.002	0.001			0.004		0.001	0.001		0.002	0.002		0.002
Bromacil	H	0.006	0.003	0.002		0.003	0.005		0.004		0.003						0.004
Carbendazim	F																0.005
Chlorpropham	H																0.001
Chlorpyrifos	I	0.003															0.001
Dichlorvos (DDVP)	I					0.001	0.006										
Eptam	H		0.001														0.001
Fludioxonil	F	0.005															
Hexazinone	H	0.014									0.002			0.004	0.004		0.002
Imazapyr	H							0.164	1.040	0.400	0.234	0.335	0.072	0.131	0.284	0.459	0.086
Imidacloprid	I																0.008
Methamidophos	D							0.002	0.003								
Metolachlor	H		0.001		0.001						0.002			0.002	0.001		
Pendimethalin	H	0.005			0.003									0.004			
Prometon	H									0.002				0.002			
Propiconazole	F								0.004								
Sulfentrazone	H	0.018															
Tebuthiuron	H										0.004						
Triazine HA Degradate	D				0.001					0.001	0.001		0.001	0.001			
Nitrite-Nitrate (mg/L)								0.017									
Ortho Phosphate (mg/L)								0.075		0.077							
Total Phosphorus (mg/L)								0.094		0.091							
Total suspended solids (mg/L)	41		7	6	18	2	2	2		1	1	1	2				
Streamflow (cubic ft/sec)	334		125	80	62	51	33	25	18	13	10	4	5	5	25	25	43
Precipitation (total in/week)†	0.00		0.30	0.09	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02

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

 Current-use exceedance  Detection

Below is a brief overview of pesticide findings in Touchet River in 2020.

- NRAS tested for 166 unique pesticides in Touchet River.
- There were 64 total pesticide detections from four different use categories: 11 types of herbicides, 3 insecticides, 4 fungicides, and 3 degradates.
- Pesticides were detected at all 16 sampling events.
- Up to nine pesticides were detected at the same time.
- Of the total pesticide detections, two were above WSDA’s assessment criteria (Table 20).
 - Of the two dichlorvos detections, one detection exceeded the invertebrate NOAEC (0.0058 µg/L).
 - The single imidacloprid detection approached the invertebrate NOAEC (0.01 µg/L).
- There were no watershed-specific POCs for the Touchet site.

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

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 2 of the 16 site visits (13%). Water quality measurements at the Touchet River site are shown below (Figure 48).

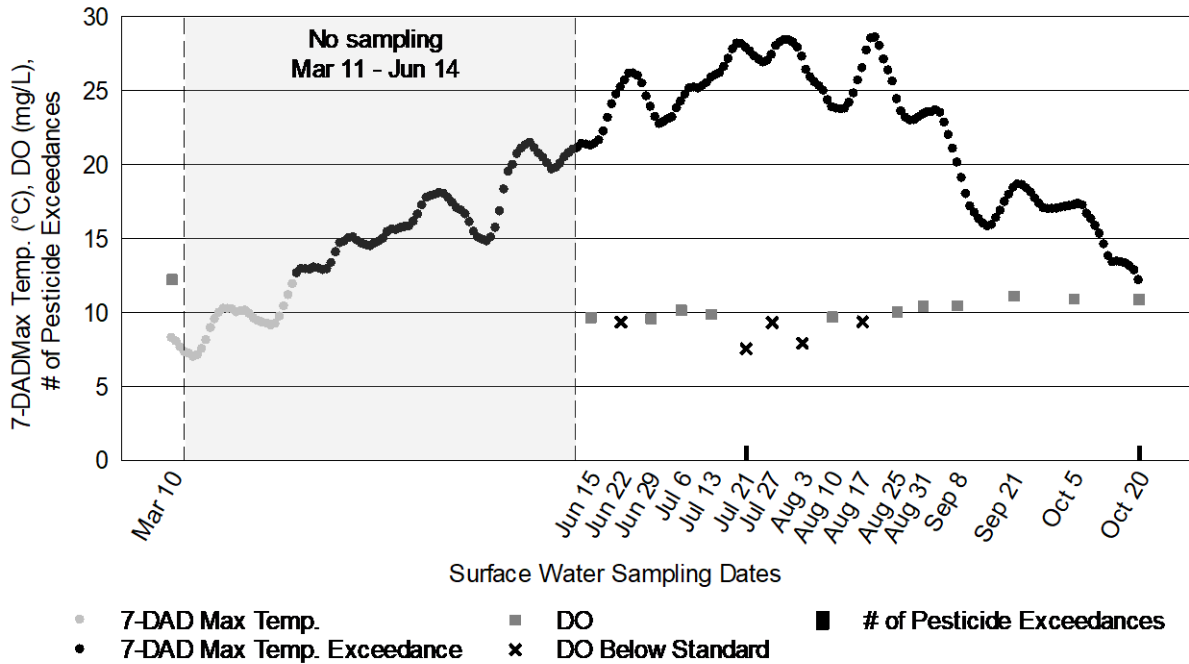


Figure 48 – Touchet River water quality measurements and exceedances of assessment criteria

The pH measurements ranged from 7.75 to 8.67 with an average of 8.26. Roughly 13% of these measurements exceeded the state water quality standard; two measurements were above 8.50. DO measurements ranged from 7.55 mg/L to 12.23 mg/L with an average of 9.91 mg/L. Less than half (31%) of these measurements did not meet the state standard; five measurements were less than 9.5 mg/L. The 7-DADMax temperatures exceeded the 12°C standard on 196 days of the sampling season, from April 8 through October 20. On July 21, a pesticide exceedance occurred with both a 7-DADMax temperature exceedance and a pH measurement exceeding the state standard. On October 5, a pesticide exceedance coincided with a 7-DADMax temperature exceedance.

The Touchet River has been designated as a freshwater body that provides habitat for char spawning and rearing by the WAC (WAC 2021). Staff observed juvenile fish of unknown species at the monitoring site. NRAS will continue to monitor this drainage because of its representative regional land use.

Palouse Region

Dry Creek

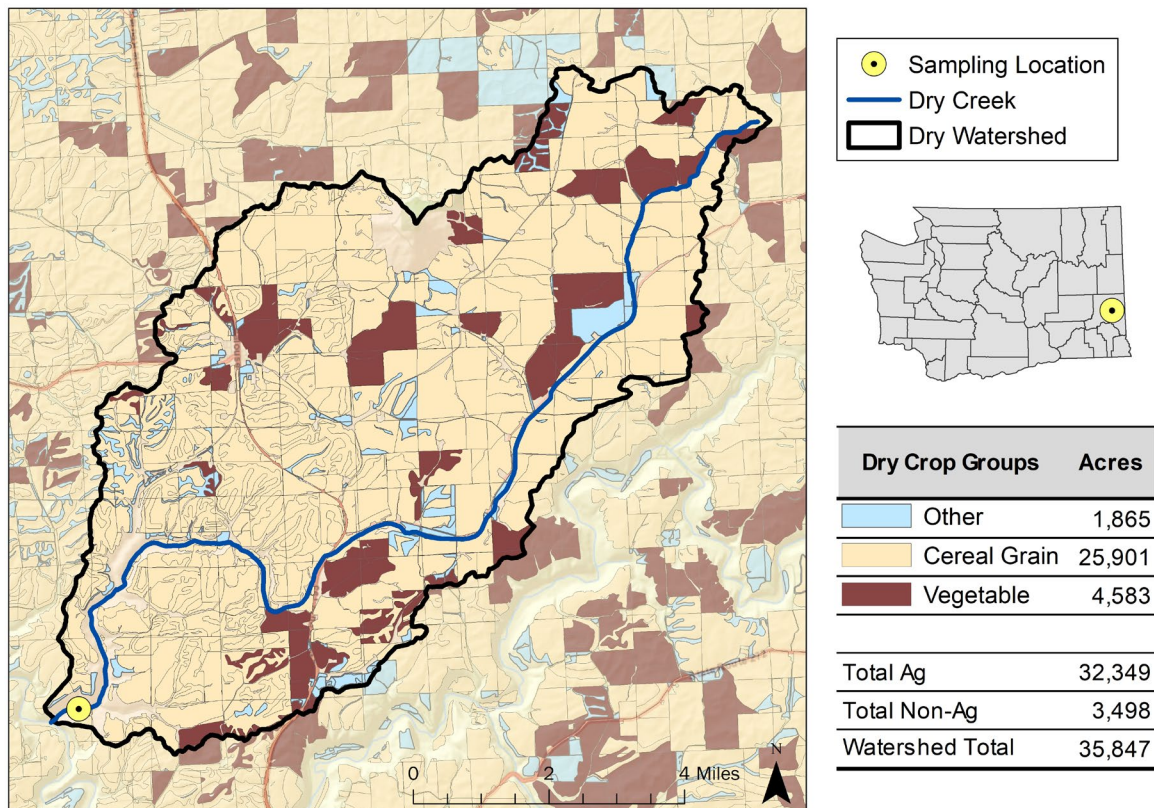


Figure 49 – Map of Dry Creek and its drainage area with associated sampling location and crop groups identified

In an effort to expand sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Dry Creek, in Whitman County, during the 2020 sampling season. The watershed was chosen as a study region due to its dryland farming practices and its location within the state. The monitoring site is located at the bridge on Manning Road near Colfax, Washington (latitude: 46.9318°, longitude: -117.4081°) (Figure 49, Figure 50).



Figure 50 – Dry Creek upstream view

Dry Creek is approximately 18 miles long and drains into the Palouse River. Melting snowpack and precipitation events generally influence streamflow in the creek. The Palouse River is a channel within the larger Columbia River Watershed which is a focus of many water quality and water quantity improvement projects. The Palouse Falls prevents salmon from migrating further into the Palouse River Watershed and in extension, Dry Creek, but the creek provides habitat for fish like rainbow trout, smallmouth bass, and pike minnows.

The watershed has low-lying, flat terrain. A majority of the creek is ditched and straightened in between agricultural fields. The agricultural land use is predominately wheat, barley, and legumes. The 'Other' crop group category consists of tilled and idle fallow fields, oilseed, and other assorted small acreage

crops (Figure 49). A wildfire in September burned part of the watershed upstream of the monitoring site although no effects were observed in the monitoring results due to that event.

NRAS tested for three additional analytes at this site in 2020 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were glyphosate, AMPA (a glyphosate breakdown product), and glufosinate-ammonium. Glyphosate is relied upon heavily in the cropping systems of the Palouse region. We do not test for it at each monitoring site due to the cost of lab analysis and the ubiquitous detections in Washington surface waters below WSDA assessment criteria. The results of the three chemicals were included in the Statewide Results section of this report that summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Dry Creek in 2020.

- NRAS tested for 169 unique pesticides in Dry Creek.
- There were 324 total pesticide detections from five different use categories: 26 types of herbicides, 5 insecticides, 5 fungicides, 6 degradates, and 1 insect repellent.
- Pesticides were detected at all 17 sampling events.
- Up to 30 pesticides were detected at the same time.
- All three chemicals tested for in the herbicide special study were detected. Glyphosate had a 100% detection frequency. However, none of the detections of the three chemicals were above WSDA assessment criteria.
- Of the total pesticide detections, 11 were above WSDA's assessment criteria (Table 21).
 - The single detection of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - Of the five dimethoate detections, one detection approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.5 µg/L).
 - Of the nine linuron detections, one detection approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.09 µg/L).

The Dry Creek watershed POC was imidacloprid. Below, the POC detections are compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Of the six imidacloprid detections, five detections approached the invertebrate NOAEC and one detection exceeded the invertebrate NOAEC (0.01 µg/L).

The Dry Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2020 monitoring season and a visual comparison to the WSDA assessment criteria (Table 21). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 21 – Dry Creek pesticide calendar, µg/L

Month		Mar	Jun			Jul				Aug				Sep		Oct		
Day of the Month	Use*	16	15	22	29	6	13	21	27	3	10	17	25	31	14	28	12	27
1-(3,4-Dichlorophenyl)-3-methylurea	D		0.004	0.003	0.006	0.006												
2,4-D	H		0.586	0.027	0.029	1.350	0.021	0.038	0.030	0.020		0.019		0.025	0.047	0.069	1.260	0.085
2,6-Dichlorobenzamide	D														0.001			
4,4'-DDE	D					0.001												
Aminomethylphosphoric acid (AMPA)	D									0.549	0.386	0.321	0.478	0.382	0.541	X	0.644	0.423
Atrazine	H		0.004	0.005	0.002	0.006		0.002										
Azoxystrobin	F		0.058	0.017	0.040	0.072	0.043	0.020	0.014	0.009	0.007	0.005	0.004	0.004	0.005	0.003	0.004	0.007
Boscalid	F			0.001	0.001				X		0.001							
Bromacil	H																	0.003
Bromoxynil	H		0.200	0.021		0.041												
Carbendazim	F		0.006	0.006	0.007	0.005				0.006	0.005	0.004	0.004	0.003	0.003	0.002	0.005	
Chlorpyrifos	I		0.003	0.001		0.005	0.002											
Chlorsulfuron	H					0.015												
Clopyralid	H		0.108														0.169	0.083
Clothianidin	I		0.006	0.003	0.004	0.004	0.005	0.004	0.003									0.003
Dicamba acid	H		0.658	0.135	0.024	0.588	0.011	0.094	0.110	0.087	0.121	0.061	0.102	0.038	0.082	0.098	1.040	0.089
Dimethoate	I		0.006		0.480	0.595	0.045											0.020
Diuron	H		0.005															
Glufosinate-ammonium	H									0.009	0.015	0.007			0.027	X	0.019	
Glyphosate	H	0.704	1.020	0.788	0.717	0.890	0.553	0.554	0.792	0.624	0.309	0.196	0.537	0.487	0.563	0.878	2.550	0.335
Imazapyr	H				0.003	0.004										0.003	0.004	0.004
Imidacloprid	I		0.012	0.009			0.007	0.005	0.007	0.005								
Indaziflam	H		0.002															
Linuron	H		0.114	0.056	0.027	0.023					0.016			0.010	0.025	0.011	0.017	
MCPA	H		4.770															
Methamidophos	D						0.003	0.003										
Metolachlor	H		0.280	0.021	0.019	0.020	0.020	0.017	0.017	0.014	0.010	0.008		0.006	0.005	0.004	0.004	
Metribuzin	H	0.004	0.124	0.046	0.035	0.029	0.024	0.017	0.018	0.014	0.010	0.009	0.008	0.010	0.015	0.011	0.013	0.009
Metsulfuron-methyl	H		0.096	0.013	0.009	0.013	0.008				0.004							0.021
N,N-Diethyl-m-tolamide (DEET)	IR		0.009							0.011								
Pendimethalin	H		0.008	0.005	0.003	0.006	0.003	0.003	0.002	0.003				0.002				0.003
Picloram	H					0.326		0.116	0.083	0.045				0.079	0.068		0.724	0.125
Prometon	H	0.003	0.004		0.005	0.008	0.006	0.006	0.006	0.005	0.005	0.005	0.004	0.005	0.005	0.004	0.004	0.003
Propiconazole	F		1.420	0.179		0.135	0.048	0.042	0.045				0.017	0.025	0.023			0.021
Pyraclostrobin	F		0.092	0.013	0.006	0.004		0.002										
Pyroxasulfone	H			0.053														
Sodium Bentazon	H			0.073	0.073													
Sulfentrazone	H		0.033	0.018	0.015	0.021	0.013	0.011	0.010	0.011	0.009	0.008	0.008	0.010	0.010	0.009	0.017	0.012
Sulfometuron methyl	H			0.006														
Tebuthiuron	H	0.006	0.008	0.010	0.009	0.010	0.007	0.007	0.007	0.007	0.007	0.005	0.006	0.006	0.006	0.004	0.006	
Thiamethoxam	I		0.029	0.011	0.009	0.007	0.005	0.005	0.005	0.005	0.004		0.003		0.004	0.003	0.004	0.004
Triallate	H		0.016	0.011	0.008	0.010	0.007	0.006	0.006	0.004	0.005	0.004	0.004	0.004	0.006	0.005	0.006	0.006
Triazine HA Degradate	D		0.002	0.002	0.002	0.001	0.002		0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.001	0.002	
Total suspended solids (mg/L)		3	15	12	10	8	9	16	8	7	3	4	3	6	6	7	2	1
Streamflow (cubic ft/sec)		7.4	6.4	3.1	1.9	1.4	1.3	0.7	0.5	0.4	0.4	0.4	0.4	0.5	--	0.9	1.1	1.5
Precipitation (total in/week)†		--	--	--	--	--	0.25	0.00	0.00	0.00	0.03	0.00	0.01	0.00	0.00	0.11	0.51	0.34

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  No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent)

† Washington State University AgWeatherNet station: Palouse.W, (latitude: 46.93°, longitude: -117.22°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 7 of the 17 site visits (41%). Water quality at the Dry Creek site is shown below (Figure 51).

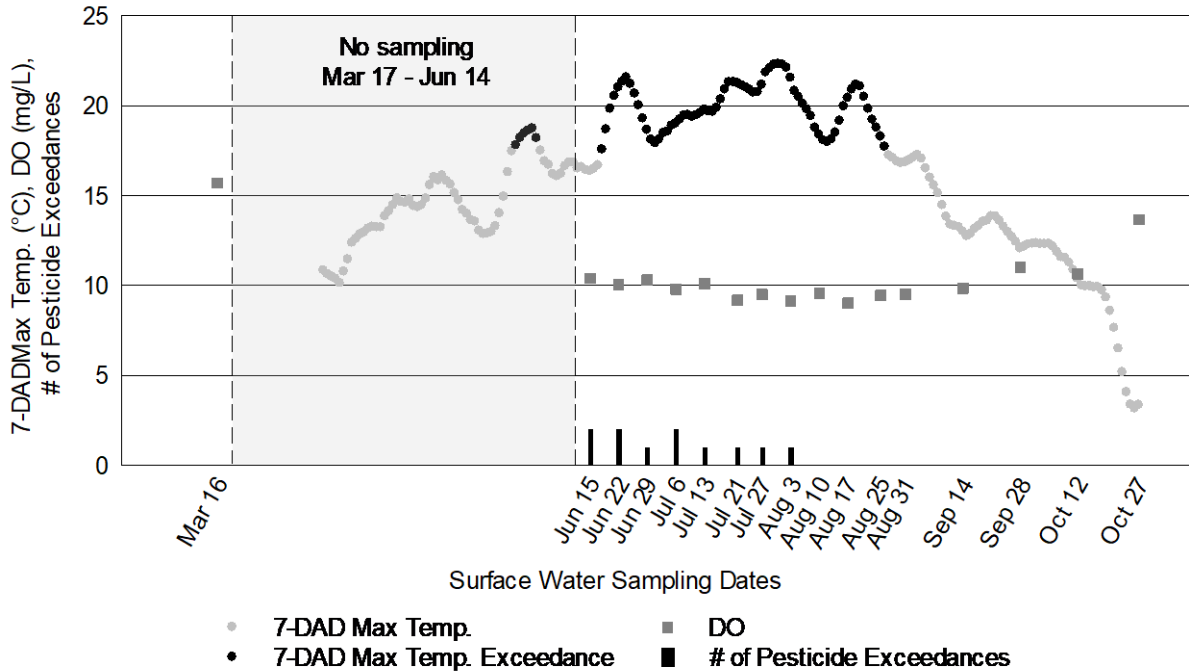


Figure 51– Dry Creek water quality measurements and exceedances of assessment criteria

All but one pH measurement met the state water quality standard, ranging from 7.92 to 8.87 with an average of 8.18. The pH measurement on March 16 exceeded the standard of 8.50 (data not shown). All DO measurements met the state standard, ranging from 9.02 mg/L to 15.69 mg/L with an average of 10.40 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 76 days of the sampling season, primarily from June 16 through August 26. At least one pesticide exceedance coincided with a 7-DADMax temperature exceedance at seven site visits.

Although Dry Creek does not provide habitat for salmonids, the water from the creek eventually flows into the Columbia River which contains many salmonid species. The WAC categorizes Dry Creek under the following guideline: “All surface waters of the state not named in Table 602 are to be protected for the designated uses of: salmonid spawning, rearing and migration” (WAC 2021). Staff observed pike minnow and other unknown species of fish within the creek throughout the sampling season.

Statewide Results

NRAS 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 (10 to 28 sampling events) and samples from several sites are tested for a subset of pesticides compared to the majority of sites (90 to 169 analytes). In addition, NRAS monitoring sites are not representative of all Washington streams in terms of levels of pesticide contamination or other characteristics. Statewide summary information (Table 22) provides a useful overview but should be used with caution.

Table 22 – 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		4
Legacy pesticides	5	5	4	76
Degradate	18	15		879
Fungicide	22	15		774
Herbicide	60	46	1	2,531
Insect repellent	1	1		82
Insecticide	59	27	9	654
Synergist	2	1		4
Wood preservative	1	1		6
Total analytes	169	112	14	5,010

There were 112 different analytes detected in 2020 (Table 22). Across 16 monitoring sites, we identified 5,010 detections. Every monitoring site had detections of at least one herbicide, one fungicide, and one insecticide. To determine if the detected concentrations could negatively affect aquatic life, NRAS compared each detection to WSDA assessment criteria.

There were 193 instances where analytes exceeded the WSDA assessment criteria listed in Appendix A: Assessment Criteria for Pesticides. The Monitoring Site Results section in this report discusses the individual exceedances in more detail while the Pesticide Detection Summary below divides the detections and associated exceedances by pesticide general use category.

Of the 193 individual exceedances, 120 (62%) were currently registered pesticides or their associated degradates. The other 73 (38%) were detections of legacy pesticides or their degradates. Approximately half of the exceedances, 102 (53%), occurred at monitoring sites in Central Washington and Palouse region including many of the statewide exceedances of DDT or its degradates (57). Imidacloprid, a neonicotinoid insecticide, accounted for 89 (46%) of the individual pesticide exceedances with 66 of the exceedances found at Western Washington monitoring sites. There was at least one exceedance detected at 14 of the 16 monitoring sites.

Pesticide Detection Summary

Below, statewide detections are summarized by pesticide general use categories. This subsection only presents analytes detected in 2020. Appendix B: 2020 Quality Assurance Summary provides a list of all analytes tested.

Herbicide Detections

Herbicides were the most frequently detected group making up approximately 51% (2,531 detections) of the total pesticide detections. Of the 60 herbicides included in the laboratory analysis, 46 were detected in surface water samples. Table 23 provides a statewide summary of the detected herbicides.

Table 23 – Statewide summary of herbicides with one or more detections in 2020

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)
Sulfentrazone	293	187 (64%)		14		0.00261 - 0.127
Diuron	276	156 (57%)		12		0.00346 - 0.469
Imazapyr	276	150 (54%)		12		0.00341 - 7.640
Metolachlor	293	137 (47%)		13		0.000673 - 0.280
Hexazinone	293	135 (46%)		15		0.00146 - 0.145
2,4-D	257	133 (52%)		13		0.0139 - 1.610
Terbacil	293	131 (45%)		9		0.00286 - 0.631
Bromacil	293	128 (44%)		12		0.00220 - 0.0702
Norflurazon	293	117 (40%)		10		0.00132 - 0.0122
Tebuthiuron	293	115 (39%)		11		0.00315 - 0.0720
Pendimethalin	293	114 (39%)		12		0.00204 - 0.0202
Dichlobenil	293	113 (39%)		10		0.00148 - 0.463
Prometon	293	109 (37%)		14		0.00219 - 0.00999
Atrazine	293	107 (37%)		12		0.00214 - 0.0251
Simazine	293	107 (37%)		10		0.00377 - 1.190
Eptam	293	82 (28%)		11		0.00110 - 0.0223
Dicamba acid	257	76 (30%)		11		0.00897 - 1.0400
Triclopyr acid	257	49 (19%)		9		0.0128 - 0.391
Picloram	257	45 (18%)		4		0.0450 - 0.823
Metribuzin	293	42 (14%)		9		0.00220 - 0.124
Trifluralin	293	30 (10%)		11		0.00136 - 0.00543
Dithiopyr	293	23 (8%)		4		0.00167 - 0.00566
Oxadiazon	293	19 (6%)		2		0.00177 - 0.00916
Dacthal (DCPA)	257	18 (7%)		3		0.0155 - 0.292
Mecoprop (MCP)	257	18 (7%)		4		0.0376 - 0.463
Napropamide	293	18 (6%)		3		0.00273 - 0.0233
Sulfometuron methyl	276	18 (7%)		7		0.00308 - 0.0338
Glyphosate	17	17 (100%)		1		0.196 - 2.550
Indaziflam	276	17 (6%)		4		0.00187 - 0.0363
Triallate	293	16 (5%)		1		0.00399 - 0.0163
Metsulfuron-methyl	276	13 (5%)		4		0.00406 - 0.0964
Imazapic	276	12 (4%)		3		0.00600 - 0.0177
Sodium bentazon	257	12 (5%)		4		0.0484 - 0.167
Aminocyclopyrachlor	276	10 (4%)		2		0.0130 - 0.0525
Linuron	276	9 (3%)	2	1	1	0.00998 - 0.114
Clopyralid	257	7 (3%)		4		0.0454 - 0.169
Glufosinate-ammonium	17	6 (35%)		1		0.00717 - 0.0272
Isoxaben	276	6 (2%)		4		0.00245 - 0.00582

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)
MCPA	257	6 (2%)		4		0.0836 - 4.770
Prometryn	293	6 (2%)		4		0.00183 - 0.0131
Bromoxynil	257	5 (2%)		3		0.0213 - 0.200
Chlorpropham	293	5 (2%)		4		0.00106 - 0.00906
Chlorsulfuron	276	4 (1%)		3		0.0147 - 0.0607
Pyroxasulfone	276	1 (0%)		1		0.0531 - 0.0531
Simetryn	293	1 (0%)		1		0.00673 - 0.00673
Triclopyr butoxyethyl ester	293	1 (0%)		1		0.00161 - 0.00161

The variability in number of samples collected was due to the variation in analytes chosen to be tested at each monitoring site by analytical method. For example, glyphosate, glufosinate-ammonia, and AMPA (in the LCMS-Glyphos analytical method) were only tested at one site. The GCMS-Herbicides analytical method chemicals weren't tested at two monitoring sites.

Sulfentrazone, diuron, and imazapyr were the most frequently detected herbicides that NRAS annually tests for with 187, 156, and 150 detections, respectively. There were 20 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Only one herbicide, linuron, was detected above the WSDA assessment criteria, accounting for roughly 1% of the total exceedances in 2020. The two exceeding detections were found at the same monitoring site, Dry Creek. Linuron is used mostly for newly emerging broadleaf and grassy weed control in agricultural and non-agricultural locations. We do not find this herbicide frequently in surface waters.

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 NRAS tests for.

- Atrazine → Triazine DEA (detected at six monitoring sites),
 - → Triazine HA (detected at 13 monitoring sites),
 - → Triazine DIA (detected at seven monitoring sites),
- Dichlobenil → 2,6-dichlorobenzamide (detected at all 16 monitoring sites),
- Dicamba acid → 3,5-dichlorobenzoic acid (detected at one monitoring site),
- Diuron → 1-(3,4-Dichlorophenyl)-3methylurea (detected at 11 monitoring sites),
- Glyphosate → Aminomethylphosphoric acid (AMPA) (detected at the only monitoring site where it was tested for).

Fungicide Detections

Fungicides were the second most frequently detected group of pesticides making up 774 detections, or 15%, of the total number of detections. Out of 22 fungicides included in the laboratory analysis, 15 were detected in surface water samples. Table 24 provides a statewide summary of the detected fungicides.

Table 24 – Statewide summary of fungicides with one or more detections in 2020

Analyte	# of samples collected*	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
Boscalid	293	218 (74%)		16		0.000898 - 0.188
Fludioxonil	293	144 (49%)		9		0.00338 - 0.350
Carbendazim	276	114 (41%)		14		0.00119 - 0.0182
Pyrimethanil	276	88 (32%)		7		0.00191 - 0.466
Propiconazole	276	71 (26%)		12		0.00380 - 1.420
Azoxystrobin	276	70 (25%)		7		0.00199 - 0.322
Myclobutanil	276	26 (9%)		5		0.00447 - 0.0235
Triadimefon	293	18 (6%)		8		0.00168 - 0.00365
Cyprodinil	276	8 (3%)		4		0.00411 - 0.0190
Pyraclostrobin	276	5 (2%)		1		0.00213 - 0.0924
Chlorothalonil	293	4 (1%)		2		0.00164 - 0.00234
Fluopicolide	276	3 (1%)		2		0.00490 - 0.00723
Difenoconazole	276	2 (1%)		1		0.00605 - 0.0274
Paclobutrazol	276	2 (1%)		2		0.00289 - 0.00330
Pentachloronitrobenzene	293	1 (0%)		1		0.00515 - 0.00515

Boscalid, fludioxonil, and carbendazim were the most commonly detected fungicides with 218, 144, and 114 detections, respectively. Boscalid and fludioxonil have been among the most commonly detected fungicides each year since 2015. Carbendazim is rarely used as a fungicide and is more often found in the environment as a degradate (Montague et al. 2014). However, it is registered in Washington as a fungicide and is categorized as a fungicide in this program. Its parent compound, thiophanate-methyl is a fungicide that NRAS does not test for and degrades very quickly into carbendazim in surface water. No fungicide detections exceeded WSDA assessment criteria in 2020.

NRAS detected the following fungicides at more than 50% of the monitoring sites throughout the sampling season:

- Boscalid
- Fludioxonil
- Propiconazole
- Carbendazim
- Triadimefon

Insecticide Detections

Current-use insecticides were the third most frequently detected group of pesticides representing approximately 13% (654 detections) of the total pesticide detections. Of the 59 current-use insecticides included in the laboratory analysis, 27 were detected in surface water samples. Table 25 provides a statewide summary of the detected insecticides.

Table 25 – Statewide summary of insecticides with one or more detections in 2020

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	276	130 (47%)		9		0.00184 - 0.0719
Imidacloprid	276	92 (33%)	89	13	13	0.00471 - 0.150

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)
Chlorpyrifos	293	66 (23%)	1	14	1	0.00111 - 0.0230
Clothianidin	276	57 (21%)	14	8	1	0.00287 - 0.0561
Dinotefuran	276	42 (15%)		5		0.00393 - 0.627
Oxamyl	276	32 (12%)		3		0.000826 - 0.0399
Malathion	293	31 (11%)	4	10	3	0.00192 - 0.0884
Dimethoate	293	26 (9%)	2	8	1	0.00282 - 0.595
Methoxyfenozide	276	26 (9%)		6		0.00234 - 0.00816
Acephate	276	25 (9%)		4		0.00383 - 0.0910
Diazinon	293	24 (8%)		6		0.00127 - 0.00691
Chlorantraniliprole	276	20 (7%)		2		0.00683 - 0.0261
Fipronil	293	20 (7%)	3	6	2	0.00189 - 0.0106
Acetamiprid	276	12 (4%)		5		0.00212 - 0.0891
Ethoprop	293	9 (3%)		6		0.00143 - 0.00521
Pyriproxyfen	293	9 (3%)		7		0.00159 - 0.00259
Phosmet	293	6 (2%)		4		0.00471 - 0.0724
Etoxazole	293	5 (2%)		5		0.00265 - 0.00693
Methomyl	276	5 (2%)		2		0.00227 - 0.00434
Carbaryl	276	4 (1%)		3		0.00314 - 0.00869
Cyantraniliprole	276	3 (1%)		3		0.00891 - 0.0530
Dichlorvos (DDVP)	293	3 (1%)	2	2	2	0.00121 - 0.00644
Bifenthrin	293	2 (1%)	2	2	2	0.00218 - 0.00526
Pyridaben	293	2 (1%)		2		0.00178 - 0.00199
Deltamethrin	293	1 (0%)	1	1	1	0.0151 - 0.0151
Hexythiazox	276	1 (0%)		1		0.00649 - 0.00649
Tefluthrin	293	1 (0%)		1		0.00105 - 0.00105

WSDA considers bolded analytes to be statewide POCs.

Thiamethoxam, imidacloprid, and chlorpyrifos were the most commonly detected insecticides with 130, 92, and 66 detections, respectively. The insecticides thiamethoxam and imidacloprid have been among the most commonly detected insecticides every year since 2015.

NRAS detected the following insecticides at more than 50% of the monitoring sites throughout the sampling season:

- Chlorpyrifos
- Clothianidin
- Dimethoate
- Imidacloprid
- Malathion
- Thiamethoxam

Detections of current-use insecticides accounted for almost 61% (118 detections) of all exceedances in 2020. All detections of bifenthrin, dichlorvos, and deltamethrin were at concentrations above the WSDA assessment criteria. Of the 27 current-use insecticides that NRAS detected, 33% (9 insecticides) had a concentration detected that exceeded WSDA assessment criteria at least once.

The three statewide POCs identified in 2020 were chlorpyrifos, malathion, and imidacloprid. Chlorpyrifos has been a WSDA POC since 2009 and is most often applied on fruit trees. There was only one exceedance of chlorpyrifos and it was found in Central Washington, where most of the state's

fruit trees are located. Staff were unable to sample during the spring season when chlorpyrifos usage is typically highest so there were many less detections and exceedances of this chemical in 2020 than in previous years. Malathion has been a POC since 2015. Malathion is applied most frequently to control fruit flies and mosquitos. It is often applied to a wide range of crops from tree fruit and berries to yards and even has indoor uses. Detections and exceedances of malathion were found in both Western and Central Washington. Imidacloprid has been a POC since 2017. This insecticide can be applied to over 250 commercial crop types and has residential uses; the exceedances and detections were found at all three monitoring regions as well. It is unknown by NRAS if the detections of imidacloprid that exceeded WSDA criteria were the result of applications to crops or residential uses.

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

- Acephate → methamidophos (detected at nine monitoring sites),
- Fipronil → fipronil sulfide (detected at seven monitoring sites),
 - → fipronil sulfone (detected at six monitoring sites),
 - → fipronil disulfinyl (detected at three monitoring sites),
- Oxamyl → oxamyl oxime (detected at three monitoring sites),
- Thiamethoxam → clothianidin. Although thiamethoxam degrades into clothianidin, 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. Degradates represented 18% (879 detections) of total detections and pesticide-related chemicals represented 2% (96 detections) of total detections. Of the 18 degradates from current-use chemicals included in the laboratory analysis, 15 were detected in surface water samples. Only one of the two synergists tested for was detected. Each antimicrobial, wood preservative, and insect repellent tested for had at least one detection. Table 26 provides a statewide summary of the detected degradates and other pesticide product ingredients.

Table 26 – Statewide summary of degradates and other pesticide products in 2020

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	293	223 (76%)		16		0.00137 - 0.376
Triazine HA	276	214 (78%)		13		0.00105 - 0.0406
Triazine DEA	276	98 (36%)		6		0.00221 - 0.0185
Triazine DIA	276	62 (22%)		7		0.00231 - 0.0442
Tetrahydrophthalimide	293	56 (19%)		8		0.00120 - 0.988
1-(3,4-Dichlorophenyl)-3-methylurea	276	51 (18%)		11		0.00332 - 0.114
Fipronil sulfide	293	36 (12%)		7		0.000921 - 0.00785
Methamidophos	276	35 (13%)		9		0.00144 - 0.0285
Oxamyl oxime	276	32 (12%)		3		0.0163 - 0.0796
Acetochlor ESA	276	30 (11%)		5		0.0238 - 0.134
Fipronil sulfone	293	26 (9%)		6		0.00214 - 0.00697
AMPA	17	9 (53%)		1		0.321 - 0.644

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)
Fipronil disulfinyl	293	5 (2%)		3		0.00160 - 0.00324
3,5-Dichlorobenzoic acid	257	1 (0%)		1		0.0187 - 0.0187
4-Nitrophenol	257	1 (0%)		1		0.448 - 0.448
Antimicrobial:						
Triclosan	293	4 (1%)		2		0.00242 - 0.0236
Insect repellent:						
DEET	293	82 (28%)		14		0.00143 - 0.0520
Synergist:						
Piperonyl butoxide	293	4 (1%)		3		0.00319 - 0.00456
Wood preservative:						
Pentachlorophenol	257	6 (2%)		2		0.0129 - 0.0465

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 223 detections, followed by triazine HA (degradate of the herbicide atrazine) with 214 positive detections. The degradate 2,6-dichlorobenzamide was found ubiquitously throughout the season at all monitoring sites. The degradates detected that did not have a parent compound detected at any of the monitoring sites were acetochlor ESA, tetrahydrophthalimide, and 4-nitrophenol. Acetochlor ESA is the breakdown product of the herbicide acetochlor, tetrahydrophthalimide is the main breakdown product of the fungicide captan, and 4-nitrophenol is a breakdown product of several natural and synthetic products.

Other associated pesticide ingredients detected were pentachlorophenol, triclosan, and piperonyl butoxide. Pentachlorophenol's main usage is for wood preservation. Also, the insect repellent DEET (N,N-diethyl-m-toluamide), detected 82 times, was found at every monitoring site but two. The only federally registered uses of DEET are for application to horses, the human body, and clothing.

Legacy Pesticides and Degradates

We test for legacy pesticides and some of their degradates as a way to identify pesticides that may be lingering in the environment or, in some circumstances, to identify when stock of a pesticide is being used up after the pesticide has been cancelled. Detected legacy pesticides and associated degradates accounted for 1% (76 detections) of the total pesticide detections. All five legacy analytes included in the lab analysis were detected. A statewide summary of the legacy analytes are shown below in Table 27.

Table 27 – Statewide summary of legacy pesticides and degradates with one or more detections in 2020

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
4,4'-DDE	293	37 (13%)	37	9	9	0.00138 - 0.0507
4,4'-DDD	293	33 (11%)	33	9	9	0.000800 - 0.00624
Fenarimol	293	3 (1%)		3		0.00411 - 0.0259
4,4'-DDT	293	2 (1%)	2	1	1	0.00777 - 0.0145
Tralomethrin	293	1 (0%)	1	1	1	0.0151 - 0.0151

There were detections of all five legacy analytes tested for. One DDT degradate, 4,4'-DDE, was the most frequently detected legacy chemical with 37 detections, closely followed by another DDT degradate, 4,4'-DDD, with 33 detections. DDT or an associated breakdown product were found at five of seven Western Washington sites, six of eight Central Washington sites, and the single Palouse region site. 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 because of its persistence in soils. Contaminated soil can enter surface water as a result of runoff or when sediment is disturbed. Fenarimol, a fungicide banned in 2013, was detected at three monitoring sites but did not exceed WSDA assessment criteria. This chemical's presence could be from legacy use, as it is known to stay in the environment for many years before breaking down. Tralomethrin, an insecticide banned in 2012, breaks down quickly into deltamethrin in the environment. The one exceedance of tralomethrin occurred at the same monitoring site and sampling event as the one deltamethrin (current-use insecticide) exceedance.

The parent compound 4,4'-DDT and its degradates (4,4'-DDE and 4,4'-DDD) accounted for 37% of the total exceedances detected in 2020. Of the 72 combined DDT exceedances, 26 (36%) were detected at the monitoring site on Brender Creek, where there was past use of the insecticide on orchards. Although every detection of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD exceeded the state water quality standards, these detections are not a result of current pesticide usage patterns.

Toxic Unit Analysis

A study by Broderius and Kahl (1985) found when a large number of chemicals are included in mixture experiments on organisms; an additive response is typically found (Lydy et al. 2004). One of the most common methods of assessing the additive effects of pesticide mixtures is by using toxic units (TUs). For this report, TUs were used to estimate the additive effects of pesticide mixtures, as described by Faust et al. in 1993 (in Lydy et al. 2004). To determine a TU for a sample, a criteria ratio is calculated for each pesticide detected in the sample by dividing the pesticide concentration by the corresponding pesticides LC₅₀ or EC₅₀ assessment criteria. Then, each of those ratios is summed to obtain an estimated TU for the whole sample. In this report, NRAS analyzed TU using the fish LC₅₀, invertebrate EC₅₀, and plant EC₅₀ assessment criteria with WSDA's safety factor for a more conservative approach. If the TU ratio is above or equal to one, there is a higher possibility of lethal or sublethal effects on aquatic life. Of the 293 sampling events analyzed using TUs, there were seven samples that had a TU above or equal to one. Of the seven samples, six samples had exceeding TUs using invertebrate criteria and one sample had an exceeding TU using plant criteria. All seven samples had exceeding TUs primarily due to an elevated concentration of one or two pesticides. The pesticides that contributed significantly to samples with TUs greater than or equal to one were malathion and chlorpyrifos. These insecticides were found in concentrations above WSDA assessment criteria predominately in the spring and early summer, often coinciding with the samples where TU was exceeded. They both have relatively high toxicity to aquatic life at low concentrations. The TU exceedances occurred at Lower Big Ditch, Brender Creek, Dry Creek, Indian Slough, Juanita Creek, and Mission Creek.

Nutrient Analysis

In 2020, we sampled nutrients for the first time at four monitoring sites. Table 28 provides a summary of nutrient results at the four sites. Collecting water samples for nutrient analysis (ammonia, nitrate+nitrite, orthophosphate, and total phosphorus) alongside samples for pesticide analysis provides an interpretive benefit for determining possible pathways of pesticide movement. For example, the concentration of nitrate in a particular sample may provide evidence as to the primary source of the water in a stream at a given point in time. Nitrate is a conservative constituent for which

high concentrations typically occur in water that has percolated through an agricultural soil and through subsurface drainage (Capel et al. 2018). If a high concentration for a particular pesticide occurs in the same sample that a relatively high nitrate concentration was found, it provides additional evidence that the pesticide may have entered the stream through a similar transport pathway or mechanism (Capel et al. 2018). Similarly, high pesticide concentrations occurring when SSC and/or total phosphorus concentrations are also high would suggest runoff/erosion is the primary transport pathway. The relationships described above are more evident with multiple years of data to assess, and since 2020 is the first year that nutrient samples have been collected, it will take several more years of collecting paired nutrient and pesticide water samples to identify consistent relationships between pesticides and nutrient levels.

Table 28 – Summary of 2020 nutrient sampling results

Nutrient	Monitoring site	# of samples collected	# of detections (% samples)	# of detections exceeding criteria	Median (mg/L)	Maximum (mg/L)
Ammonia as N	Upper Big Ditch	25	25 (100%)		0.078	0.194
	Dry Creek	16	8 (50%)		0.012	0.014
	Marion Drain	27	10 (37%)		0.028	0.065
	Sulfur Creek Wasteway	19	16 (84%)		0.015	0.045
Nitrate+nitrite as N	Upper Big Ditch	26	26 (100%)	26	0.438	0.863
	Dry Creek	17	17 (100%)	17	2.57	7.69
	Marion Drain	28	28 (100%)	28	2.48	4.83
	Sulfur Creek Wasteway	20	20 (100%)	20	3.79	12.9
Total phosphorus as P	Upper Big Ditch	26	26 (100%)	26	0.0926	0.646
	Dry Creek	17	17 (100%)	17	0.162	0.187
	Marion Drain	28	28 (100%)	28	0.134	0.374
	Sulfur Creek Wasteway	20	20 (100%)	20	0.269	1.86
Ortho-phosphate as P	Upper Big Ditch	26	26 (100%)	N/A	0.0150	0.0289
	Dry Creek	17	17 (100%)	N/A	0.127	0.165
	Marion Drain	28	28 (100%)	N/A	0.111	0.332
	Sulfur Creek Wasteway	20	20 (100%)	N/A	0.176	1.78

All detections of nitrate-nitrite and total phosphorus exceeded EPA’s Ambient Water Quality Criteria Recommendations (EPA 2000a, EPA 2000b). This means that the concentrations were above estimated environmental background concentrations. Water contaminated with pollutants such as pesticides and excess nutrients can compound in their adverse effects to aquatic life. None of the ammonia detections exceeded the Water Quality Standards for Washington State (WAC 2020). There were no known orthophosphate criteria to compare to.

Conclusions

Staff collected surface water monitoring data at 16 locations across Western Washington, Central Washington, and the Palouse region in 2020. Water samples were collected during the first two weeks in March and then mid-June through December (March – December) a total of 294 times. The pause in monitoring during the peak pesticide usage season (spring) was due to COVID-19 restrictions. Samples taken from 12 of the monitoring sites were tested in a lab for 166 pesticide and pesticide-related chemicals, while one monitoring site was tested for 169 chemicals, one site was tested for 152 chemicals, and two more sites were tested for a subset of 90 chemicals.

- Of 169 pesticides tested for, 112 unique pesticides were detected.
- NRAS detected pesticides in water samples a total of 5,010 times.
- Sulfentrazone, diuron, and imazapyr were the most frequently detected herbicides (187, 156, and 150 times, respectively).
- Thiamethoxam, imidacloprid, and chlorpyrifos were the most frequently detected insecticides (130, 92, and 66 times, respectively).
- Boscalid, fludioxonil, and carbendazim were the most frequently detected fungicides (218, 144, and 114 times, respectively).
- Nine chemicals were detected at more than 50% of sampling events they were tested for. Triazine HA (a degradate), 2,6-dichlorobenzamide (a degradate), and boscalid were detected each at more than 70% of sampling events.

In order to assess the potential effects of pesticide exposure to aquatic life and endangered species, we compared detected pesticide concentrations to WSDA assessment criteria. There were 193 exceedances total with at least one exceedance at 14 of the 16 monitoring sites (Table 29). Approximately 62% of the total exceedances (120 exceedances) were from 10 current-use pesticides. Every detection of bifenthrin and deltamethrin exceeded WSDA assessment criteria. However, not every detection of the other eight pesticides did. A summary of current-use pesticides with exceedances is below in Table 29. Detections of legacy pesticides and associated degradates accounted for the remaining 38% (73 exceedances) of the total exceedances. The single detection of tralomethrin, a banned insecticide, exceeded WSDA assessment criteria. DDT and/or one of its degradates tested for were detected at five Western Washington sites, ranging from one exceeding detection at the Lower Bertrand site to a maximum of six exceeding detections at the Lower Big Ditch site. In Central Washington and Palouse region, DDT and/or one of its degradates was detected at six sites; detections ranged from one exceedance at Dry Creek to a maximum of 26 exceedances at Brender Creek. Every detection of DDT exceeded WSDA assessment criteria.

Exceedances by current-use pesticide types are as follows.

- Out of 2,531 total herbicide detections, two detections exceeded criteria (<1%).
- Out of 774 total fungicide detections, no detection exceeded criteria (0%).
- Out of 654 total insecticide detections, 118 detections exceeded criteria (18%).

Table 29 – Summary of WSDA assessment criteria exceedances from current-use pesticides

Analyte	# of detections	# of detections above assessment criteria
Imidacloprid	92	89 (97%)
Chlorpyrifos	66	1 (2%)
Clothianidin	57	14 (25%)
Malathion	31	4 (13%)
Dimethoate	26	2 (8%)
Fipronil	20	3 (15%)
Linuron	9	2 (22%)
Dichlorvos (DDVP)	3	2 (67%)
Bifenthrin	2	2 (100%)
Deltamethrin	1	1 (100%)

In 2020, monitoring sites commonly contained mixtures of pesticides in samples. Of the 16 monitoring sites, 15 sites had two or more pesticide detections at every sampling event during the entire field season. Only the Touchet River monitoring site had a sampling event with less than two detections. The maximum number of detections (42) at a single sampling event occurred June 23 at the Indian Slough 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). Further adverse effects can occur if certain nutrients and other conventional water quality parameters such as dissolved oxygen, pH, and water temperature exceed water quality standards. At least one water quality parameter did not meet state water quality standards at 14 of the 16 monitoring sites. All sampling events at the four monitoring sites that were tested for nutrients also had exceedances of nitrate-nitrite and total phosphorus recommended criteria. When these exceedances coincide with exceeding pesticide detections and exceeding water quality parameters, it increases stress on aquatic life.

NRAS maintains and updates a POC list annually, consisting solely of current-use pesticides, in order to identify the highest priority pesticides for education and outreach programs. The agricultural community, regulatory community, and public may also reference the POC list to keep informed about current pesticide trends in Washington State. In 2019, WSDA and all other Region 10 states adopted a new decision matrix for selecting watershed and statewide POCs. The decision matrix provides a uniform methodology for selecting POCs and significantly reduced the number of POCs identified. Identifying a smaller number of pesticides as statewide POCs allows for more consistent communication to pesticide applicators across the state. Maintaining watershed POC lists allows WSDA to communicate watershed-specific priorities based on results from each monitoring site. WSDA's statewide POCs were the insecticides chlorpyrifos, imidacloprid, and malathion. The Monitoring Site Results section in this report lists each watershed's individual POCs. Even though DDT and its degradates exceeded assessment criteria, they are not considered POCs because they are legacy chemicals that have not been registered for use in the U.S. since 1972.

Washington State had approximately 1,240 pesticide active ingredients (including pesticides, synergists, adjuvants, and additives) registered for use at the beginning of 2021 (WSPMRS 2021). Surface water samples in 2020 were tested for roughly 14% of the total registered pesticide active ingredients. NRAS 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 affect ESA-listed salmonids. Invertebrates are the main food source of juvenile salmonids, and those invertebrates rely on aquatic plants to sustain their populations. If a pesticide is causing impairment to any organism, food webs and ecosystem functions can be potentially disrupted. Pesticide monitoring in Washington waterways is essential for understanding the fate and transport of pesticides that can cause water quality concerns. WSDA POCs should be given additional prioritization for management by WSDA and partners to ensure their concentrations are maintained or reduced below WSDA assessment criteria. WSDA will continue to implement the Pesticide Management Strategy as a way to identify and address specific pesticide issues, as well as promote public education and outreach efforts through presentations, reports, and watershed-specific fact sheets in order to support appropriate pesticide use.

Program Changes

Several changes occurred between the 2020 and 2021 sampling seasons. In Central Washington, sampling of Lower Crab Creek was discontinued after the 2020 monitoring season due to few pesticide detections exceeding WSDA assessment criteria for several years. A new monitoring site was established at Ahtanum Creek near Union Gap to investigate a new part of the region. Staff sampled the remaining seven Central Washington sites sampled in 2020, in 2021. The seven monitoring sites sampled in Western Washington in 2020 were sampled in 2021 as well. NRAS partnered with the Palouse Conservation District to monitor Dry Creek for a second sampling season and also started sampling Thorn Creek near Pine City and Kamiache Creek near Ewan.

The 169 analytes tested for in 2020 were tested for in 2021 minus three analytes (azinphos-ethyl, azinphos-methyl, and aldicarb sulfoxide) and with the addition of eight analytes (Table 30). We only tested for glyphosate, AMPA, and glufosinate-ammonium at the three Palouse-region monitoring sites during 2021 to expand the special project to other watersheds in that part of Washington.

Table 30 – Additional analytes tested for in 2021

Analytes added	CAS number	General Use
Clethodim sulfone	111031-17-5	Herbicide degradate
Clethodim sulfoxide	111031-14-2	Herbicide degradate
Dimethenamid ESA	1418095-09-6	Herbicide degradate
Dimethenamid OA	380412-59-9	Herbicide degradate
Flupyradifurone	951659-40-8	Insecticide
Inpyrfluxam	1352994-67-2	Fungicide
Sulfoxaflor	946578-00-3	Insecticide
Tolfenpyrad	129558-76-5	Insecticide

Historically, NRAS has sampled for total suspended solids at each sampling event. During the 2021 field season, staff started analyzing samples for suspended sediment concentration instead as a way to capture more of the material such as gravels and larger particles within the sample that the total suspended solids analytical method could miss.

Similar to the 2020 field season, staff sampled for nutrients at Upper Big Ditch, Marion Drain, Sulphur Creek Wasteway, and Dry Creek monitoring sites in 2021, but additionally sampled nutrients at the Thorn Creek and Kamiache Creek monitoring sites.

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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, aquatic invertebrates, and aquatic plants. Staff reviewed various EPA derived risk assessments to determine the most comparable and up-to-date toxicity guidelines for freshwater species.

WSDA applies a 0.5x safety factor to state and national water quality standards and criteria in order to be adequately protective of aquatic life. This safety factor was applied to each criteria found in Table 31a. 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:
 - ACR-acute to chronic ratio
 - AS-Atlantic salmon
 - AG-astacopsis gouldi (crayfish)
 - BS-bluegill sunfish
 - BT-brook trout
 - CC-carp
 - CF-catfish
 - FF-flagfish
 - FM-fathead minnow
 - GC-grass carp (ctenopharyngodon idellus)
 - JM-Japanese medaka
 - LT-lake trout
 - ND-not described
 - RT-rainbow trout
 - PS-pumpkinseed sunfish
 - SB-striped bass

- Invertebrate:
 - ACR-acute to chronic ratio
 - CG-chloroperia grammatical (stonefly)
 - CP-chironomus plumosus (midge)
 - CR-chironomus riparius
 - DM-daphnia magna
 - GF-gammarus fasciatus (scud)
 - MATC-maximum allowed toxic concentration
 - ND-not described
 - PC-pteronarcys californica (stonefly)

- Aquatic plant:
 - AF-anabaena flos-aquae (cyanobacteria)
 - AI-anabaena inaequalis (blue-green cyanophyceae)
 - EN-elodea nuttali (waterweed)
 - LG- lemna gibba
 - LM-Lemna minor
 - ND-not described
 - NP-navicula pelliculosa
 - OL-oscillatoria lutea (blue-green algae)
 - SC-pseudokirchneriella subcapitata
 - SD-skeltonema costatum (diatom)
 - SP-scenedesmus pannonicus
 - SS-scenedesmus 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 31a contains only chemicals detected in 2020. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2020 Quality Assurance Summary.

Table 31a – WSDA Freshwater assessment criteria (WSDA safety factors applied, µg/L)

Pesticide	<u>Fish</u>				<u>Invertebrate</u>			<u>Aquatic Plant</u>		<u>WAC</u>		<u>NRWQC</u>	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
1-(3,4-Dichlorophenyl)-3-methylurea													
2,4-D ^{1,b}	2,040	20,400	11,800	RT/FM	6,250	8,025	DM	149.6	LG				
2,6-Dichlorobenzamide ²	3,000	30,000	5,000	BS/RT	46,000	160,000	DM	50,000	SP				
3,5-Dichlorobenzoic Acid													
4,4'-DDD ³										0.55 ^a	0.0005 ^a	0.55 ^a	0.0005 ^a
4,4'-DDE ³										0.55 ^a	0.0005 ^a	0.55 ^a	0.0005 ^a
4,4'-DDT ³										0.55 ^a	0.0005 ^a	0.55 ^a	0.0005 ^a
4-Nitrophenol ⁴	100	1,000		RT	1,250		DM						
Acephate ⁵	20,800	208,000	2,880	RT	275	75	DM	25,000	SD				
Acetamiprid ⁶	2,500	25,000	9,600	RT/FM	5.25	1.05	CR/ACR	500	LG				
Acetochlor ESA ⁷	4,500	45,000		RT	31,250		DM	4,950	SC				
Aminocyclopyrachlor ⁸	3,000	30,000	5,500	BS/RT	9,925	185	DM	3,700	AF				
Aminomethylphosphoric acid ⁹	12,475	124,750		RT	170,750		DM						
Atrazine ¹⁰	132.5	1,325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin ¹¹	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Bifenthrin ¹²	0.00375	0.0375	0.02	RT/FM	0.4	0.00065	DM						
Boscalid ¹³	67.5	675	58		1,332.50	395		670					
Bromacil ¹⁴	900	9,000	1,500	RT	30,250	4,100	DM	3.4	SC				
Bromoxynil ¹⁵	52.5	525		RT	4,805		DM						
Carbaryl ¹⁶	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	330	NP			1.05	1.05
Carbendazim ¹⁷	0.25	2.5	0.495		27.5	1.55							
Chlorantraniliprole ¹⁸	345	3,450	55	RT/RT	2.9	2.235	DM/DM	890	SC				
Chlorothalonil ¹⁹	0.2625	2.625	1.5	RT/AG	0.9	0.3	DM	3.4	SC				
Chlorpropham ²⁰	75.25	752.5		RT	927.5		DM						
Chlorpyrifos ²¹	0.045	0.45	0.285	RT/FM	0.025	0.02	DM	70		0.0415	0.0205	0.0415	0.0205
Chlorsulfuron ²²	7,500	75,000	16,000	RT	92,500	10,000	DM	0.175	LG				
Clopyralid ²³	2,587.5	25,875		RT	58,250		DM	3,450	SC				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Clothianidin ²⁴	2,537.5	25,375	4,850	RT/FM	5.5	0.025	CR	32,000					
Cyantraniliprole ²⁵	250	2,500	5,350	CF/RT	5.1	3.28	DM	5,000	SD				
Cyprodinil ²⁶	54.5	545	115	BS/FM	8	4.1	DM	985	AF				
Dacthal (DCPA) ²⁷	165	1,650		RT	4,505		DM						
Deltamethrin ²⁸	0.0145	0.145	0.0085	PS/FM	0.0275	0.00205	DM						
Diazinon ²⁹	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1,850	SC			0.085	0.085
Dicamba acid ³⁰	700	7,000		RT	25,000		DM	30.5	AF				
Dichlobenil ²	123.25	1,232.5	165	RT	1,550	280	DM	15	LG				
Dichlorvos (DDVP) ³¹	4.575	45.75	2.6	LT/RT	0.0175	0.0029	DM	7,000	ND				
Difenoconazole ³²	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP				
Dimethoate ³³	155	1,550	215	RT	10.75	0.25	PC	10,000	AF				
Dinotefuran ³⁴	2,477.5	24,775	3,180	CC/RT	242,075	47,650	DM	48,800	SC				
Dithiopyr ³⁵	11.75	117.5	28	BS/RT	425	40.5	DM	10	SC				
Diuron ³⁶	10	100	13.2	SB/FM	40	100	GF/DM	1.2	SC				
Eptam ³⁷	350	3,500	20	BS/FM-ACR	1,625	400	DM	700	SC				
Ethoprop ³⁸	7.5	75	12	RT/FM	11	0.4	DM	4,200					
Etoxazole ³⁹	9.25	92.5	7.5	RT	1.825	0.065	DM	25.95	NP				
Fenarimol ⁴⁰	22.5	225	90	RT	1,700	56.5	DM	50	SC				
Fipronil ⁴¹	2.075	20.75	3.3	BS	0.055	0.0055	DM/ACR	50					
Fipronil disulfanyl ⁴¹	0.5	5	0.295		50	5.155		50					
Fipronil sulfide ⁴¹	2.075	20.75	3.3		0.5325	0.055		50	ND				
Fipronil sulfone ⁴¹	0.625	6.25	0.335	RT/ND	0.18	0.0185	DM/ND	50	ND				
Fludioxonil ⁴²	11.75	117.5	9	RT/FM	225	7	DM	140	SC				
Fluopicolide ⁴³	8.725	87.25	75.5	RT/FM	425	95	DM	1,300	SC				
Glufosinate-ammonium ⁴⁴	7,800	78,000	25,000	RT	162,750	15,500	DM	36	AF				
Glyphosate ⁹	1,075	10,750	12,850	BS/FM	13,300	24,950	CP/DM	5,950	LG				
Hexazinone ⁴⁵	6,850	68,500	8,500	RT/FM	37,900	10,000	DM	3.5	SC				
Hexythiazox ⁴⁶	3	30		RT		3.05	DM	60	LG				
Imazapic ⁴⁷	2,500	25,000	48,000	RT/FM	25,000	48,000	DM	3.11	LM				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Imazapyr ⁴⁸	2,500	25,000	21,550	RT/FM	25,000	48,550	DM	12	LM				
Imidacloprid ⁴⁹	5,725	57,250	4,500	RT	0.1925	0.005		5,000	ND				
Indaziflam													
Isoxaben ⁵⁰	25	250	200	RT	325	345	DM	5	LG				
Linuron ⁵¹	75	750	2.79	RT	30	0.045	DM	1.25	EN				
Malathion ⁵²	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1,020				0.05	
MCPA ⁵³								85	SC				
Mecoprop (MCP) ⁵⁴	2,325	23,250		RT	22,750	25,400	DM	7	SC				
Methamidophos ⁵⁵	625	6,250	86.8	RT	6.5	2.25	DM	25,000	SD				
Methomyl ⁵⁶	12.5	125	28.5	CF/FM	2.2	0.3	DM/MATC						
Methoxyfenozide ⁵⁷	105	1,050	265	RT/FM	14.25	1.55	CR	1,700	SC				
Metolachlor ⁵⁸	95	950	15	RT	275	0.5	DM	4	SC				
Metribuzin ⁵⁹	1,050	10,500	1,500	RT	1,050	645	DM	4.05					
Metsulfuron-methyl ⁶⁰	3,750	37,500	2,250	BS	37,500		DM	0.18	LG				
Myclobutanil ⁶¹	60	600	490	BS/FM	2,750		DM	415	SC				
N,N-diethyl-m-toluamide ⁶²	1,875	18,750		RT	18,750		DM						
Napropamide ⁶³	160	1,600	550	RT	3,575	550	DM	1,700	SC				
Norflurazon ⁶⁴	202.5	2,025	385	RT	3,750	500	DM	4.85	SC				
Oxadiazon ⁶⁵	30	300	16.5	RT/FM	545	16.5	DM	2.6	SC				
Oxamyl ⁶⁶	105	1,050	250	RT/FM	45	13.5	ACR	60	SC				
Oxamyl oxime ⁶⁶	105	1,050	250	RT/FM	45	13.5	ACR	60	SC				
Paclobutrazol ⁶⁷	397.5	3,975	24.5	GC/RT	60	4.5	DM	4	LG				
Pendimethalin ⁶⁸	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC				
Pentachloronitrobenzene ⁶⁹	2.5	25	6.5		192.5	9							
Pentachloropheno ⁷⁰	0.375	3.75	5.5	RT	23	2.05	DM	25	SC			9.5	7.5
Phosmet ⁷¹	1.75	17.5	1.6	RT	0.5	0.4	DM						
Picloram ⁷²	137.5	1,375	275	RT	8,600	5,900	DM	17,450	SC				
Piperonyl butoxide (PBO) ⁷³	47.5	475	20	RT	127.5	15	DM						
Prometon ⁷⁴	300	3,000	9,850	RT/FM	6,425	1725	DM	49	SC				
Prometryn ⁷⁵	72.75	727.5	310	RT/FM	2,425	500	DM	0.52	NP				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Propiconazole ⁷⁶	21.25	212.5	47.5	RT/FM	325	130	DM	10.5	ND				
Pyraclostrobin ⁷⁷	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP				
Pyridaben ⁷⁸	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG				
Pyrimethanil ⁷⁹	252.5	2,525	10	RT	750	500	DM	900	ND				
Pyriproxyfen ⁸⁰	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG				
Pyroxasulfone													
Simazine ⁸¹	160	1,600	30	FM	250	20	DM/ACR	3	SC				
Simetryn													
Sodium bentazon ⁸²	4,750	47,500	4,915	RT/FM	15,575	50,600	CR/DM	2,250	SC				
Sulfentrazone ⁸³	2,345	23,450	1,475	BS/RT	15,100	100	DM	14.4	SC				
Sulfometuron methyl ⁸⁴	3,700	37,000		RT	37,500	48,500	DM	0.225	LG				
Tebuthiuron ⁸⁵	2,650	26,500	4,650	FM	74,250	10,900	DM	25	SC				
Tefluthrin ⁸⁶	0.0015	0.015	0.002	RT/FM	0.0175	0.004	DM						
Terbacil ⁸⁷	1,155	11,550	600	RT	16,250	25	DM	5.5	NP				
Tetrahydrophthalimide ⁸⁸	3,150	31,500		RT	28,250		DM	90,500	SC				
Thiamethoxam ⁸⁹	2,850	28,500	10,000	BS/RT	8.75	0.37	CR	45,100	LM				
Tralomethrin ⁹⁰	0.04	0.4	0.044	RT/FM	0.00975	0.0022	DM						
Triadimefon ⁹¹	102.5	1,025	85	RT	400	26	DM	1,000	SC				
Triallate ⁹²	30	300	19	RT	22.75	7	DM	10.5	SC				
Triazine DEA degradate ⁹³								500					
Triazine DIA degradate ⁹³	425	4,250			31,500			1,250					
Triazine HA Degradate ⁹³	75	750		RT	1,025		DM	5,000	AI				
Triclopyr acid ⁹⁴	2,925	29,250	52,000	RT/FM	33,225	40,350	DM	2,950	SC				
Triclopyr butoxyethyl ester ⁹⁴	9	90	13	BS/RT	425		DM	50	NP				
Triclosan ⁹⁵	7.2	72		FM	97.5		DM	0.35	SS				
Trifluralin ⁹⁶	0.4625	4.625	0.95		62.75	1.2		10.95					

CMC: Criteria Maximum Concentration

CCC: Criteria Continuous Concentration

^a Criteria is specific to total DDT but is used here for individual metabolites as well.

^b 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: 2020 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 2020, QA/QC samples were 11% of all the samples collected in the field. There were 171 QC samples in total: 77 field replicates, 49 field blanks, 30 MS/MSD samples and 15 conductivity check samples. The lab contributed the remaining LCS/LCSD and method blank samples.

Data Qualification

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

The Manchester Environmental Laboratory (MEL) qualify all sample results based on the analysis of LCS/LCSDs, MS/MSDs, surrogates, and method blanks. LCS/LCSD were generated by adding analytes at known concentrations to purified water free of all organics. An LCS/LCSD pair was extracted and analyzed with every batch of field samples and other QC samples. They were used to evaluate method performance for a specific analyte and to check for bias and precision of the lab's extraction and analytical processes. Detections from a batch may be qualified based on high/low recovery and/or high RPD between the paired LCS and LCSD. Similarly, samples collected in the field that had analytes added at known concentrations and analyzed are MS/MSD samples. The analysis of this type of QC sample can assess the potential for matrix interactions or interaction between analytes within field samples that can affect analytical results. Staff collected an MS/MSD sample once during the season at each site for each analysis method, except in a few cases where budgetary restrictions were prohibitive. In 2019, almost all analytes tested for during the season were used to spike MS/MSDs and LCS/LCSDs, although the lab rotated between two spike mixtures for the GCMS-Pesticides analytical method to avoid coelution of analytes. Surrogates are analytes not normally found in environmental samples that were spiked into all field and QC samples to evaluate recoveries for groups of organic compounds. Results of surrogates can evaluate extraction efficiency and matrix interference within the sample.

WSDA staff qualify the remainder of the field sample data based on field replicates, field blanks, and MS/MSD results. Field replicates were used to evaluate variability in analytical results. No field sample results were qualified due solely to field replicate results in 2020. Field blank results were used to examine bias caused by contamination in the field during transport to the lab and during processing at the lab. No field samples were qualified due solely to MS/MSD results.

MEL reports the lower limit of quantitation (LLOQ), which is the lowest concentration at which the laboratory has demonstrated analytes can be reliably reported with a level of confidence, for pesticide

and pesticide-related chemicals. They report the method reporting limit (MRL), the lowest concentration used in the initial calibration for each analyte, for general chemistry such as TSS, specific conductivity, and nutrients. The LLOQ and MRL were adjusted for each individual sample according to sample volume and dilution (if needed). Results outside the instrument calibration range may be qualified as estimates (J). Mean LLOQ or MRL (calculated for each individual sample in 2020) and standard deviation are presented in Table 32b.

Table 32b – Mean performance of analytical method reporting limits (LLOQ or MRL) in ng/L

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
<u>Method: LCMS-Pesticides; Reporting Limit: LLOQ</u>				
1-(3,4-Dichlorophenyl)-3-methylurea	3567-62-2	Degradate	1.00E+01	0.00E+00
Acephate	30560-19-1	Insecticide	2.00E+01	0.00E+00
Acetamiprid	135410-20-7	Insecticide	2.00E+01	0.00E+00
Acetochlor ESA	187022-11-3	Degradate	1.00E+02	0.00E+00
Afidopyropen	915972-17-7	Insecticide	2.00E+02	0.00E+00
Aldicarb Sulfoxide	1646-87-3	Degradate	1.00E+01	0.00E+00
Aminocyclopyrachlor	858956-08-8	Herbicide	1.00E+02	0.00E+00
Azinphos-ethyl	2642-71-9	Insecticide	1.00E+02	0.00E+00
Azinphos-methyl	86-50-0	Insecticide	2.00E+02	0.00E+00
Azoxystrobin	131860-33-8	Fungicide	2.00E+01	0.00E+00
Bensulide	741-58-2	Herbicide	1.00E+02	0.00E+00
Carbaryl	63-25-2	Insecticide	2.00E+01	0.00E+00
Carbendazim	10605-21-7	Fungicide	2.19E+01	3.93E+01
Chlorantraniliprole	500008-45-7	Insecticide	5.00E+01	0.00E+00
Chlorsulfuron	64902-72-3	Herbicide	1.00E+02	0.00E+00
Clothianidin	210880-92-5	Insecticide	1.00E+02	0.00E+00
Cyantraniliprole	736994-63-1	Insecticide	1.00E+02	0.00E+00
Cyprodinil	121552-61-2	Fungicide	1.00E+01	0.00E+00
Difenoconazole	119446-68-3	Fungicide	2.00E+01	0.00E+00
Diflubenzuron	35367-38-5	Insecticide	5.00E+01	0.00E+00
Dinotefuran	165252-70-0	Insecticide	2.00E+01	0.00E+00
Diuron	330-54-1	Herbicide	1.00E+01	0.00E+00
Fenbuconazole	114369-43-6	Fungicide	2.00E+01	0.00E+00
Fenbutatin oxide	13356-08-6	Insecticide	2.42E+01	7.94E+00
Fluopicolide	239110-15-7	Fungicide	1.00E+01	0.00E+00
Hexythiazox	78587-05-0	Insecticide	1.12E+01	5.00E+00
Imazapic	104098-48-8	Herbicide	1.00E+02	0.00E+00
Imazapyr	81334-34-1	Herbicide	1.01E+02	2.33E+01
Imidacloprid	138261-41-3	Insecticide	2.00E+01	0.00E+00
Indaziflam	950782-86-2	Herbicide	1.00E+01	0.00E+00
Isoxaben	82558-50-7	Herbicide	1.00E+01	0.00E+00
Linuron	330-55-2	Herbicide	5.00E+01	0.00E+00
Malaoxon	1634-78-2	Degradate	1.00E+01	0.00E+00
Methamidophos	10265-92-6	Degradate	2.00E+01	0.00E+00
Methidathion	950-37-8	Insecticide	2.23E+01	8.07E+00
Methiocarb	2032-65-7	Insecticide	2.00E+01	0.00E+00
Methomyl	16752-77-5	Insecticide	1.00E+01	0.00E+00
Methomyl oxime	13749-94-5	Degradate	1.00E+02	0.00E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Methoxyfenozide	161050-58-4	Insecticide	1.00E+01	0.00E+00
Metsulfuron-methyl	74223-64-6	Herbicide	5.00E+01	0.00E+00
Myclobutanil	88671-89-0	Fungicide	2.00E+01	0.00E+00
Oryzalin	19044-88-3	Herbicide	2.09E+02	3.69E+01
Oxamyl	23135-22-0	Insecticide	1.00E+01	0.00E+00
Oxamyl oxime	30558-43-1	Degradate	1.00E+02	0.00E+00
Paclobutrazol	76738-62-0	Fungicide	1.02E+01	9.09E-01
Phorate	298-02-2	Insecticide	2.00E+01	0.00E+00
Propiconazole	60207-90-1	Fungicide	5.00E+01	0.00E+00
Propoxur	114-26-1	Insecticide	1.00E+01	0.00E+00
Pyraclostrobin	175013-18-0	Fungicide	5.00E+01	0.00E+00
Pyrethrins	121-21-1	Insecticide	2.00E+02	0.00E+00
Pyrimethanil	53112-28-0	Fungicide	1.00E+01	0.00E+00
Pyroxasulfone	447399-55-5	Herbicide	2.00E+02	0.00E+00
Spirotetramat	203313-25-1	Insecticide	2.00E+02	0.00E+00
Sulfometuron methyl	74222-97-2	Herbicide	2.00E+01	0.00E+00
Thiacloprid	111988-49-9	Insecticide	1.00E+01	0.00E+00
Thiamethoxam	153719-23-4	Insecticide	2.00E+01	0.00E+00
Thiram	137-26-8	Fungicide	1.86E+02	1.72E+02
Triazine DEA degradate	6190-65-4	Degradate	1.00E+01	0.00E+00
Triazine DIA degradate	1007-28-9	Degradate	1.00E+01	0.00E+00
Triazine HA degradate	2163-68-0	Degradate	1.00E+01	0.00E+00
Trifloxystrobin	141517-21-7	Fungicide	2.00E+01	0.00E+00
Zoxamide	156052-68-5	Fungicide	1.00E+01	0.00E+00
<u>Method: LCMS-Glyphos; Reporting Limit: LLOQ</u>				
AMPA	1066-51-9	Degradate	7.74E+02	1.32E+03
Glufosinate-ammonium	77182-82-2	Herbicide	1.74E+01	2.01E+01
Glyphosate	1071-83-6	Herbicide	1.82E+01	1.15E+01
<u>Method: GCMS-Herbicides; Reporting Limit: LLOQ</u>				
2,4-D	94-75-7	Herbicide	5.98E+01	7.67E-01
3,5-Dichlorobenzoic Acid	51-36-5	Degradate	5.98E+01	7.67E-01
4-Nitrophenol	100-02-7	Degradate	5.98E+01	7.67E-01
Bromoxynil	1689-84-5	Herbicide	5.98E+01	7.67E-01
Clopyralid	1702-17-6	Herbicide	5.98E+01	7.67E-01
Dacthal (DCPA)	1861-32-1	Herbicide	5.98E+01	7.67E-01
Dicamba acid	1918-00-9	Herbicide	5.98E+01	7.67E-01
Dichlorprop	120-36-5	Herbicide	5.98E+01	7.67E-01
MCPA	94-74-6	Herbicide	6.18E+01	3.32E+01
Mecoprop (MCPP)	93-65-2	Herbicide	5.98E+01	7.67E-01
Pentachlorophenol	87-86-5	Wood Preservative	5.98E+01	7.67E-01
Picloram	1918-02-1	Herbicide	2.99E+02	3.85E+00
Sodium bentazon	25057-89-0	Herbicide	5.98E+01	7.67E-01
Triclopyr acid	55335-06-3	Herbicide	5.98E+01	7.67E-01
<u>Method: GCMS-Pesticides; Reporting Limit: LLOQ</u>				
2,6-Dichlorobenzamide	2008-58-4	Degradate	5.57E+00	1.89E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
4,4'-DDD	72-54-8	Degradate	5.24E+00	5.55E-01
4,4'-DDE	72-55-9	Degradate	5.00E+00	1.46E-01
4,4'-DDT	50-29-3	Insecticide	7.36E+00	2.78E+00
Acetochlor	34256-82-1	Herbicide	4.97E+00	6.26E-02
Alachlor	15972-60-8	Herbicide	4.97E+00	6.26E-02
Atrazine	1912-24-9	Herbicide	5.00E+00	1.46E-01
Benfluralin	1861-40-1	Herbicide	4.97E+00	6.26E-02
Bifenazate	149877-41-8	Insecticide	1.03E+01	8.49E+00
Bifenthrin	82657-04-3	Insecticide	4.97E+00	6.26E-02
Boscalid	188425-85-6	Fungicide	5.23E+00	7.67E-01
Bromacil	314-40-9	Herbicide	4.97E+00	6.26E-02
Captan	133-06-2	Fungicide	5.05E+00	6.21E-01
Chlorethoxyfos	54593-83-8	Insecticide	9.93E+00	1.30E-01
Chlorothalonil	1897-45-6	Fungicide	5.18E+00	8.49E-01
Chlorpropham	101-21-3	Herbicide	5.32E+00	1.14E+00
Chlorpyrifos	2921-88-2	Insecticide	5.10E+00	5.88E-01
Chlorpyrifos-methyl	5598-13-0	Insecticide	4.97E+00	6.26E-02
cis-Permethrin	54774-45-7	Insecticide	4.97E+00	6.26E-02
Coumaphos	56-72-4	Insecticide	5.03E+00	5.63E-01
Cycloate	1134-23-2	Herbicide	1.49E+01	1.95E-01
Deltamethrin	52918-63-5	Insecticide	5.03E+00	5.63E-01
Diazinon	333-41-5	Insecticide	4.97E+00	6.26E-02
Dichlobenil	1194-65-6	Herbicide	5.29E+00	1.28E+00
Dichlorvos (DDVP)	62-73-7	Insecticide	4.97E+00	6.26E-02
Dicofol	115-32-2	Insecticide	3.13E+01	1.10E+01
Dimethoate	60-51-5	Insecticide	5.15E+00	1.65E+00
Dithiopyr	97886-45-8	Herbicide	4.97E+00	6.26E-02
Eptam	759-94-4	Herbicide	4.97E+00	6.26E-02
ES fenvalerate	51630-58-1	Insecticide	4.97E+00	6.26E-02
Ethalfuralin	55283-68-6	Herbicide	4.97E+00	6.26E-02
Ethoprop	13194-48-4	Insecticide	5.11E+00	6.41E-01
Etoxazole	153233-91-1	Insecticide	1.49E+01	1.95E-01
Etridiazole	2593-15-9	Fungicide	4.97E+00	6.26E-02
Fenarimol	60168-88-9	Fungicide	1.82E+01	1.35E+01
Fenpropathrin	39515-41-8	Insecticide	4.97E+00	6.26E-02
Fipronil	120068-37-3	Insecticide	4.97E+00	6.26E-02
Fipronil disulfanyl	205650-65-3	Degradate	4.97E+00	6.26E-02
Fipronil sulfide	120067-83-6	Degradate	4.97E+00	6.26E-02
Fipronil sulfone	120068-36-2	Degradate	9.93E+00	1.30E-01
Fludioxonil	131341-86-1	Fungicide	4.97E+00	6.26E-02
Flumioxazin	103361-09-7	Herbicide	2.48E+01	3.22E-01
Fluroxypyr 1-methylheptyl ester	81406-37-3	Herbicide	2.48E+01	3.20E-01
gamma-Cyhalothrin	76703-62-3	Insecticide	5.03E+00	5.63E-01
Hexazinone	51235-04-2	Herbicide	6.63E+00	4.03E+00
Malathion	121-75-5	Insecticide	4.97E+00	6.26E-02
Metalaxyl	57837-19-1	Fungicide	9.93E+00	1.30E-01
Metolachlor	51218-45-2	Herbicide	5.49E+00	1.10E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Metribuzin	21087-64-9	Herbicide	5.03E+00	5.63E-01
MGK264	113-48-4	Synergist	4.97E+00	6.26E-02
N,N-diethyl-m-toluamide	134-62-3	Insect Repellent	8.57E+01	2.03E+02
Naled	300-76-5	Insecticide	4.97E+01	6.26E-01
Napropamide	15299-99-7	Herbicide	4.97E+00	6.26E-02
Norflurazon	27314-13-2	Herbicide	4.97E+00	6.26E-02
Oxadiazon	19666-30-9	Herbicide	4.97E+00	6.26E-02
Oxyfluorfen	42874-03-3	Herbicide	4.97E+01	6.26E-01
Pendimethalin	40487-42-1	Herbicide	4.97E+00	6.26E-02
Pentachloronitrobenzene	82-68-8	Fungicide	4.97E+00	6.26E-02
Phenothrin	26002-80-2	Insecticide	9.93E+00	1.30E-01
Phosmet	732-11-6	Insecticide	7.32E+00	6.01E+00
Piperonyl butoxide (PBO)	51-03-6	Synergist	5.03E+00	5.63E-01
Prallethrin	23031-36-9	Insecticide	4.97E+00	6.26E-02
Prodiamine	29091-21-2	Herbicide	2.48E+01	3.20E-01
Prometon	1610-18-0	Herbicide	4.97E+00	6.26E-02
Prometryn	7287-19-6	Herbicide	9.93E+00	1.30E-01
Propargite	2312-35-8	Insecticide	9.93E+00	1.30E-01
Propyzamide (pronamide)	23950-58-5	Herbicide	4.97E+00	6.26E-02
Pyraflufen-ethyl	129630-19-9	Herbicide	4.97E+00	6.26E-02
Pyridaben	96489-71-3	Insecticide	4.97E+00	6.26E-02
Pyriproxyfen	95737-68-1	Insecticide	9.95E+00	1.86E-01
Simazine	122-34-9	Herbicide	1.01E+01	2.24E+00
Simetryn	1014-70-6	Herbicide	2.48E+01	3.20E-01
Sulfentrazone	122836-35-5	Herbicide	5.03E+00	5.63E-01
Tebuthiuron	34014-18-1	Herbicide	9.93E+00	1.30E-01
Tefluthrin	79538-32-2	Insecticide	4.97E+00	6.26E-02
Terbacil	5902-51-2	Herbicide	5.16E+00	1.67E+00
Tetrachlorvinphos	961-11-5	Insecticide	5.03E+00	5.63E-01
Tetrahydrophthalimide	27813-21-4	Degradate	5.12E+00	1.24E+00
Tetramethrin	7696-12-0	Insecticide	5.03E+00	5.63E-01
Total cyfluthrin	68359-37-5	Insecticide	5.03E+00	5.63E-01
Total cyhalothrin	91465-08-6	Insecticide	5.03E+00	5.63E-01
Total cypermethrin	52315-07-8	Insecticide	5.03E+00	5.63E-01
tau-Fluvalinate	102851-06-9	Insecticide	5.03E+00	5.63E-01
Tralomethrin	66841-25-6	Insecticide	5.03E+00	5.63E-01
trans-Permethrin	61949-77-7	Insecticide	4.97E+00	6.26E-02
Triadimefon	43121-43-3	Fungicide	5.79E+00	2.04E+00
Triallate	2303-17-5	Herbicide	4.97E+00	6.26E-02
Triclopyr butoxyethyl ester	64700-56-7	Herbicide	9.93E+00	1.30E-01
Triclosan	3380-34-5	Antimicrobial	1.90E+01	1.11E+01
Trifluralin	1582-09-8	Herbicide	9.93E+00	1.30E-01
Various Methods; Reporting Limit: MRL				
Specific conductivity			15.0 µmhos/cm	0.00E+00
Total suspended solids			1.57 mg/L	1.09E+00
Ammonia as N	7664-41-7	Nutrient	0.0164 mg/L	2.92E-02

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Nitrate-Nitrite as N		Nutrient	0.0334 mg/L	3.36E-02
ortho-Phosphate as P		Nutrient	0.00545 mg/L	7.19E-03
Total phosphorus as P		Nutrient	0.0108 mg/L	5.66E-03

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 33b that are used for sample analysis of pesticides, TSS, nutrients, and specific conductivity (MEL, 2016).

Table 33b – 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

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

During 2020, 5% of pesticide, nutrient, and TSS samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 254 consistently identified pairs for pesticide analysis, 13 consistently identified pairs for nutrient analysis, and 15 consistently identified pairs for TSS analysis. Consistently identified pairs are those where the analytes were identified in both the original sample and field replicate with unqualified, *J* and *E* results. Conversely, inconsistently identified replicate pairs are those where the analyte was detected in only one of the two samples collected. Only 58 inconsistently identified pairs for pesticide analysis, 1 inconsistently identified pair for nutrients, and no inconsistently identified pairs for TSS were found.

Of the 174 analytes tested for, 48% (84 analytes) were detected in field replicates. Table 34b presents the variability of detections in field replicates with at least one detection in a replicate pair. RPDs were only calculated for consistently identified replicate pairs. Variability of detection and RPDs could not be calculated for the 90 analytes without replicate detections and, therefore, are not found in Table 34b.

Table 34b – Variability of pesticide detections in field replicates and mean RPDs

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Fluopicolide	LCMS-Pesticides	14	0		1	100	100
Methamidophos	LCMS-Pesticides	14	0		1	100	100
Metsulfuron-methyl	LCMS-Pesticides	14	0		1	100	100
Glufosinate-ammonium	LCMS-Glyphos	0	0		1	100	100
4-Nitrophenol	GCMS-Herbicides	13	0		1	100	100
Sodium bentazon	GCMS-Herbicides	13	0		1	100	100
Fipronil	GCMS-Pesticides	16	0		1	100	100
Pyridaben	GCMS-Pesticides	16	0		1	100	100
Pyriproxyfen	GCMS-Pesticides	16	0		1	100	100

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Tefluthrin	GCMS-Pesticides	16	0		1	100	100
Triadimefon	GCMS-Pesticides	16	0		1	100	100
Fipronil sulfone	GCMS-Pesticides	14	1	6	2	67	97
Methoxyfenozide	LCMS-Pesticides	13	1	11	1	50	95
Sulfometuron methyl	LCMS-Pesticides	13	1	12	1	50	95
Picloram	GCMS-Herbicides	12	1	2	1	50	95
Triclopyr acid	GCMS-Herbicides	12	1	5	1	50	95
4,4'-DDD	GCMS-Pesticides	15	1	4	1	50	95
4,4'-DDE	GCMS-Pesticides	15	1	4	1	50	95
Fipronil sulfide	GCMS-Pesticides	15	1	2	1	50	95
Metribuzin	GCMS-Pesticides	15	1	8	1	50	95
Trifluralin	GCMS-Pesticides	15	1	3	1	50	95
Chlorpyrifos	GCMS-Pesticides	11	2	11	4	67	91
Acephate	LCMS-Pesticides	14	1	2	0	0	90
Aminocyclopyrachlor	LCMS-Pesticides	14	1	19	0	0	90
Cyantraniliprole	LCMS-Pesticides	14	1	21	0	0	90
Imazapic	LCMS-Pesticides	14	1	31	0	0	90
AMPA	LCMS-Glyphos	0	1	11	0	0	90
Glyphosate	LCMS-Glyphos	0	1	8	0	0	90
Bromoxynil	GCMS-Herbicides	13	1	3	0	0	90
Dacthal (DCPA)	GCMS-Herbicides	13	1	34	0	0	90
Pentachlorophenol	GCMS-Herbicides	13	1	6	0	0	90
Dithiopyr	GCMS-Pesticides	16	1	9	0	0	90
Napropamide	GCMS-Pesticides	16	1	6	0	0	90
Triallate	GCMS-Pesticides	16	1	4	0	0	90
Dicamba acid	GCMS-Herbicides	10	2	13	2	50	86
Myclobutanil	LCMS-Pesticides	12	2	8	1	33	80
Oxamyl	LCMS-Pesticides	12	2	13	1	33	80
2,4-D	GCMS-Herbicides	6	4	9	4	50	76
Acetochlor ESA	LCMS-Pesticides	13	2	10	0	0	68
Chlorantraniliprole	LCMS-Pesticides	13	2	49	0	0	68

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Cyprodinil	LCMS-Pesticides	13	2	16	0	0	68
Dinotefuran	LCMS-Pesticides	13	2	4	0	0	68
Indaziflam	LCMS-Pesticides	13	2	18	0	0	68
Oxamyl oxime	LCMS-Pesticides	13	2	22	0	0	68
Diazinon	GCMS-Pesticides	15	2	14	0	0	68
Malathion	GCMS-Pesticides	15	2	9	0	0	68
Oxadiazon	GCMS-Pesticides	15	2	10	0	0	68
Tetrahydrophthalimide	GCMS-Pesticides	15	2	11	0	0	68
Ammonia	NH3	0	3	1	1	25	68
Propiconazole	LCMS-Pesticides	9	4	17	2	33	67
Hexazinone	GCMS-Pesticides	10	5	4	2	29	60
Norflurazon	GCMS-Pesticides	10	5	7	2	29	60
1-(3,4-Dichlorophenyl)-3-methylurea	LCMS-Pesticides	10	4	14	1	20	58
Clothianidin	LCMS-Pesticides	10	4	17	1	20	58
Triazine DIA degradate	LCMS-Pesticides	10	4	11	1	20	58
Sulfentrazone	GCMS-Pesticides	5	8	12	4	33	56
Imidacloprid	LCMS-Pesticides	7	6	10	2	25	54
Pendimethalin	GCMS-Pesticides	9	6	8	2	25	54
Pyrimethanil	LCMS-Pesticides	12	3	7	0	0	54
ortho-Phosphate	OP	0	3	3	0	0	54
Total Phosphorus	TP8-H	0	3	2	0	0	54
Eptam	GCMS-Pesticides	10	6	5	1	14	45
Prometon	GCMS-Pesticides	10	6	3	1	14	45
Diuron	LCMS-Pesticides	5	8	10	2	20	45
Nitrate-Nitrite as N	NO2NO3	0	4	0	0	0	44
DEET	GCMS-Pesticides	13	4	6	0	0	44
Simazine	GCMS-Pesticides	13	4	7	0	0	44
Tebuthiuron	GCMS-Pesticides	9	7	7	1	13	41
Terbacil	GCMS-Pesticides	9	7	5	1	13	41
Dimethoate	GCMS-Pesticides	12	5	10	0	0	37

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)	Uncertainty: 90% upper confidence bound (%)
Azoxystrobin	LCMS-Pesticides	10	5	7	0	0	37
Carbendazim	LCMS-Pesticides	9	6	9	0	0	32
Triazine DEA degradate	LCMS-Pesticides	9	6	14	0	0	32
Thiamethoxam	LCMS-Pesticides	9	6	7	0	0	32
Atrazine	GCMS-Pesticides	11	6	12	0	0	32
Dichlobenil	GCMS-Pesticides	11	6	8	0	0	32
Metolachlor	GCMS-Pesticides	11	6	6	0	0	32
Triazine HA degradate	LCMS-Pesticides	3	11	11	1	8	29
Imazapyr	LCMS-Pesticides	7	8	4	0	0	25
Bromacil	GCMS-Pesticides	8	9	11	0	0	23
Fludioxonil	GCMS-Pesticides	8	9	5	0	0	23
Boscalid	GCMS-Pesticides	5	12	5	0	0	17
2,6-dichlorobenzamide	GCMS-Pesticides	3	14	8	0	0	15
Total suspended solids	TSS	1	15	12	0	0	14

Staff used two methods to estimate the uncertainty of replicate variability. The first was the percentage of inconsistently identified replicate pairs and the second was an evaluation of the upper confidence bound associated with the percentage of inconsistently identified replicate pairs. If the percentage of inconsistently identified replicate pairs (can be 0%) out of the total count of consistently and inconsistently identified replicate pairs was 25% or less, a low variability of detection was assumed; whereas, a percentage of 50% or greater was indicative of high variability of detection (Martin, 2002). Almost 64% of analytes (54 analytes) with consistently identified pairs and/or 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 2020 using the second method indicate only six analytes have a low detection variability rather than the 54 analytes estimated through the first method. These six were triazine HA degradate, imazapyr, bromacil, fludioxonil, 2,6-dichlorobenzamide, and TSS. All six of these analytes were frequently detected throughout the season at most monitoring sites. This analysis shows that there was not a high reproducibility of detections between replicates for most analytes. Likely, some of the high variability was due in part to a small number of replicate pairs with at least one detection.

The RPD of analytes for consistently identified pairs was good overall. For pesticide analysis, the mean RPD of the consistently identified replicate-paired analytes was 9%. Of the 254 consistently identified replicate pairs for pesticides, two had RPDs that were equal to or greater than the 40% RPD criterion. For TSS analysis, the mean RPD of the consistently identified replicate-paired analyte was 12%. Of the 15

consistently identified TSS pairs, three had an RPD equal to or greater than the 20% RPD criterion. For nutrients analysis, the mean RPD of the consistently identified replicate-paired analytes was 2%. Of the 13 consistently identified nutrient pairs, none had an RPD that was equal to or greater than the 20% RPD criterion. Results for pesticide, nutrient, and TSS field sample and replicate detections were not qualified as a result of the replicate analysis 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, nutrient, and TSS field replicates were of acceptable data quality.

The majority of the 59 inconsistently identified pairs were detections at concentrations between the LLOQ and the method detection limit (MDL) (below which the laboratory is unable to distinguish between instrument response due to the presence of analytes or background noise). Most of these replicate pairs consisted of a *J* qualified detection and a *U* or *UJ* qualified detection. There were no sample detections qualified due solely to inconsistent field replicate results.

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 2020, there were 19 detections in the 49 field blank samples collected for nutrients, TSS, and pesticide analysis (Table 35b). If a detection occurred in a field blank, all sample detections of the same analyte in the analytical batch were reviewed for qualification. Sample detection concentrations that were greater than five times the field blank detection concentration were not qualified. Sample detection concentrations that were lower than five times the field blank detection concentration were qualified to *U*. There were 59 sample detections qualified to *U* in 2020 due to field blank detections.

Table 35b – Analyte detections in field blanks

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	LLOQ (ng/L)	MDL (ng/L)	Qualifier
6/22	Dry Creek	NO2NO3	Nitrate-Nitrite as N	0.0230 mg/L	0.010 mg/L	0.004 mg/L	J
7/28	Stemilt Creek	GCMS-Pesticides	Boscalid	1.13	4.98	0.544	J
7/28	Stemilt Creek	GCMS-Pesticides	Metolachlor	1.39	4.98	0.580	J
7/28	Stemilt Creek	GCMS-Pesticides	DEET	89.0	4.98	1.33	
7/28	Stemilt Creek	GCMS-Pesticides	Triclosan	7.92	9.95	1.72	J
7/27	Snipes Creek	LCMS-Pesticides	Carbendazim	34.8	10.0	1.16	
8/10	Touchet River	LCMS-Pesticides	Carbaryl	2.33	20.0	2.15	J
8/17	Marion Drain	GCMS-Pesticides	Chlorpropham	1.97	4.95	0.971	J
8/17	Marion Drain	GCMS-Pesticides	Dichlobenil	2.19	4.95	1.39	J
8/17	Marion Drain	GCMS-Pesticides	DEET	169	4.95	1.32	J
9/8	Burnt Bridge	GCMS-Pesticides	2,6-Dichlorobenzamide	2.36	4.98	1.28	J
9/22	Upper Big Ditch	NH3	Ammonia	0.0350 mg/L	0.010 mg/L	0.005 mg/L	
9/28	Dry Creek	LCMS-Glyphos	AMPA	184	64.7	2.41	

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	LLOQ (ng/L)	MDL (ng/L)	Qualifier
9/28	Dry Creek	LCMS-Glyphos	Glufosinate-ammonium	17.7	6.47	3.29	
9/28	Snipes Creek	GCMS-Pesticides	Chlorpropham	1.50	5.00	0.980	J
9/28	Snipes Creek	GCMS-Pesticides	DEET	41.3	5.00	1.33	
10/5	Bertrand Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	1.96	5.03	1.29	J
10/26	Snipes Creek	GCMS-Pesticides	Chlorpropham	1.09	4.90	0.961	J
10/26	Snipes Creek	GCMS-Pesticides	DEET	38.3	4.90	1.31	J

Matrix Spike/Matrix Spike Duplicate Results

Summary MS/MSD results for each analyte are shown in Table 36b, with control limits, percent recoveries, and RPDs. The table describes the number of MS/MSD recoveries that were above or below the laboratory control limits set for each analyte and the number of detections from all grab samples throughout the season for each analyte. Only the MS/MSD recoveries that were unqualified, *E*, or *J* qualified are included in the table. Some RPDs were unable to be calculated because of a *U*, *NAF*, or *NC* qualified MS/MSD recovery result. The summary table excluded the uncalculated RPDs.

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

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
1-(3,4-Dichlorophenyl)-3-methylurea	22	54	163	101	87 - 121	0	0	11	7	1 - 19	51
2,4-D	16	10	150	77	38 - 97	0	0	8	8	2 - 18	133
2,6-dichlorobenzamide	20	29	175	103	87 - 122	0	0	10	4	0.4 - 9	223
3,5-dichlorobenzoic acid	16	21	144	66	50 - 84	0	0	8	5	0.7 - 13	1
4,4'-DDD	20	61	161	109	93 - 128	0	0	10	4	1 - 8	33
4,4'-DDE	2	40	115	95	93 - 96	0	0	1	3	3 - 3	37
4,4'-DDE	18	46	115	93	75 - 107	0	0	9	5	0.2 - 10	37
4,4'-DDT	20	40	140	83	57 - 105	0	0	10	9	3 - 19	2
4-nitrophenol	16	10	172	120	72 - 145	0	0	8	13	0.09 - 39	1
Acephate	22	65	135	92	83 - 103	0	0	11	5	0.1 - 9	25
Acetamiprid	22	61	172	124	102 - 155	0	0	11	5	1 - 13	12
Acetochlor	20	37	156	112	102 - 125	0	0	10	3	0.4 - 5	
Acetochlor ESA	22	59	136	103	72 - 155	0	1	11	10	4 - 30	30

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
Afidopyropen	22	64	135	96	66 - 135	0	0	11	19	2 - 36	
Alachlor	20	48	174	113	99 - 126	0	0	10	4	2 - 8	
Aldicarb sulfoxide	22	65	135	98	70 - 107	0	0	11	4	1 - 9	
Aminocyclopyrachlor	20	50	150	135	71 - 346	0	4	10	5	1 - 11	10
AMPA	2	50	150	91	88 - 94	0	0	1	5	5 - 5	9
Atrazine	20	47	140	109	101 - 118	0	0	10	5	0.09 - 10	107
Azinphos-ethyl	22	50	150	98	82 - 131	0	0	11	10	0.3 - 22	
Azinphos-methyl	22	50	150	97	59 - 119	0	0	11	11	3 - 33	
Azoxystrobin	22	65	135	114	89 - 137	0	3	11	6	0.005 - 22	70
Benfluralin	20	50	155	102	93 - 116	0	0	10	4	0.07 - 10	
Bensulide	22	65	145	93	60 - 122	1	0	11	12	2 - 23	
Bifenazate	18	50	150	245	103 - 882	0	9	9	9	0.2 - 29	
Bifenthrin	20	50	159	89	63 - 104	0	0	10	10	2 - 20	2
Boscalid	20	48	168	113	92 - 128	0	0	10	7	0.3 - 24	218
Bromacil	20	43	181	131	116 - 148	0	0	10	3	0.6 - 5	128
Bromoxynil	16	28	138	91	74 - 100	0	0	8	6	0.09 - 17	5
Captan	20	18	160	74	41 - 107	0	0	10	10	0.1 - 26	
Carbaryl	22	65	135	101	86 - 117	0	0	11	7	0.4 - 13	4
Carbendazim	22	65	135	97	74 - 119	0	0	11	5	0.5 - 10	114
Chlorantraniliprole	22	65	135	108	90 - 130	0	0	11	9	1 - 19	20
Chlorethoxyfos	20	36	157	100	92 - 115	0	0	10	5	0.3 - 13	
Chlorothalonil	20	39	147	106	94 - 117	0	0	10	3	0.2 - 6	4
Chlorpropham	20	37	178	115	105 - 126	0	0	10	5	1 - 9	5
Chlorpyrifos	20	62	171	101	92 - 108	0	0	10	4	1 - 8	66
Chlorpyrifos-methyl	20	33	165	107	92 - 119	0	0	10	3	0.3 - 8	
Chlorsulfuron	22	37	158	98	42 - 131	0	0	11	10	1 - 18	4
cis-Permethrin	20	56	216	95	69 - 107	0	0	10	7	0.1 - 19	
Clopyralid	16	10	106	46	31 - 54	0	0	8	9	0.8 - 34	7
Clothianidin	22	50	150	80	63 - 118	0	0	11	5	0.6 - 10	57
Coumaphos	20	30	130	126	113 - 139	0	7	10	5	0.3 - 15	
Cyantraniliprole	22	50	150	101	80 - 130	0	0	11	8	1 - 22	3

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
Cycloate	20	53	166	114	94 - 146	0	0	10	6	0.6 - 9	
Cyprodinil	22	65	135	97	83 - 120	0	0	11	5	2 - 13	8
Dacthal (DCPA)	16	38	173	97	81 - 112	0	0	8	5	0.3 - 19	18
Deltamethrin	20	53	181	107	74 - 122	0	0	10	7	0.5 - 17	1
Diazinon	20	49	197	111	101 - 119	0	0	10	5	0.7 - 12	24
Dicamba acid	16	10	146	74	58 - 89	0	0	8	8	2 - 21	76
Dichlobenil	20	24	146	103	97 - 110	0	0	10	6	0.9 - 10	113
Dichlorprop	16	22	160	86	74 - 96	0	0	8	6	0.3 - 17	
Dichlorvos (DDVP)	20	23	191	130	118 - 144	0	0	10	4	0.09 - 10	3
Dicofol	20	30	130	214	155 - 287	0	20	10	6	1 - 12	
Difenoconazole	22	59	135	90	64 - 114	0	0	11	8	0.005 - 25	2
Diflubenzuron	22	65	171	102	69 - 129	0	0	11	12	2 - 20	
Dimethoate	20	38	203	116	100 - 135	0	0	10	5	3 - 10	26
Dinotefuran	22	58	167	116	97 - 157	0	0	11	4	0.4 - 9	42
Dithiopyr	20	44	179	99	85 - 110	0	0	10	4	0.7 - 10	23
Diuron	22	65	135	108	92 - 121	0	0	11	5	0.1 - 12	156
Eptam	20	15	171	102	85 - 115	0	0	10	7	4 - 11	82
ES fenvalerate	20	51	190	97	70 - 111	0	0	10	8	0.3 - 18	
Ethalfuralin	20	53	153	107	96 - 123	0	0	10	6	0.7 - 13	
Ethoprop	20	45	205	116	107 - 129	0	0	10	4	0.7 - 8	9
Etoxazole	20	33	198	100	88 - 114	0	0	10	6	0.6 - 21	5
Etridiazole	20	26	151	105	87 - 122	0	0	10	6	1 - 10	
Fenarimol	20	48	216	134	118 - 157	0	0	10	4	0.1 - 14	3
Fenbuconazole	22	63	135	106	72 - 142	0	2	11	8	1 - 26	
Fenbutatin oxide	22	10	144	96	69 - 150	0	2	11	9	2 - 24	
Fenpropathrin	20	30	130	94	71 - 110	0	0	10	8	0.3 - 19	
Fipronil	20	67	217	120	105 - 148	0	0	10	5	1 - 10	20
Fipronil disulfanyl	20	72	206	109	94 - 124	0	0	10	5	1 - 7	5
Fipronil sulfide	20	53	187	109	98 - 124	0	0	10	5	1 - 9	36
Fipronil sulfone	20	62	216	116	102 - 138	0	0	10	5	0.2 - 11	26
Fludioxonil	20	41	181	117	105 - 133	0	0	10	4	0.3 - 9	144

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
Flumioxazin	20	44	254	112	93 - 138	0	0	10	6	0.02 - 21	
Fluopicolide	22	50	150	108	77 - 136	0	0	11	8	0.02 - 23	3
Fluroxypyr 1-methylheptyl ester	20	57	164	113	87 - 132	0	0	10	5	0.2 - 12	
gamma-Cyhalothrin	20	30	130	99	73 - 116	0	0	10	8	0.7 - 17	
Glufosinate-ammonium	2	50	150	96	87 - 105	0	0	1	14	14 - 14	6
Glyphosate	2	50	150	77	69 - 85	0	0	1	8	8 - 8	17
Hexazinone	20	69	194	112	83 - 123	0	0	10	6	0.6 - 21	135
Hexythiazox	22	57	156	89	56 - 110	1	0	11	8	0.7 - 24	1
Imazapic	22	50	150	118	64 - 181	0	2	11	5	0.1 - 13	12
Imazapyr	22	50	150	107	65 - 160	0	2	11	5	0.4 - 11	150
Imidacloprid	22	50	150	104	91 - 120	0	0	11	6	0.2 - 12	92
Indaziflam	22	65	135	93	80 - 115	0	0	11	7	0.09 - 13	17
Isoxaben	22	65	135	114	83 - 142	0	1	11	8	0.4 - 21	6
Linuron	22	62	139	105	90 - 123	0	0	11	10	3 - 20	9
Malaoxon	22	65	135	109	94 - 128	0	0	11	5	1 - 14	
Malathion	20	49	197	117	103 - 132	0	0	10	4	0.2 - 9	31
MCPA	16	14	148	84	72 - 99	0	0	8	8	2 - 21	6
Mecoprop (MCP)	16	23	162	90	69 - 111	0	0	8	5	0.08 - 14	18
Metalaxyl	20	46	160	116	107 - 125	0	0	10	2	0.2 - 5	
Methamidophos	22	53	135	77	55 - 105	0	0	11	3	0.4 - 9	35
Methidathion	22	64	144	102	73 - 129	0	0	11	7	0.04 - 25	
Methiocarb	22	65	139	108	90 - 130	0	0	11	7	0.08 - 14	
Methomyl	22	65	135	106	95 - 122	0	0	11	4	0.7 - 10	5
Methomyl oxime	22	65	135	74	52 - 100	6	0	11	5	0.3 - 11	
Methoxyfenozide	22	59	165	114	82 - 154	0	0	11	9	0.9 - 27	26
Metolachlor	20	53	164	113	99 - 127	0	0	10	3	0.6 - 6	137
Metribuzin	20	42	122	104	86 - 116	0	0	10	4	0.2 - 11	42
Metsulfuron-methyl	22	29	190	104	50 - 137	0	0	11	7	0.5 - 12	13
MGK264	20	40	164	107	96 - 116	0	0	10	3	0.1 - 8	
Myclobutanil	22	65	135	114	90 - 135	0	0	11	9	2 - 31	26

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
N,N-diethyl-m-toluamide	20	37	179	116	102 - 127	0	0	10	4	0.1 - 10	82
Naled	20	10	187	89	69 - 119	0	0	10	8	0.5 - 18	
Napropamide	20	49	189	114	98 - 126	0	0	10	3	0.7 - 13	18
Norflurazon	20	61	198	116	107 - 128	0	0	10	4	2 - 9	117
Oryzalin	22	50	150	120	57 - 225	0	4	11	18	3 - 58	
Oxadiazon	20	41	141	108	92 - 120	0	0	10	4	0.2 - 8	19
Oxamyl	22	65	135	106	91 - 120	0	0	11	3	0.3 - 7	32
Oxamyl oxime	22	45	180	109	83 - 179	0	0	11	5	0.2 - 13	32
Oxyfluorfen	20	76	220	131	118 - 153	0	0	10	5	1 - 9	
Paclobutrazol	22	65	135	105	80 - 117	0	0	11	6	0.3 - 18	2
Pendimethalin	20	56	161	116	102 - 128	0	0	10	3	1 - 7	114
Pentachloronitrobenzene	20	37	134	104	96 - 119	0	0	10	6	0.4 - 12	1
Pentachlorophenol	16	32	136	79	55 - 95	0	0	8	8	1 - 26	6
Phenothrin	20	25	126	55	32 - 91	0	0	10	15	0.6 - 40	
Phorate	22	50	150	81	50 - 119	0	0	11	13	3 - 30	
Phosmet	20	32	246	114	102 - 138	0	0	10	5	0.1 - 16	6
Picloram	16	10	110	42	19 - 53	0	0	8	17	1 - 56	45
Piperonyl butoxide (PBO)	20	32	151	120	100 - 146	0	0	10	3	0.3 - 6	4
Prallethrin	20	30	130	118	95 - 130	0	0	10	5	0.3 - 11	
Prodiamine	20	54	185	112	97 - 134	0	0	10	5	1 - 14	
Prometon	20	36	179	111	102 - 122	0	0	10	4	0.009 - 9	109
Prometryn	20	43	183	113	100 - 122	0	0	10	3	0.4 - 9	6
Propargite	20	41	179	92	61 - 122	0	0	10	4	2 - 8	
Propiconazole	22	65	135	104	72 - 150	0	2	11	8	0.2 - 18	71
Propoxur	22	65	135	105	94 - 124	0	0	11	4	0.2 - 13	
Propyzamide	20	44	171	117	111 - 126	0	0	10	5	1 - 10	
Pyraclostrobin	22	65	135	102	78 - 130	0	0	11	7	0.3 - 21	5
Pyraflufen-ethyl	20	54	134	114	102 - 129	0	0	10	5	2 - 10	
Pyrethrins	21	50	150	88	16 - 146	1	0	10	12	5 - 26	
Pyridaben	20	53	212	100	83 - 115	0	0	10	6	0.5 - 15	2
Pyrimethanil	22	65	135	100	85 - 122	0	0	11	6	2 - 14	88

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
Pyriproxyfen	20	59	162	102	88 - 114	0	0	10	5	0.04 - 16	9
Pyroxasulfone	22	50	150	103	68 - 146	0	0	11	19	5 - 54	1
Simazine	20	43	138	108	96 - 118	0	0	10	5	1 - 8	107
Simetryn	20	31	165	107	97 - 118	0	0	10	4	0.6 - 7	1
Sodium bentazon	16	25	159	101	84 - 117	0	0	8	6	0.7 - 17	12
Spirotetramat	22	47	141	113	72 - 140	0	0	11	11	2 - 24	
Sulfentrazone	20	10	230	124	100 - 148	0	0	10	5	0.2 - 15	187
Sulfometuron methyl	22	52	156	109	75 - 143	0	0	11	6	0.4 - 19	18
Tebuthiuron	20	36	216	127	107 - 142	0	0	10	5	0.1 - 10	115
Tefluthrin	20	31	135	93	69 - 110	0	0	10	9	0.8 - 16	1
Terbacil	18	48	225	141	122 - 157	0	0	9	5	0.07 - 12	131
Tetrachlorvinphos	20	53	278	134	112 - 149	0	0	10	5	0.7 - 10	
Tetrahydrophthalimide	20	19	171	115	100 - 133	0	0	10	4	0.7 - 9	56
Tetramethrin	20	43	215	103	89 - 130	0	0	10	9	2 - 16	
Thiacloprid	22	65	156	116	95 - 129	0	0	11	6	2 - 14	
Thiamethoxam	22	50	150	84	65 - 131	0	0	11	4	0.4 - 12	130
Thiram	22	50	150	98	15 - 222	4	4	11	10	0.8 - 29	
Total cyfluthrin	20	50	150	105	77 - 124	0	0	10	9	0.9 - 16	
Total cyhalothrin	20	30	130	100	74 - 116	0	0	10	8	0.8 - 17	
Total ypermethrin	20	50	150	109	78 - 127	0	0	10	8	0.2 - 17	
tau-Fluvalinate	20	23	194	107	75 - 128	0	0	10	7	0.05 - 18	
Tralomethrin	20	10	184	107	74 - 122	0	0	10	7	0.5 - 17	1
trans-Permethrin	20	59	197	97	70 - 114	0	0	10	8	0.1 - 20	
Triadimefon	20	59	181	118	104 - 128	0	0	10	4	1 - 7	18
Triallate	20	24	160	98	85 - 109	0	0	10	4	0.3 - 9	16
Triazine DEA degradate	22	65	147	98	84 - 127	0	0	11	4	0.4 - 8	98
Triazine DIA degradate	22	65	142	98	81 - 141	0	0	11	5	0.4 - 12	62
Triazine HA degradate	22	65	152	102	80 - 136	0	0	11	4	1 - 9	214
Triclopyr acid	16	10	190	98	86 - 109	0	0	8	6	0.5 - 15	49
Triclopyr butoxyethyl ester	20	52	163	111	95 - 132	0	0	10	4	0.6 - 9	1

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	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 RPDs* (%)	Total detections (n)
Triclosan	20	42	147	131	107 - 154	0	1	10	6	0.8 - 25	4
Trifloxystrobin	22	64	147	97	70 - 134	0	0	11	8	1 - 24	
Trifluralin	20	49	174	103	91 - 121	0	0	10	4	0.4 - 9	30
Zoxamide	22	65	135	101	77 - 128	0	0	11	8	0.2 - 23	

* RPD control limit for all pesticide analytes was 40%.

There were a total of 3,387 spiked results (1,693 MS/MSD pairs) from MS and MSD recoveries that were unqualified or *J* qualified. Overall, the mean recovery was 106% with a standard deviation of 29%. The percentage of analyte recoveries from MS/MSD samples that were above, below, or fell within the laboratory control limits are as follows:

- < 1% of analyte recoveries (13 recoveries) fell below the control limits for MS/MSD samples,
- 98% of analyte recoveries (1,616 recoveries) were within the control limits for MS/MSD samples,
- 2% of analyte recoveries (64 recoveries) were above the control limits for MS/MSD samples.

RPDs calculated for 1,693 MS/MSD pairs were below the 40% RPD control limit 99% of the time; only four pairs had RPDs above the control limit. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 7% with a standard deviation of 6%. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 52% with a standard deviation of 8%.

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

Laboratory Blanks

MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. Lab blanks also provide a method to measure the response of an analytical process to the analyte at a theoretical concentration of zero, helping to determine at what concentration samples can be distinguished from background noise. If lab blank detections occur, the sample LLOQ may be increased, and detections may be qualified as estimates. Table 37b lists the analyte detections that occurred in the laboratory blanks (325 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 37b – Analyte detections in laboratory blanks

Analyte	Analytical method	Blank detections (n)	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
2,6-Dichlorobenzamide	GCMS-Pesticides	12	1.0	0.344	3.09	5	1.3
4,4'-DDD	GCMS-Pesticides	16	1.1	0.860	1.40	5	0.7
4,4'-DDE	GCMS-Pesticides	13	0.7	0.027	1.11	5	1.4
4,4'-DDT	GCMS-Pesticides	28	1.4	0.700	3.03	5	0.8
AMPA	LCMS-Glyphos	7	241.1	41.4	1,110	31	2.5
Atrazine	GCMS-Pesticides	2	0.9	0.619	1.11	5	2.2
Azoxystrobin	LCMS-Pesticides	2	0.4	0.378	0.477	20	1.9
Boscalid	GCMS-Pesticides	4	1.2	1.02	1.47	5	0.5
Carbaryl	LCMS-Pesticides	2	0.6	0.520	0.683	20	2.2
Carbendazim	LCMS-Pesticides	19	1.3	0.247	5.86	10	1.2
Chlorothalonil	GCMS-Pesticides	2	1.3	0.843	1.72	5	1.2
Chlorpyrifos	GCMS-Pesticides	1	1.5	1.54	1.54	5	1.1
Cyprodinil	LCMS-Pesticides	1	1.5	1.50	1.50	10	4.0
Dichlobenil	GCMS-Pesticides	20	0.5	0.097	1.12	5	1.4
Dichlorvos (DDVP)	GCMS-Pesticides	1	0.3	0.271	0.271	5	0.5
Difenoconazole	LCMS-Pesticides	3	1.9	1.10	2.75	20	4.9
Dithiopyr	GCMS-Pesticides	1	0.4	0.426	0.426	5	1.7
Ethoprop	GCMS-Pesticides	2	1.3	1.02	1.59	5	1.4
Fenarimol	GCMS-Pesticides	26	4.4	1.16	20.8	5	1.1
Fenbutatin oxide	LCMS-Pesticides	16	4.8	2.32	9.11	20	3.0
Fluopicolide	LCMS-Pesticides	1	0.8	0.790	0.790	10	3.0
Glufosinate-ammonium	LCMS-Glyphos	3	6.0	4.20	8.47	7	3.4
Glyphosate	LCMS-Glyphos	5	17.1	8.53	22.9	13	2.5
Hexazinone	GCMS-Pesticides	5	2.6	1.53	3.98	5	1.0
Hexythiazox	LCMS-Pesticides	4	2.9	0.455	6.51	10	1.6
Indaziflam	LCMS-Pesticides	1	0.4	0.394	0.394	10	1.8
Methomyl	LCMS-Pesticides	9	0.4	0.288	0.674	10	0.7
Methomyl oxime	LCMS-Pesticides	1	9.5	9.46	9.46	100	8.7
Methoxyfenozide	LCMS-Pesticides	1	0.5	0.504	0.504	10	2.3
Metolachlor	GCMS-Pesticides	4	1.6	1.39	1.68	5	0.6
Metsulfuron-methyl	LCMS-Pesticides	1	7.2	7.15	7.15	50	3.7
Myclobutanil	LCMS-Pesticides	1	2.3	2.32	2.32	20	4.3

Analyte	Analytical method	Blank detections (n)	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
N,N-diethyl-m-toluamide	GCMS-Pesticides	26	1.7	0.693	4.06	5	1.3
Oryzalin	LCMS-Pesticides	1	73.5	73.5	73.5	200	62.3
Oxamyl	LCMS-Pesticides	2	0.3	0.295	0.337	10	0.8
Paclobutrazol	LCMS-Pesticides	1	2.8	2.80	2.80	10	1.6
Phosmet	GCMS-Pesticides	4	3.2	1.27	6.15	5	1.6
Propiconazole	LCMS-Pesticides	11	1.9	0.756	2.97	50	3.5
Propyzamide (pronamide)	GCMS-Pesticides	3	0.5	0.449	0.714	5	1.4
Pyraclostrobin	LCMS-Pesticides	6	1.1	0.632	2.48	50	2.1
Pyridaben	GCMS-Pesticides	2	0.8	0.758	0.805	5	1.1
Pyrimethanil	LCMS-Pesticides	6	0.8	0.372	1.06	10	1.8
Pyriproxyfen	GCMS-Pesticides	8	1.6	0.982	2.13	10	1.4
Tetrahydrophthalimide	GCMS-Pesticides	1	1.5	1.54	1.54	5	1.2
Thiamethoxam	LCMS-Pesticides	1	0.5	0.513	0.513	20	4.2
Thiram	LCMS-Pesticides	9	68.5	5.82	135	72	9.2
Triadimefon	GCMS-Pesticides	3	2.1	1.83	2.52	5	1.5
Triazine HA degradate	LCMS-Pesticides	3	0.4	0.246	0.612	10	1.1
Triclopyr butoxyethyl ester	GCMS-Pesticides	1	0.7	0.722	0.722	10	1.3
Triclosan	GCMS-Pesticides	20	4.4	1.01	13.9	10	1.7
Trifloxystrobin	LCMS-Pesticides	3	0.6	0.461	0.767	20	1.7

Surrogates

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

Table 38b – Pesticide surrogates

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
<u>Carbamate pesticides:</u>						
Carbaryl C13	LCMS-Pesticides	303	99	100.0	67	132
Carbendazim-D4	LCMS-Pesticides	303	91	100.0	50	150

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
<u>Acid-derivitizable herbicides:</u>						
2,4,6-Tribromophenol	GCMS-Herbicides	279	87	100.0	41	116
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	279	82	100.0	31	149
<u>Nitrogen containing pesticides:</u>						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	333	92	98.2	53	124
<u>Chlorinated pesticides:</u>						
4,4'-DDE-13C12	GCMS-Pesticides	333	90	99.1	61	113
Decachlorobiphenyl (DCB)	GCMS-Pesticides	333	67	99.7	30	124
<u>Glyphosate related pesticides:</u>						
AMPA-C13N15	LCMS-Glyphos	19	103	94.7	20	200
Glyphosate-C13N15	LCMS-Glyphos	21	88	95.2	20	200
<u>Neonicotinoid pesticides:</u>						
Clothianidin-D3	LCMS-Pesticides	303	79	100.0	50	150
Clothianidin-D3-Neg	LCMS-Pesticides	303	95	99.3	50	150
Difenoconazole-D4	LCMS-Pesticides	303	84	96.0	50	150
<u>Organophosphate pesticides:</u>						
Chlorpyrifos-D10	GCMS-Pesticides	333	103	98.5	76	157
Triphenyl phosphate	GCMS-Pesticides	333	118	99.4	49	167
<u>Chlorine and nitrogen containing pesticides:</u>						
Trifluralin-D14	GCMS-Pesticides	333	100	99.7	64	165
Atrazine-D5	GCMS-Pesticides	333	106	97.0	80	147

This was the first year neonicotinoid surrogates were used by the laboratory to identify possible matrix interference. In 2020, the overall mean recovery for surrogates was 93% and 99% of surrogate recoveries were within control limits.

Laboratory Control Samples

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

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

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
1-(3,4-Dichlorophenyl)-3 methylurea	52	63	154	106	91 - 124	0	0	26	7	0.6 - 16
2,4-D	56	10	147	85	49 - 108	0	0	28	9	0.7 - 45
2,6-Dichlorobenzamide	58	30	140	101	24 - 131	1	0	29	7	0.4 - 122
3,5-Dichlorobenzoic Acid	56	14	135	70	42 - 91	0	0	28	9	0.4 - 47
4,4'-DDD	58	64	138	110	34 - 129	1	0	29	6	0.3 - 109
4,4'-DDE	58	43	140	100	42 - 113	1	0	29	6	0.2 - 86
4,4'-DDT	58	49	148	112	44 - 132	1	0	29	6	0.09 - 93
4-Nitrophenol	56	11	187	109	47 - 161	0	0	28	18	0.08 - 67
Acephate	52	65	135	108	93 - 124	0	0	26	5	0.06 - 17
Acetamiprid	52	65	135	108	93 - 128	0	0	26	6	0.07 - 20
Acetochlor	58	30	130	108	20 - 121	1	0	29	7	0.2 - 137
Acetochlor ESA	52	54	155	100	66 - 165	0	1	26	15	0.9 - 43
Afidopyropen	52	57	135	100	62 - 137	0	1	26	12	0.4 - 42
Alachlor	58	13	184	109	21 - 123	0	0	29	7	0.5 - 138
Aldicarb sulfoxide	52	65	138	106	94 - 127	0	0	26	6	0.4 - 17
Aminocyclopyrachlor	52	50	150	94	61 - 115	0	0	26	6	0.2 - 20
AMPA	18	50	150	108	80 - 185	0	2	9	9	0.8 - 20
Atrazine	58	14	178	106	25 - 125	0	0	29	7	0.05 - 127
Azinphos-ethyl	52	50	150	95	62 - 133	0	0	26	14	0.3 - 35
Azinphos-methyl	52	50	150	98	64 - 125	0	0	26	13	0.4 - 33
Azoxystrobin	52	65	135	109	73 - 144	0	2	26	9	0.5 - 25
Benfluralin	58	44	143	98	22 - 113	1	0	29	8	0.02 - 127
Bensulide	52	46	153	94	63 - 124	0	0	26	11	0.3 - 39
Bifenazate	58	50	150	102	17 - 433	6	7	29	12	0.07 - 117
Bifenthrin	58	30	130	95	39 - 116	0	0	29	8	0.4 - 85
Boscalid	58	50	150	111	20 - 128	1	0	29	8	0.1 - 140
Bromacil	58	58	170	123	30 - 146	1	0	29	7	0.1 - 131
Bromoxynil	56	32	128	94	59 - 112	0	0	28	7	0.1 - 38
Captan	52	36	168	29	2 - 124	40	0	26	23	1 - 125

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Carbaryl	52	65	140	108	92 - 134	0	0	26	6	0.2 - 18
Carbendazim	52	65	140	104	84 - 125	0	0	26	5	0.2 - 17
Chlorantraniliprole	52	64	135	105	72 - 139	0	1	26	10	0.3 - 32
Chlorethoxyfos	58	30	130	96	18 - 119	1	0	29	9	0.4 - 135
Chlorothalonil	58	86	221	104	24 - 117	4	0	29	8	0.02 - 128
Chlorpropham	58	58	150	111	24 - 135	1	0	29	7	0.1 - 129
Chlorpyrifos	58	64	146	101	24 - 119	1	0	29	7	0.3 - 127
Chlorpyrifos-methyl	58	58	135	102	20 - 122	1	0	29	7	0.1 - 134
Chlorsulfuron	52	22	150	88	42 - 131	0	0	26	10	0.4 - 28
cis-Permethrin	58	48	178	101	45 - 126	1	0	29	7	0.08 - 81
Clopyralid	56	10	119	48	26 - 71	0	0	28	14	0.5 - 59
Clothianidin	52	61	135	106	90 - 128	0	0	26	9	1 - 25
Coumaphos	58	65	207	120	25 - 141	1	0	29	8	0.2 - 134
Cyantraniliprole	52	50	150	104	74 - 146	0	0	26	8	0.2 - 25
Cycloate	58	50	141	105	24 - 126	1	0	29	8	0.08 - 125
Cyprodinil	52	64	135	100	79 - 121	0	0	26	6	0.6 - 19
Dacthal (DCPA)	56	40	154	101	57 - 118	0	0	28	7	0.1 - 49
Deltamethrin	58	30	130	102	40 - 121	0	0	29	8	0.4 - 92
Diazinon	58	70	142	105	19 - 128	1	0	29	7	0.03 - 139
Dicamba acid	56	12	138	77	47 - 94	0	0	28	8	0.006 - 45
Dichlobenil	58	44	139	100	24 - 115	1	0	29	8	0.3 - 123
Dichlorprop	56	16	153	85	50 - 102	0	0	28	7	0.02 - 47
Dichlorvos (DDVP)	58	39	145	106	23 - 136	1	0	29	8	0.3 - 128
Dicofol	58	31	179	271	51 - 510	0	52	29	9	0.2 - 128
Difenoconazole	52	64	135	97	69 - 122	0	0	26	9	0.1 - 30
Diflubenzuron	52	50	171	102	73 - 128	0	0	26	11	0.3 - 29
Dimethoate	58	48	206	107	23 - 132	1	0	29	7	0.2 - 130
Dinotefuran	52	65	135	106	62 - 130	2	0	26	5	0.08 - 17
Dithiopyr	58	30	130	98	18 - 119	1	0	29	8	0.02 - 140
Diuron	52	65	135	107	89 - 129	0	0	26	7	0.7 - 16
Eptam	58	48	142	98	21 - 120	1	0	29	8	0.007 - 127

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
ES fenvalerate	58	30	130	94	40 - 110	0	0	29	8	0.5 - 86
Ethalfuralin	58	31	167	100	18 - 117	1	0	29	8	0.1 - 138
Ethoprop	58	55	163	110	22 - 134	1	0	29	8	0.2 - 132
Etoxazole	58	50	150	101	28 - 124	1	0	29	8	0.03 - 114
Etridiazole	58	30	130	109	27 - 124	1	0	29	7	0.2 - 123
Fenarimol	58	30	130	119	19 - 152	1	14	29	9	0.06 - 141
Fenbuconazole	52	65	135	107	66 - 144	0	2	26	9	0.05 - 29
Fenbutatin oxide	52	10	135	85	46 - 126	0	0	26	9	0.9 - 28
Fenpropathrin	58	30	130	98	37 - 114	0	0	29	8	0.3 - 92
Fipronil	58	30	130	110	20 - 132	1	1	29	8	0.2 - 143
Fipronil disulfanyl	58	30	130	104	19 - 125	1	0	29	7	0.3 - 140
Fipronil sulfide	58	30	130	104	17 - 124	1	0	29	8	0.2 - 146
Fipronil sulfone	58	30	130	110	19 - 136	1	2	29	8	0.2 - 147
Fludioxonil	58	30	130	119	23 - 144	1	10	29	7	0.005 - 131
Flumioxazin	56	30	130	42	0 - 104	15	0	26	18	1 - 145
Fluopicolide	52	50	150	107	74 - 145	0	0	26	9	0.7 - 25
Fluroxypyr 1-methylheptyl ester	58	30	130	106	35 - 131	0	2	29	8	0.3 - 101
gamma-Cyhalothrin	58	30	130	94	38 - 113	0	0	29	9	0.05 - 91
Glufosinate-ammonium	18	50	150	108	81 - 136	0	0	9	10	3 - 30
Glyphosate	18	50	150	96	85 - 110	0	0	9	4	0.8 - 14
Hexazinone	58	69	150	114	24 - 132	1	0	29	8	0.4 - 130
Hexythiazox	52	62	141	97	70 - 134	0	0	26	9	0.1 - 22
Imazapic	52	63	145	104	79 - 130	0	0	26	8	0.3 - 27
Imazapyr	52	65	135	101	74 - 132	0	0	26	6	0.2 - 27
Imidacloprid	52	52	148	103	85 - 129	0	0	26	8	0.5 - 33
Indaziflam	52	65	135	103	80 - 128	0	0	26	8	0.3 - 22
Isoxaben	52	65	135	109	74 - 145	0	4	26	9	0.07 - 32
Linuron	52	64	145	103	79 - 126	0	0	26	11	0.9 - 28
Malaoxon	52	65	135	107	87 - 128	0	0	26	7	0.6 - 18
Malathion	58	61	138	107	20 - 128	1	0	29	8	0.2 - 139

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
MCPA	56	13	139	85	51 - 108	0	0	28	8	0.2 - 40
Mecoprop (MCP)	56	23	148	92	56 - 112	0	0	28	7	0.3 - 40
Metalaxyl	58	59	153	112	22 - 125	1	0	29	7	0.1 - 137
Methamidophos	52	65	135	107	89 - 131	0	0	26	6	0.1 - 19
Methidathion	52	65	145	104	72 - 150	0	1	26	9	0.04 - 26
Methiocarb	52	65	151	107	82 - 137	0	0	26	9	0.06 - 28
Methomyl	52	65	135	107	91 - 122	0	0	26	6	0.09 - 16
Methomyl oxime	52	65	143	96	67 - 130	0	0	26	7	0.2 - 22
Methoxyfenozide	52	49	162	110	74 - 138	0	0	26	9	0.6 - 29
Metolachlor	58	68	158	109	20 - 122	1	0	29	7	0.2 - 142
Metribuzin	58	30	130	99	21 - 116	1	0	29	7	0.2 - 132
Metsulfuron-methyl	52	19	159	90	35 - 124	0	0	26	9	0.04 - 27
MGK264	58	71	169	102	20 - 120	3	0	29	7	0.07 - 140
Myclobutanil	52	65	135	108	75 - 136	0	1	26	9	0.3 - 23
N,N-diethyl-m-toluamide	58	30	130	109	24 - 129	1	0	29	7	0.06 - 128
Naled	58	22	159	100	27 - 139	0	0	29	8	0.1 - 127
Napropamide	58	82	176	109	20 - 135	3	0	29	7	0.2 - 137
Norflurazon	58	85	143	113	29 - 139	3	0	29	7	0.07 - 123
Oryzalin	52	50	150	105	53 - 156	0	2	26	19	1 - 52
Oxadiazon	58	30	130	104	19 - 121	1	0	29	8	0.4 - 139
Oxamyl	52	65	135	108	94 - 129	0	0	26	5	0.5 - 16
Oxamyl oxime	52	53	135	98	42 - 126	2	0	26	7	0.3 - 17
Oxyfluorfen	58	42	154	121	38 - 146	1	0	29	7	0.3 - 115
Paclobutrazol	52	65	135	107	82 - 128	0	0	26	7	0.2 - 18
Pendimethalin	58	49	159	109	29 - 123	1	0	29	7	0.04 - 121
Pentachloronitrobenzene	58	30	130	101	26 - 115	1	0	29	7	0.02 - 121
Pentachlorophenol	56	32	125	81	52 - 102	0	0	28	8	0.1 - 47
Phenothrin	58	20	95	60	22 - 79	0	0	29	15	0.5 - 72
Phorate	52	50	150	85	48 - 117	1	0	26	12	0.7 - 29
Phosmet	58	44	190	66	4 - 110	11	0	29	13	0.2 - 130
Picloram	56	10	110	39	8 - 110	2	0	28	31	1 - 103

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Piperonyl butoxide (PBO)	58	30	130	110	22 - 138	1	8	29	7	0.4 - 134
Prallethrin	58	30	130	102	19 - 134	1	1	29	9	0.02 - 137
Prodiamine	58	30	130	105	23 - 129	1	0	29	8	0.07 - 135
Prometon	58	59	161	107	24 - 133	1	0	29	7	0.02 - 129
Prometryn	58	60	160	108	23 - 130	1	0	29	7	0.3 - 133
Propargite	58	30	130	92	24 - 125	1	0	29	8	0.2 - 115
Propiconazole	52	61	135	102	65 - 146	0	3	26	10	2 - 32
Propoxur	52	65	140	108	86 - 131	0	0	26	7	0.6 - 16
Propyzamide (pronamide)	58	74	150	110	22 - 131	3	0	29	7	0.03 - 131
Pyraclostrobin	52	65	137	103	76 - 129	0	0	26	8	0.4 - 22
Pyraflufen-ethyl	58	30	130	108	24 - 141	1	3	29	8	0.3 - 128
Pyrethrins	52	50	150	88	13 - 197	6	2	26	15	0.5 - 53
Pyridaben	58	30	130	103	34 - 123	0	0	29	8	0.1 - 105
Pyrimethanil	52	65	137	106	83 - 127	0	0	26	6	0.1 - 16
Pyriproxyfen	58	30	130	104	28 - 123	1	0	29	7	0.08 - 115
Pyroxasulfone	52	50	150	104	56 - 154	0	1	26	14	0.2 - 41
Simazine	58	80	184	107	25 - 129	3	0	29	7	0.5 - 128
Simetryn	58	44	168	103	23 - 122	1	0	29	7	0.02 - 129
Sodium bentazon	56	35	152	105	59 - 123	0	0	28	7	0.2 - 44
Spirotetramat	52	46	135	102	46 - 148	0	1	26	11	1 - 34
Sulfentrazone	58	30	130	56	18 - 137	8	1	29	27	1 - 125
Sulfometuron methyl	52	52	135	100	73 - 132	0	0	26	6	0.2 - 17
Tebuthiuron	58	10	94	111	15 - 146	0	46	29	9	0.2 - 127
Tefluthrin	58	30	130	89	42 - 110	0	0	29	6	0.4 - 66
Terbacil	58	57	183	123	27 - 143	1	0	29	8	0.2 - 129
Tetrachlorvinphos	58	84	176	121	26 - 139	2	0	29	7	0.03 - 135
Tetrahydrophthalimide	58	50	150	82	24 - 102	1	0	29	8	0.08 - 113
Tetramethrin	58	30	130	74	18 - 107	3	0	29	11	0.4 - 138
Thiacloprid	52	65	135	107	89 - 128	0	0	26	6	0.06 - 26
Thiamethoxam	52	53	143	107	87 - 141	0	0	26	8	0.1 - 25
Thiram	52	50	150	91	12 - 176	6	5	26	12	0.06 - 36

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Total cyfluthrin	58	30	130	103	37 - 123	0	0	29	7	0.06 - 97
Total cyhalothrin	58	30	130	98	38 - 117	0	0	29	8	0.4 - 92
Total cypermethrin	58	30	130	105	39 - 131	0	1	29	8	0.3 - 93
tau-Fluvalinate	58	30	130	101	44 - 127	0	0	29	8	0.5 - 88
Tralomethrin	58	30	130	102	40 - 121	0	0	29	8	0.6 - 92
trans-Permethrin	58	30	130	101	43 - 125	0	0	29	8	0.3 - 85
Triadimefon	58	74	166	112	22 - 131	1	0	29	7	0.02 - 137
Triallate	58	58	126	97	21 - 120	1	0	29	8	0.009 - 126
Triazine DEA degradate	52	65	152	101	60 - 122	2	0	26	5	0.2 - 18
Triazine DIA degradate	52	65	139	101	63 - 125	2	0	26	5	0.2 - 19
Triazine HA degradate	52	65	156	104	83 - 123	0	0	26	6	0.2 - 17
Triclopyr acid	56	10	183	100	59 - 124	0	0	28	7	0.06 - 48
Triclopyr butoxyethyl ester	58	30	130	106	23 - 138	1	2	29	7	0.2 - 130
Triclosan	58	30	130	111	29 - 186	1	8	29	9	0.04 - 147
Trifloxystrobin	52	63	149	99	74 - 126	0	0	26	9	0.2 - 25
Trifluralin	58	41	173	98	20 - 114	1	0	29	8	0.4 - 133
Zoxamide	52	65	137	103	79 - 129	0	0	26	9	0.6 - 22

*RPD control limit for all pesticide analytes was 40%.

There were a total of 9,274 spiked results from LCS and LCSD recoveries that were unqualified or *J* qualified. Overall, the mean recovery was 101% with a standard deviation of 27%. The percentage of analyte recoveries from LCS/LCSD samples that were above, below, or fell within the laboratory control limits are as follows:

- 2% of analyte recoveries (184 recoveries) fell below the control limits for LCS/LCSD samples,
- 96% of analyte recoveries (8,903 recoveries) were within the control limits for LCS/LCSD samples,
- 2% of analyte recoveries (187 recoveries) were above the control limits for LCS/LCSD samples.

RPDs calculated for 4,635 LCS/LCSD pairs were below the 40% RPD control limit 97% of the time; 129 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 6% with a standard deviation of 6%. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 102% with a standard deviation of 36%.

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.

Additional Inorganic Chemical and Parameter Analysis

MEL uses split sample duplicates to evaluate the precision of nutrients, TSS, and specific conductivity analyses per batch (Table 40b). No field TSS samples were qualified due solely to RPD exceedances. Overall, laboratory duplicate results were of acceptable data quality.

Table 40b – Laboratory duplicate results

Analyte or parameter	Results (n)	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Ammonia	28	20	0	0
Nitrate-Nitrite as N	28	20	0	0
ortho-Phosphate	55	20	0	0
Specific conductivity	5	20	0	0
Total phosphorus	22	20	0	0
Total suspended solids	92	20	2	2

Unlike the pesticide analytes assessed with LCS/LCSD, the analytes and parameters in Table 41b did not have a duplicate spiked LCS sample so there were no RPDs to assess. LCS/LCSD analysis does not have to be completed for inorganic analytes or parameters as per their prescribed laboratory methods. LCS recoveries of the additional analytes or parameters were of acceptable data quality.

Table 41b: Summary statistics for LCS recoveries of additional analytes and parameters

Analyte or parameter	LCS recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)
Ammonia	28	80	120	101	93 - 106
Nitrate-Nitrite as N	28	80	120	99	96 - 102
ortho-Phosphate	55	80	120	102	92 - 118
Specific conductivity	5	95	105	100	100 - 100
Total phosphorus	22	80	120	103	98 - 108
Total suspended solids	58	80	120	96	78 - 108

Field Data Quality Control Measures

A YSI ProDSS field meter was used at every sampling event. The field meters were calibrated the evening before, or the morning of the first field day of the week according to NRAS SOP: YSI ProDSS (Bischof 2020). All field meters were post-checked, using known standards, at the end of the sampling week.

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

Streamflow measurements were taken with OTT MF Pro flow meters and top-setting wading rods for sites that did not already have established gaging stations managed by other agencies. Each flow meter was calibrated the morning of the first day of the week as described in the OTT MF Pro Basic User Manual (OTT, 2018). A streamflow replicate measurement was taken once a week at a randomly selected site for each flow meter used in Central and Western monitoring sites.

Field Data Collection Performance

Quality control results for two different conventional water quality parameter replicates are shown below in Table 42b. Precision of the conductivity and streamflow replicates was gauged by relative standard deviation (RSD). Data that did not meet measurement quality objectives (MQOs) were qualified. Replicates were conducted at every site but Dry Creek.

Table 42b – Quality control results for conventional water quality parameter replicates

Replicate parameter	MQO	Western Washington		Central Washington	
		Mean	Maximum	Mean	Maximum
Specific conductivity (field meter vs. laboratory)	10% RSD	1% RSD	1% RSD	1% RSD	3% RSD
Streamflow	10% RSD	2% RSD	5% RSD	3% RSD	9% RSD

The field meters for the streamflow replicates met MQOs for all monitoring locations the replicates were conducted at. The specific conductivity replicate at Indian Slough was considered an outlier and excluded from this analysis (10% RSD). Indian Slough's specific conductivity can vary thousands of $\mu\text{S}/\text{cm}$ within a 2 ft. water depth.

Field Meter Performance

Table 43b describes measurement quality objectives for field meter post-checks as described in the WSDA QAPP (Bischof et al. 2020).

Table 43b – Measurement quality objectives for YSI ProDSS post-checks

Parameter	Units	Accept	Qualify	Reject	Resolution
pH	standard units	$\leq \pm 0.25$	$> \pm 0.25$ and $\leq \pm 0.5$	$> \pm 0.5$	0.1
Water temperature	$^{\circ}\text{C}$	± 0.2	N/A	$> \pm 0.2$	0.1
Conductivity*	$\mu\text{S}/\text{cm}$	$\leq \pm 5\%$ RSD	$> \pm 5\%$ and $\leq \pm 15\%$ RSD	$> \pm 15\%$ RSD	0.1
DO*	mg/L	$\leq \pm 5\%$ RSD	$> \pm 5\%$ and $\leq \pm 10\%$ RSD	$> \pm 10\%$ RSD	0.1

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

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

- Central YSI meter pH post-check failed MQOs the week of November 9.
 - The two field pH readings taken by the Central YSI meter between the pre-check and post-check were rejected.
- Central YSI meter DO post-check failed MQOs the weeks of July 6, July 20 and August 10.
 - The 24 field DO readings taken by the Central YSI meter between the pre-checks and post-checks were qualified as estimates due to a 6% RSD for each of the three pre/post-checks.
- Westside YSI meter pH post-check failed MQOs the week of July 13.
 - The seven field pH readings taken by the Westside YSI meter between the pre-check and post-check were rejected. The pH sensor was replaced before the next week's calibration.

Field Audit

The purpose of the field audit was to ensure sampling methodologies were consistent for all field teams. For field audits, teams met at a wadable stream to measure 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 March 5, 2020, the Central and Westside NRAS surface water monitoring teams and the Palouse Conservation District monitoring team conducted a field audit to compare 2020 sampling procedures. Each team calibrated their YSI ProDSS meter the morning of March 5 in the WSDA Yakima Office located in Yakima, Washington. Each team then proceeded to Ahtanum Creek (46.538512, -120.480397) near Union Gap in Yakima County, Washington to conduct the field audit. All ProDSS meters were placed in the same location in the stream upon site arrival to allow ample time to equilibrate to stream conditions while each team measured streamflow. Using the same transect, each team consecutively measured streamflow using their own OTT MF Pro flow meter. The Central team was the first to measure streamflow, followed by Westside, and then Palouse. Each team's flow measurement required approximately 40 minutes to complete. After flow was measured, values from each team's ProDSS meters were recorded. Results and RSDs are displayed in Table 44b.

Table 44b - Conventional water quality parameters and flow data from field audit

Team	Temperature (°C)	pH	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Westside	7.2	8.1	175.1	12.5	107.1	38.8
Central	7.2	8.2	174.9	12.7	108.8	41.7
Palouse	7.2	8.1	182.8	12.8	109.3	47.5
All 3	±0.0° C	1% RSD	3% RSD	±0.3 mg/L	1% RSD	>10% RSD
MQO	±0.2° C	10% RSD	10% RSD	±0.2 mg/L	10% RSD	10% RSD

Field meters met MQOs except for DO (mg/L) and streamflow. Variability in DO was likely due to calibrating new DO sensor caps for the first use at the field audit. DO data for the sampling season was used with caution and qualified. Streamflow did not meet the MQO due to variation in each team's measured velocities. Palouse's flow meter had higher velocities in general compared to Central or West team's flow meter. Staff compared the Central flow meter with the Palouse flow meter one more time before the field season and the Palouse meter still had high velocities so the meter was replaced with a new one.

Only the Westside team was able to post-check their YSI field meter. The YSI meter post-check passed MQOs found in Table 43b.

Quality Assurance Summary References

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