Ambient Monitoring for Pesticides in Washington State Surface Water

2021 Technical Report

February 2024

Washington State Department of Agriculture
Natural Resources and Agricultural Sciences
Derek I. Sandison, Director

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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 2021, WSDA's Natural Resources and Agricultural Sciences team (NRAS) collected surface water samples weekly or biweekly from March into November at 18 monitoring sites. 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, King, Skagit, Walla Walla, Whatcom, Whitman and Yakima counties with watershed areas ranging from 2,000 acres to over 350,000 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 the watersheds sampled in 2021 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, diuron, and imidacloprid. Additional pesticides identified as watershed POCs were bifenthrin, clothianidin, deltamethrin, diazinon, fipronil, gamma-cyhalothrin, indaziflam, malathion, metsulfuron-methyl, permethrin, pyriproxyfen, pyroxasulfone, and tau-fluvalinate.

This report summarizes activities and data from the 18 separate sites selected for the 2021 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 316 surface water sampling events between March 15 and November 9.
- Out of 173 pesticide active ingredients and breakdown products tested for, there were 120 unique pesticides detected.
- There were 4,928 positively identified pesticide detections.
- Mixtures of two or more pesticides were detected at each sampling event.
- Sulfentrazone was the most frequently detected herbicide (167 times), boscalid was the most frequently detected fungicide (207 times), and thiamethoxam was the most frequently detected insecticide (111 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 234. Detections of this analyte occurred at over 75% of sampling events.

- There were 388 unique pesticide detections with concentrations exceeding WSDA assessment criteria (8% of total detections), approaching levels that could adversely affect aquatic life.
  - Legacy pesticides and their breakdown products accounted for 178 of the exceedances (~46% of total exceedances). The chemicals include:
    - 4,4'-DDD (89 exceedances),
    - 4,4'-DDE (66 exceedances),
    - 4,4'-DDT (23 exceedances).
  - Current-use pesticides accounted for 210 of the exceedances (~54% of total exceedances). The chemicals include:
    - bifenthrin (1 exceedance),
    - carbaryl (1 exceedance),
    - chlorpyrifos (81 exceedances),
    - cis-permethrin (1 exceedance),
    - clothianidin (7 exceedances),
    - diazinon (2 exceedances),
    - dichlorvos (DDVP) (1 exceedance),
    - diuron (11 exceedances),
    - fenbutatin oxide (1 exceedance),
    - fipronil (18 exceedances),
    - gamma-cyhalothrin (5 exceedances),
    - imidacloprid (68 exceedances),
    - malathion (7 exceedances),
    - metsulfuron-methyl (2 exceedances),
    - pyriproxyfen (Nylar) (3 exceedances), and
    - pyroxasulfone (1 exceedance).

Of the 388 detections that exceeded WSDA assessment criteria, many (73% or 284 detections) also exceeded state, national, or toxicity study criteria. Current-use pesticides accounted for 37% (106 detections) of those exceedances without the WSDA safety factor. The detection of bifenthrin exceeded not only the WSDA assessment criteria, but also its acute fish toxicity study criterion and chronic fish and chronic invertebrate toxicity study criteria. Chlorpyrifos, found at 12 of the 18 monitoring sites, exceeded the chronic invertebrate toxicity study criterion 43 times out of a total of 84 detections; 15 of those detections also exceeded the acute invertebrate criterion. Another insecticide detected frequently, imidacloprid, exceeded the chronic invertebrate toxicity study criterion 43 times out of 75 detections and was found at 14 of the 18 monitoring sites. Two reasons chlorpyrifos and imidacloprid are detected so often exceeding toxicity study criteria is that they have very low laboratory method detection levels, low chronic toxicity criteria, and common usage across the state. Other pesticides detected less often that still exceeded state, national, or toxicity study criteria included carbaryl, cis-permethrin, clothianidin, diazinon, diuron, fipronil, gamma-cyhalothrin, malathion, and pyriproxyfen. Legacy insecticide DDT and its associated degradates accounted for the remaining 63% (178 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 2022). At least one conventional water quality parameter did not meet state water quality standards on one or more occasions at 17 of the 18 monitoring sites. Nutrient samples were collected at six monitoring sites; four that were sampled in 2020 with the addition of two sites in the Palouse Region. 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 six 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 and Agricultural Sciences team 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 2021.
- 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 2021 in March through October throughout the state. During the first year of monitoring (2003), NRAS sampled nine monitoring sites in agricultural and urban areas. By 2021, the program has expanded to 18 monitoring sites, including two of the nine original sites. WSDA has monitored surface water in 25 unique watersheds since the start of the program. For the 2021 monitoring season, the Lower Crab Creek site in Grant County was discontinued and replaced with the Ahtanum Creek site in Yakima County; and the Kamiache Creek and Thorn Creek sites in Whitman County were added.

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 2021, NRAS tested for 173 chemicals, with 120 confirmed chemicals detected in surface water samples. Between the 2020 and 2021 monitoring seasons, 8 chemicals were added to the testing list. The list of chemicals analyzed for every year may change because of new use restrictions, changes in pesticide registration, analytical cost, or lack of detections in surface water.

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 2022). Figure 1 shows the boundaries of the 9 subbasins that NRAS sampled in 2021, identified by their WRIA codes and corresponding subbasin names.

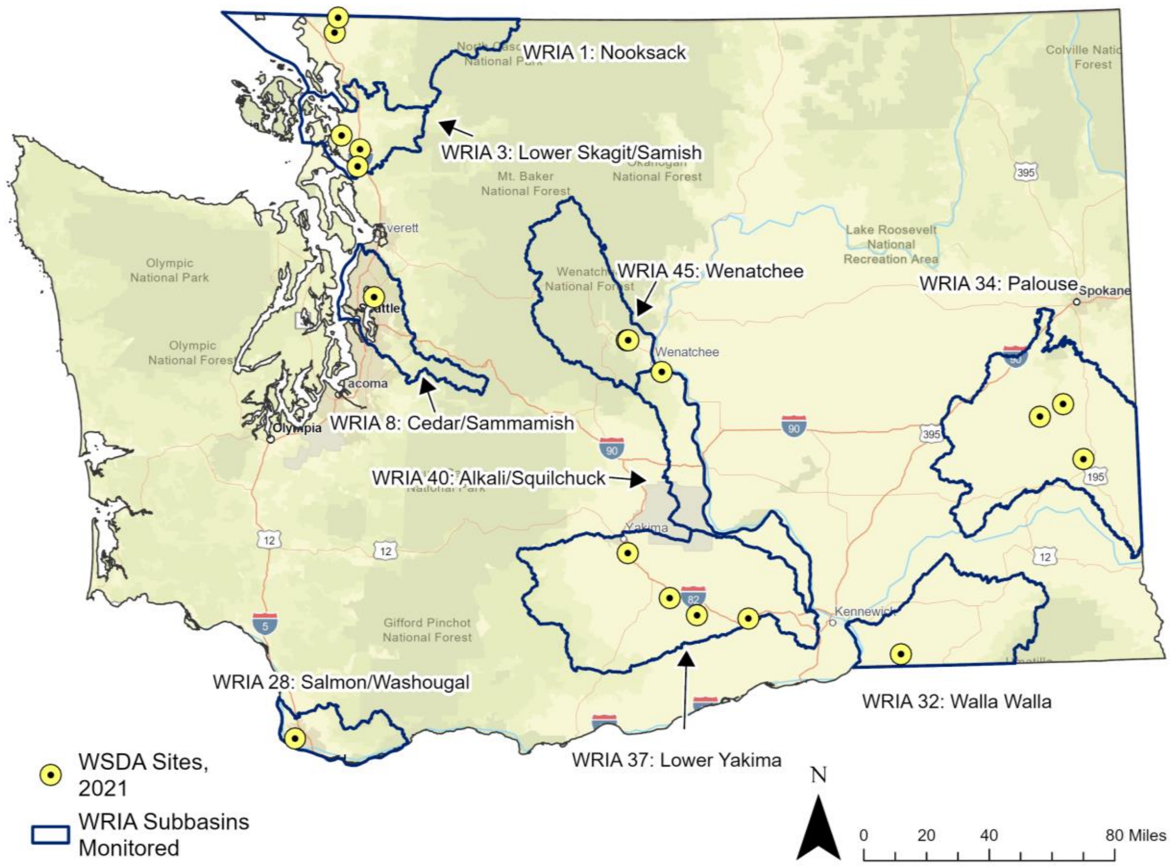


Figure 1 – Subbasins monitored in Washington State in 2021

All 9 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 seven 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. Staff collected surface water samples at 18 monitoring sites across the state, which MEL analyzed for total suspended solids (TSS), suspended sediment concentration (SSC), and 173 pesticide active ingredients and pesticide-related products. Additionally, MEL analyzed nutrients for Upper Big Ditch, Marion Drain, Sulphur Creek Wasteway, Dry Creek, Kamiache Creek, and Thorn Creek. The nutrients sampled were total phosphorus, ortho-phosphate, ammonia as N, and nitrate-nitrite as N. The sampling schedule and analytes tested was determined individually for each site.

Conventional water quality parameters such as pH, specific conductance, continuous air and water temperature data (collected at 30-minute intervals), dissolved oxygen (DO), and streamflow were monitored at the monitoring sites. 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. 2021).

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 2021a). Before delivery to MEL, staff labeled and preserved all samples according to the Quality Assurance Project Plan (Bischof et al. 2021). 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 2021b) and YSI ProDSS User Manual (YSI 2020). NRAS followed Ecology's SOP for Continuous Temperature Monitoring of Fresh Water Rivers and Streams for continuous, 30-minute-interval temperature data collection at 14 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 12 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 six 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.

- Ahtanum – USGS gauging station located near Union Gap (Station ID: 12502500)
- 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)
- 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 2021 field data quality results are summarized in Appendix B of this report.

Laboratory Analyses

MEL analyzed the surface water grab samples for pesticides, TSS, SSC, nutrients, and specific 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 (Derivitizable acid herbicides)	3535A	SW8270E	GC/MS
LCMS-Glyphos	3535A	SW8321B	LC/MS/MS
LCMS-Pesticides	n/a	SW8321B	LC/MS/MS
SSC	n/a	ASTM D3977B	Gravimetric
Specific Conductivity	n/a	APHA SM2510B	Electrode
TSS	n/a	SM2540D	Gravimetric
Nitrate+Nitrite-N	n/a	APHA SM4500NO3I	Lachat
Ammonia-N (NH3)	n/a	APHA SM4500NH3H	Lachat
Phosphate, Ortho- (OP)	n/a	APHA SM4500PG	Lachat
Phosphorus, Total	n/a	APHA 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, method 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 2021, 12% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2021 Quality Assurance Summary.

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

Field Replicates

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 analyte was positively detected in both the sample and field replicate. Conversely, inconsistently identified replicate pairs are those where the analyte 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 12 of the 302 consistently identified replicate pairs detected for pesticide, nutrient, SSC, and TSS analysis exceeded an RPD criterion (40% RPD for pesticides; 20% RPD for nutrients, SSC, and TSS). The results were not qualified for the 12 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 2,6-dichlorobenzamide had low replicate variability among the 89 analytes detected in replicate pairs. There was not a high reproducibility of detections between replicate pairs for analytes detected in 2021. The analyte, in part, had high variability because of the small number of replicate pairs with at least one identified detection. Even so, all pesticide, nutrient, SSC, 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 specific 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 teams and 3 replicate streamflow measurements were taken at random by the Palouse sampling team. A conductivity sample was collected once at each monitoring site for comparison to a YSI ProDSS meter. In 2021, all but 9 of relative percent differences between the streamflow or specific conductivity measurements and replicate measurements/samples were below the measurement quality objective of 10%.

Blanks

Field and method blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were 18 detections in field blanks and 220 detections in method blanks. Detections in field blanks included analytes such as DEET, nitrate-nitrite, and ortho-phosphate, while detections in method blanks included analytes such as fenarimol, DEET, and triclosan. The origin of these detections was unknown. There were 54 regular field sample detections corresponding to a field or method blank sample in the same batch that were qualified as non-detects due to the regular sample concentration being 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 2021. 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 94% 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 99% 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 2022b), and Washington State regulations (WAC 2022). 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 2022a).

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

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

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 $1/20^{th}$ of the most sensitive LC_{50} 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 2022b). Acute and chronic toxicity data from pesticide registration toxicity studies provide the pesticide criteria in the NRWQC. NRAS used the 2021 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 2022). 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 2021, 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 33% of monitored watersheds. In 2021, three watershed POCs were found in 6 or more of the 18 monitored watersheds (>33% of the 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 2022), 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 2021 was fresh water and was only compared to WAC freshwater 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 – Water quality standards for Washington State by aquatic life use

WAC aquatic life uses	7-DADMax (ºC), 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 2021 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 (NO_2 + NO_3) 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, Kamiache Creek, Marion Drain, Sulphur Creek Wasteway, Thorn Creek	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 2022). 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 2021 except for Dry Creek, Kamiache Creek, and Thorn Creek were considered salmonid present waterway as per the State Water Quality Standards.

For salmonids present:

$$\frac{0.275}{1+10^{7.204-pH}}+\frac{39.0}{1+10^{\mathrm{pH}-7.204}}$$

For salmonids absent:

$$\frac{0.411}{1+10^{7.204-pH}}+\frac{58.4}{1+10^{\mathrm{pH}-7.204}}$$

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

Monitoring Site Results

In 2021, NRAS monitored 18 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 2021 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 µg/L, rounded to the thousandths place. The addition of a “<” identifies concentrations of imidacloprid less than 0.005 µg/L to show that those detections did not exceed WSDA assessment criterion of 0.005 µg/L.

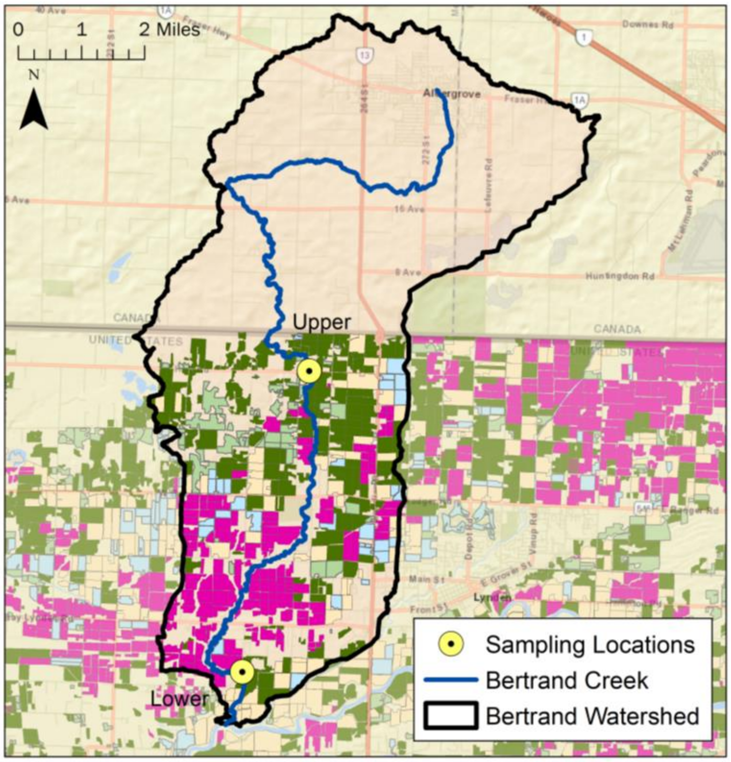
Detection of a pesticide concentration above the WSDA assessment criteria does not necessarily indicate an exceedance has occurred because the temporal component of the criteria must also be exceeded. For WSDA assessment criteria, measurements of instantaneous concentrations are assumed to represent 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	157
Berry	2,334
Cereal Grain	1,264
Hay/Silage	3,162
Pasture	702
Vegetable	478
Total U.S. Ag	8,097
Total U.S. Non-Ag	4,733
Watershed Total	26,893

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

Figure 3 – Upper Bertrand Creek site upstream view

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.

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 2021.

- NRAS tested for 170 unique pesticides in Upper and Lower Bertrand Creek.
- Pesticides were detected at each sampling event.
- Up to 41 pesticides were detected at the same time in Upper Bertrand Creek and up to 31 in Lower Bertrand Creek.
- There were 48 pesticides that were detected at least once in both the Upper and Lower Bertrand Creek sites throughout the sampling season. Conversely, there were five pesticides that were found only at the upper site and 15 pesticides that were found only at the lower site.
- There were 488 total pesticide detections in Upper Bertrand Creek from six different use categories: 20 types of herbicides, 13 insecticides, 11 fungicides, 2 legacies, 6 degradates, and 1 insect repellent.
- Of the total pesticide detections in Upper Bertrand Creek, 24 were above WSDA's assessment criteria (Table 6).
    - The single detection of 4,4'-DDD, a legacy degradate, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
- There were 569 total pesticide detections in Lower Bertrand Creek from six different use categories: 22 types of herbicides, 18 insecticides, 12 fungicides, 1 legacy, 9 degradates, and 1 insect repellent.
- Of the total pesticide detections in Lower Bertrand Creek, 26 were above WSDA's assessment criteria (Table 7).
    - The single detection of cis-Permethrin exceeded the invertebrate NOAEC (0.0042 µg/L) and approached invertebrate LC_{50} (0.0066 µg/L).
    - The single detection of pyriproxyfen approached the invertebrate NOAEC (0.015µg/L).

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

- All two detections of chlorpyrifos approached the invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
- All 21 detections of imidacloprid approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- The single detection of diuron did not exceed any assessment criteria in 2021, but this herbicide was still classified as watershed POCs because of 2020 detections that did exceed criteria.

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

- Of the 10 diazinon detections, one detection approached the invertebrate LC_{50} (0.21 µg/L) and invertebrate NOAEC (0.17 µg/L).
- Of the 21 imidacloprid detections, 18 detections approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- The five detections of malathion approached the invertebrate LC_{50} (0.098 µg/L) and invertebrate NOAEC (0.06 µg/L).
- The 13 detections of diuron in 2021 did not exceed any assessment criteria, but the herbicide was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site. Similarly, bifenthrin and permethrin were not detected in 2021, but were considered a watershed POC because of the same logic.

The Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Table 6, Table 7). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 6 – Upper Bertrand pesticide calendar, µg/L

Month		**Apr**				**May**				**Jun**					**Jul**				**Aug**				**Oct**	**Nov**
Day of the Month	Use*	6	13	20	26	4	10	18	24	2	7	15	21	29	6	13	19	26	2	9	16	23	18	1
2,4-D	H		0.037		0.063	0.065	0.151				0.893	0.096	0.050											
2,6-Dichlorobenzamide	D	0.169	0.185	0.244	0.319	0.248	0.281	0.238	0.191	0.338	0.324	0.389	0.405	0.276	0.258	0.226	0.206	0.162	0.142	0.127	0.125	0.115	0.323	0.287
4,4'-DDD	L									0.003														
Acephate	I					2.350	0.478	0.051	0.071	0.159	0.065	0.015	0.014											
Acetamiprid	I											0.131												
Atrazine	H	0.018	0.018	0.072	0.125	0.076		0.028				0.029		0.009						0.006		0.005	0.040	0.019
Azoxystrobin	F											0.095	0.011	0.005	0.003									
Boscalid	F	0.093	0.072	0.115	0.244	0.151	0.133	0.117	0.119	0.134	0.124	0.189	0.109	0.086	0.075	0.095	0.084	0.075	0.073	0.070	0.066	0.062	0.174	0.163
Carbaryl	I											0.108											0.045	
Carbendazim	F	0.070	0.011	0.021	0.015	X	0.012	0.012	0.005	0.011	0.012	0.013	0.011	0.011	0.008	0.007	0.007		0.007				0.007	
Chlorothalonil	F		0.003																					
Chlorpyrifos	I		0.004				0.004																	
Clothianidin	I							0.011	0.009															
Cyprodinil	F								0.011			0.104												
Diazinon	I				0.005	0.003		0.004	0.009	0.003	0.002													
Dicamba acid	H				0.009		0.011					0.013												
Dichlobenil	H	0.133	0.109	0.086	0.121	0.204	0.191	0.072	0.042	0.227	0.094	0.298	0.189	0.078	0.034	0.020	0.015	0.012	0.011	0.010	0.009	X	0.232	0.099
Dimethoate	I									0.009	0.065	0.006												
Diuron	H											0.005												
Eptam	H	0.005	0.003		0.001	0.001	0.002					0.001											0.006	
Fludioxonil	F		0.004	0.004	0.004	0.004	0.004	0.004	0.018	0.011	0.009	0.101	0.014	0.010	0.007	0.005	0.005	0.004	0.005	0.006	0.005	0.004	0.006	0.006
Flupyradifurone	I			0.004	0.029	0.007	0.008			0.006	0.025	0.338	0.052	0.032		0.020				0.008	0.008	0.007	0.053	0.034
Hexazinone	H	0.003	0.004	0.005		0.005	X	0.005	0.005		0.005	0.006	0.005		0.005	0.005								
Imazapyr	H									0.005			0.007										0.007	
Imidacloprid	I	0.035	0.044	0.029	0.091	0.046	0.032	0.019	0.017	0.021	0.021	0.056	0.020	0.017	0.011		0.011	0.008		0.007	0.006	0.005	0.044	0.046
Malathion	I															0.007	0.006	0.010		0.009				
MCPA	H										0.150	0.045												
Mecoprop (MCPP)	H	0.032			0.028		0.128					0.055											0.015	
Metalaxyl	F	0.027	0.020	0.012	0.013	0.032	0.019	0.011	0.009	0.128	0.097	0.044	0.035	0.036	0.064	0.097	0.051	0.029	0.026	0.024	0.018	0.015	0.103	0.059
Methamidophos	L					0.198	0.059	0.012	0.013	0.028	0.014	0.007	0.008											
Methomyl	I										0.002													
Metolachlor	H	0.016	0.036	0.014	0.013	0.013	0.023	0.009	0.011	0.013	0.014	0.040	0.012	0.006	0.005	0.004	0.005		0.005	0.005	0.005	0.005	0.016	0.014
Metribuzin	H																						0.090	0.028
Myclobutanil	F			0.006	0.008		0.006	0.005	0.009	0.005	0.008	0.012												
N,N-Diethyl-m-toluamide (DEET)	IR	X	0.003			X						0.029		0.019	0.053								0.026	0.007
Napropamide	H											0.020											0.080	0.029
Oxadiazon	H	0.005	0.006	0.004	0.005	0.004	0.004	0.003	0.003	0.003		0.006	0.003										0.006	
Oxamyl	I	0.003	0.002	0.002	0.003		0.001				0.001	0.001												0.001
Oxamyl oxime	D			0.025	0.026		0.016	0.018	0.022	0.015	0.045	0.026												
Paclobutrazol	F		0.005																					
Prometryn	H									0.004														
Propiconazole	F	0.075	0.044	0.015	0.038	0.014	0.019	0.012	0.007			0.074	0.016		0.007									0.012
Pyrimethanil	F						0.002	0.012	0.009	0.005	0.008	0.013		0.002										
Simazine	H	0.015	0.013	0.021	0.023	0.022	0.288	0.083	0.540	0.114	0.107	0.073	0.047	0.035	0.029	0.028	0.031	0.025	0.024	0.022	0.021	0.018	0.034	0.025
Sulfentrazone	H	0.011	0.010	0.012	0.022	0.013	0.013	0.011	0.010	0.010	0.022	0.027	0.011	0.007	0.007	0.009							0.025	0.016
Sulfometuron-methyl	H					0.009			0.005						0.003									
Tebuthiuron	H											0.005												
Terbacil	H	0.035	0.029	0.058	0.083	0.065	0.076	0.068	0.051	0.042	0.083	0.101	0.048	0.026	0.014	0.010	0.007	0.006					0.022	0.044
Tetrahydrophthalimide (THPI)	D	0.003		0.002	0.003	0.011	0.047	0.039	0.011	0.008	0.006	0.059	0.002				0.002			0.004			0.006	0.006
Thiamethoxam	I				0.003		0.011	0.020	0.015	0.005	0.011	0.011	0.004	0.004										
Triazine DEA degradate	D			0.004	0.014	0.010	0.005	0.002	0.003	0.002		0.004	0.003										0.003	
Triazine DIA degradate	D			0.005	0.018	0.009	0.018	0.018	0.052	0.020	0.035	0.032	0.013	0.011	0.015	0.011	0.009	0.007		0.004		0.004	0.007	
Triazine HA degradate	D	0.005	0.004	0.005	0.007	0.007	0.006	0.005	0.004	0.007	0.007	0.009	0.005	0.004	0.004	0.004	0.003			0.003	0.004	0.004	0.007	0.007
Suspended sediment concentration		-	-	2	2	4	2	3	2	4	2	9	2	2	3	2	2	2	7	2	2	2	5	2
Total suspended solids		2	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		17.9	13.4	7.2	8.9	6.4	6.2	4.4	4.3	4.0	5.2	20.4	2.5	1.6	1.4	0.9	0.7	0.9	0.9	0.7	0.5	0.5	62.1	29.8
Precipitation (total in/week)†		0.07	0.51	0.00	0.40	0.33	0.59	0.19	0.36	0.45	0.51	0.89	0.34	0.00	0.00	0.00	0.00	-	-	-	-	-	2.39	1.91

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, L: Legacy)

† Washington State University AgWeatherNet station: Lynden.N, (latitude: 48.98°, longitude: -122.43°)

Table 7 – Lower Bertrand pesticide calendar, µg/L

Month		Apr				May				Jun					Jul				Aug				Oct	Nov
Day of the Month	Use*	6	13	20	26	4	10	18	24	2	7	15	21	29	6	13	19	26	2	9	16	23	18	1
1-(3,4-Dichlorophenyl)-3-methylurea	D													0.006										
2,4-D	H			0.034		0.080	0.123			0.065													0.015	
2,6-Dichlorobenzamide	D	0.155	0.125	0.152	0.165	0.191	0.235	0.143	0.141	0.234	0.180	0.197	0.204	0.154	0.139	0.164	0.157	0.141	0.147	0.155	0.145	0.157	0.312	0.240
Acephate	I	0.008				2.610	0.390	0.025	0.007	0.074	0.047	0.004												
Acetamiprid	I																				0.006			
Acetochlor ESA	D																					0.041		
Atrazine	H	0.011	0.012	0.024	0.028	0.027	0.026											0.005	0.005	0.006		0.006	0.035	0.017
Azoxystrobin	F												0.003											
Boscalid	F	0.042	0.035	0.040	0.067	0.057	0.069	0.044	0.044	0.044	0.044	0.049	0.057	0.035	0.030	0.044	0.048	0.040	0.035	0.057	0.068	0.044	0.151	0.132
Bromacil	H	0.017	0.016	0.020	0.020	0.020	0.018	0.025	0.023	0.020	0.021	0.018	0.030	0.032	0.041	0.058	0.062	0.049	0.054	0.050	0.041	0.048		0.014
Carbaryl	I																						0.028	
Carbendazim	F	0.020	0.006	0.017	0.011	X			0.004	0.010	0.010		0.009										0.007	
Chlorantraniliprole	I																				0.009			
Chlorothalonil	F	0.003																						
cis-Permethrin	I	0.005																						
Clopyralid	H																0.025							
Clothianidin	I	0.003							0.003			0.005												
Cyprodinil	F								0.009			0.005		0.005			0.004							
Diazinon	I			0.017	0.012	0.005	0.003	0.081	0.048	0.007	0.004	0.005	0.004											
Dichlobenil	H	0.094	0.034	0.025	0.033	0.061	0.124	0.023	0.014	0.091	0.026	0.066	0.054	0.017	0.007	0.005	0.004	0.003	0.002	0.002	0.003	X	0.249	0.067
Dinotefuran	I	0.012	0.009	0.006	0.003																			
Diuron	H	0.004		0.004	0.006			0.025				0.014	0.017	0.015	0.019	0.009	0.010		0.004		0.006	0.004		
Eptam	H	0.003	0.002																				0.004	
Ethoprop	I	0.005																						
Fludioxonil	F		0.004	0.004	0.004	0.004	0.004	0.005	0.011	0.007	0.008	0.009	0.009	0.007	0.007	0.009	0.012	0.009	0.006	0.017	0.011	0.007	0.007	0.006
Flupyradifurone	I					0.006	0.004							0.007									0.044	0.022
Hexazinone	H	0.004	0.006	0.007		0.006	X	0.006	0.006		0.006	0.006	0.007	0.007	0.007	0.010		0.009	0.009	0.008	0.009			0.005
Imazapyr	H																						0.008	
Imidacloprid	I	0.022	0.018	0.013	0.035	0.028	0.021	0.030	0.010	0.013	0.014	0.015	0.011	0.010	0.007	0.006	0.006		0.004	0.004	0.004		0.043	0.026
Malaoxon	D				0.005							0.017												
Malathion	I	0.016	0.019	0.016	0.031	0.012	0.012	0.010	0.005	0.007	0.005	0.048			0.012	0.009	0.042	0.038	0.009	0.026			0.015	0.019
MCPA	H						0.016																	
Mecoprop (MCPP)	H						0.078																0.019	
Metalaxyl	F	0.051	1.340	0.169	0.117	0.122	0.078	0.095	0.124	0.109	0.121	0.107	0.129	0.112	0.108	0.126	0.133	0.133	0.180	0.245	0.125		0.166	0.099
Methamidophos	L					0.217	0.043	0.008	0.005	0.016	0.014													
Methomyl	I										0.003													
Methoxyfenozide	I					0.003																		
Metolachlor	H		0.023	0.010	0.008	0.011	0.013	0.008	0.009	0.010	0.008	0.010	0.009	0.007	0.007	0.010	0.009	0.010	0.010	0.010	0.009	0.009	0.022	0.013
Metribuzin	H		0.004							0.004													0.068	0.020
Myclobutanil	F								0.007															
N,N-Diethyl-m-toluamide (DEET)	IR	X				X																	0.011	0.006
Napropamide	H																						0.096	0.021
Norflurazon	H		0.004	0.003		0.004	0.003			0.003	0.004	0.004	0.004		0.005	0.008	0.007	0.007	0.008	0.007	0.008	0.008		
Oxadiazon	H		0.002	0.002		0.002	0.002																	
Oxamyl	I	0.038	0.038	0.043	0.042	0.045	0.038	0.045	0.043	0.037	0.033	0.036	0.034	0.031	0.024	0.025	0.021	0.021	0.017	0.017	0.013	0.013	0.002	0.008
Oxamyl oxime	D	0.040	0.051	0.093	0.106	0.117	0.074	0.094	0.092	0.094	0.091	0.079	0.086	0.120	0.101	0.119	0.087	0.087	0.085	0.074	0.067	0.068		
Paclobutrazol	F		0.004																					
Phosmet	I		0.005				X																	
Picloram	H																		0.038					
Propiconazole	F	0.042		0.005		0.005							0.005											
Pyrimethanil	F								0.003	0.015	0.014	0.009	0.006			0.003				0.003				
Pyriproxyfen	I		0.008																					
Simazine	H	0.011	0.011	0.010	0.020	0.014	0.055	0.317	0.098	0.056	0.049	0.077	0.081	0.045	0.041	0.027	0.018	0.013	0.011	0.013	0.024	0.014	0.034	0.023
Sulfentrazone	H	0.035	0.032	0.044	0.038	0.044	0.038	0.047	0.041	0.036	0.036	0.038	0.047	0.048	0.050	0.082	0.066	0.069	0.077	0.073	0.082	0.068	0.027	0.031
Sulfometuron-methyl	H		0.004		0.007						0.005	0.009												
Tebuthiuron	H	0.005	0.004	0.005		0.005	0.004		0.005		0.005	0.004	0.005			0.005		0.005	0.005		0.007			
Terbacil	H	0.014	0.016	0.017	0.020	0.035	0.025		0.011	0.014	0.016	0.014	0.011	0.004									0.015	0.029
Tetrahydrophthalimide (THPI)	D	0.003	0.004	0.011	0.004	0.006	0.013	0.077	0.026	0.014	0.014	0.011	0.008	0.003	0.008	0.007	0.021	0.007	0.004	0.118	0.137	0.111	0.011	0.017
Thiamethoxam	I	0.021	0.024	0.023	0.025	0.033	0.032	0.041	0.032	0.029	0.029	0.027	0.030	0.037	0.034	0.042	0.041	0.042	0.041	0.039	0.039	0.037		0.008
Triadimefon	F		0.004																					
Triazine DEA degradate	D			0.002	0.004	0.004	0.003	0.002	0.002					0.002								0.003	0.004	
Triazine DIA degradate	D			0.006	0.005	0.005	0.007	0.025	0.011	0.010	0.012	0.026	0.022	0.016	0.019	0.012				0.004	0.004		0.004	
Triazine HA degradate	D	0.007	0.005	0.004	0.005	0.005	0.005	0.004	0.003	0.004	0.004	0.004	0.004	0.003	0.003	0.003	0.002				0.002	0.003	0.007	0.006
Suspended sediment concentration		-	-	3	2	3	3	2	2	1	1	2	1	1	2	2	2	2	1	1		1	7	3
Total suspended solids		3	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		46.8	43.8	28.8	33.9	25.8	23.3	20.2	18.1	38.2	16.6	29.4	14.3	17.9	4.0	5.7	4.5	3.1	3.5	5.7	5.1	6.9	157.0	68.9
Precipitation (total in/week)†		0.07	0.51	0.00	0.40	0.33	0.59	0.19	0.36	0.45	0.51	0.89	0.34	0.00	0.00	0.00	0.00	-	-	-	-	-	2.39	1.91

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 | Detection | No criteria

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

† Washington State University AgWeatherNet station: Lynden.N, (latitude: 48.98°, 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. Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in *Figure 6* are shown below.

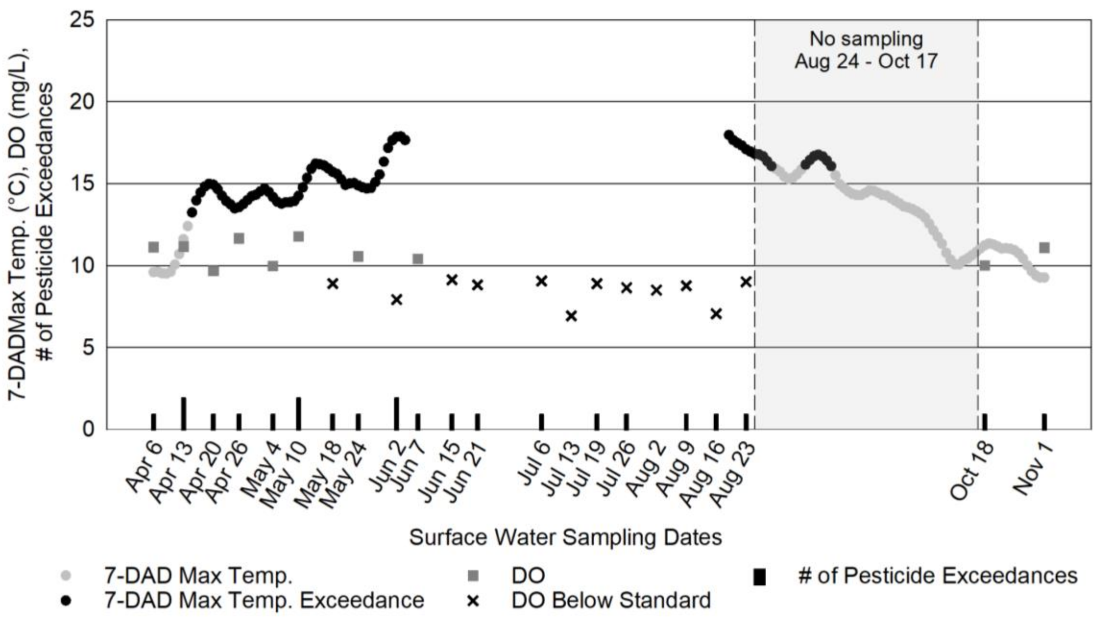


Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria

Water temperature data for Upper Bertrand Creek was not available for the period between June 10 and August 16 due to detection equipment being out of the water. Pesticide exceedances in Upper Bertrand Creek coincided with water quality measurements that did not meet state standards at 15 of the 23 site visits (65%). All pH measurements met the state standard, ranging from 7.14 to 7.83 with an average of 7.41. Dissolved oxygen (DO) measurements ranged from 6.26 mg/L to 11.78 mg/L with an average of 9.36 mg/L. Over half (57%) of these measurements did not meet the state standard; 13 measurements were less than 9.5 mg/L. All DO measurements that did not meet standards coincided with one pesticide exceedance, except for two. At three site visits (13%), 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 ºC, while June 16 through the end of the sampling season should remain below 16 ºC (WAC 2021). The 7-DADMax temperature exceeded the standard on 69 days, primarily from April 15 through June 4, before the data gap begins. There was at least one pesticide exceedance at every site visit with a 7-DADMax temperature exceedance.

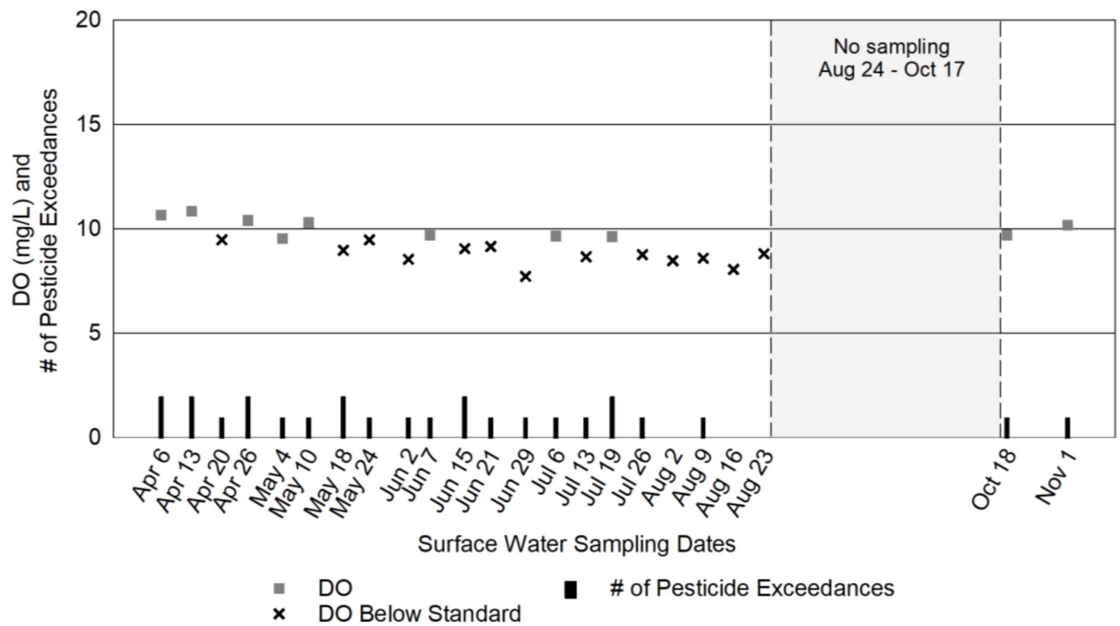
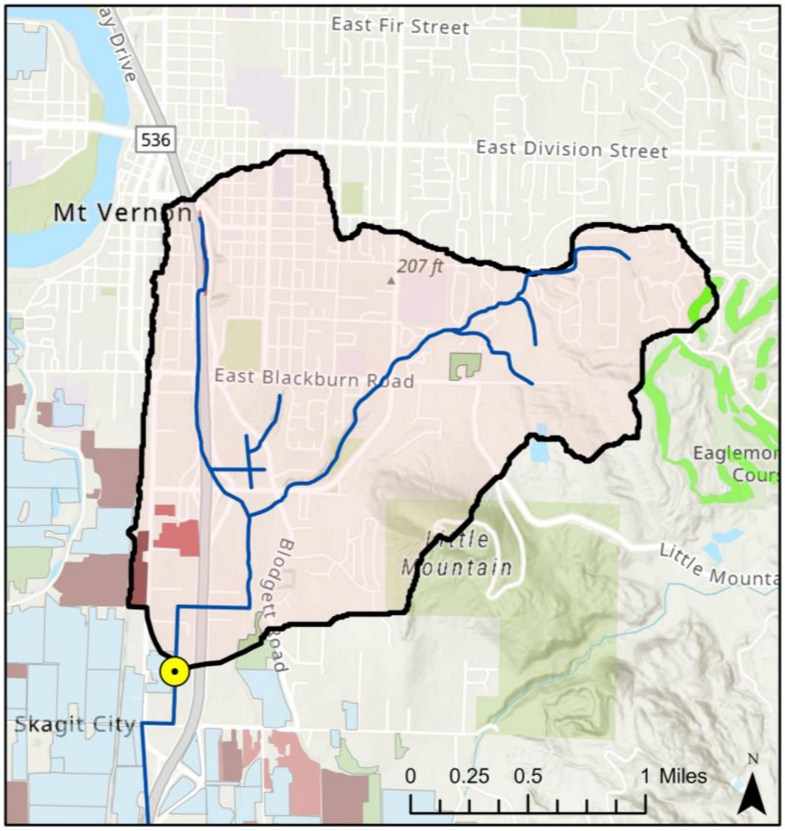


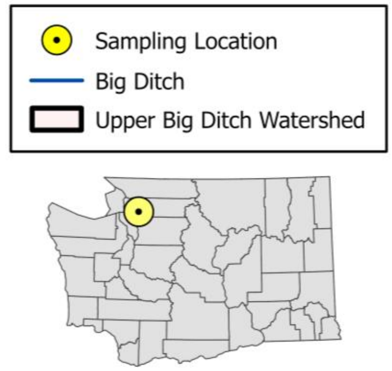
Figure 6 – Lower Bertrand Creek water quality measurements and exceedances of assessment criteria

Pesticide exceedances in Lower Bertrand Creek coincided with water quality measurements that did not meet state standards at 10 of the 23 site visits (43%). All pH measurements met the state standard, ranging from 6.66 to 7.40 with an average of 7.11. DO measurements ranged from 7.72 mg/L to 10.84 mg/L with an average of 9.31 mg/L. Over half (57%) of the DO measurements did not meet the standard; 13 measurements were less than 9.5 mg/L. Continuous water temperature was unable to be assessed because the temperature logger in the creek was buried in sediment on and off during the sampling season, which caused inaccurate measurements.

Bertrand 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 land use, historical sampling, and consistent, yearly detections of POCs.

Upper Big Ditch





Upper Big Ditch Crop Groups	Acres
Nursery	20
Pasture	11
Turfgrass	6
Vegetable	11
Other	<1
Total Ag	48
Total Non-Ag	1,992
Watershed Total	2,040

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 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).

Figure 8 – Upper Big Ditch upstream view

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.

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 watersheds NRAS monitors have nursery or greenhouse crop groups as their main agricultural commodity. The ‘Other’ crop group category was a seed crop in 2021 (Figure 7).

Below is a brief overview of the pesticide findings in Upper Big Ditch in 2021.

- NRAS tested for 170 unique pesticides in Upper Big Ditch.
- There were 539 total pesticide detections from seven different use categories: 22 types of herbicides, 14 insecticides, 12 fungicides, 1 legacy, 5 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 29 sampling events.
- Up to 36 pesticides were detected at the same time.
- Of the total pesticide detections, five were above WSDA’s assessment criteria (Table 8).
    - The two detections of fipronil approached the invertebrate NOAEC (0.011 µg/L).

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

- The single bifenthrin detection exceeded the Endangered Species Level of Concern (0.0075 µg/L), fish NOAEC (0.004 µg/L), invertebrate LC_{50} (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- The single chlorpyrifos detection approached invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
- The single imidacloprid detection approached invertebrate NOAEC (0.01 µg/L).
- The eight detections of indaziflam in 2021 did not exceed any assessment criteria, but the herbicide was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site. Similarly, tau-fluvalinate was not detected in 2021, 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 2021 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.

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

Month		Apr				May				Jun					Jul				Aug					Sep				Oct		
Day of the Month	Use*	6	13	20	27	4	11	18	25	2	8	15	22	29	7	13	20	27	3	10	17	24	31	7	13	21	29	5	12	19
1-(3,4-Dichlorophenyl)-3-methylurea	D																										0.005			
2,4-D	H				0.862	0.049		1.480	0.167		0.063	0.162								0.367			0.244	0.185	0.285	0.115	0.045		0.022	0.014
2,6-Dichlorobenzamide	D	0.199	0.184	0.166	0.190	0.148	0.133	0.151	0.124	0.090	0.095	0.128	0.101	0.080	0.085	0.100	0.095	0.108	0.090	0.115	0.095	0.092	0.101	0.092	0.142	0.202	0.273	0.147	0.158	0.187
4-Nitrophenol	D							0.053																			0.063			
Acephate	I							0.004																						
Atrazine	H		0.003		0.003			0.004	0.007		0.003	0.004								0.004										
Azoxystrobin	F	0.004	0.005	0.080	0.010	0.065	0.090	0.050	0.106	0.015	0.005	0.005	0.008	0.040	0.003					0.003			0.002	0.002	0.003					
Bifenthrin	I			0.007																										
Boscalid	F	0.011	0.010	0.038	0.017	0.036	0.041	0.019	0.030	0.045	0.008	0.012	0.047	0.101	0.009	0.009	0.008	0.008	0.008	0.010	0.009	0.009	0.012	0.010	0.017	0.011	0.010	0.009	0.007	0.006
Bromacil	H		0.003																											
Carbendazim	F			0.010	0.013		0.014	0.012	0.007	0.010	0.010	0.012	0.010	0.023			0.007	0.007	0.007	0.008		0.009	0.009		0.011	0.009	0.008	0.006	0.007	0.007
Chlorothalonil	F																										0.009			
Chlorpyrifos	I			0.004																										
Cyantraniliprole	I	0.089		0.518	0.220	0.720	0.638	0.045	0.092	0.042			0.014	0.941																
Cyprodinil	F													0.008																
Diazinon	I				0.002																									
Dicamba acid	H				0.015			1.020	0.017			0.010																		
Dichlobenil	H	0.005	0.003	0.007	0.015	0.004	0.004	0.022	0.017	0.003	0.004	0.009	0.003	0.002		0.001				0.002				0.001	0.004	0.008	0.010	0.003	0.004	0.005
Dimethoate	I							0.013	0.005																					
Dinotefuran	I	0.228	0.203	0.291	0.175	0.231	0.234	0.036	0.326	0.103	0.058	0.096	0.138	0.045	0.015	0.043	0.066	0.066	0.068	0.041	0.022	0.020	0.014	0.011	0.016	0.003		0.060	0.033	0.052
Dithiopyr	H	0.003							0.002																	0.003	0.005			
Diuron	H				0.009	0.004	0.003	0.007	0.006			0.008	0.004							0.006	0.004				0.005	0.008	0.015	0.006	0.008	0.007
Eptam	H			0.002	0.003	0.003	0.002	0.003	0.001		0.001	0.001	0.001													0.010	0.002	0.002	0.002	0.002
Fipronil	I				0.006			0.007																						
Fludioxonil	F	0.114	0.055	0.321	0.075	0.203	0.253	0.113	0.187	0.140	0.056	0.059	0.437	0.648	0.099	0.072	0.048	0.039	0.031	0.052	0.032	0.034	0.057	0.043	0.053	0.036	0.021	0.030	0.023	0.021
Flumioxazin	H						X						X																0.062	
Fluopicolide	F	0.029	0.022	0.214	0.043	0.103	0.274	0.030	0.036	0.010	0.004		0.016	0.012								0.004								
Flupyradifurone	I	0.050	0.029	0.080			0.219	0.057	0.146	0.043	0.016		0.124	0.058	0.008															
Imazapic	H		0.007		0.006			0.013																		0.006	0.007			
Imazapyr	H	0.036	0.033	0.041	0.047	0.040	0.040	0.041	0.042	0.039	0.043	0.044	0.035	0.031	0.021	0.019	0.018	0.014	0.016	0.028	0.017	0.018	0.016	0.017	0.022	0.046	0.038	0.021	0.021	0.021
Imidacloprid	I													0.009																
Indaziflam	H				0.006		0.002	0.003	0.003		0.002	0.003	0.004	0.005																
Isoxaben	H																									0.009				
Mecoprop (MCPP)	H							0.074																						
Metalaxyl	F	0.019		0.019		0.019	0.055		0.015				0.007	0.029																
Methamidophos	L																													0.002
Methiocarb	I				0.553	0.031	0.094	0.008	0.008																					
Metolachlor	H			0.004	0.006	0.005	0.004	0.021	0.013	0.004	0.007	0.013	0.005	0.004						0.005					0.007	0.021	0.013	0.007	0.006	0.007
Metsulfuron-methyl	H							0.005	0.005																					
N,N-Diethyl-m-toluamide (DEET)	IR	X	0.003		0.011	X		0.021	0.009			0.014		0.006		0.023				0.019					0.029	0.019	0.034		0.013	0.013
Paclobutrazol	F	0.010		0.012			0.013	0.003						0.010											0.005					
Pentachlorophenol	WP			0.013				0.019																			0.016			
Phosmet	I						X				0.005																			
Picloram	H	0.141	0.179	0.084	0.163	0.145	0.069		0.124	0.178	0.147	0.107	0.272	0.261		0.208	0.187	0.172	0.202	0.082	0.196	0.232	0.250	0.165	0.078	0.181		0.057	0.144	0.120
Prometon	H	0.009	0.009	0.012	0.010	0.010	0.010	0.014	0.008	0.009	0.009	0.008	0.010	0.008	0.010	0.010	0.009	0.011	0.009	0.009	0.010	0.010	0.011	0.010	0.008	0.008	0.009	0.010	0.008	0.008
Propiconazole	F											0.013													0.016					0.011
Pyraclostrobin	F													0.005																
Spirotetramat	I								4.800	0.094																				
Sulfentrazone	H				0.005			0.010	0.005			0.007															0.014			
Sulfometuron-methyl	H				0.050	0.013	0.010	0.017	0.024		0.012	0.046								0.004										
Tebuthiuron	H	0.026	0.023	0.031	0.025	0.032	0.034	0.028	0.029	0.040	0.036	0.030	0.052		0.042	0.065	0.066	0.066	0.060	0.049	0.058	0.057	0.059	0.057	0.027	0.032	0.007	0.047		0.048
Tetrahydrophthalimide (THPI)	D							0.006																						
Thiamethoxam	I	0.006	0.006	0.006	0.004	0.005	0.005		0.005	0.007																				
Triazine HA degradate	D	0.006	0.006	0.007	0.006	0.007	0.008	0.006	0.004	0.006	0.006	0.005	0.007	0.007	0.006	0.005	0.007	0.007	0.006	0.006	0.009	0.007	0.008	0.007	0.007	0.006	0.003	0.006	0.005	0.006
Triclopyr acid	H				1.190	0.064	0.039	0.357	0.149		0.029	0.176								0.029					0.221	0.164	0.136	0.023	0.030	0.031
Trifloxystrobin	F													0.003																
Suspended sediment concentration		-	-	7	5	8	6	14	7	8	6	5	5	6	4	5	4	3	3	1	2	2	2	2	1	2	6	3	3	11
Total suspended solids		4	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		2.1	1.7	1.1	1.7	1.1	1.1	1.3	1.3	1.2	0.9	1.1	0.9	0.6	0.6	0.6	0.4	0.6	0.5	0.2	0.3	0.2	0.3	0.3	0.4	0.9	3.1	1.0	0.8	0.6
Precipitation (total in/week)†		0.01	0.50	0.00	0.65	0.03	0.33	0.02	0.39	0.12	0.26	0.60	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.04	0.08	0.04	0.24	1.64	0.86	0.64	0.83	0.92

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 | Detection | No criteria

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

† 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 state standards at 3 of the 29 site visits (10%). Water quality at the Upper Big Ditch site is shown below (Figure 9).

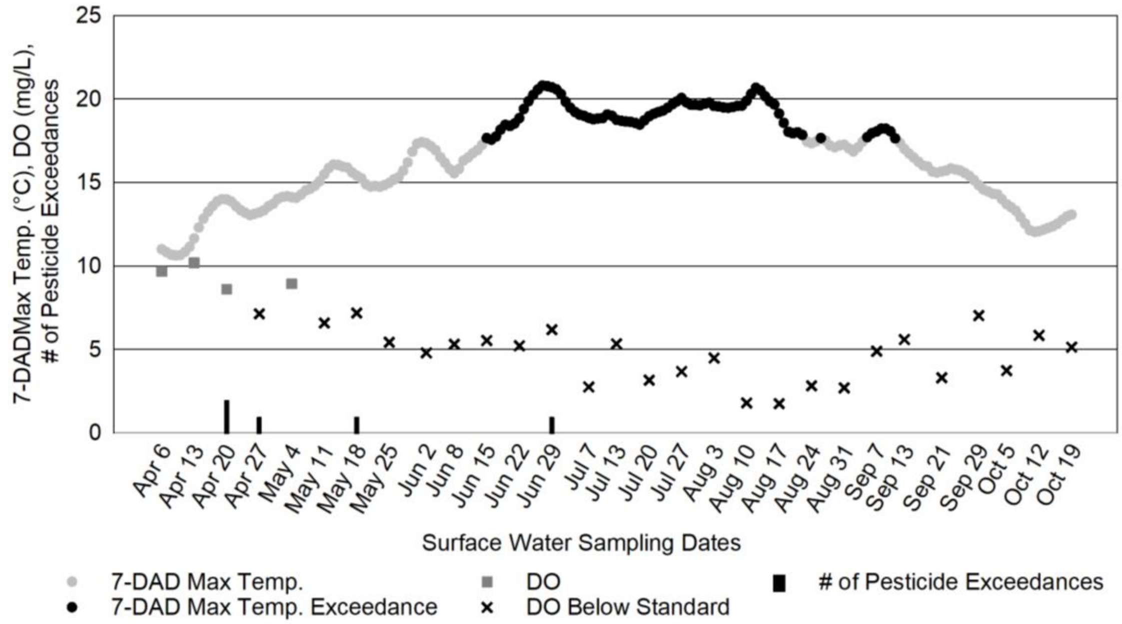
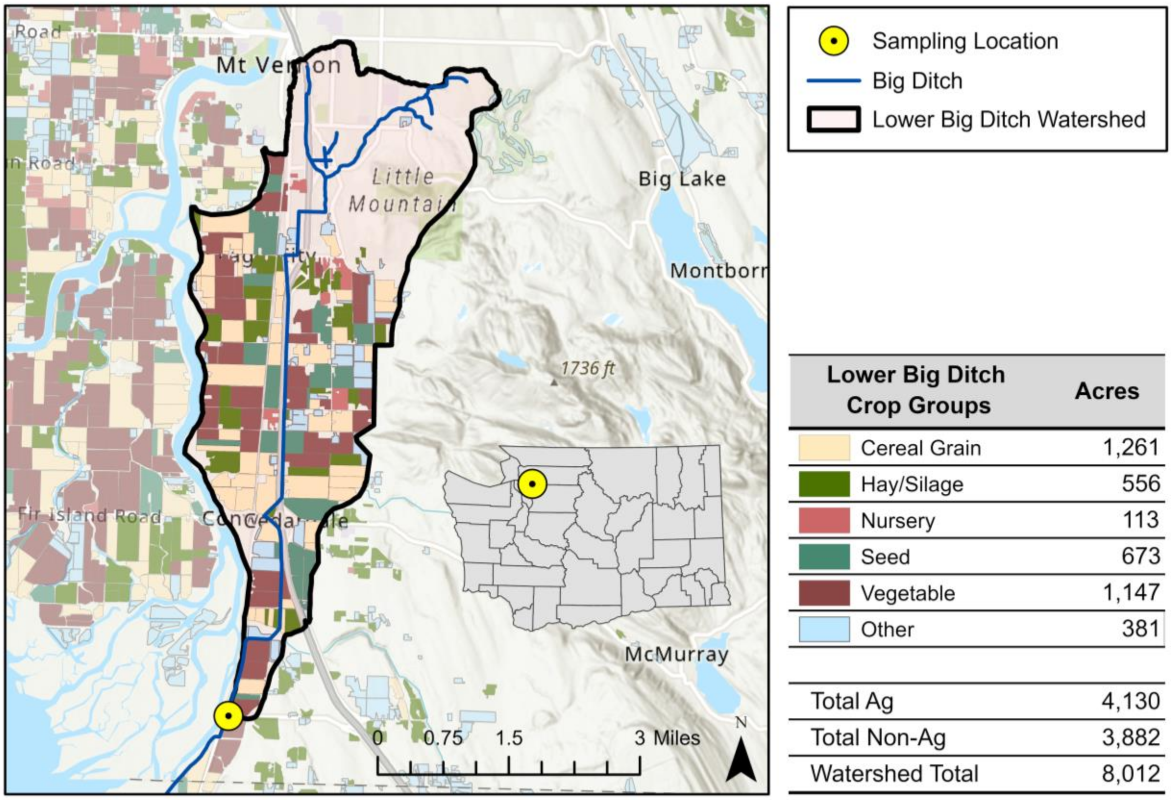


Figure 9 – Upper Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 6.52 to 7.14 with an average of 6.93. DO measurements ranged from 1.75 mg/L to 10.19 mg/L with an average of 5.33 mg/L. More than three-quarters (86%) of the DO measurements did not meet the state standard; 25 measurements were less than 8 mg/L. Three 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 previous four years of monitoring. The 7-DADMax temperature standard of 17.5°C was exceeded 77 days of the sampling season, intermittently from June 15 through September 11.

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



Lower Big Ditch Crop Groups	Acres
Cereal Grain	1,261
Hay/Silage	556
Nursery	113
Seed	673
Vegetable	1,147
Other	381
Total Ag	4,130
Total Non-Ag	3,882
Watershed Total	8,012

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).

Figure 11 – Lower Big Ditch upstream view

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. 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).

Below is a brief overview of the pesticide findings in Lower Big Ditch in 2021.

- NRAS tested for 170 unique pesticides in Lower Big Ditch.
- There were 348 total pesticide detections from six different use categories: 28 types of herbicides, 11 insecticides, 9 fungicides, 2 legacies, 8 degradates, and 1 insect repellent.
- Pesticides were detected at all 17 sampling events.
- Up to 41 pesticides were detected at the same time.
- Of the total pesticide detections, 26 were above WSDA's assessment criteria (Table 9).
    - All detections of 4,4'-DDD and 4,4'-DDE, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Out of eight fipronil detections, two exceeded the invertebrate NOAEC and four approached the invertebrate NOAEC (0.011 µg/L).
- All three detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- All detections of diuron in 2021 did not exceed any assessment criteria, but the herbicide was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site. Similarly, bifenthrin was not detected in 2021, but was considered a watershed POC because of the same logic.

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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		Apr				May				Jun					Sep		Oct	
Day of the Month	Use*	5	12	19	27	3	11	17	25	1	8	14	22	28	21	29	5	12
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.005							0.004						
2,4-D	H		0.081		0.507					0.043		0.055			0.480	0.130	0.049	0.041
2,6-Dichlorobenzamide	D	0.092	0.104	0.084	0.127	0.071	0.007	0.017	0.019	0.007	0.001	0.008			0.035	0.140	0.169	0.129
4,4'-DDD	L	0.003	0.003	0.004	0.003	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003				
4,4'-DDE	L							0.002		0.002			0.002	0.002				
Aminocyclopyrachlor	H	0.019	0.019	0.021		0.029												
Atrazine	H																0.004	
Azoxystrobin	F	0.055	0.068	0.087	0.054	0.037	0.006	0.007	0.021	0.022		0.015			0.010	0.011	0.009	0.007
Boscalid	F	0.004	0.006	0.008	0.017	0.014	0.004	0.005	0.009	0.005		0.005		0.003	0.007	0.010	0.009	0.007
Bromacil	H		0.004															
Bromoxynil	H							0.023										
Carbendazim	F				0.011							0.009			0.007	0.006	0.007	0.006
Chlorpropham	H	0.002	0.002	0.003	0.003	0.002												
Clothianidin	I				0.005													
Cyantraniliprole	I			0.026	0.400	0.344			0.045									
Diazinon	I			0.002	0.003													
Dicamba acid	H				0.011			0.032				0.028						
Dichlobenil	H	0.003	0.005	0.006	0.011	0.003		0.001	0.001						0.002	0.003	0.004	0.003
Difenoconazole	F	0.010	0.013	0.013	0.012	0.011												
Dimethenamid ESA	D	0.103	0.085	0.174														
Dimethoate	I			0.101	0.043													
Dinotefuran	I	0.035	0.035	0.051	0.143	0.068		0.012	0.023	0.005		0.005				0.003	0.005	0.007
Dithiopyr	H				0.003													
Diuron	H	0.036	0.041	0.020	0.034	0.017	0.007	0.004	0.004			0.006				0.009	0.008	0.007
Eptam	H	0.009	0.008	0.028	0.009	0.011	0.051	0.005	0.002	0.003		0.002			0.003	0.003		0.002
Ethoprop	I											0.003						
Fipronil	I	0.004	0.004	0.007	0.007	0.007			0.007	0.024		0.011						
Fipronil disulfinyl	D		0.003							0.007								
Fipronil sulfide	D	0.006	0.007	0.005	0.002	0.003				0.001		0.004			0.005	0.006	0.005	
Fipronil sulfone	D	0.006	0.006	0.004	0.003	0.003				0.005		0.004						
Fludioxonil	F	0.129	0.325	0.297	0.231	0.201	0.060	0.057	0.067	0.036	0.011	0.047	0.017	0.018	0.023	0.029	0.030	0.024
Fluopicolide	F	0.004		0.015	0.019	0.019		0.018	0.008									
Flupyradifurone	I			0.014	0.032	0.029		0.053	0.035									
Hexazinone	H	0.003	0.004	0.006		0.006			0.004						0.005			0.004
Imazapic	H		0.009		0.013													
Imazapyr	H	0.180	0.167	0.183	0.081	0.088	0.011	0.016	0.022	0.008		0.017			0.028	0.024	0.036	0.058
Imidacloprid	I				0.012												0.067	0.018
Indaziflam	H				0.021										0.018	0.007		
Isoxaben	H															0.002		
MCPA	H			0.101														
Metalaxyl	F					0.020		0.010	0.005									
Methiocarb	I					0.034		0.003										
Metolachlor	H		0.016	0.013	0.089	0.032	0.013	0.011	0.088	0.033	0.005	0.361	0.007	0.005	0.030	0.022	0.217	0.361
Metribuzin	H	0.007	0.006		0.005			0.010	0.005	0.004		0.005			0.008			
N,N-Diethyl-m-toluamide (DEET)	IR	X	0.008		0.011	X								0.005	0.012	0.013	0.014	0.011
Paclobutrazol	F				0.003													
Picloram	H		0.051	0.061	0.077												X	
Prometon	H	0.006	0.012	0.009	0.010	0.008			0.005						0.008	0.008	0.008	0.004
Propiconazole	F			0.008														
Simazine	H		0.018															
Sodium bentazon	H		0.022		0.013							0.074						
Sulfentrazone	H					0.005												
Sulfometuron-methyl	H				0.081	0.005									0.042	0.015	0.002	
Tebuthiuron	H	0.020	0.022	0.027	0.024	0.027	0.005	0.007	0.008			0.006			0.016	0.015	0.012	
Terbacil	H			0.008		0.008												
Tetrahydrophthalimide (THPI)	D			0.002		0.003												
Thiamethoxam	I			0.009	0.023	0.003												
Triazine HA degradate	D	0.047	0.043	0.044	0.030	0.037	0.010	0.010	0.008	0.005	0.002	0.013		0.002	0.030	0.017	0.019	0.015
Triclopyr acid	H				0.707	0.025									0.023	0.091	0.056	0.023
Suspended sediment concentration		-	-	19	17	40	15	13	10	14	15	8	10	13	2	3	2	5
Total suspended solids		29	23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		9.6	6.6	3.6	4.5	2.7	9.5	20.8	9.5	10.2	25.4	14.3	-	20.2	-	-	2.9	4.2
Precipitation (total in/week)†		0.01	0.50	0.00	0.65	0.11	0.33	0.00	0.39	0.12	0.26	0.30	0.05	0.00	1.64	0.86	0.64	0.83

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, L: Legacy)

† 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 11 of the 17 site visits (65%). Water quality at the Lower Big Ditch site is shown below (Figure 12).

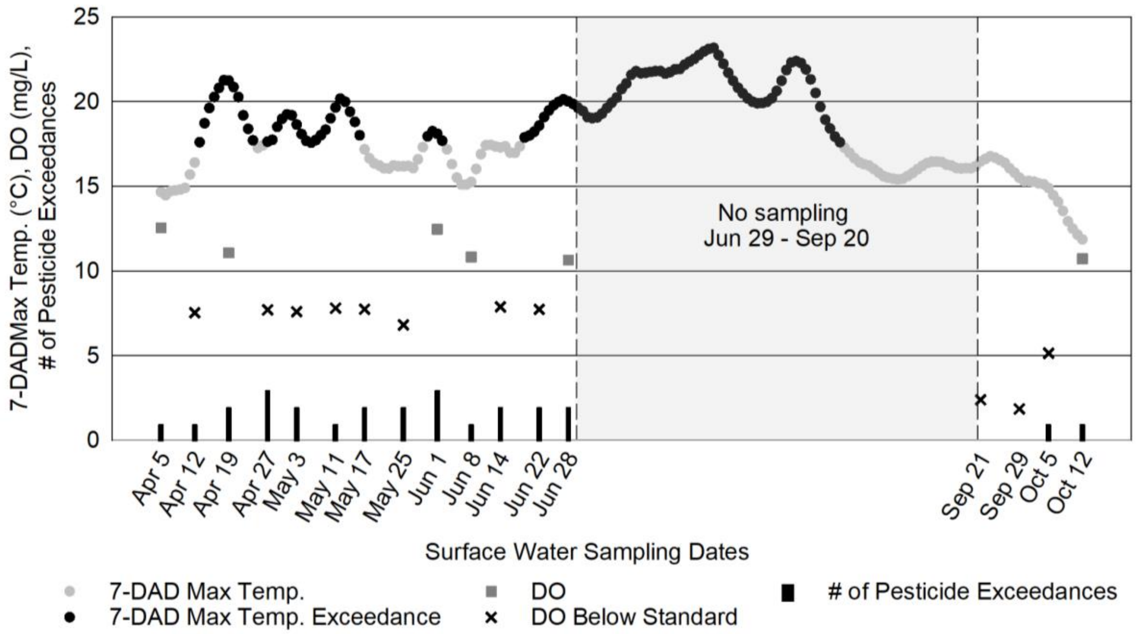
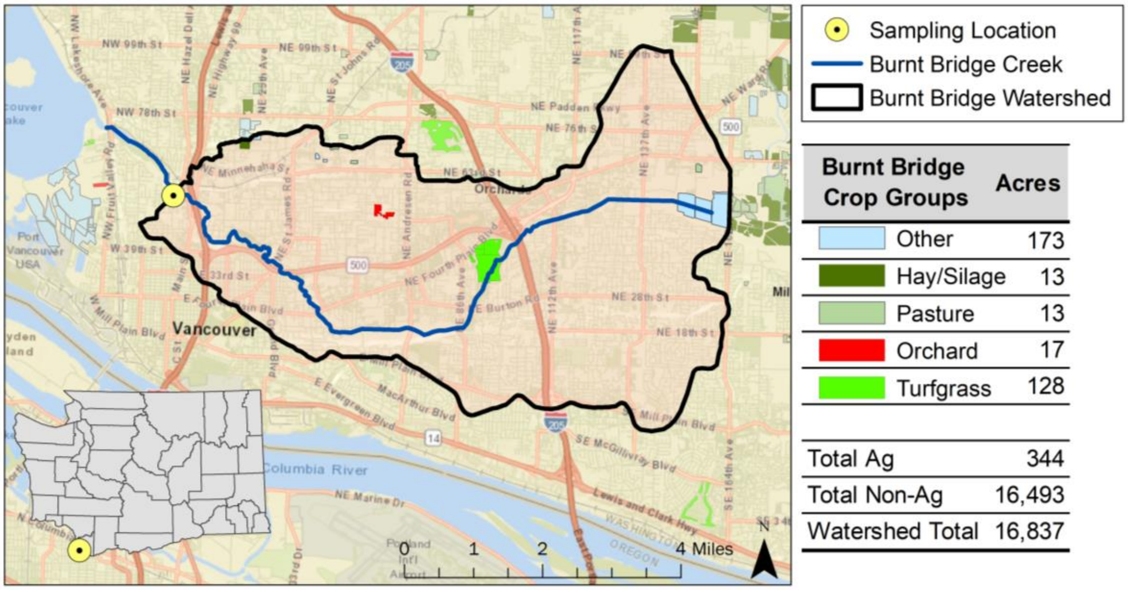


Figure 12 – Lower Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 6.57 to 8.27 with an average of 7.20. DO measurements ranged from 1.85 mg/L to 12.55 mg/L with an average of 8.14 mg/L. More than half (65%) of these measurements did not meet the DO standard; 11 measurements were less than 8 mg/L. DO variability potentially can be attributed to the effects of tidal fluctuations. The 7-DADMax temperatures were greater than the 17.5°C standard on 102 days of the sampling season, primarily from April 13 through August 23. A 7-DADMax temperature exceedance coincided with at least one pesticide exceedance at eight 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 four 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



Burnt Bridge Crop Groups	Acres
Other	173
Hay/Silage	13
Pasture	13
Orchard	17
Turfgrass	128
Total Ag	344
Total Non-Ag	16,493
Watershed Total	16,837

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: 45.6614º, longitude: -122.6720º) (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 2021.

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 observed fish of unknown species at this site.

Below is a brief overview of the pesticide findings in Burnt Bridge Creek in 2021.

- NRAS tested for 170 unique pesticides in Burnt Bridge Creek.
- There were 207 total pesticide detections from seven different use categories: 24 types of herbicides, 7 insecticides, 4 fungicides, 2 legacies, 9 degradates, 1 insect repellent and 1 wood preservative.
- Pesticides were detected at all 13 sampling events.
- Up to 30 pesticides were detected at the same time.
- Of the total pesticide detections, 17 were above WSDA's assessment criteria (Table 10).
    - All detections of 4,4'DDD and 4,4'-DDE, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the eight diuron detections, two detections approached the plant EC_{50} (0.13 µg/L).
- Out of three detections of fipronil, two detections approached the invertebrate NOAEC (0.011 µg/L).
- The detection of imidacloprid approached the invertebrate NOAEC (0.01 µg/L).
- There was no detection of permethrin at the site, however, permethrin was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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		Apr		May		Jun			Jul		Aug		Sep	Oct
Day of the Month	Use*	7	21	5	19	2	16	23	14	28	11	25	20	4
1-(3,4-Dichlorophenyl)-3-methylurea	D						0.006	0.004					0.007	
2,4-D	H		0.034		0.129		0.082						0.108	
2,6-Dichlorobenzamide	D	0.186	0.229	0.210	0.207	0.201	0.192	0.248	0.259	0.278	0.255	0.248	0.188	0.249
4,4'-DDD	L	0.003	0.003	0.003	0.003	0.003	0.004	0.003		0.002				
4,4'-DDE	L				0.002	0.001		0.001					0.002	
Atrazine	H	0.005	0.005	0.005	0.006	0.004	0.006	0.004	0.005	0.005	0.005	0.005		0.007
Boscalid	F						0.005			0.005			0.006	
Bromacil	H	0.003	0.005	0.005		0.005	0.006	0.005	0.008	0.012	0.007			
Carbaryl	I				0.008									
Carbendazim	F	0.002	0.010		0.013	0.009	0.010	0.009	0.009				0.014	0.006
Chlorpropham	H				0.001									
Chlorsulfuron	H						0.020							
Diazinon	I			0.002										
Dicamba acid	H												0.011	
Dichlobenil	H	0.008	0.013	0.009	0.005	0.005	0.014	0.005	0.002	0.003	0.003	X	0.016	0.004
Dinotefuran	I				0.009								0.005	
Dithiopyr	H		0.002			0.003	0.004			0.002			0.007	
Diuron	H			0.004	0.007	0.025	0.078	0.008	0.008				0.071	0.006
Eptam	H												0.010	
Ethoprop	I												0.004	
Fipronil	I						0.009						0.009	0.004
Fipronil disulfinyl	D												0.006	
Fipronil sulfide	D									0.005			0.005	0.005
Fipronil sulfone	D									0.004				
Hexazinone	H			0.004	0.005									
Imazapic	H												0.007	
Imazapyr	H	0.013	0.018	0.019	0.021	0.019	0.019	0.027	0.023	0.023	0.023	0.024	0.021	0.015
Imidacloprid	I						0.010							
Isoxaben	H												0.003	
Mecoprop (MCPP)	H												0.019	
Metolachlor	H				0.004	0.004	0.005			0.005			0.049	0.009
Metribuzin	H					0.004								
N,N-Diethyl-m-toluamide (DEET)	IR			X	0.007	0.032	0.021	0.019					0.061	0.025
Oxamyl	I												0.006	
Pendimethalin	H	0.002		0.006	0.008	0.005	0.012	0.005		0.005			0.034	0.011
Pentachlorophenol	WP												0.013	
Prometryn	H									0.008				
Propiconazole	F	0.016	0.016	0.014	0.013		0.021	0.011	0.012		0.013		0.069	0.014
Simazine	H	0.007	0.006	0.009	0.017	0.008	0.011			0.009		0.009	0.157	0.017
Sulfentrazone	H			0.005	0.007		0.007	0.005	0.008				0.010	0.008
Tebuthiuron	H							0.004						
Terbacil	H	0.004	0.004											
Tetrahydrophthalimide (THPI)	D				0.003									
Triadimefon	F						0.004							
Triazine DEA degradate	D	0.003	0.004	0.004	0.003	0.004	0.003	0.005	0.004	0.005	0.004	0.006		0.004
Triazine DIA degradate	D				0.004								0.010	
Triazine HA degradate	D						0.001							
Triclopyr acid	H			0.030	0.219		0.089	0.058	0.071		0.065	0.025	0.617	0.044
Suspended sediment concentration		-	9	8	8	6	12	6	4	5	5	4	8	2
Total suspended solids		6	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		9.8	7.4	6.7	7.1	5.1	7.9	3.9	3.6	2.8	3.2	3.5	15.0	4.7
Precipitation (total in/week)†		-	-	0.18	0.15	0.24	1.35	0.00	0.00	0.00	0.01	0.01	1.76	0.60

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, L: Legacy, 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 4 of the 13 site visits (31%). Water quality at the Burnt Bridge Creek site is shown below (Figure 15).

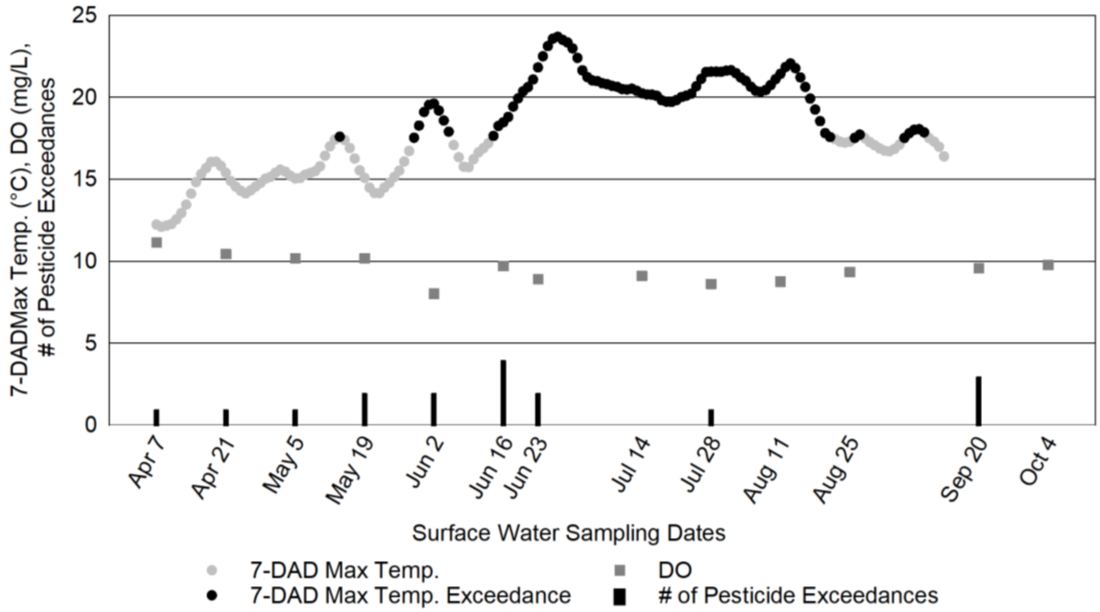


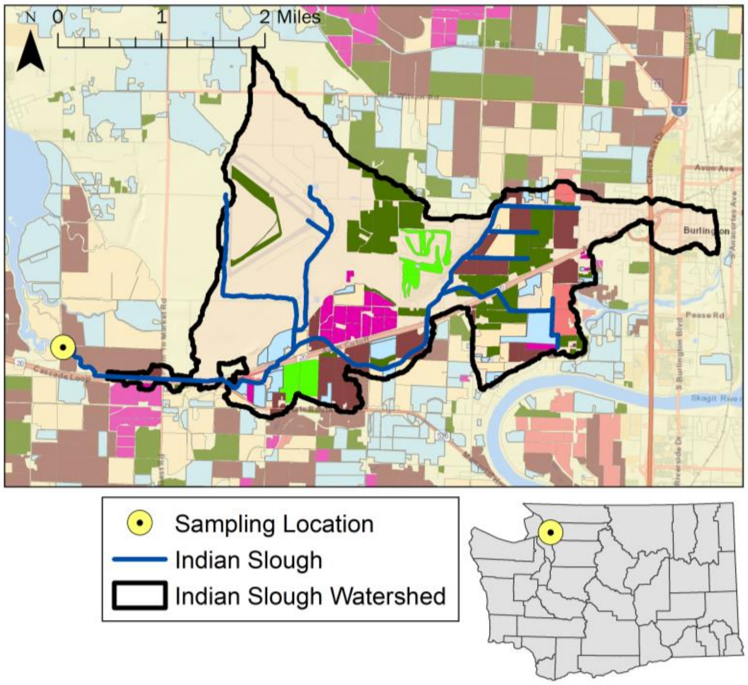
Figure 15 – Burnt Bridge Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.33 to 8.00 with an average of 7.74. All DO measurements also met the standard, ranging from 8.01 mg/L to 11.15 mg/L with an average of 9.51 mg/L. The 7-DADMax temperature was greater than the 17.5°C standard on 85 days of the sampling season, primarily from June 14 to August 21. Pesticide exceedances coincided with 7-DADMax temperature exceedances at four 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 above WSDAs monitoring site (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



Indian Slough Crop Groups	Acres
Other	256
Berry	181
Cereal Grain	231
Hay/Silage	586
Nursery	91
Turfgrass	152
Vegetable	480
Total Ag	1,977
Total Non-Ag	3,048
Watershed Total	5,025

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, also referred to as Little Indian Slough, in Skagit County. The monitoring site is located just upstream from the tide gate at Bayview-Edison Road near Mt. Vernon (latitude: 48.4506º, longitude: -122.4650º) (Figure 16, Figure 17).

Figure 17 – Indian Slough upstream view

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 brassicas. The ‘Other’ crop group category consists mostly of fallow fields, pasture, and assorted small acreage crops (Figure 16). Indian Slough is another site where the presence of invasive New Zealand mud snails has been confirmed.

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

Below is a brief overview of the pesticide findings in Indian Slough in 2021.

- NRAS tested for 170 unique pesticides in Indian Slough.
- There were 454 total pesticide detections from six different use categories: 29 types of herbicides, 11 insecticides, 7 fungicides, 3 legacies, 7 degradates, and 1 insect repellent.
- Pesticides were detected at all 18 sampling events.
- Up to 39 pesticides were detected at the same time.
- Of the total pesticide detections, 28 were above WSDA's assessment criteria (Table 11).
    - All the 4,4'-DDD and 4,4'-DDE detections, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the five detections of fipronil, three detections approached the invertebrate NOAEC (0.011 µg/L).
- Of the 11 detections of imidacloprid, three detections exceeded the invertebrate NOAEC and six approached the invertebrate NOAEC (0.01 µg/L).
- Diuron was detected every sampling event (18); none of which exceeded assessment criteria. The seven indaziflam detections and the malathion detection did not exceed any assessment criteria in 2021 either. Diuron, indaziflam, and malathion were still considered watershed POCs because they have been detected at this site exceeding assessment criteria in recent years. Bifenthrin was not detected in 2021 but was considered a watershed POC because of the same logic.

The Indian Slough monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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		Apr				May				Jun					Jul		Sep	Oct	
Day of the Month	Use*	5	12	19	27	3	11	17	25	1	8	14	22	28	7	12	29	5	12
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.006									0.005					
2,4-D	H		0.040	0.102	0.210												0.037	0.024	0.026
2,6-Dichlorobenzamide	D	0.125	0.116	0.116	0.151	0.107	0.098	0.090	0.082	0.081	0.076	0.071	0.088	0.059	0.045	0.049	0.219	0.299	0.239
4,4'-DDD	L	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.003	0.003	0.003	0.003						
4,4'-DDE	L							0.001		0.001			0.001		0.001				
4-Nitrophenol	D							0.031											
Acephate	I			0.012	0.156	0.024	0.003	0.034											
Aminocyclopyrachlor	H		0.019				0.020				0.018								
Atrazine	H	0.004	0.010	0.004	0.049		0.003			0.003		0.003			0.003			0.004	0.005
Azoxystrobin	F	0.030	0.021	0.005	0.038	0.005	0.023	0.008	0.059	0.008	0.035	0.006	0.006	0.005	0.006	0.004	0.006	0.007	0.006
Benfluralin	H								0.001										
Boscalid	F	0.009	0.009	0.009	0.010	0.009	0.007	0.008	0.008	0.008	0.008	0.009	0.011	0.011	0.010	0.013	0.015	0.016	0.015
Bromacil	H	0.008	0.008	0.007	0.051	0.006	0.006		0.007	0.005	0.006	0.006	0.006				0.044	0.129	0.055
Carbaryl	I				0.003														
Carbendazim	F				0.011						0.008	0.011	0.009				0.008	0.008	0.007
Chlorpropham	H	0.032	0.018	0.002	0.029	0.003	0.011	0.002	0.018	0.004	0.007								0.003
Dacthal (DCPA)	H		0.036			0.049	0.062	0.048		0.057	0.020	0.030							
Diazinon	I			0.003	0.007														
Dicamba acid	H			0.021	0.099														
Dichlobenil	H	0.005	0.007	0.004	0.031	0.005	0.004	0.002	0.003	0.002	0.002	0.002	0.003				0.008	0.161	0.034
Dinotefuran	I		0.446	0.003															
Diuron	H	0.011	0.010	0.010	0.011	0.008	0.006	0.007	0.006	0.005	0.006	0.004	0.007	0.006	0.004	0.005	0.014	0.027	0.012
Eptam	H	0.002	0.002	0.003	0.006	0.004	0.006	0.002	0.003	0.002		0.008	0.003	0.001	0.002	0.002	0.003	0.002	0.002
Fipronil	I	0.004			0.008				0.007								0.005	0.007	
Fipronil sulfide	D		0.003														0.005	0.005	
Fludioxonil	F	0.020	0.014	0.007	0.037	0.009	0.022	0.011	0.044	0.011	0.026	0.008	0.009	0.010	0.012	0.007	0.010	0.021	0.026
Hexazinone	H	0.017	0.016	0.020		0.018	X	0.016	0.015		0.016	0.016	0.019	0.014	0.013	0.015	0.032	0.037	0.035
Imazapic	H																	0.007	
Imazapyr	H	0.028	0.023	0.024	0.054	0.030	0.239	0.043	0.308	0.147	0.038	0.032	0.110	0.043	0.024	0.025	3.640	3.000	2.640
Imidacloprid	I			0.010	0.007	0.004		0.006	0.004	0.075	0.024	0.010	0.010	0.005			0.009		
Indaziflam	H		0.011		0.026	0.002	0.002						0.002				0.003	0.003	
Isoxaben	H										0.006								
Malathion	I		0.009																
MCPA	H				0.727		0.537	1.310											
Metalaxyl	F				0.011								0.021				0.017	0.024	0.023
Methamidophos	L				0.011	0.007	0.004	0.005											
Methoxyfenozide	I										0.003						0.003	0.003	
Metolachlor	H		0.005	0.006	0.010	0.006	0.007	0.006	0.010	0.012	0.010	0.033	0.012	0.007	0.012	0.010	0.013	0.017	0.043
Metribuzin	H								0.005	0.006		0.006	0.005						
Metsulfuron-methyl	H								0.008										0.014
N,N-Diethyl-m-toluamide (DEET)	IR	X			0.012													0.012	0.008
Phosmet	I						X				0.005								
Prometon	H				0.006				0.005								0.005	0.019	0.008
Propiconazole	F	0.016	0.016	0.009	0.070	0.018	0.023	0.012	0.017	0.018	0.044	0.017	0.021	0.025	0.023	0.015	0.057		0.068
Pyrimethanil	F																	0.003	
Simazine	H	0.008	0.008		0.008			0.006		0.005									
Sodium bentazon	H			0.016							0.017		0.023						
Sulfentrazone	H	0.021	0.021	0.026	0.022	0.025	0.019	0.019	0.021	0.018	0.022	0.021	0.023	0.018	0.017	0.019	0.037	0.040	0.045
Sulfometuron-methyl	H		0.006		0.006				0.013		0.006			0.006	0.004		0.002	0.003	
Tebuthiuron	H	0.060	0.052	0.068	0.045	0.064	0.060	0.059	0.049	0.051	0.047	0.056	0.060	0.044	0.042	0.056	0.036	0.032	0.034
Terbacil	H	0.012	0.010	0.019		0.020	0.020	0.020	0.022	0.021	0.025	0.026	0.025	0.025	0.024	0.033			0.019
Tetrahydrophthalimide (THPI)	D				0.214		0.001		0.004	0.001	0.007								
Tetramethrin	I				0.046														
Thiamethoxam	I	0.011	0.011	0.011	0.021	0.008	0.006	0.008	0.006	0.005	0.007	0.007	0.007	0.005	0.004	0.004	0.008	0.011	0.007
Triazine DEA degradate	D				0.007														
Triazine HA degradate	D	0.014	0.011	0.011	0.011	0.011	0.010	0.009	0.007	0.007	0.009	0.009	0.011	0.008	0.008	0.007	0.007	0.009	0.009
Triclopyr acid	H				0.023				0.029								0.137	0.095	0.156
Trifluralin	H								0.008										
Suspended sediment concentration		-	-	11	11	12	11	13	11	11	10	9	8	7	5	4	5	8	6
Total suspended solids		8	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		32.8	36.0	23.6	31.8	17.2	17.2	16.5	22.8	9.3	14.7	12.6	10.5	10.3	13.6	-	23.5	13.4	6.2
Precipitation (total in/week)†		0.01	0.50	0.00	0.65	0.11	0.33	0.00	0.39	0.12	0.26	0.30	0.05	0.00	0.00	0.00	0.86	0.64	0.83

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, L: Legacy)

† 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 15 of the 18 site visits (83%). Water quality at the Indian Slough site is shown below (Figure 18).

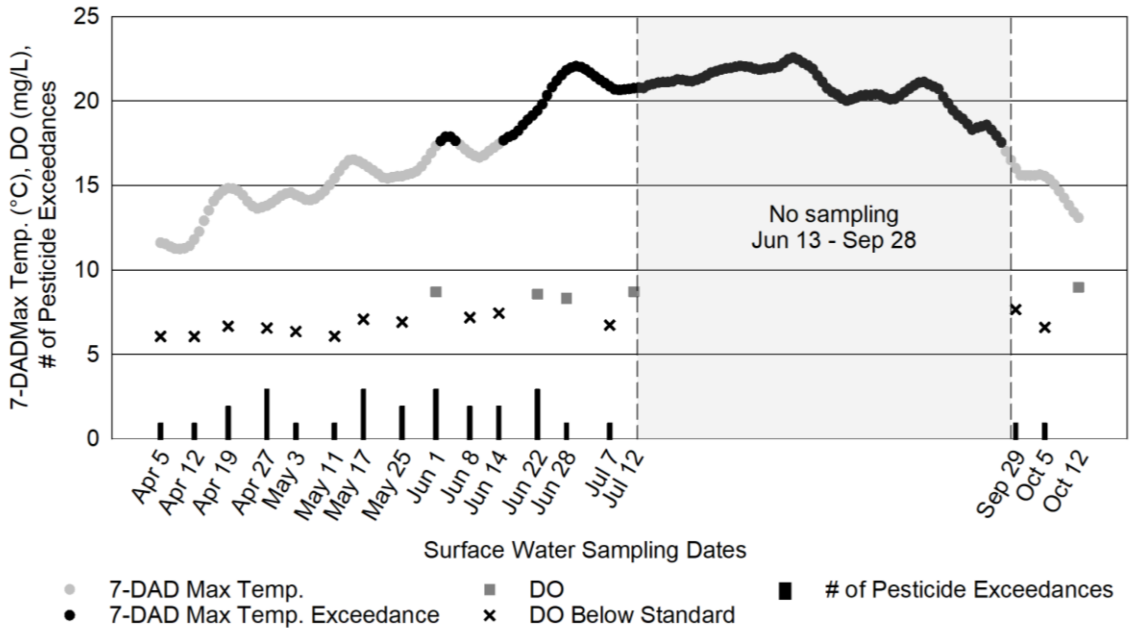


Figure 18 – Indian Slough water quality measurements and exceedances of assessment criteria

All pH measurements were within the state standard, ranging from 6.60 to 7.38 with an average of 6.90. DO measurements ranged from 6.05 mg/L to 8.97 mg/L with an average of 7.26 mg/L. Over half (72%) of the measurements did not meet the state DO standard; 13 measurements were less than 8 mg/L. There were thirteen instances when the DO measurement coincided with one, two, or three pesticide exceedances. The 7-DADMax temperatures were greater than the 17.5°C temperature standard on 108 days of the sampling season, specifically from June 2 through June 5 and then June 15 through September 2. Pesticide exceedances overlapped with 7-DADMax temperature exceedances at three 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 were 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 water 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

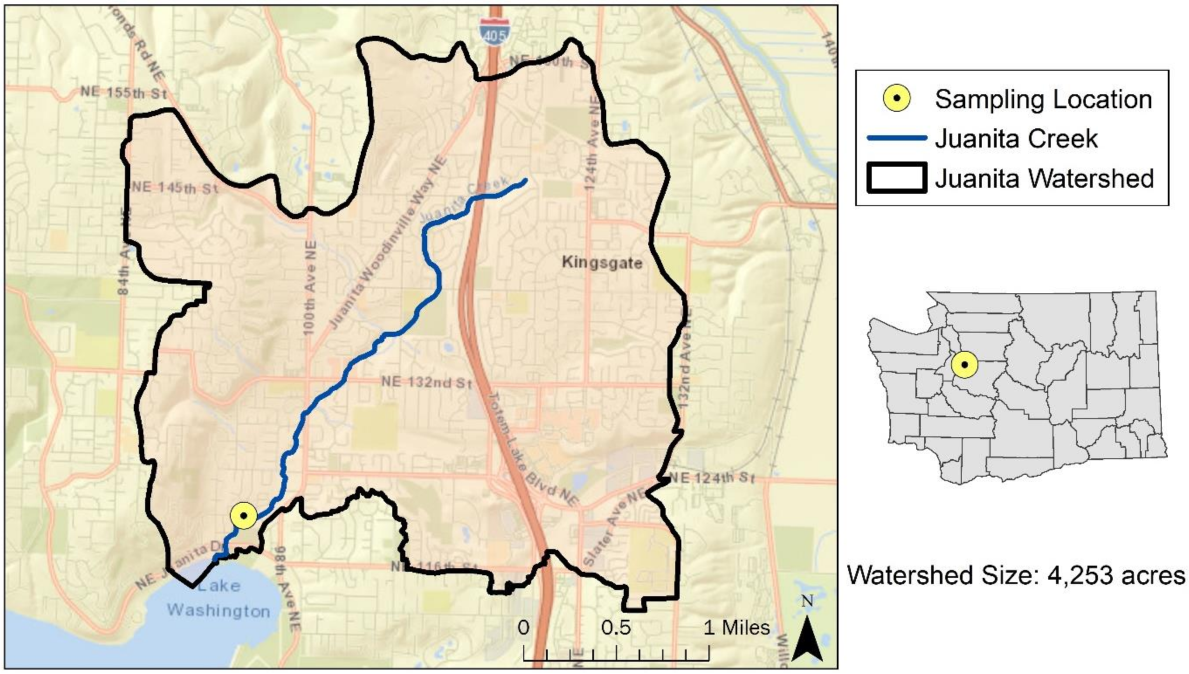


Figure 19 – Map of Juanita Creek and its drainage area with associated sampling location and crop groups identified

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: 47.7077º, longitude: -122.2148º). 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 2021.

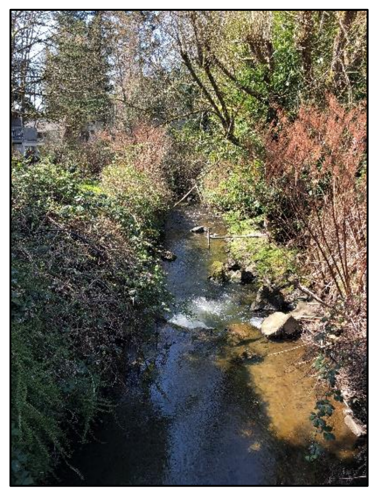


Figure 20 – Juanita Creek downstream view

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.

Below is a brief overview of pesticide findings in Juanita Creek in 2021.

- NRAS tested for 170 unique pesticides in Juanita Creek.
- There were 159 total pesticide detections from eight different use categories: 22 types of herbicides, 4 insecticides, 2 fungicides, 4 degradates, 1 antimicrobial, 1 insect repellent, and 2 synergists.
- Pesticides were detected at all 13 sampling events.
- Up to 23 pesticides were detected at the same time.
- Of the total pesticide detections, five were above WSDA's assessment criteria (Table 12).

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

- The single imidacloprid detection exceeded the invertebrate NOAEC (0.01 µg/L).
- Of six fipronil detections, one detection exceeded the invertebrate NOAEC and three approached the invertebrate NOAEC (0.011 µg/L).
- There was no detection of deltamethrin at the site in 2021, however, deltamethrin was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Juanita Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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		Apr		May		Jun		Jul		Aug			Sep	
Day of the Month	Use*	13	26	10	24	7	21	6	20	3	17	31	13	28
1-(3,4-Dichlorophenyl)-3-methylurea	D					0.004			0.003					0.010
2,4-D	H		0.051		0.054	0.165			0.393					0.050
2,6-Dichlorobenzamide	D	0.297	0.286	0.276	0.269	0.198	0.294	0.270	0.314	0.278	0.271	0.309	0.283	0.262
Atrazine	H	0.004		0.003	0.003		0.003			0.004		0.004	X	
Boscalid	F					0.003								
Bromacil	H	0.004								0.007				
Carbendazim	F		0.011		0.003	0.013	0.010		0.016	0.006		0.009	0.009	0.018
Diazinon	I		0.003											
Dicamba acid	H					0.011								
Dichlobenil	H	0.006	0.020	0.005	0.006	0.015	0.005	0.003	0.003	0.002				0.016
Dinotefuran	I		0.003			0.003								0.004
Dithiopyr	H		0.003			0.015	0.004							0.004
Diuron	H	0.006	0.011	0.004	0.006	0.012	0.006	0.004	0.034		0.004	0.005	0.004	0.041
Eptam	H													0.005
Fipronil	I		0.007		0.012	0.009			0.005				0.004	0.008
Fipronil sulfide	D	0.003								0.005	0.005			0.005
Flumioxazin	H		0.050	X			X							
Imazapic	H					0.006								
Imazapyr	H	0.011	0.024	0.009	0.012	0.022	0.009	0.006	0.006	0.006	0.007	0.007	0.005	0.012
Imidacloprid	I				0.018									
Indaziflam	H													0.003
Isoxaben	H		0.003			0.002								
MGK264	Sy				0.008									
Mecoprop (MCPP)	H					0.041								0.021
Metolachlor	H													0.008
N,N-Diethyl-m-toluamide (DEET)	IR	0.003	0.009		0.008	0.154			0.084					0.035
Pendimethalin	H		0.005			0.005								
Piperonyl butoxide (PBO)	Sy				0.023									
Prometon	H		0.011	0.007	0.009	0.006	0.008	0.006	0.007		0.006	0.006	0.005	0.006
Simazine	H	0.005	0.008		0.005									
Sulfentrazone	H		0.006		0.004	0.008								0.013
Tebuthiuron	H	0.007			0.006	0.008	0.007		0.006		0.004			0.016
Triazine HA degradate	D	0.004	0.005	0.004	0.003	0.007	0.005	0.003	0.003		0.004		0.003	0.009
Triclopyr acid	H					0.038	0.045		0.143			0.049		0.047
Triclosan	A				0.011									
Trifluralin	H		0.008	0.007	0.007	0.008								
Suspended sediment concentration		-	4	1	5	14	3	5	6	2	2	1		4
Total suspended solids		2	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		5.6	8.9	3.8	4.2	22.9	3.3	2.3	2.0	1.9	2.1	2.0	2.0	8.7
Precipitation (total in/week)†		0.28	0.80	0.26	0.43	0.66	0.08	0.00	0.00	0.00	0.00	0.13	0.01	0.94

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 | Detection | No criteria

* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellant, Sy: Synergist)

† 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 13 site visits (8%). Water quality at the Juanita Creek site is shown below (Figure 21).

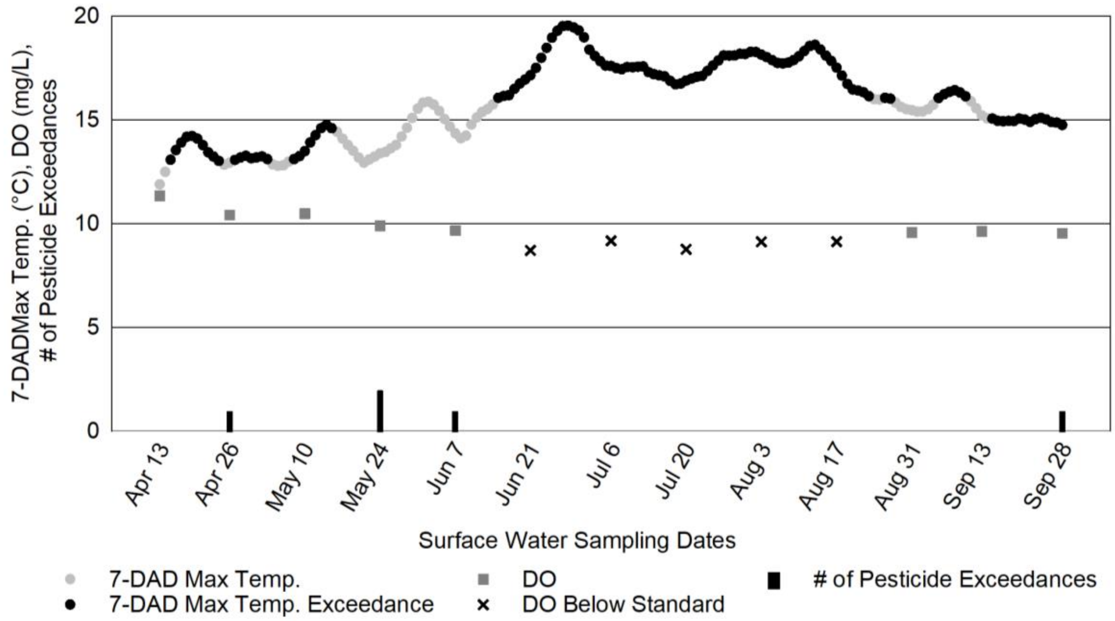


Figure 21 – Juanita Creek water quality measurements and exceedances of assessment criteria

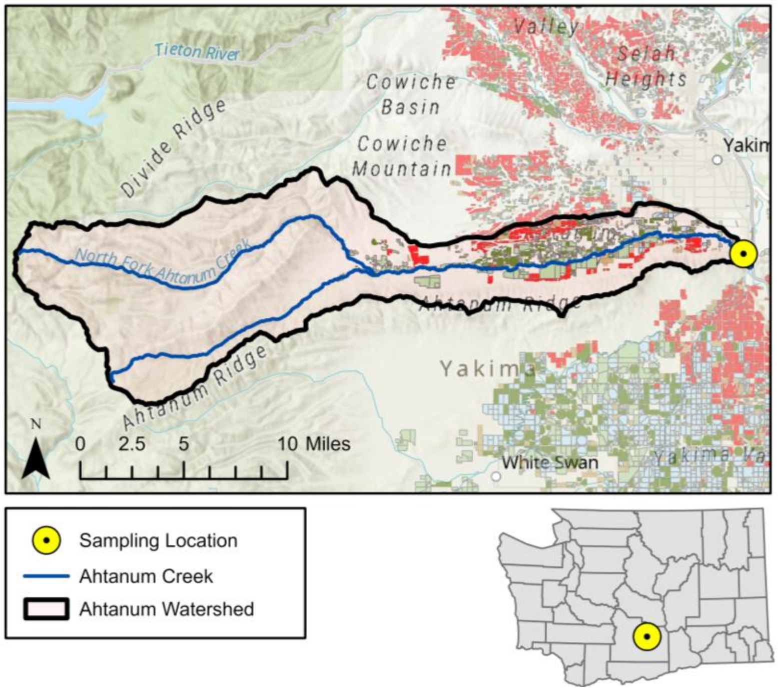
All pH measurements met the state water quality standard, ranging from 6.79 to 7.72 with an average of 7.27. DO measurements ranged from 8.71 mg/L to 11.33 mg/L with an average of 9.65 mg/L. Less than half (38%) of the DO measurements did not meet the standard; five measurements were less than 9.5 mg/L.

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 were applied during different periods of the sampling season. From September 15 through May 15, the 7-DADMax temperature should remain below 13ºC. From May 16 through September 14, the 7-DADMax temperature should remain below 16ºC (WAC 2021). The 7-DADMax temperature exceeded the standard on 117 days, primarily from April 15 through May 15 and June 15 through August 23.

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

Ahtanum Creek



Ahtanum Creek Crop Groups	Acres
Hay/Silage	1,853
Orchard	2,852
Fallow	941
Pasture	4,923
Other	345
Total Ag	10,914
Total Non-Ag	98,326
Watershed Total	109,240

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

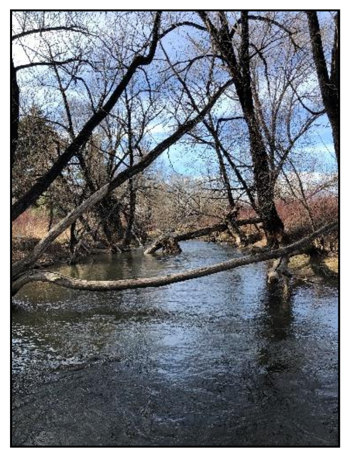


Figure 23 – Ahtanum Creek downstream view

In 2021, NRAS started monitoring the Ahtanum watershed in Yakima County. We selected the watershed for its diverse agricultural land uses and large watershed drainage area. The Ahtanum Creek monitoring site is located upstream of the Main Street bridge crossing the creek in Fullbright Park (latitude: 46.5386°, longitude: -120.4805°) (Figure 22, Figure 23). WDFW has documented the presence of spring Chinook salmon, coho salmon, bull trout, and summer steelhead trout within the Ahtanum Creek watershed (WDFW 2021). Staff observed juvenile fish of unknown species at this site.

The western half of the watershed contains two tributaries to Ahtanum Creek, the North Fork Ahtanum Creek and the South Fork Ahtanum Creek. Both tributaries are mostly within the mountainous Ahtanum State Forest and converge near Tampico. The eastern half of the watershed contains low, flat-lying terrain where most of the watershed's agriculture is. The 46-mile-long Ahtanum Creek, including the length of the North Fork Ahtanum Creek, pours into the Yakima River just south of Union Gap, Washington. Water is taken from the creek to irrigate the surrounding crops. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. Within the Ahtanum Creek drainage area, land use is predominantly grazing, apples, and grass hay. The 'Other' crop group category consists of hops, a golf course, oats, and other assorted small acreage crops (Figure 22).

Below is a brief overview of pesticide findings in Ahtanum Creek in 2021.

- NRAS tested for 170 unique pesticides in Ahtanum Creek.

- There were 47 total pesticide detections from six different use categories: 7 types of herbicides, 3 insecticides, 2 fungicides, 1 legacy, 1 degradate, and 1 insect repellent.
- Pesticides were detected at all 13 sampling events.
- Up to six pesticides were detected at the same time.
- Of the total pesticide detections, four were above WSDA's assessment criteria (Table 13).
    - The single detection of 4,4'-DDE, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
- Chlorpyrifos was the only 2021 watershed-specific POC at this site. All detections of chlorpyrifos approached the invertebrate NOAEC (0.005 µg/L).

The Ahtanum Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Table 13). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 13 – Ahtanum Creek pesticide calendar, µg/L

Month		Mar	Apr		May		Jun		Jul		Aug			Sep
Day of the Month	Use*	29	12	27	10	24	7	21	6	19	2	17	30	13
2,6-Dichlorobenzamide	D	0.002	0.002	0.002	0.002	0.001		0.003	0.006	0.005	0.004	0.006	0.005	0.004
4,4'-DDE	L								0.002					
Aminocyclopyrachlor	H									0.028				
Boscalid	F	X			0.003					0.003	0.005			
Carbaryl	I				0.007	0.007								
Chlorpyrifos	I	0.004	0.004	0.004										
Diazinon	I			0.002										
Dichlobenil	H													0.001
Dithiopyr	H				0.003									
Fludioxonil	F		0.004	0.005	0.004	0.003	0.004	0.007	0.006	0.008	0.008	0.009	0.007	0.006
N,N-Diethyl-m-toluamide (DEET)	IR									0.011				
Norflurazon	H					0.003								
Picloram	H										0.046			
Prometon	H								0.005			0.005		
Sulfentrazone	H	0.004			0.006	0.006	0.005		0.004					
Suspended sediment concentration		-	-	13	13	19	11	5	46	3	3	2	2	2
Total suspended solids		12	12	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		58.1	65.7	51.5	61.8	73.9	68.1	26.8	25.5	17.5	15.3	10.6	15.0	17.9
Precipitation (total in/week)†		0.00	0.00	0.15	0.00	0.02	0.00	0.16	0.00	0.27	0.01	0.00	0.00	0.30

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, L: Legacy)
† Washington State University AgWeatherNet station: Ahtanum, (latitude: 46.55°, longitude: -120.71°)

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 13 site visits (8%). Water quality at the Ahtanum Creek site is shown below (Figure 24).

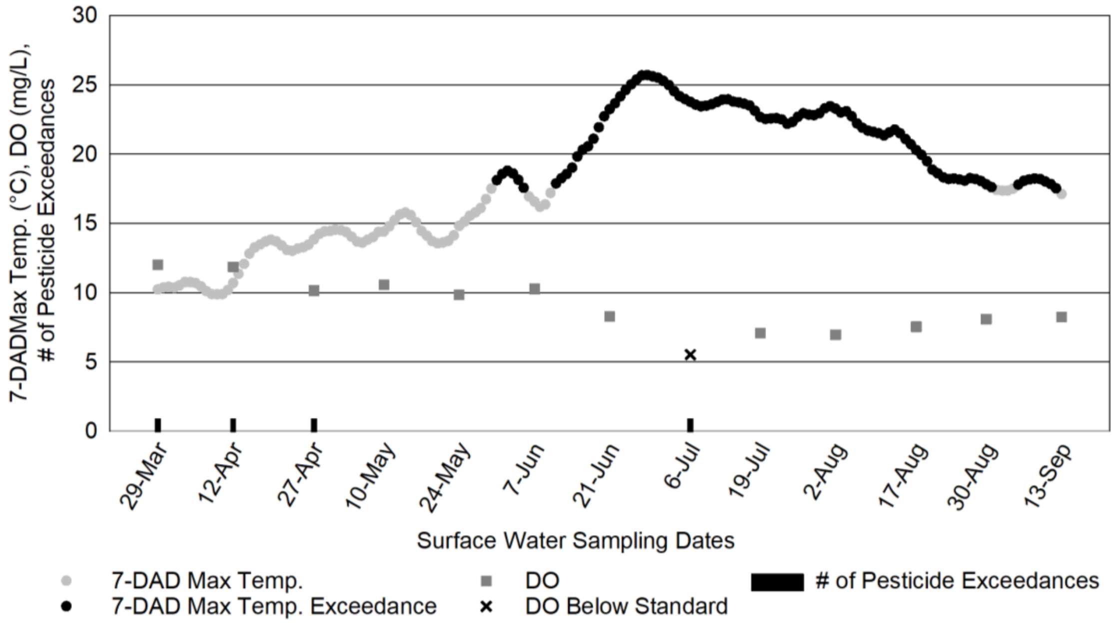
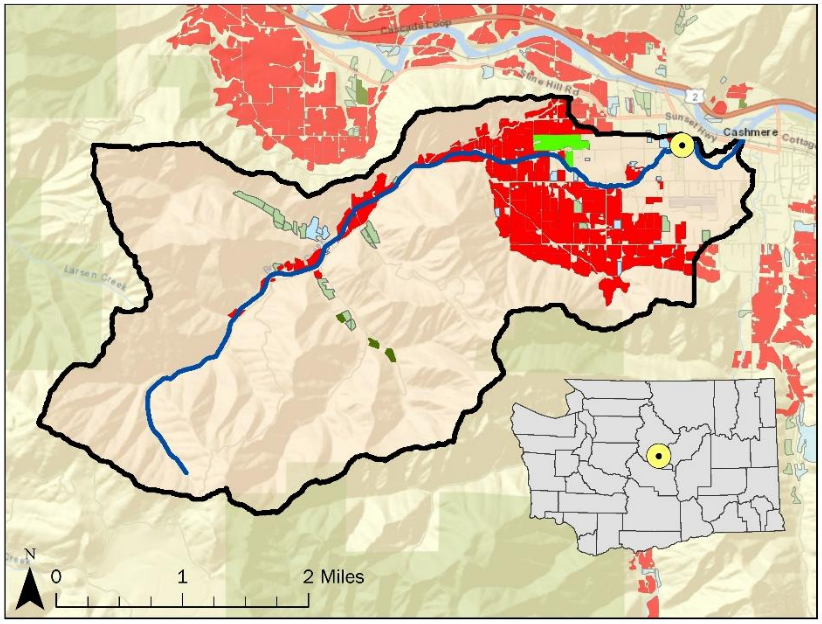


Figure 24 – Ahtanum Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 7.17 to 7.93, with an average of 7.44. All DO measurements except for one met the state standard, ranging from 5.52 mg/L to 11.86 mg/L with an average of 8.70 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 96 days of the sampling season from May 31 through September 12.

Ahtanum Creek has been designated as a freshwater body that provides habitat for salmonid rearing and migration by the WAC (WAC 2021). NRAS will continue to monitor this drainage because of its representative regional land use.

Brender Creek



Brender Crop Groups	Acres
Other	38
Hay/Silage	9
Orchard	774
Pasture	64
Turfgrass	35
Total Ag	920
Total Non-Ag	5,944
Watershed Total	6,864

Figure 25 – 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.

Figure 26 – Brender Creek upstream view

The Brender site is located in Cashmere, on the upstream side of the culvert at Evergreen Drive (latitude: 47.5211°, longitude: -120.4863°) (Figure 25, Figure 26). 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).

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 25).

Below is a brief overview of the pesticide findings in Brender Creek in 2021.

- NRAS tested for 156 unique pesticides in Brender Creek.
- Pesticides were detected at all 23 sampling events.
- There were 260 total pesticide detections from seven different use categories: 7 types of herbicides, 16 insecticides, 3 fungicides, 3 legacies, 1 degradate, 1 insect repellent, and 1 synergist.
- Up to 17 pesticides were detected at the same time.
- Of the total pesticide detections, 89 were above WSDA's assessment criteria (Table 14).
  - DDT and its degradates account for 58 of these exceedances. The 21 detections of 4,4'-DDD, 23 detections of 4,4'-DDE, and 14 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
  - The single detection of fenbutatin oxide exceeded the Endangered Species Level of Concern (0.085 µg/L).
  - Of two pyriproxyfen detections, one approached the invertebrate NOAEC (0.015 µg/L).

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

- Of four carbaryl detections, one detection exceeded the invertebrate NOAEC (0.5 µg/L) and approached NRWQC and WAC chronic criteria (both 2.1 µg/L).
- Of 22 chlorpyrifos detections, 17 detections exceeded the invertebrate NOAEC, and four detections approached the invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
  - The detection on March 30 exceeded the Endangered Species Level of Concern (0.085 µg/L) and the invertebrate LC_{50}. It also exceeded the NRWQC and WAC acute criteria (both 0.083 µg/L), and NRWQC and WAC chronic criteria (both 0.041 µg/L).
  - The detection on April 6 approached the Endangered Species Level of Concern and exceeded the invertebrate LC_{50}.
  - The detection on April 26 exceeded the Endangered Species Level of Concern, invertebrate LC_{50}, NRWQC chronic criteria, and WAC chronic criteria.
  - The detection on May 4 exceeded the invertebrate LC_{50}.
- The four gamma-Cyhalothrin detections exceeded the Endangered Species Level of Concern (0.00145 µg/L) and the invertebrate LC_{50} (0.00008 µg/L). All the detections also approached or exceeded the invertebrate NOAEC (0.00193 µg/L).
  - The detection on March 30 also approached the fish LC_{50} (0.029 µg/L).
- Two imidacloprid detections approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the eight malathion detections, one detection exceeded the Endangered Species Level of Concern (0.205 µg/L), invertebrate LC_{50} (0.098 µg/L), invertebrate NOAEC (0.06 µg/L), and NRWQC chronic criteria (0.1 µg/L).

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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. There were 11 herbicides, 2 herbicide degradates, and 1 wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 14 – Brender Creek pesticide calendar, µg/L

Month		Mar		Apr				May				Jun					Jul				Aug			
Day of the Month	Use*	23	30	6	13	20	26	4	11	18	25	2	8	15	22	29	6	13	20	27	2	9	16	24
2,6-Dichlorobenzamide	D	0.006	0.006	0.005	0.006	X	0.010	0.007	0.005	0.005	0.004	0.008	0.007	0.006	0.006	0.007	0.005	0.007	0.006	0.005	0.006	0.006	0.007	0.006
4,4'-DDD	L	X	0.004	0.005		0.004	0.006	0.005	0.004	0.005	0.006	0.006	0.004	0.008	0.006	0.006	0.004	0.005	0.005	0.005	0.006	0.005	0.004	0.005
4,4'-DDE	L	0.015	0.014	0.013	0.007	0.008	0.026	0.015	0.014	0.017	0.023	0.036	0.012	0.038	0.023	0.025	0.020	0.010	0.013	0.027	0.028	0.023	0.012	0.023
4,4'-DDT	L		0.005	0.004		0.004	0.009			0.007		0.013		0.013		0.009		0.005	0.006		0.010	0.009	0.006	0.009
Acetamiprid	I				0.006	0.003	0.007	0.007	0.006	0.057	0.005			0.002								0.005		0.085
Bifenazate	I																							0.120
Boscalid	F	X		0.003	0.004	0.004	0.004	0.004	0.003	0.003	0.006	0.003		0.004	0.003	0.004	0.004		0.004	0.005	0.005	0.006	0.005	0.005
Bromacil	H	0.008	0.012	0.017	0.022	0.022	0.008	0.014	0.007	0.008	0.005	0.006	0.011	0.003	0.004	0.005	0.005	0.027	0.012	0.006	0.007	0.007	0.008	
Carbaryl	I							1.390	0.005	0.003	0.004													
Carbendazim	F																					0.010	0.015	0.061
Chlorpyrifos	I	0.002	0.113	0.039	0.013	0.010	0.065	0.015	0.013	0.010	0.009	0.007	0.005	0.007	0.006	0.006	0.005	0.005	0.005	0.005	0.005	0.004	0.004	
Clothianidin	I	0.003	0.003									0.005				0.005								
Cyhalothrin-Total	I		0.020								0.002	0.002		0.002										
Diazinon	I					0.005																		
Etoxazole	I										0.006	0.034	0.006	0.009										
Fenbutatin oxide	I																			0.057				
gamma-Cyhalothrin	I		0.016		0.002						0.002			0.002										
Hexazinone	H	0.001						0.004	X															
Imidacloprid	I																					0.012	0.007	
Malathion	I	0.008	2.280	0.018	0.005		0.014		0.006		0.004	0.004												
Metolachlor	H		0.003																					
N,N-Diethyl-m-toluamide (DEET)	IR															0.006								
Norflurazon	H	0.007	0.008	0.009	0.009	0.009	0.008	0.008	0.006	0.010	0.006	0.022	0.011	0.008	0.016	0.011	0.009	0.012	0.012	0.012	0.011	0.016	0.011	0.011
Pendimethalin	H			0.002	0.004	0.005	0.006	0.005	0.004	0.005	0.005		0.005	0.005	0.005								0.006	
Phosmet	I		0.004						X															
Piperonyl butoxide (PBO)	Sy	0.009	0.029	0.013			0.022																	
Pyridaben	I		0.003																					
Pyriproxyfen	I		0.002		0.008																			
Simazine	H				0.004							0.005								0.010				
Spirotetramat	I									0.060			0.086											
Sulfentrazone	H	0.005	0.007	0.006	0.009	0.008	0.005	0.005	0.005	0.005	0.005	0.005	0.005		0.004									
Thiamethoxam	I	0.002	0.002									0.010			0.004	0.003	0.234	0.004	0.005			0.005		
Trifloxystrobin	F							0.010																
Suspended sediment concentration		-	-	-	-	6	44	32	21	29	31	91	130	68	34	31	25	6	9	33	38	30	23	33
Total suspended solids		17	16	16	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		1.7	2.0	1.9	1.6	1.6	5.4	2.0	4.1	3.3	4.9	3.1	1.1	7.0	3.6	2.3	-	0.4	1.2	3.8	-	3.1	1.4	5.2
Precipitation (total in/week)		0.10	0.38	0.00	0.04	0.00	0.05	0.00	0.00	0.00	0.35	0.01	0.03	0.22	0.00	0.00	0.00	0.01	0.00	0.00	0.04	0.01	0.00	0.30

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, L: Legacy, Sy: Synergist)

† Washington State University AgWeatherNet station: Cashmere.N, (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 8 of the 23 site visits (35%). Water quality at the Brender site is shown below (Figure 27).

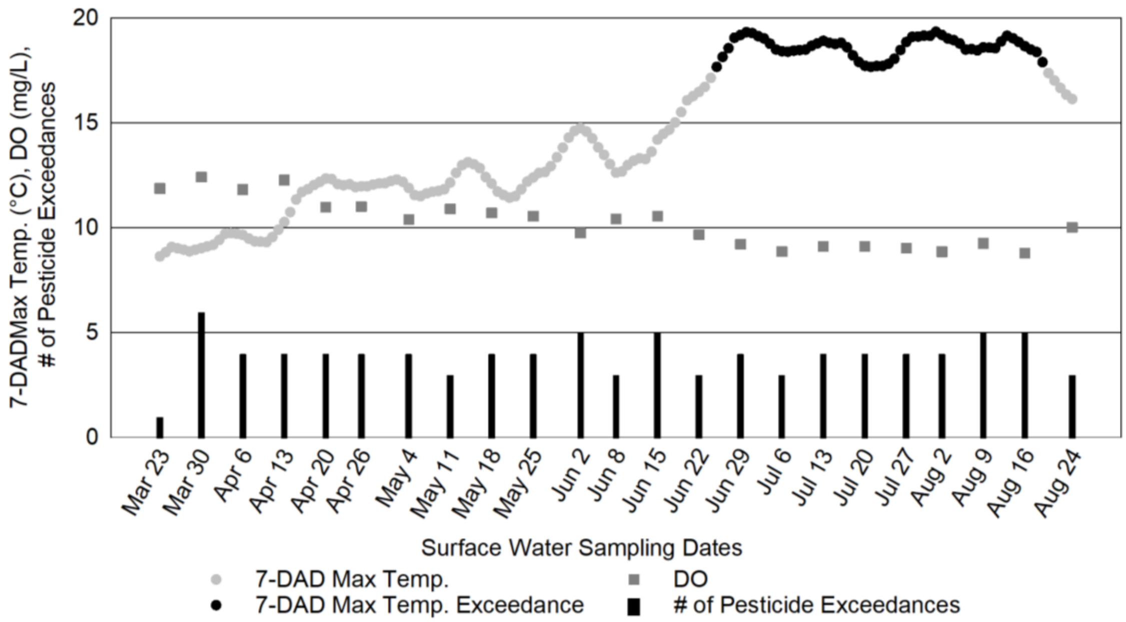
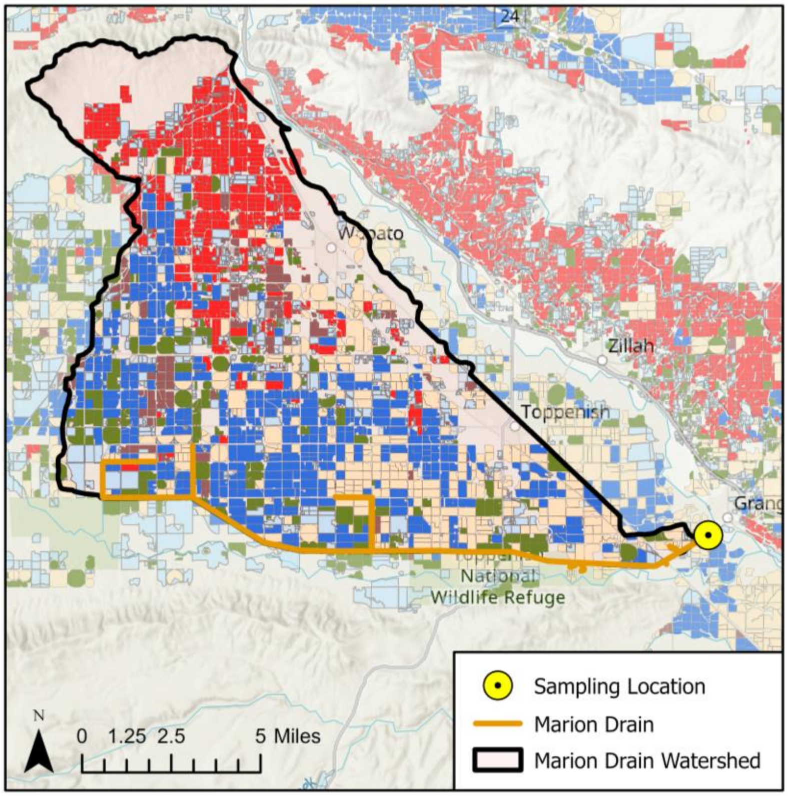


Figure 27– Brender Creek water quality measurements and exceedances of assessment criteria

All pH measurements met state standards, ranging from 7.58 to 8.33 with an average of 7.97. All DO measurements also met state standards, ranging from 8.79 mg/L to 12.41 mg/L with an average of 10.24 mg/L. The 7-DADMax temperatures exceeded the 17.5°C temperature standard on 56 days of the sampling season, from June 25 through August 19. Pesticide exceedances coincided with 7-DADMax temperature exceedances eight times.

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.

Marion Drain



Marion Drain Crop Groups	Acres
Cereal Grain	12,834
Hay/Silage	6,570
Herb	16,279
Orchard	9,531
Vegetable	2,629
Other	7,981
Total Ag	55,824
Total Non-Ag	26,591
Watershed Total	82,415

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: 46.3306º, longitude: -120.2000º) (Figure 28, Figure 29). WSDA selected this watershed to represent irrigated agricultural practices in Central Washington.

Figure 29 – Marion Drain upstream view

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 2021. WDFW and the Yakama Nation have documented fall Chinook salmon, coho salmon, and summer steelhead within the Marion Drain watershed (WDFW 2021).

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).

Below is a brief overview of the pesticide findings in Marion Drain in 2021.

- NRAS tested for 170 unique pesticides in Marion Drain.
- There were 474 total pesticide detections from six different use categories: 21 types of herbicides, 12 insecticides, 7 fungicides, 2 legacies, 6 degradates, and 1 insect repellent.
- Pesticides were detected at all 28 sampling events.
- Up to 26 pesticides were detected at the same time.
- Of the total pesticide detections, 25 were above WSDA's assessment criteria (Marion Drain *pesticide calendar, µg/L Table 15*).
    - One detection of 4,4'-DDD and four detections of 4,4'-DDE 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.

- The 11 detections of chlorpyrifos approached or exceeded the invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
- Of the 28 detections of clothianidin, five approached the invertebrate NOAEC and two exceeded the invertebrate NOAEC (0.05 µg/L).
- The two imidacloprid detections approached the invertebrate NOAEC (0.01 µg/L).

The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Marion Drain *pesticide calendar, µg/L Table 15*). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. The last three sampling visits were only tested for the LCMS-Pesticides analytical method (67 analytes) and SSC due to budgetary limits.

Marion Drain pesticide calendar, µg/L Table 15 – Marion Drain pesticide calendar, µg/L

Month		Mar			Apr				May				Jun					Jul				Aug				Oct		Nov	
Day of the Month	Use*	15	22	29	5	12	19	27	3	10	17	24	1	7	14	21	28	6	12	19	26	2	9	17	23	18	25	1	8
1-(3,4-Dichlorophenyl)-3-methylurea	D			0.007										0.004											0.004				
2,4-D	H				0.045	0.046	0.057	0.112	0.052		0.045	0.060		0.055	0.151	0.057	0.052		0.026	0.037		0.069	0.039	0.108	0.032	-	-	-	-
2,6-Dichlorobenzamide	D				0.001		X		0.001			0.001	0.001	0.002		0.002	0.002	0.002	0.002	0.002	0.002			0.002		-	-	-	-
4,4'-DDD	L			0.002																						-	-	-	-
4,4'-DDE	L			0.001							0.001		0.001											0.002		-	-	-	-
Acephate	I														0.007	0.030													
Aminocyclopyrachlor	H																			0.018									
Atrazine	H	0.007	0.007	0.033	0.006	0.006	0.009	0.006	0.018	0.008	0.007	0.009	0.010	0.031	0.036	0.026	0.013	0.032	0.013	0.011	0.008	0.009	0.009	0.008	0.010	-	-	-	-
Azoxystrobin	F					0.005	0.008	0.011	0.007	0.005	0.007	0.003	0.004		0.003	0.002													
Boscalid	F	<0.001		0.010	0.004	0.007	0.007	0.007	0.007	0.007	0.006	0.005	0.007	0.008	0.013	0.013	0.009	0.006	0.012	0.011	0.011	0.010	0.011	0.010	0.009	-	-	-	-
Bromacil	H			0.020	0.005	0.003	0.010	0.020	0.009	0.007	0.006	0.005	0.004	0.005	0.006				0.004		0.007					-	-	-	-
Bromoxynil	H						0.019	0.030																		-	-	-	-
Carbaryl	I							0.002	0.003	0.004	0.004																		
Carbendazim	F													0.012						0.007									
Chlorantraniliprole	I	0.013	0.012	0.011													0.007	0.010			0.008	0.011	0.010			0.024	0.025	0.024	
Chlorothalonil	F					0.003																				-	-	-	-
Chlorpyrifos	I			0.005	0.006	0.005	0.004	0.019	0.010	0.006	0.004		0.004	0.004		0.004										-	-	-	-
Clothianidin	I	0.038	0.032	0.031	0.013	0.011	0.013	0.013	0.013	0.010	0.016	0.013	0.012	0.009	0.011	0.012	0.016	0.008	0.018	0.016	0.020	0.022	0.021	0.020	0.021	0.049	0.055	0.055	0.049
Diazinon	I			0.004																					0.004	-	-	-	-
Dicamba acid	H						0.010	0.020				0.011		0.019	0.013	0.015		0.019	0.013	0.011	0.010	0.018	0.011			-	-	-	-
Dimethoate	I							0.004	0.024					0.003	0.007											-	-	-	-
Diuron	H			0.036	0.014	0.006	0.009	0.023	0.022	0.006	0.004	0.006	0.006	0.028	0.006	0.006	0.005		0.007	0.004			0.004	0.008	0.008		0.005		
Eptam	H							0.001	0.001					0.017	0.002	0.001										-	-	-	-
Fludioxonil	F				0.018	0.046	0.026	0.021	0.017	0.021	0.011	0.021	0.025	0.029	0.034	0.017	0.011	0.007	0.015	0.013	0.016	0.025	0.024	0.025	0.025	-	-	-	-
Hexazinone	H	0.001	0.001	0.003	0.002	0.003	0.004		0.005	X		0.004		0.005		0.005										-	-	-	-
Imidacloprid	I													0.005												0.008			
MCPA	H								0.020		0.013															-	-	-	-
Methoxyfenozide	I																									0.003			
Metolachlor	H			0.003					0.004		0.004				0.004	0.004	0.004									-	-	-	-
Metribuzin	H				0.006																					-	-	-	-
N,N-Diethyl-m-toluamide (DEET)	IR				X				X								0.006									-	-	-	-
Norflurazon	H		0.002	0.006	0.003		0.004		0.003		0.003	0.003	0.003	0.003	0.003											-	-	-	-
Oxamyl	I																									0.002			
Pendimethalin	H	0.005	0.004	0.014	0.015	0.009	0.034	0.043	0.022	0.028	0.032	0.020	0.022	0.014	0.011	0.007	0.005	0.004	0.005		0.006	0.008		0.007	0.006	-	-	-	-
Phosmet	I									X		0.005														-	-	-	-
Picloram	H																					0.035				-	-	-	-
Prometon	H															0.005							0.005			-	-	-	-
Propiconazole	F						0.008		0.012			0.021			0.009														
Pyrimethanil	F				0.019	0.016	0.007	0.004	0.005	0.004	0.004	0.005	0.004	0.018	0.006	0.006	0.005		0.011	0.006	0.004	0.003	0.008		0.004	0.006			
Simazine	H	0.008	0.007	0.026	0.007	0.004	0.011	0.008	0.012	0.010	0.006	0.012	0.008	0.032	0.019	0.015	0.010	0.019	0.010	0.009	0.010	0.011	0.010	0.010	0.010	-	-	-	-
Sodium bentazon	H	0.043		0.044											0.029					0.018			0.088			-	-	-	-
Sulfentrazone	H	0.003		0.004		0.006	0.011	0.044		0.011	0.008		0.007	0.005	0.015	0.004	0.007	0.011	0.010	0.011	0.013	0.014	0.011		0.011	-	-	-	-
Terbacil	H			0.123			0.132	0.231	0.276	0.080	0.143	0.042	0.104	0.103	0.092	0.034	0.033	0.032	0.096	0.124	0.104	0.150	0.054	0.039	0.073	-	-	-	-
Tetrahydrophthalimide (THPI)	D				0.002		0.002																			-	-	-	-
Thiamethoxam	I	0.019	0.019	0.011	0.007	0.006	0.005	0.005	0.006	0.004	0.007	0.007	0.006		0.004	0.004	0.004		0.005	0.005	0.005	0.009	0.008	0.011	0.012	0.047	0.051	0.060	0.045
Triazine DEA degradate	D	0.010	0.010	0.012	0.003	0.003	0.004	0.004	0.006	0.004	0.004	0.003	0.003	0.005	0.004	0.006	0.005	0.010	0.004	0.005	0.004	0.004	0.003	0.003	0.006	0.007		0.008	0.008
Triazine DIA degradate	D			0.008			0.004			0.004					0.005	0.005		0.011							0.003				
Triazine HA degradate	D	0.001		0.004				0.002	0.003		0.002			0.003	0.003	0.003	0.003	0.002	0.004	0.003		0.003	0.003	0.003	0.003	0.001			
Trifluralin	H	0.002					0.009	0.008	0.010	0.008	0.008	0.008	0.007	0.008												-	-	-	-
Suspended sediment concentration		-	-	-	-	-	6	5	4	14	6	23	13	4	2	1		1	2	2	6	27	8	35	9	11	12	6	7
Total suspended solids		21	16	12	54	7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		153.9	157.9	142.9	-	43.9	26.8	32.7	15.6	115.5	50.8	127.9	96.0	28.9	18.9	11.3	9.9	-	9.6	9.0	21.1	54.6	43.5	-	84.9	-	233.4	215.4	202.9
Precipitation (total in/week)†		0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.08	0.08	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.67	0.00	0.18

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 repellant, L: Legacy)

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

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 12 of the 28 site visits (42%). Water quality at the Marion Drain site is shown below (Figure 30 and Figure 31).

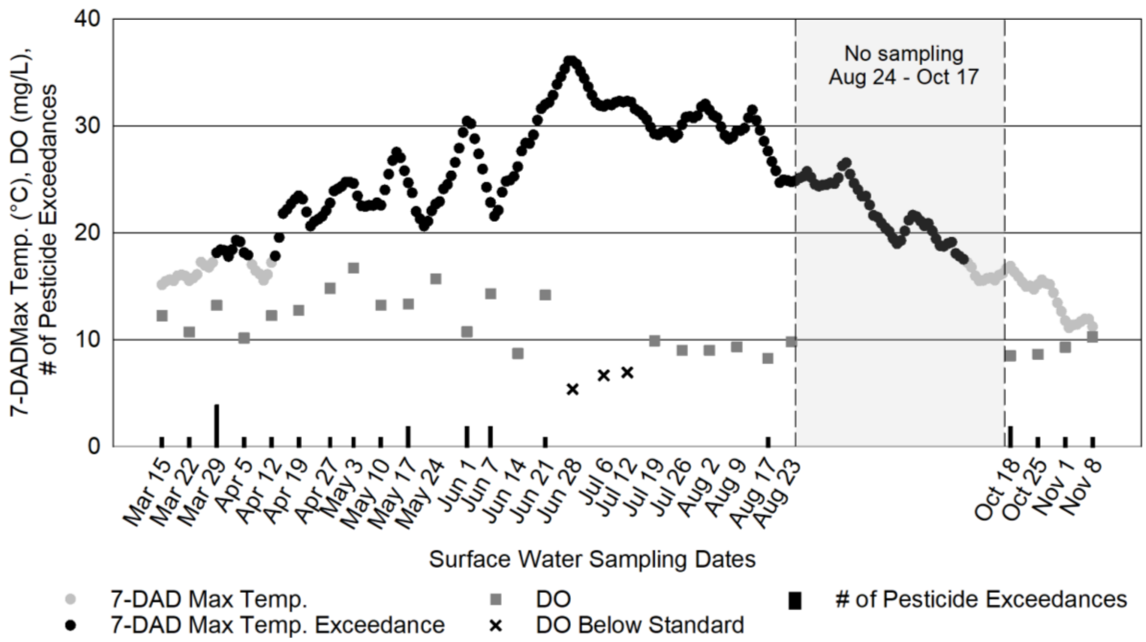


Figure 30 – Marion Drain water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

A majority (89%) of the DO measurements met the state standard, ranging from 5.36 mg/L to 16.70 mg/L with an average of 10.86 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 186 days of the sampling season, primarily from April 13 through October 6. Pesticide exceedances coincided with 7-DADMax temperature exceedances 11 times.

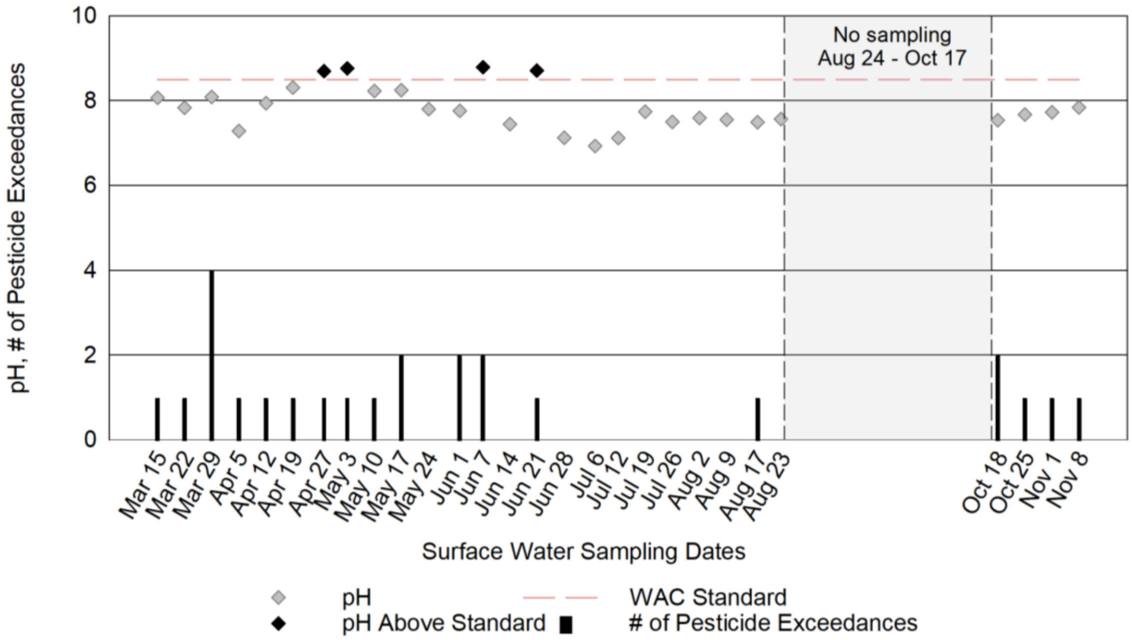
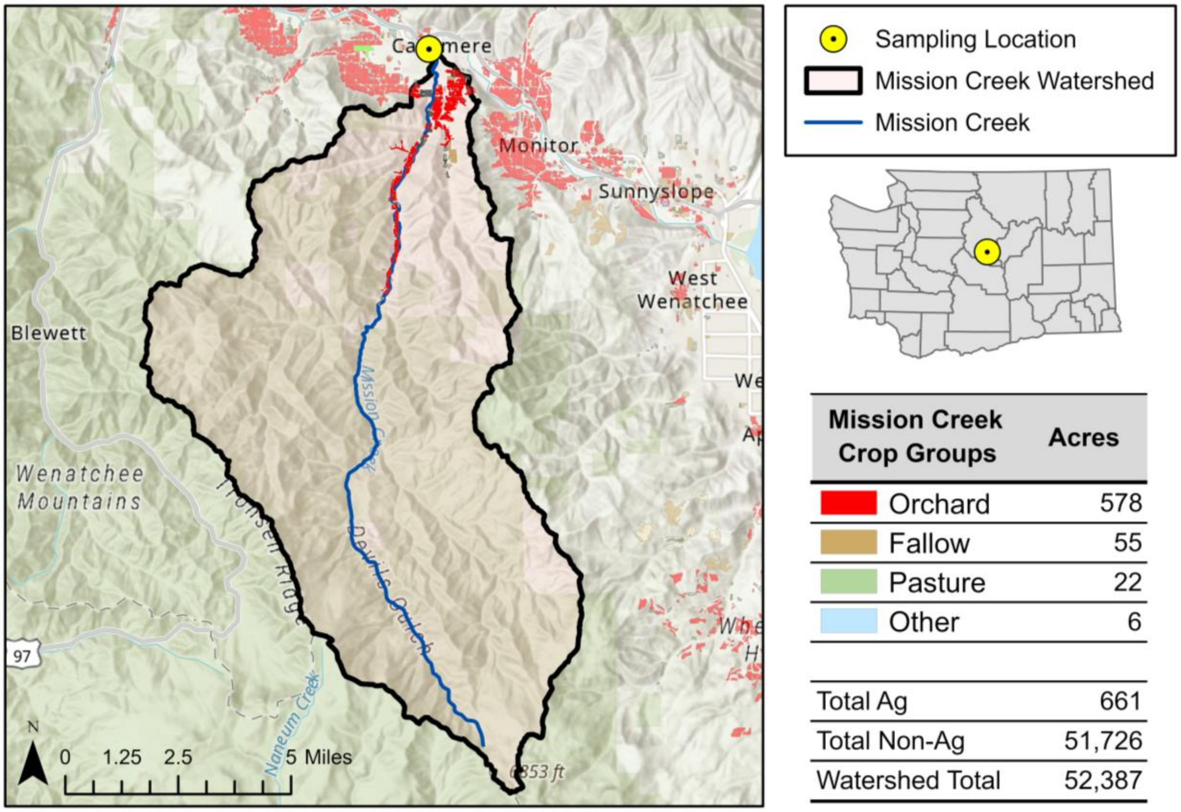


Figure 31 – Marion Drain pH measurements and exceedances of assessment criteria

The pH measurements ranged from 6.93 to 8.79 with an average of 7.83. Less than a quarter (14%) of these measurements exceeded the state standard; four measurements were above 8.50. All pH exceedances coincided with at least one pesticide exceedance.

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



Mission Creek Crop Groups	Acres
Orchard	578
Fallow	55
Pasture	22
Other	6
Total Ag	661
Total Non-Ag	51,726
Watershed Total	52,387

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: 47.5212º, longitude: -120.4760º) (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

Below is a brief overview of the pesticide findings in Mission Creek in 2021.

- NRAS tested for 89 unique pesticides.
- There were 80 total pesticide detections from five different use categories: six types of herbicides, six insecticides, one fungicide, three legacies, and one degradate.
- Pesticides were detected at all 12 sampling events.

- Up to 13 pesticides were detected at the same time.
- Of the total pesticide detections, 31 were above WSDA's assessment criteria (Table 16).
    - DDT and its degradates account for 18 of these exceedances. The 10 detections of 4,4'-DDD, 3 detections of 4,4'-DDE, and 5 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- All the 11 chlorpyrifos detections approached or exceeded the assessment criteria.
    - Two detections exceeded the invertebrate NOAEC (0.005 µg/L). The detection on March 30 also exceeded the invertebrate LC_{50} (0.0138 µg/L) and approached the NRWQC chronic criteria (0.041 µg/L).
    - Nine detections approached the invertebrate LC_{50} (0.0138 µg/L) and the invertebrate NOAEC (0.005 µg/L).
- Of the five detections of malathion, one approached the invertebrate LC_{50} (0.098 µg/L) and invertebrate NOAEC (0.06 µg/L).
- The single detection of pyriproxyfen exceeded the invertebrate NOAEC (0.015 µg/L).

The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Table 16). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. 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		Apr				May				Jun	
Day of the Month	Use*	23	30	6	13	20	26	4	11	18	25	2	8
2,6-Dichlorobenzamide	D		0.002	0.002		X	0.002	0.002			0.002	0.004	0.002
4,4'-DDD	L		0.002	0.003		0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003
4,4'-DDE	L		0.002							0.003		0.003	
4,4'-DDT	L		0.002			0.005	0.004			0.006		0.004	
Boscalid	F		X									0.003	
Chlorpyrifos	I		0.023	0.010	0.005	0.004	0.004	0.005	0.004	0.004	0.004	0.004	0.004
Diazinon	I					0.002						0.002	
Etoxazole	I											0.007	
Hexazinone	H	0.024	0.036	0.050	0.046	0.085	0.075	0.042	0.023	0.014	0.013		0.012
Malathion	I	0.003	0.042	0.008	0.004								0.004
Metolachlor	H											0.004	
Norflurazon	H		0.003		0.004	0.003		0.003			0.003	0.004	0.004
Oxyfluorfen	H		0.050										
Pendimethalin	H	0.005	0.085	0.007	0.006	0.007	0.006	0.006	0.005	0.005	0.005	0.005	0.005
Phosmet	I								X			0.005	
Pyriproxyfen	I				0.018								
Trifluralin	H											0.007	
Suspended sediment concentration		-	-	-	-	175	69	41	22	23	15	14	6
Total suspended solids		24	44	47	26	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		43.8	51.3	54.9	35.4	-	58.7	48.2	32.0	35.1	26.9	19.8	17.3
Precipitation (total in/week)†		0.10	0.38	0.00	0.04	0.00	0.05	0.00	0.00	0.00	0.35	0.01	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

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

† 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. There were no pesticide exceedances that coincided with water quality measurements that did not meet the state standards. Water quality at the Mission Creek site is shown below (Figure 34).

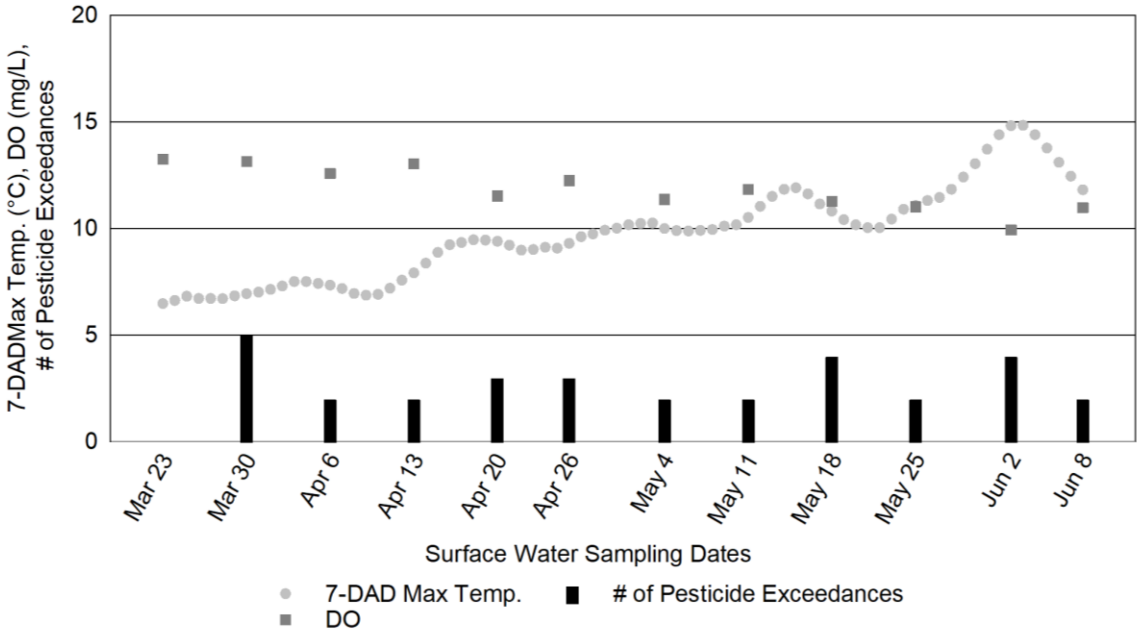
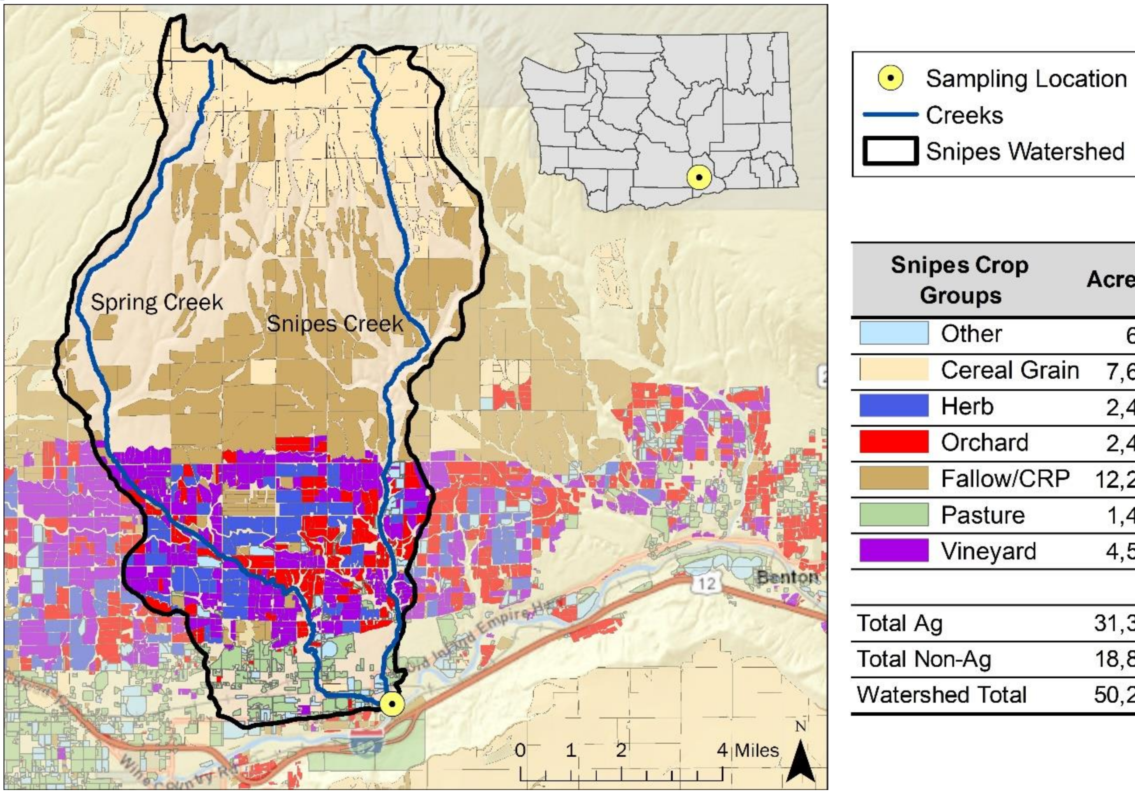


Figure 34 – Mission Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 7.84 to 8.28 with an average of 8.12. All DO measurements met the state standard, ranging from 9.92 mg/L to 13.24 mg/L with an average of 11.84 mg/L. The 7-DADMax temperatures met the state standard during the sampled period, staying below 17.5°C.

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



Snipes Crop Groups	Acres
Other	669
Cereal Grain	7,621
Herb	2,431
Orchard	2,401
Fallow/CRP	12,246
Pasture	1,482
Vineyard	4,520
Total Ag	31,370
Total Non-Ag	18,896
Watershed Total	50,266

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

Figure 36 – Snipes Creek upstream view with average streamflow

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).

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 creek. Roza Irrigation District releases water from the Roza Canal into Snipes Creek at times during the irrigation season. In addition, the Sunnyside Valley Irrigation District releases water from the Sunnyside Canal into Spring Creek, which discharges into Snipes Creek just upstream of the monitoring site. 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 2021.

- NRAS tested for 170 unique pesticides in Snipes Creek.
- There were 302 total pesticide detections from six different use categories: 18 types of herbicides, 13 insecticides, 6 fungicides, 3 legacies, 5 degradates, and 1 insect repellent.
- Pesticides were detected at all 17 sampling events.
- Up to 22 pesticides were detected at the same time.
- Of the total pesticide detections, 38 were above WSDA's assessment criteria (Table 17).
    - The eight detections of 4,4'-DDD, eight detections of 4,4'-DDE, and one detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The three statewide POCs in 2021, chlorpyrifos, diuron, and imidacloprid, were also watershed-specific POCs in Snipes Creek. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- All the 13 detections of chlorpyrifos approached or exceeded the invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
    - The detection on March 29 also exceeded NRWQC and WAC acute (both 0.083 µg/L) and chronic criteria (both 0.041 µg/L).
- Of the 15 detections of diuron, three detections exceeded the plant EC_{50} and two approached the plant EC_{50} (0.13 µg/L).
    - The detection on March 22 approached the invertebrate NOAEC and the detection on March 29 exceeded the invertebrate NOAEC (0.83 µg/L).
- Of the three detections of imidacloprid, one detection approached the invertebrate NOAEC, and two detections exceeded the invertebrate NOAEC (0.01 µg/L).

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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		Mar		Apr				May				Jun					Jul	
Day of the Month	Use*	22	29	5	12	19	27	3	10	17	24	1	7	14	21	28	6	12
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.014	0.057	0.013	0.011	0.020	0.010	0.008		0.007		0.008	0.009	0.004	0.007			
2,4-D	H		0.037	0.059	0.147	0.069	0.057	0.097	0.077	0.092	0.088	0.059	0.083	0.080	0.061			0.026
2,6-Dichlorobenzamide	D	0.003	0.005	0.006	0.004	X	0.003	0.003	0.005	0.004	0.004	0.006	0.003	0.003	0.010	0.014	0.005	0.006
4,4'-DDD	L		0.003			0.003	0.003	0.003	0.003	0.003	0.003	0.003						
4,4'-DDE	L	0.006	0.002							0.002		0.002			0.002	0.001	0.002	0.003
4,4'-DDT	L		0.002															
Acetamiprid	I					0.006											0.004	
Atrazine	H		0.004	0.006	0.007	0.006	0.004	0.004	0.005	0.005	0.004	0.005	0.004	0.009	0.009	0.007	0.005	0.006
Boscalid	F	0.002	0.012	0.004	0.006	0.006	0.005	0.006	0.006	0.008	0.006	0.007	0.007	0.011	0.012	0.009	0.006	0.007
Bromacil	H	0.005	0.006	0.004		0.007												
Carbaryl	I						0.008	0.051	0.019	0.007	0.004		0.012					
Chlorantraniliprole	I															0.009		
Chlorpyrifos	I	0.036	0.107	0.033	0.019	0.010	0.006	0.005	0.005	0.004	0.004	0.004	0.004		0.004			
Diazinon	I	0.010	0.004	0.004	0.003	0.004	0.002					0.002	0.002	0.003	0.004			
Dicamba acid	H				0.015	0.017	0.018				0.024			0.011				
Dichlobenil	H	0.002	0.001				0.002											
Dimethoate	I						0.004	0.015	0.003	0.002				0.022				
Diuron	H	0.442	1.560	0.185	0.122	0.106	0.037	0.026	0.031	0.016	0.015	0.019	0.025	0.009	0.019	0.006		
Eptam	H									0.001	0.001		0.007	0.002				
Etoxazole	I															0.007	0.004	
Fludioxonil	F	0.012	0.022	0.017	0.005	0.013	0.010	0.010	0.009	0.010	0.009	0.006	0.008	0.011	0.009	0.005	0.003	
Flupyradifurone	I																0.057	0.061
Hexazinone	H	0.001	0.002		0.003	0.004		0.005	X	0.005					0.005	0.005		
Imidacloprid	I											0.011			0.010	0.006		
Indaziflam	H			0.003	0.003													
Malathion	I	0.002											0.004	0.013		0.005		
Methoxyfenozide	I							0.003							0.003	0.003		
Metolachlor	H							0.005	0.004		0.004	0.004			0.004	0.004	0.004	0.004
Myclobutanil	F					0.004												0.007
N,N-Diethyl-m-toluamide (DEET)	IR	0.002						X										
Norflurazon	H	0.008	0.047	0.006	0.007	0.007	0.005		0.006	0.005	0.006	0.007	0.004	0.005	0.006	0.008	0.006	0.007
Oxamyl	I							0.001										
Oxyfluorfen	H			0.034	0.047	0.050	0.041											
Pendimethalin	H	0.011	0.017	0.048	0.020	0.014	0.012	0.011	0.008	0.008	0.009	0.006	0.007	0.007	0.006	0.005	0.007	0.009
Prometon	H	0.005																
Pyraclostrobin	F					0.007												
Pyrimethanil	F	0.019	0.031	0.025	0.005	0.008	0.006	0.003	0.005	0.010	0.005	0.003	0.011	0.007	0.006			
Simazine	H															0.005		
Sulfentrazone	H	0.003		0.010		0.005					0.004					0.005		
Terbacil	H						0.004		0.004	0.003								
Tetrahydrophthalimide (THPI)	D			0.004		0.002												
Thiamethoxam	I											0.004		0.015	0.005	0.004		
Triazine DEA degradate	D			0.002		0.004	0.002		0.002	0.003	0.002	0.004		0.003	0.005	0.008	0.003	0.003
Triazine HA degradate	D						0.002			0.002			0.001	0.003			0.002	0.002
Triclopyr acid	H									0.024	0.012							
Trifloxystrobin	F																0.011	0.002
Suspended sediment concentration		-	-	-	-	35	39	33	38	36	44	12	33	24	8	5	63	20
Total suspended solids		327	52	25	22	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		-	-	39.5	-	43.3	78.0	-	57.7	50.9	55.4	22.2	-	-	19.7	10.8	-	28.7
Precipitation (total in/week)†		0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.00	0.00	0.12	0.00	0.00	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 | No criteria

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

† 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 12 of the 17 site visits (71%). Water quality at the Snipes Creek site is shown below (Figure 37 and *Figure 38*).

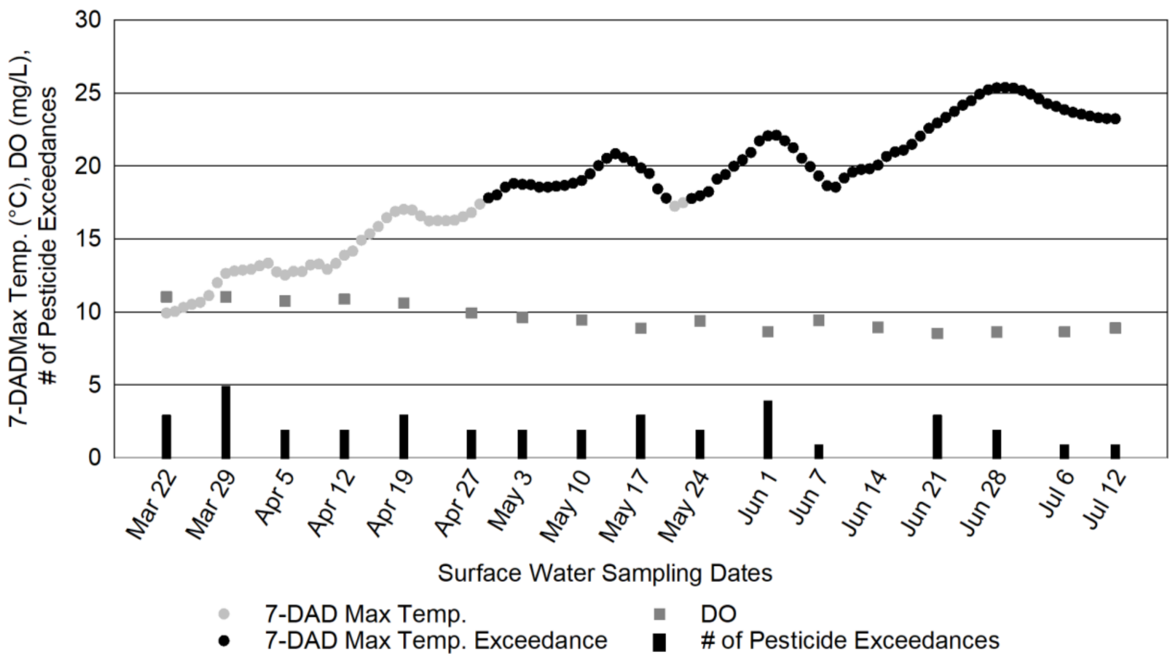


Figure 37 – Snipes Creek water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

All DO measurements met state water quality standards, ranging from 8.52 mg/L to 11.03 mg/L with an average of 9.60 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 73 days of the sampled period, primarily from April 29 through July 12. Pesticide exceedances coincided with 7-DADMax temperature exceedances at ten site visits.

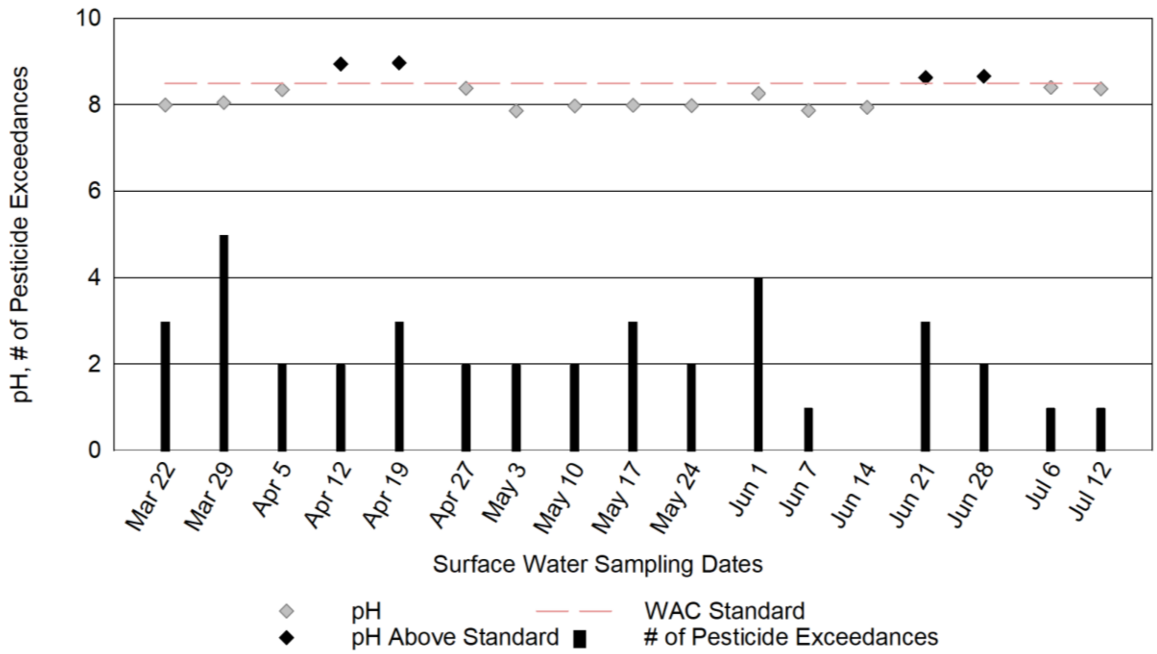
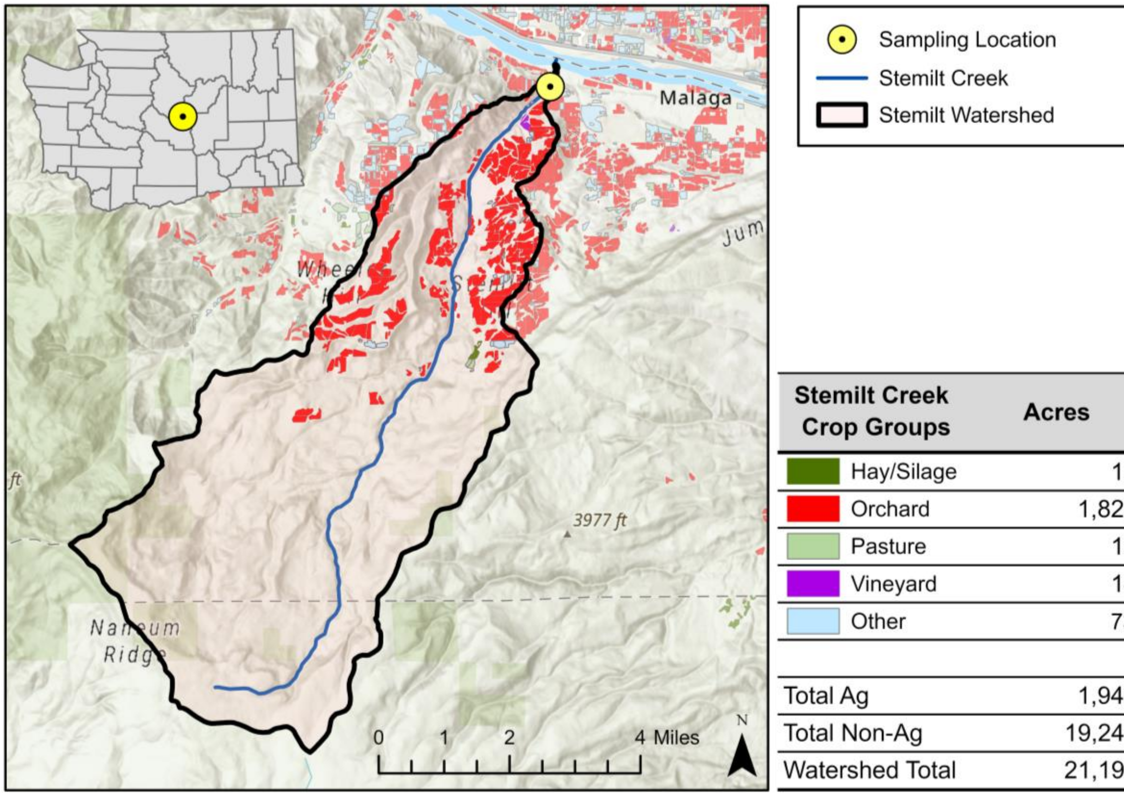


Figure 38 – Snipes Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.86 to 8.97 with an average of 8.27. Roughly 24% (4) of the pH measurements exceeded the state standard. Each of the four pH exceedances coincided with at least one pesticide exceedance (*Figure 38*). Pesticide exceedances overlapped with both pH and 7-DADMax temperature exceedances on June 21 and June 28.

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



Stemilt Creek Crop Groups	Acres
Hay/Silage	15
Orchard	1,828
Pasture	15
Vineyard	14
Other	73
Total Ag	1,945
Total Non-Ag	19,248
Watershed Total	21,193

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.

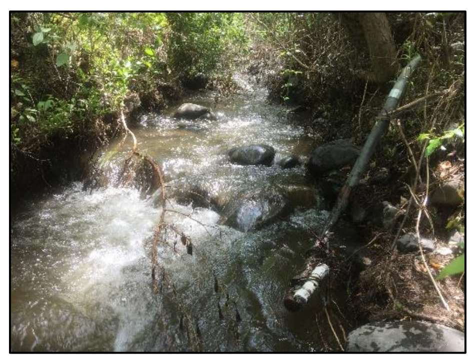


Figure 40 – Stemilt Creek upstream view

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).

Below is a brief overview of pesticide findings in Stemilt Creek in 2021.

- NRAS tested for 89 unique pesticides in Stemilt Creek.
- There were 70 total pesticide detections from five different use categories: 5 types of herbicides, 3 insecticides, 1 fungicide, 3 legacies, and 1 degradate.

- Pesticides were detected at all nine sampling events.
- Up to 10 pesticides were detected at the same time.
- Of the total pesticide detections, 22 were above WSDA's assessment criteria (Table 18).
    - The eight detections of 4,4'-DDD, one detections of 4,4'-DDE, and three detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the nine detections of chlorpyrifos, three detections approached the invertebrate NOAEC, and six detections exceeded the invertebrate NOAEC (0.005 µg/L).
    - The detections on April 6 and April 20 also exceeded the invertebrate LC_{50} (0.0138 µg/L) and one approached NRWQC and WAC chronic criteria (both 0.041 µg/L).
    - All detections of chlorpyrifos except for one approached the invertebrate LC_{50} (0.0138 µg/L).
- Of the eight detections of diazinon, one detection exceeded the invertebrate LC_{50} (0.21 µg/L), invertebrate NOAEC (0.17 µg/L), NRWQC acute and chronic criteria (both 0.17 µg/L).

The Stemilt Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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	Apr				May			
Day of the Month	Use*	30	6	13	20	26	4	11	18	25
2,6-Dichlorobenzamide	D	0.021	0.022	0.022	0.019	0.024	0.020	0.015	0.009	0.016
4,4'-DDD	L	0.003	0.003		0.004	0.004	0.004	0.004	0.004	0.003
4,4'-DDE	L								0.002	
4,4'-DDT	L				0.004	0.003			0.005	
Boscalid	F	X	0.007	0.007	0.008	0.007	0.006	0.006	0.007	0.007
Chlorpyrifos	I	0.003	0.025	0.012	0.017	0.006	0.005	0.005	0.005	0.004
Diazinon	I	0.004	0.008	0.042	0.250	0.015	0.003	0.003	0.004	
Dichlobenil	H						0.004			
Hexazinone	H			0.004	0.005		0.004			
Malathion	I	0.004	0.007	0.012	0.007	0.004			0.006	
Pendimethalin	H				0.005				0.005	
Simazine	H	0.005	0.005	0.004						
Sulfentrazone	H	0.014	0.020	0.019	0.013	0.018	0.012	0.011	0.008	0.010
Suspended sediment concentration		-	-	-	26	11	18	24	69	14
Total suspended solids		4	11	3	-	-	-	-	-	-
Streamflow (cubic ft/sec)		4.6	3.7	3.3	8.3	3.8	2.4	3.0	7.2	2.4
Precipitation (total in/week)†		0.02	0.00	0.00	0.00	0.10	0.00	0.05	0.00	0.09

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, L: Legacy)

† Wash. State Univ. AgWeatherNet station: Stemilt (latitude: 47.33°, longitude: -120.26°)

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 6 of the 9 site visits (67%). Water quality at the Stemilt Creek site is shown below (Figure 41).

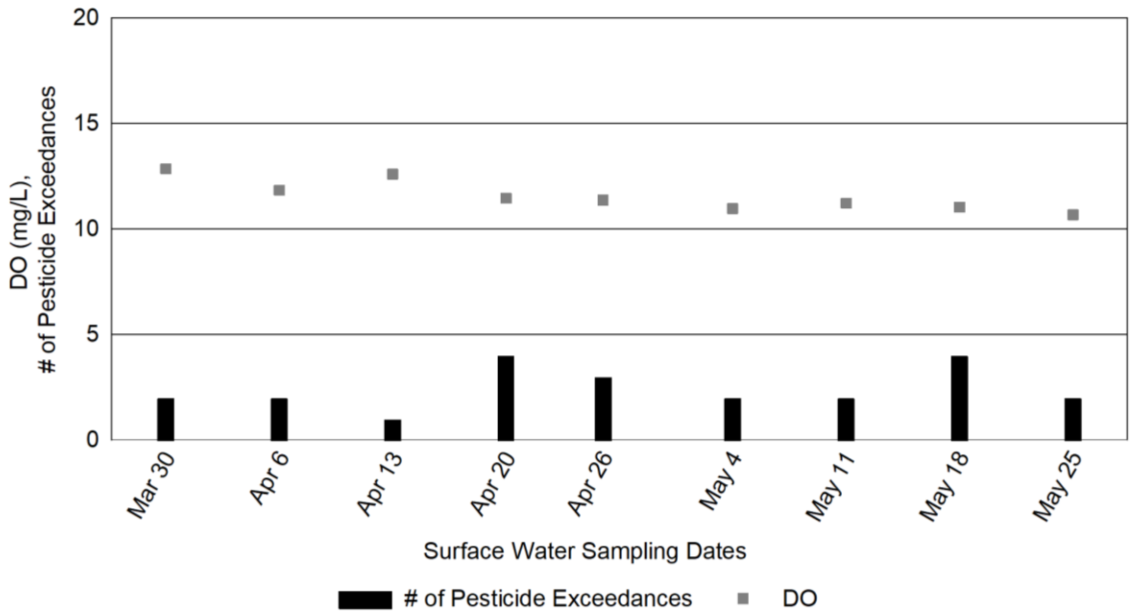


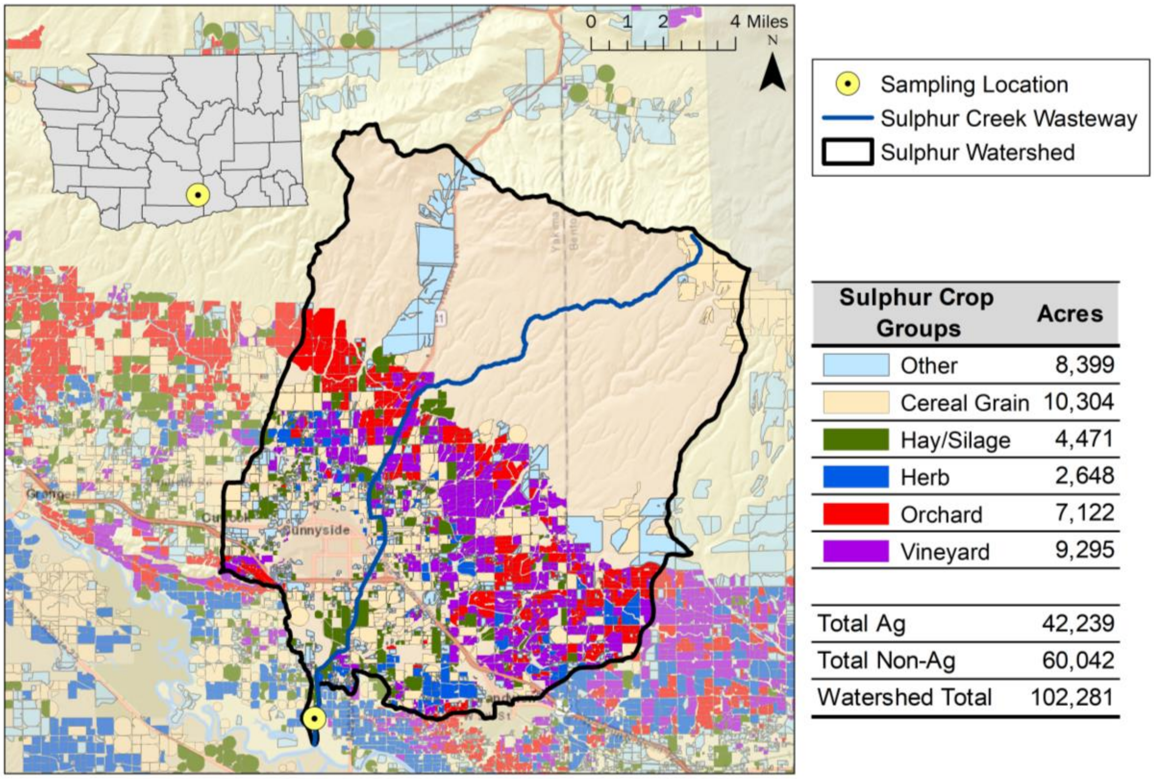
Figure 41 – Stemilt Creek water quality measurements (DO) and exceedances of assessment criteria

Over half (67%) of the pH measurements met the state standard, ranging from 7.84 to 8.68 with an average of 8.24. All DO measurements met the state standard, ranging from 10.67 mg/L to 12.85 mg/L with an average of 11.55 mg/L.

Extremely high streamflow in the spring dislodged and carried the temperature data logger away in 2019. Staff decided not to reinstall the data logger. 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



Sulphur Crop Groups	Acres
Other	8,399
Cereal Grain	10,304
Hay/Silage	4,471
Herb	2,648
Orchard	7,122
Vineyard	9,295
Total Ag	42,239
Total Non-Ag	60,042
Watershed Total	102,281

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).

Figure 43 – Sulphur Creek Wasteway downstream view

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.

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 2021.

- NRAS tested for 170 unique pesticides in Sulphur Creek Wasteway.
- There were 401 total pesticide detections from six different use categories: 24 types of herbicides, 9 insecticides, 7 fungicides, 2 legacies, 7 degradates, and 1 insect repellent.
- Pesticides were detected at all 18 sampling events.
- Up to 25 pesticides were detected at the same time.
- Of the total pesticide detections, 30 were above WSDA's assessment criteria (Table 19).
    - The seven detections of 4,4'-DDD and eight detections of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the nine detections of chlorpyrifos, six exceeded the invertebrate NOAEC (0.005 µg/L), and three of those approached the invertebrate LC_{50} (0.0138 µg/L).
    - The detections on March 22 and March 29 exceeded the invertebrate LC_{50} (0.0138 µg/L), NRWQC and WAC chronic criteria (both 0.041 µg/L). The two detections also approached the endangered species (0.0425 µg/L), NRWQC, and WAC acute criteria (both 0.083 µg/L).
    - The detection on April 5 exceeded the invertebrate LC_{50} (0.0138 µg/L).
- Of the 18 detections of diuron, three detections approached the plant EC_{50}, one detection exceeded the invertebrate NOAEC (0.83 µg/L) and plant EC_{50} (0.13 µg/L).
- The single detection of gamma-Cyhalothrin exceeded the invertebrate LC_{50} (0.00008 µg/L) and the invertebrate NOAEC (0.00193 µg/L). It also exceeded the Endangered Species Level of Concern (0.00145 µg/L).
- The single detection of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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.

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

Month		Mar		Apr				May			Jun		Jul		Aug			Sep	
Day of the Month	Use*	22	29	5	12	19	27	3	10	24	7	21	6	19	2	17	30	13	27
1-(3,4-Dichlorophenyl)-3-methylurea	D		0.031	0.004	0.006	0.010	0.005		0.005	0.006	0.009	0.005	0.007					0.007	
2,4-D	H	0.035		0.071	0.123	0.102	0.097	0.094	0.131	2.070	0.326	0.098	0.286	0.097	0.120	0.137	0.019	1.180	0.042
2,6-Dichlorobenzamide	D	0.004	0.005	0.005	0.008	X	0.007	0.007	0.007	0.004	0.006	0.007	0.009	0.013	0.011	0.010	0.011	0.007	0.012
4,4'-DDD	L	X	0.002	0.003	0.003	0.003	0.003	0.003		0.003									
4,4'-DDE	L	0.003	0.002									0.002	0.002	0.003		0.002		0.003	0.003
Acetochlor ESA	D												0.031	0.051	0.028		0.080		
Atrazine	H	0.003	0.006	0.005	0.008	0.006	0.007	0.007	0.007	0.004	0.006	0.011	0.006	0.009	0.008	0.007	0.008	X	0.007
Boscalid	F		X	0.003	0.005	0.006	0.011	0.005	0.005	0.005	0.006	0.010	0.015	0.017	0.027	0.028	0.010	0.007	0.008
Bromacil	H	0.008	0.026	0.011	0.018	0.030	0.010	0.012	0.010	0.007	0.013	0.012	0.010	0.016	0.017	0.017	0.018	0.016	0.024
Bromoxynil	H			0.019	0.025														
Carbaryl	I						0.020	0.008	0.009										
Carbendazim	F				0.002						0.009						0.009		
Chlorothalonil	F				0.003														
Chlorpyrifos	I	0.044	0.052	0.015	0.008	0.008	0.008	0.004	0.004	0.004									
Clopyralid	H																	0.067	
Clothianidin	I											0.005		0.009	0.008	0.010	0.008	0.006	0.006
Diazinon	I	0.005	0.004													0.004	0.003		
Dicamba acid	H				0.013	0.018	0.041			0.022	0.027	0.038	0.029	0.027	0.027	0.017		0.038	
Dichlobenil	H						0.001									0.006			
Dimethoate	I						0.012	0.011				0.004							
Diuron	H	0.060	2.830	0.061	0.067	0.104	0.086	0.035	0.046	0.042	0.044	0.013	0.017	0.008	0.011	0.008	0.005	0.034	0.006
Eptam	H				0.001						0.010	0.002							
Fludioxonil	F	0.024	0.020	0.007	0.011	0.009	0.007	0.009	0.008	0.015	0.007	0.008	0.014	0.045	0.023	0.013	0.015	0.021	0.021
gamma-Cyhalothrin	I	0.005																	
Hexazinone	H	0.002	0.003	0.003	0.005	0.006		0.007	X	0.005	0.005	0.007	0.006		0.008	0.008	0.008	0.007	0.009
Imazapyr	H	0.004	0.019	0.005	0.007	0.010	0.007	0.007	0.005	0.004	0.003	0.006	0.005	0.006	0.009	0.010	0.008	0.009	0.010
Imidacloprid	I								0.036										
Malathion	I	0.005								0.004									
Metalaxyl	F																0.016		
Metolachlor	H		0.003			0.004	0.005	0.008	0.008	0.004	0.006	0.007	0.005	0.005	0.006	0.005			
Metribuzin	H		0.007			0.005	0.008	0.005			0.005								
Myclobutanil	F												0.005						
N,N-Diethyl-m-toluamide (DEET)	IR	0.001						X					0.012					0.014	
Norflurazon	H	0.002	0.007	0.003	0.005	0.004	0.004		0.005	0.003	0.004		0.005	0.007	0.007	0.007	0.008	0.006	0.013
Oxamyl	I							<0.001											
Oxyfluorfen	H					0.042													
Pendimethalin	H	0.011	0.026	0.053	0.062	0.055	0.039	0.032	0.027	0.014	0.013	0.007	0.007	0.008	0.008	0.006		0.008	0.007
Picloram	H														0.043				
Prometon	H	0.002								0.005		0.005							
Pyrimethanil	F	0.025	0.019	0.010	0.024	0.006	0.002		0.004	0.008	0.013	0.005		0.006	0.003		0.005	0.024	0.008
Simazine	H		0.005					0.005							0.009	0.009			
Sodium bentazon	H					0.010					0.012				0.067	0.041			
Sulfentrazone	H	0.003	0.004	0.005	0.007	0.007	0.040	0.021	0.006	0.004	0.005	0.005	0.008	0.011	0.023	0.011	0.011		0.014
Terbacil	H	0.005	0.008	0.030	0.052	0.036	0.032	0.034	0.021	0.011	0.012	0.010	0.011	0.026	0.036	0.016	0.011	0.049	0.141
Tetrahydrophthalimide (THPI)	D	0.002	0.004	0.001						0.002									
Triazine DEA degradate	D	0.003	0.004	0.004	0.005	0.004	0.005	0.006	0.005	0.003	0.004	0.007	0.008	0.008	0.006	0.007	0.008	0.006	0.007
Triazine DIA degradate	D														0.004				0.004
Triazine HA degradate	D		0.003	0.001			0.001				0.002		0.003	0.003		0.003		0.003	0.002
Triclopyr acid	H					0.020												0.042	
Trifluralin	H		0.008	0.007		0.007	0.010	0.007	0.007	0.008	0.008	0.007	0.008						
Suspended sediment concentration		-	-	-	-	35	45	15	15	54	15	6	5	7	8	6	6	21	6
Total suspended solids		110	33	37	19	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		366	201	173	98	122	137	107	127	280	-	-	-	110	119	127	151	265	144
Precipitation (total in/week)†		0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.00	0.01	0.00	0.00	0.43	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 | No criteria

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

† Washington State Univ. AgWeatherNet station: Sunnyside.N, (latitude: 46.39°, longitude: -120.00°)

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 18 site visits (44%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 44).

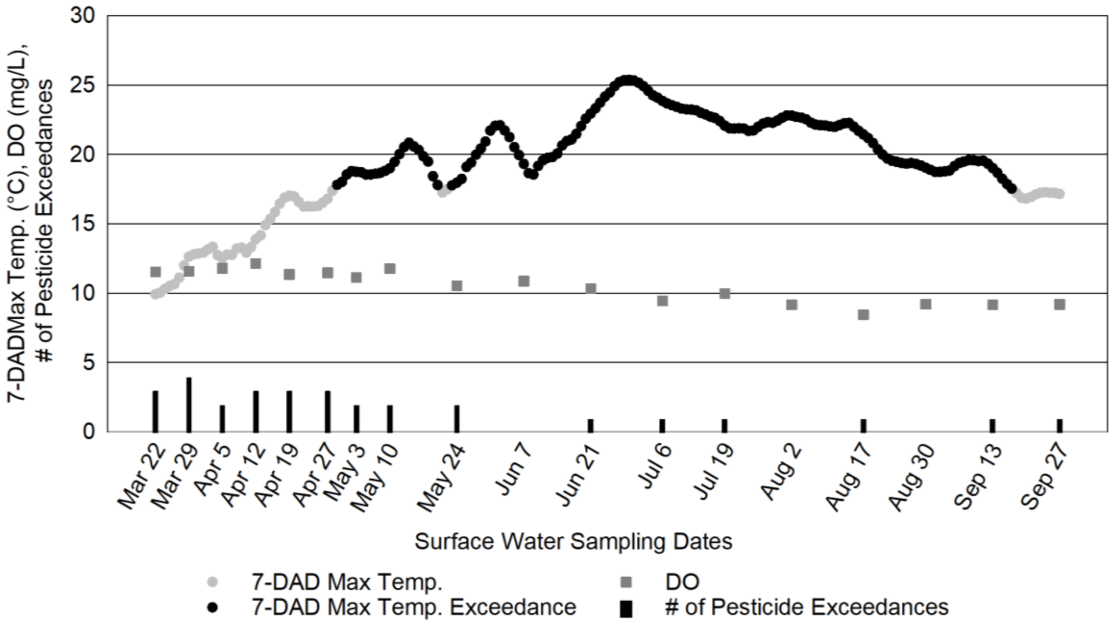
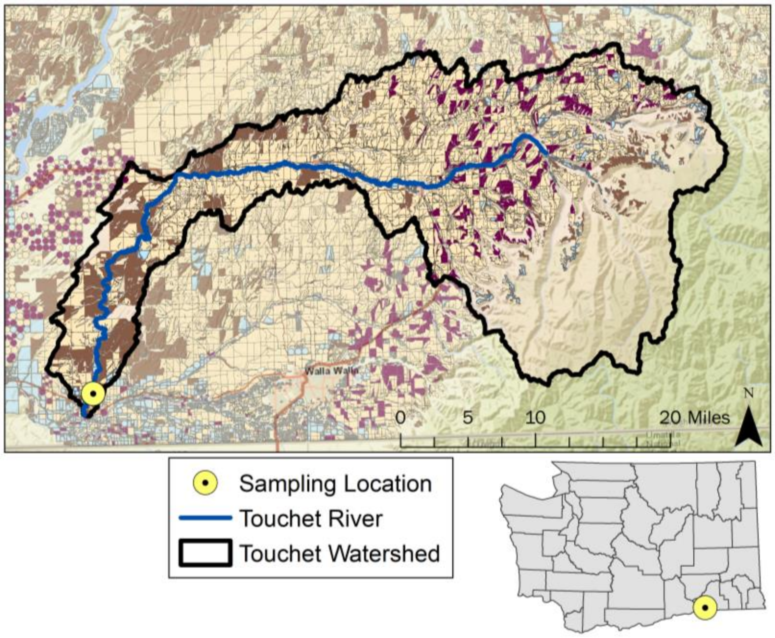


Figure 44 – Sulphur Creek Wasteway water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

All DO measurements met the state standard, ranging from 8.44 mg/L to 12.14 mg/L with an average of 10.50 mg/L. Only two (11%) of the pH measurements exceeded the standard, ranging from 7.80 to 8.71 with an average of 8.23. The 7-DADMax temperatures exceeded the 17.5°C standard on 140 days of the sampling season, primarily from April 29 through September 17. Pesticide exceedances coincided with 7-DADMax temperature exceedances at eight site visits.

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



Touchet Crop Groups	Acres
Other	9,506
Cereal Grain	159,669
CRP/Fallow	39,936
Vegetable	18,884
Total Ag	227,995
Total Non-Ag	169,461
Watershed Total	397,456

Figure 45 – 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. This year, 2021, was the final year of monitoring at Touchet River. 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 45, Figure 46).

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).

Figure 46 - Touchet River downstream view

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 predominantly 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 45).

NRAS tested for three additional analytes at this site in 2021 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 this 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 pesticide findings in Touchet River in 2021.

- NRAS tested for 173 unique pesticides in Touchet River.
- There were 76 total pesticide detections from four different use categories: 10 types of herbicides, 3 insecticides, 3 fungicides, and 2 degradates.
- Pesticides were detected at all 15 sampling events.
- Up to eight pesticides were detected at the same time.
- Of the total pesticide detections, two were above WSDA's assessment criteria (Table 20).
    - The single dichlorvos detection approached the invertebrate NOAEC (0.0058 µg/L).
- Chlorpyrifos was the only 2021 watershed-specific POC at this site. The single detection of chlorpyrifos approached the invertebrate NOAEC (0.005 µg/L).

The Touchet River monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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. The last three sampling visits were only tested for glyphosate, AMPA, and glufosinate-ammonium due to budgeting.

Table 20 – Touchet River pesticide calendar, µg/L

Month		Mar	Apr		May		Jun			Jul		Aug		Sep		Oct
Day of the Month	Use*	22	5	19	3	17	1	15	28	12	26	9	23	7	20	5
2,6-Dichlorobenzamide	D						0.002							-	-	-
Aminomethylphosphoric acid (AMPA)	D	0.024	0.037	0.040		0.048	0.054	0.106	0.106	0.110	0.123	0.125	0.120	0.133	0.189	0.029
Atrazine	H						0.003	0.003						-	-	-
Azoxystrobin	F			0.002										-	-	-
Boscalid	F							0.003	0.003		0.005		0.005	-	-	-
Bromacil	H	0.003						0.003						-	-	-
Chlorothalonil	F											0.025		-	-	-
Chlorpyrifos	I	0.003												-	-	-
Dichlorvos (DDVP)	I									0.005				-	-	-
Eptam	H				0.001	0.002	0.001	0.002						-	-	-
Fipronil	I										0.003			-	-	-
Glyphosate	H	0.031	0.075	0.052	0.019	0.053	0.041	0.061	0.036	0.023	0.033	0.025	0.130	0.164	0.642	0.030
Hexazinone	H	0.002	0.002	0.005	0.004									-	-	-
Imazapyr	H	0.016	0.008	0.009	0.006	0.006	0.006	0.005	0.013	0.007		0.011	0.055	-	-	-
Metolachlor	H				0.004	0.005		0.004	0.005					-	-	-
Metribuzin	H	0.002	0.004	0.005										-	-	-
Pendimethalin	H	0.004	0.003	0.005	0.005	0.005	0.005							-	-	-
Sulfentrazone	H		0.005											-	-	-
Suspended sediment concentration		-	-	16	14	8	5	1		1	2	1	2	3	1	
Total suspended solids		41	45	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		346.0	430.0	280.0	296.0	174.0	85.4	50.3	12.1	4.3	4.0	1.2	18.2	0.4	9.7	16.3
Precipitation (total in/week)†		0.08	0.00	0.02	0.15	0.37	0.03	0.07	0.00	0.00	0.17	0.01	0.00	0.00	0.02	0.09

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

Current-use exceedance (yellow) Detection (blue)

* (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 1 of the 15 site visits (7%). Water quality measurements at the Touchet River site are shown below (Figure 47 and Figure 48).

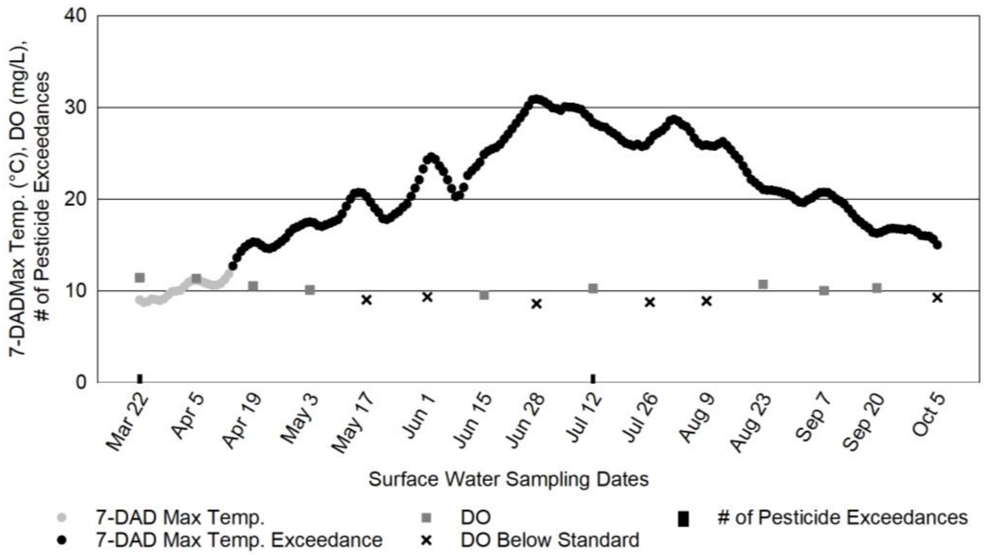


Figure 47 - Touchet River water quality measurements and exceedances of assessment criteria

DO measurements ranged from 8.60 mg/L to 11.43 mg/L with an average of 9.88 mg/L. Less than half (40%) of these measurements did not meet the state standard; six measurements were less than 9.5 mg/L. The 7-DADMax temperatures exceeded the 12°C standard on 175 days of the sampling season, from April 14 through October 5. On July 12, a pesticide exceedance occurred with both a 7-DADMax temperature exceedance and a pH measurement exceeding the state standard.

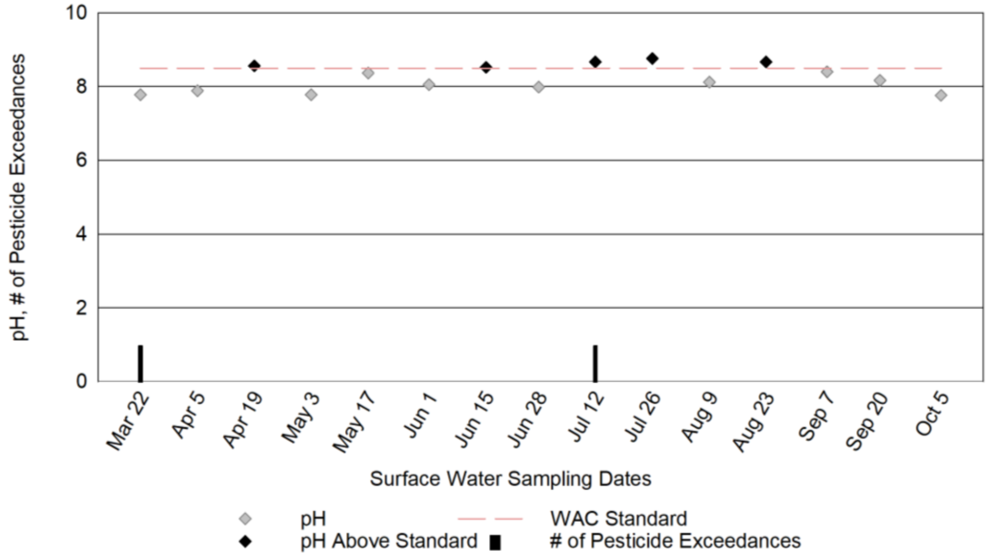


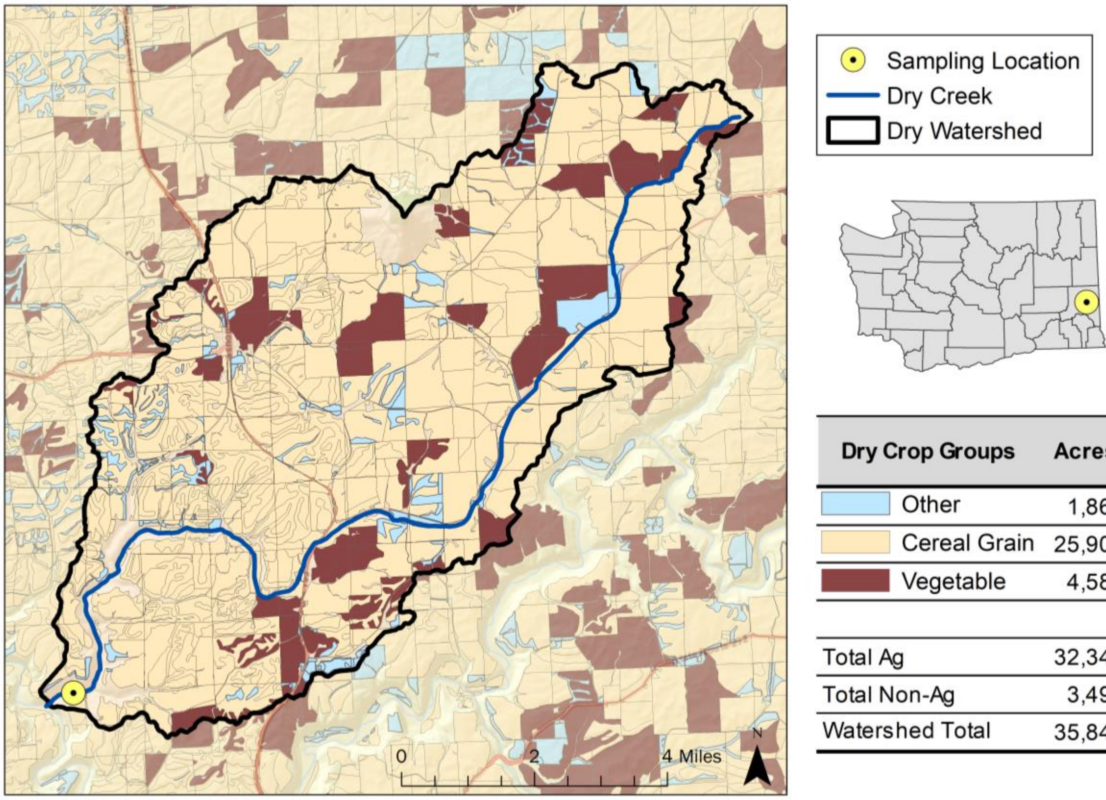
Figure 48 – Touchet Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.76 to 8.76 with an average of 8.23. Roughly 33% of these measurements exceeded the state water quality standard; five measurements were above 8.50. The pH exceedance observed on July 12 coincided with a pesticide 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 discontinued monitoring at this drainage because of relatively few exceeding pesticide concentrations over several years.

Palouse Region

Dry Creek



Dry Crop Groups	Acres
Other	1,865
Cereal Grain	25,901
Vegetable	4,583
Total Ag	32,349
Total Non-Ag	3,498
Watershed Total	35,847

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 continued to collaborate with the Palouse Conservation District to monitor Dry Creek, in Whitman County, for a second 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).

Dry Creek is approximately 18 miles long and drains into the Palouse River. 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 prevent 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. Melting snowpack and precipitation events generally influence streamflow in the creek.

Figure 50 – Dry Creek upstream view

The watershed has low-lying, flat terrain with rolling hills. 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 idle fallow fields, oilseed, and other assorted small acreage crops (Figure 49).

NRAS tested for three additional analytes at this site in 2021 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 2021.

- NRAS tested for 173 unique pesticides in Dry Creek.
- There were 223 total pesticide detections from five different use categories: 23 types of herbicides, 4 insecticides, 5 fungicides, 1 legacy, and 5 degradates.
- Pesticides were detected at all 13 sampling events.
- Up to 26 pesticides were detected at the same time.
- Of the total pesticide detections, 10 were above WSDA's assessment criteria (Table 21).
    - The three detections of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Dry Creek watershed POCs were chlorpyrifos, imidacloprid, metsulfuron-methyl, and pyroxasulfone. Below, each POC is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Of the six imidacloprid detections, four detections approached the invertebrate NOAEC (0.01 µg/L).
- Of the eight metsulfuron-methyl detections, two detections approached the plant EC_{50} (0.36 µg/L).
- The single detection of pyroxasulfone approached the nonvascular plant EC_{50} (0.38 µg/L).
- There was no detection of chlorpyrifos at the site, however, chlorpyrifos was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Dry Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 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	Apr		May		Jun		Jul	Aug			Sep	Oct
Day of the Month	Use*	22	13	26	10	24	14	28	12	2	10	23	27	25
2,4-D	H	0.048		0.045		0.083		0.190	0.022	0.242	0.030	0.021		1.380
2,6-Dichlorobenzamide	D							0.001						
4,4'-DDE	L							0.002	0.003		0.002			
Aminomethylphosphoric acid (AMPA)	D	0.585	0.766	1.010	0.612	1.030	1.180	2.770	4.000	2.500	2.530	1.850	0.725	0.786
Atrazine	H				0.003	0.003	0.003			0.004				
Azoxystrobin	F	0.004	0.004		0.022	0.021	0.002	0.003						
Boscalid	F						0.003	0.003		0.005				
Bromacil	H						0.004							
Bromoxynil	H			0.192	0.051	0.219	0.019	0.038	0.014	0.014				
Carbendazim	F			0.008	0.013	0.008	0.010	0.012	0.008	0.008		0.009		0.009
Chlorsulfuron	H							0.129	0.071	0.055	0.048	0.033	0.012	0.022
Clethodim sulfone	D							0.095						
Clethodim sulfoxide	D				0.029		0.045	0.267						
Clopyralid	H			0.160	0.058	0.710		0.240	0.051	0.035				
Clothianidin	I	0.003			0.004			0.005		0.004				
Dicamba acid	H	0.015				0.014		0.100		0.054	0.011			0.714
Dimethoate	I					0.004								
Eptam	H				0.001	0.001								
Glyphosate	H	0.592	0.960	1.380	0.236	1.270	0.310	2.950	1.620	0.818	0.736	0.562	0.219	2.050
Imazapyr	H	0.005		0.004	0.003	0.004								
Imidacloprid	I	0.005		0.006	0.004			0.010		0.006	0.005			
MCPA	H			0.254	0.075	0.653								
Metalaxyl	F							0.008						
Metolachlor	H	0.002		0.005	0.004	0.005	0.005	0.005	0.004	0.005	0.005	0.005		0.003
Metribuzin	H	0.053	0.016	0.050	0.067	0.270	0.008	0.016	0.008	0.007	0.006	0.006	0.007	0.008
Metsulfuron-methyl	H					0.026	0.022	0.283	0.226	0.111	0.097	0.060	0.015	
Pendimethalin	H		0.005	0.006	0.006	0.005								
Picloram	H	0.061	0.057						0.049	0.770	0.187	0.104	0.069	0.075
Prometon	H	0.003	0.006	0.008	0.007	0.007	0.007						0.006	
Propiconazole	F		0.017	0.195	0.052	0.083	0.032	0.092	0.053	0.051	0.047	0.037		0.021
Pyroxasulfone	H			0.312										
Sodium bentazon	H	0.070	0.033	0.052	0.057									
Sulfentrazone	H	0.006	0.009	0.014	0.007	0.014	0.009	0.011	0.021	0.021	0.016		0.015	0.065
Sulfometuron-methyl	H							0.006	0.004	0.004				
Tebuthiuron	H	0.010		0.008	0.008	0.007	0.007	0.006	0.007	0.008	0.006			0.011
Thiamethoxam	I	0.010	0.007	0.006	0.006	0.010		0.012	0.005	0.005		0.003		
Triallate	H	0.006	0.004	0.016										
Triazine HA degradate	D			0.001		0.002	0.002	0.003	0.002				0.002	
Suspended sediment concentration		-	-	6	7	9	9	34	8	9	54	12	12	4
Total suspended solids		4	3	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		9.6	6.1	4.8	2.9	2.8	0.8	0.3	0.2	0.1	0.3	0.4	0.5	0.7
Precipitation (total in/week)†		0.28	0.02	0.06	0.00	0.54	0.11	0.00	0.00	0.22	0.01	0.01	0.00	0.51

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

Current-use exceedance | DDT/degradate exceedance | Detection | No criteria

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

† 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 4 of the 13 site visits (31%). Water quality at the Dry Creek site is shown below (Figure 51).

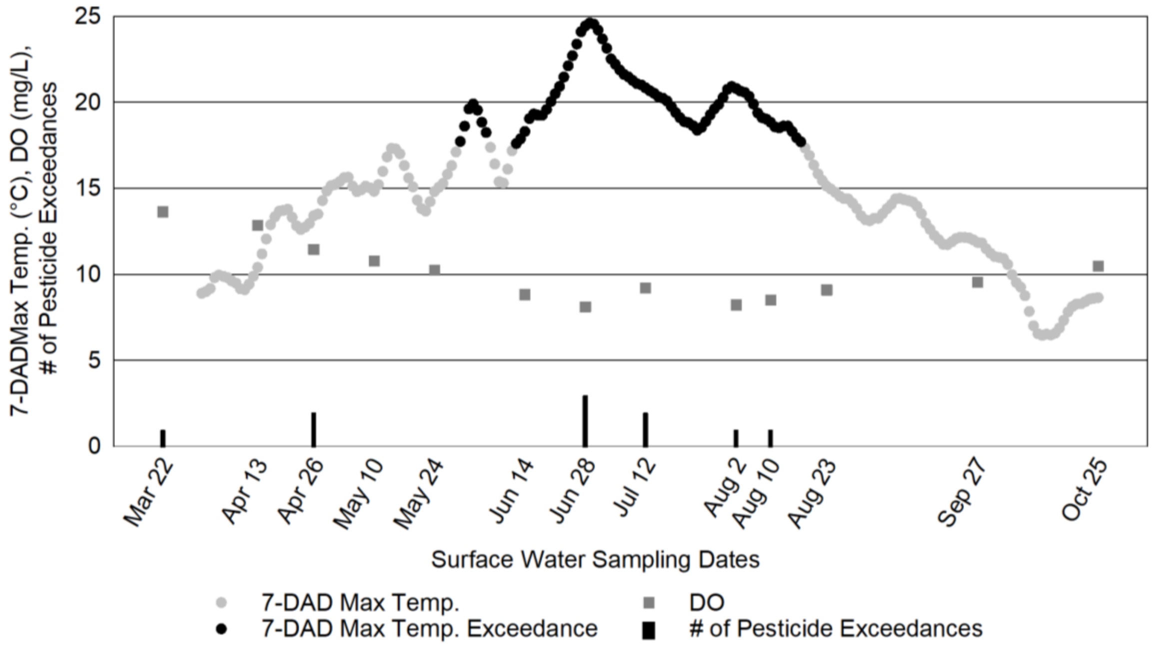
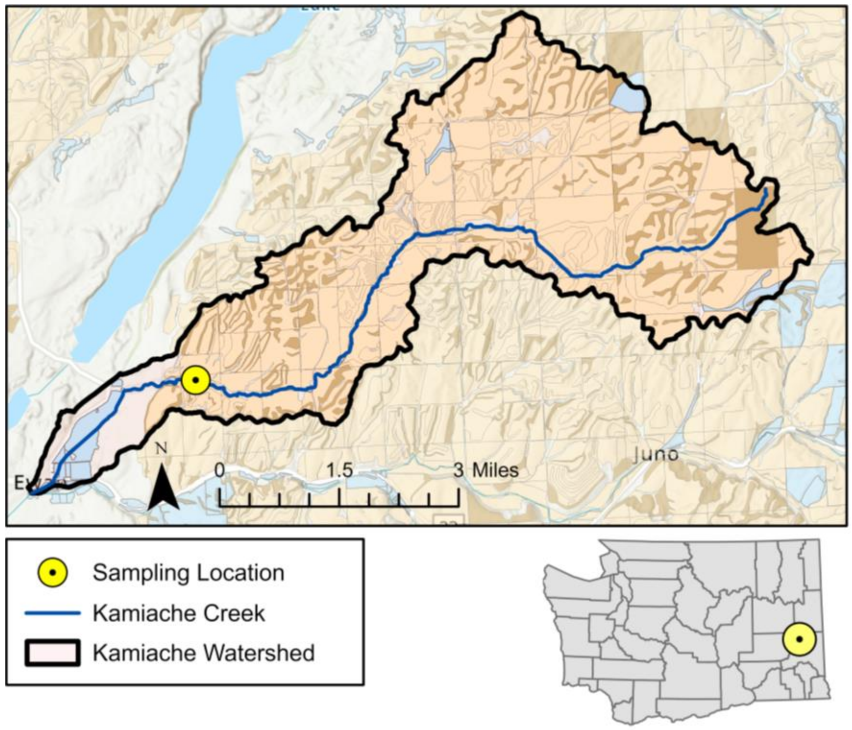


Figure 51 – Dry Creek water quality measurements and exceedances of assessment criteria

All but two (15%) pH measurements met the state water quality standard, ranging from 7.79 to 8.84 with an average of 8.18. The pH measurements on March 22 and April 13 exceeded the standard of 8.50 (data not shown). All DO measurements met the state standard, ranging from 8.10 mg/L to 13.63 mg/L with an average of 10.07 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 74 days of the sampling season, primarily from June 12 through August 17. At least one pesticide exceedance coincided with a 7-DADMax temperature exceedance at four 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. NRAS will continue to monitor this drainage because of its representative regional dryland agriculture land use.

Kamiache Creek



Kamiache Creek Crop Groups	Acres
Cereal Grain	8,880
CRP/Conservation	1,655
Other	494
Total Ag	11,029
Total Non-Ag	1,129
Watershed Total	12,158

Figure 52 – Map of Kamiache Creek and its drainage area with associated sampling location and crop groups identified

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Kamiache Creek, in Whitman County, during the 2021 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 along Gene Webb Road near Ewan, Washington, southeast of Rock Lake. (latitude: 47.1344°, longitude: -117.6917°) (Figure 52, Figure 53).

Figure 53 – A colleague measuring streamflow in Kamiache Creek

Kamiache Creek is approximately 12.6 miles long and drains into Cottonwood Creek, which drains into Rock Creek, and then finally the Palouse River. 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 prevent salmon from migrating further into the Palouse River Watershed and in extension, Kamiache Creek, but the creek provides habitat for fish like rainbow trout. Melting snowpack and precipitation events generally influence streamflow in the creek.

The Kamiache Creek watershed contains rolling hills, which are indicative of the Palouse Region topography. A majority of the creek is ditched and straightened in between agricultural fields. The agricultural land use is predominately wheat and alfalfa. The 'Other' crop group category consists of idle fallow fields, oilseed, and peas (Figure 52). There were efforts between 2016 and 2021 by a regional conservation partnership group to control sediment and nutrient loading into the creek. They used a voluntary incentive-based conservation program to convert or keep over 45,000 acres of farmland as conservation tilled in the area. Roughly 80% of the agricultural fields in this watershed were managed with mulch tilling instead of conventional tilling. Even after 2021, many farms were still managed with these conservation techniques.

NRAS tested for three additional analytes at this site in 2021 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 Kamiache Creek in 2021.

- NRAS tested for 173 unique pesticides in Kamiache Creek.
- There were 88 total pesticide detections from six different use categories: 13 types of herbicides, 5 insecticides, 2 fungicides, 1 legacy, 2 degradates, and 1 insect repellent.
- Pesticides were detected at all 16 sampling events.
- Up to 12 pesticides were detected at the same time.
- Of the total pesticide detections, four were above WSDA's assessment criteria (Table 22).
    - The two detections of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

Statewide POCs detected in Kamiache Creek were chlorpyrifos and imidacloprid. Below, the POC detections are compared to any corresponding state, national, or toxicity criteria that were exceeded.

- The single detection of chlorpyrifos did not exceed any assessment criteria.
- The single detection of imidacloprid approached the invertebrate NOAEC (0.01 µg/L).

The Kamiache Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Table 22). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 22 – Kamiache Creek pesticide calendar, µg/L

Month		Mar	Apr		May		Jun		Jul	Aug			Sep		Oct		Nov
Day of the Month	Use*	22	13	26	10	24	14	28	12	2	10	23	14	27	11	25	9
2,4-D	H	0.024		0.041		0.043	0.136	0.122	0.079	0.156	0.057	0.053	0.284	0.326	0.056	0.133	0.027
2,6-Dichlorobenzamide	D														0.002		
4,4'-DDE	L							0.002									0.003
Aminomethylphosphoric acid (AMPA)	D	0.778	0.279	0.302	0.217	0.283	0.248	0.214	6.130	0.897	0.634	0.369	0.505	0.217	0.205	0.126	0.074
Atrazine	H		0.003	0.003	0.003												
Azoxystrobin	F			0.005													
Bromoxynil	H			0.252													
Carbaryl	I			0.003													
Chlorpyrifos	I	0.002															
Clopyralid	H			0.047													
Diazinon	I	0.002															
Dicamba acid	H						0.056	0.026	12.600	0.211	0.095	0.048	0.112	0.025		0.060	
Eptam	H			0.002	0.002	0.002											
Fipronil	I					0.008											
Glufosinate-ammonium	H															0.022	
Glyphosate	H	4.970	0.838	0.416	0.428	0.439	0.308	0.207	26.700	0.955	0.726	0.399	1.010	0.197	0.314	0.291	0.149
Imidacloprid	I		0.005														
MCPA	H			0.372													
Metolachlor	H					0.004										0.003	
Metribuzin	H	0.004	0.004	0.004		0.004											
N,N-Diethyl-m-toluamide (DEET)	IR															0.005	
Picloram	H									0.035							
Propiconazole	F			0.034	0.008		0.006	0.005			0.006						
Triallate	H		0.002														
Suspended sediment concentration		-	-	7	22	16	9	106	17	11	8	3	5	9	8	11	23
Total suspended solids		12	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		1.8	1.4	1.2	1.4	1.0	0.6	<0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.6	0.8	0.7
Precipitation (total in/week)†		0.05	0.01	0.24	0.00	0.30	0.21	0.00	0.00	0.06	0.00	0.03	0.54	0.00	0.04	0.55	0.29

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

Current-use exceedance | DDT/degradate exceedance | Detection

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

† Washington State University AgWeatherNet station: St.John.E, (latitude: 47.08°, longitude: -117.51°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 1 of the 16 site visits (6%). Water quality at the Kamiache Creek site is shown below (Figure 54).

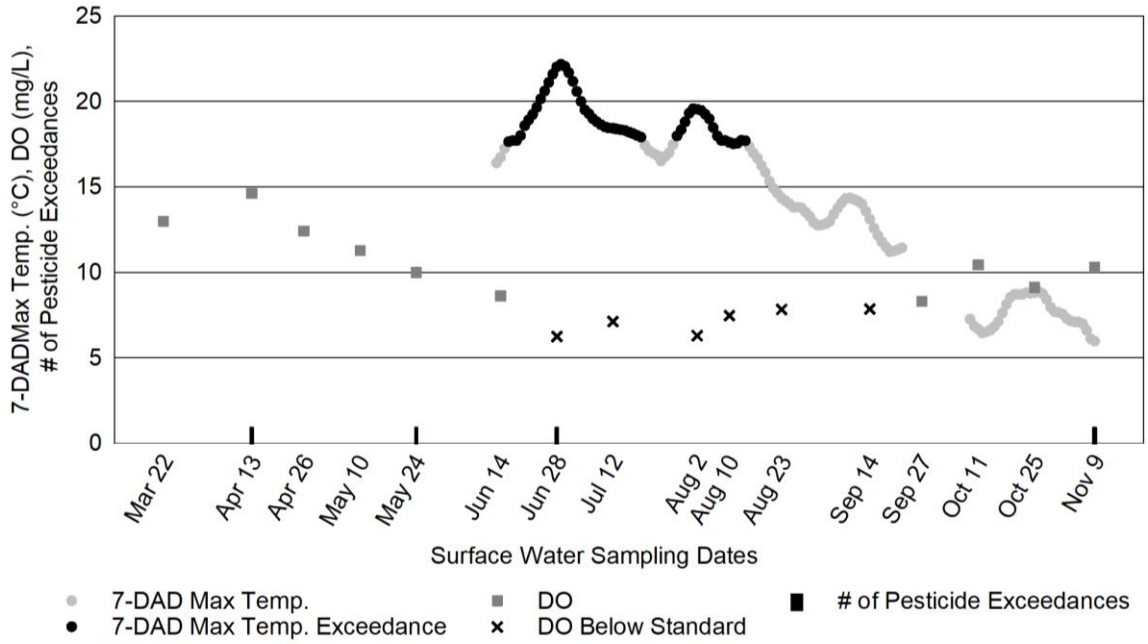
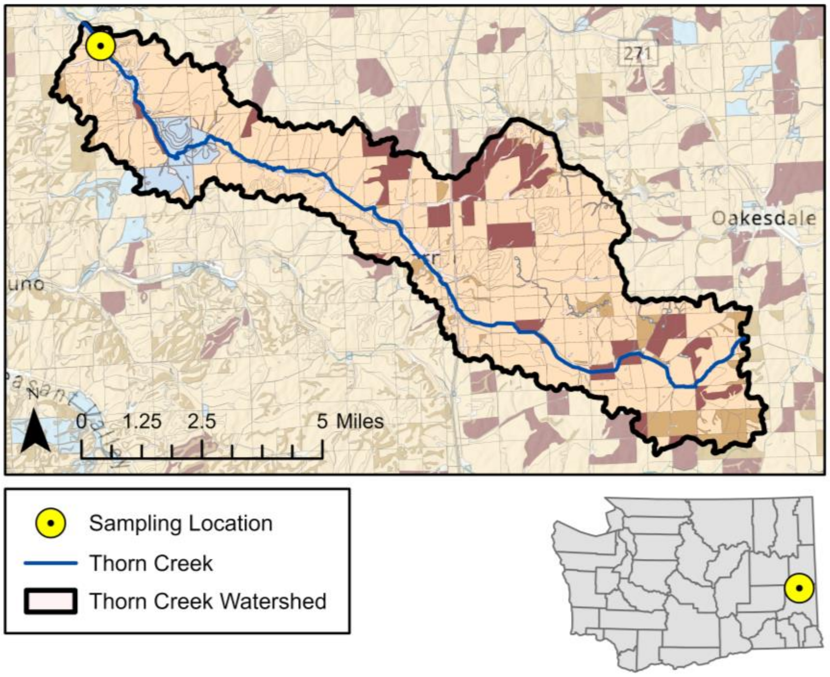


Figure 54 – Kamiache Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.72 to 8.5 with an average of 7.99. Over half (62%) of the DO measurements met the state standard, with all DO measures ranging from 6.24 mg/L to 14.62 mg/L with an average of 9.43 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 52 days of the sampling season, from June 16 through July 19, and July 28 through August 14. At least one pesticide exceedance coincided with a 7-DADMax temperature exceedance at one site visit.

Although Kamiache 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 Kamiache 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 small, unknown fish during the sampling season. NRAS will continue to monitor this drainage because of its representative regional dryland agriculture land use.

Thorn Creek



Thorn Creek Crop Groups	Acres
Cereal Grain	20,161
CRP/Conservation	1,629
Vegetable	2,936
Other	1,102
Total Ag	25,828
Total Non-Ag	1,646
Watershed Total	27,474

Figure 55 – Map of Thorn Creek and its drainage area with associated sampling location and crop groups identified

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Thorn Creek, in Whitman County, during the 2021 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 Pine City-Malden Road near Pine City, Washington (latitude: 47.1884°, longitude: -117.5315°) (Figure 55, Figure 56).

Figure 56 – Thorn Creek upstream view

Thorn Creek is approximately 31.6 miles long and drains into Pine Creek, which drains into Rock Creek, and then finally the Palouse River. 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, Thorn Creek, but the creek provides habitat for fish like rainbow trout. Melting snowpack and precipitation events generally influence streamflow in the creek.

The Thorn Creek watershed contains rolling hills, which are indicative of the Palouse Region topography. 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 idle fallow fields, oilseed, and other assorted small acreage crops (Figure 55). Almost 80% of the agricultural fields in this watershed used conventional tillage practices.

NRAS tested for three additional analytes at this site in 2021 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 Thorn Creek in 2021.

- NRAS tested for 173 unique pesticides in Thorn Creek.
- There were 143 total pesticide detections from six different use categories: 21 types of herbicides, 4 insecticides, 4 fungicides, 1 legacy, 4 degradates, and 1 insect repellent.
- Pesticides were detected at all 16 sampling events.
- Up to 21 pesticides were detected at the same time.
- Of the total pesticide detections, two were above WSDA's assessment criteria (Table 23).
    - The single detection of 4,4'-DDE exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

Statewide POCs detected in Thorn Creek were chlorpyrifos and imidacloprid. Below, the POC detections are compared to any corresponding state, national, or toxicity criteria that were exceeded.

- The single detection of chlorpyrifos did not exceed any assessment criteria.
- The single detection of imidacloprid approached the invertebrate NOAEC (0.01 µg/L).

The Thorn Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2021 monitoring season and a visual comparison to the WSDA assessment criteria (Table 23). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 23 – Thorn Creek pesticide calendar, µg/L

Month		Mar	Apr		May		Jun		Jul	Aug			Sep		Oct		Nov
Day of the Month	Use*	22	13	26	10	24	14	28	12	2	10	23	14	27	11	25	9
2,4-D	H			0.093		0.101	0.165		0.040	0.797	0.036	0.039	0.025	0.036	0.015	0.087	0.013
2,6-Dichlorobenzamide	D								0.002								0.002
4,4'-DDE	L																0.003
4-Nitrophenol	D	0.099															
Aminocyclopyrachlor	H	0.021															
Aminomethylphosphoric acid (AMPA)	D	1.090	0.546	0.270	0.452	0.278	0.500	0.403	0.317	0.235	0.233	0.321	0.442	0.211	0.147	0.142	0.119
Atrazine	H					0.003	0.003										
Azoxystrobin	F	0.004		0.008	0.007	0.010											
Boscalid	F					0.003											
Bromacil	H	0.009		0.007	0.006	0.005	0.005										
Bromoxynil	H			0.017		0.172		0.020									
Carbendazim	F						0.010										
Chlorpyrifos	I	0.002															
Clopyralid	H			0.060		0.699				0.069						0.055	
Diazinon	I	0.002															
Dicamba acid	H					0.032	0.019	0.010		0.020							
Eptam	H			0.001	0.001	0.001											
Glyphosate	H	3.390	0.600	0.192	0.361	0.185	0.298	0.203	0.122	0.216	0.135	0.223	0.682	0.164	0.174	0.519	0.196
Hexazinone	H	0.002	0.005		X	0.005											
Imidacloprid	I										0.007						
MCPA	H					0.664											
Metolachlor	H					0.004	0.004										
Metribuzin	H	0.003		0.008	0.005	0.005											
Metsulfuron-methyl	H					0.007		0.007									
N,N-Diethyl-m-toluamide (DEET)	IR							0.007				X			0.005	0.032	
Pendimethalin	H			0.005													
Picloram	H	0.029		0.055						0.339		0.024		0.024		0.024	
Prometon	H	0.002	0.006	0.005	0.005	0.005	0.005										
Propiconazole	F		0.007	0.028	0.025	0.045		0.010				0.004					
Sodium bentazon	H			0.014							0.027	0.021		0.025	0.016		
Sulfentrazone	H	0.006	0.006	0.018		0.009	0.006	0.006	0.010	0.016	0.008	0.009				0.035	
Sulfometuron-methyl	H			0.004	0.003					0.004							
Tebuthiuron	H			0.005	0.004		0.004										
Thiamethoxam	I	0.006	0.004	0.003		0.003											
Triazine HA degradate	D	0.002	0.002			0.002	0.001										
Suspended sediment concentration		-	-	4	5	3	3	5	4	4	3	3	5	2	2	2	3
Total suspended solids		5	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Streamflow (cubic ft/sec)		5.6	4.7	3.4	2.3	2.0	1.1	0.6	0.4	0.4	0.6	0.4	0.4	0.4	0.4	0.7	0.8
Precipitation (total in/week)†		0.05	0.01	0.24	0.00	0.30	0.21	0.00	0.00	0.06	0.00	0.03	0.54	0.00	0.04	0.55	0.29

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

Current-use exceedance DDT/degradate exceedance Detection

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, L: Legacy)
† Washington State University AgWeatherNet station: St.John.E, (latitude: 47.08°, longitude: -117.51°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. There were no pesticide exceedances that coincided with water quality measurement that did not meet the state standards. Water quality at the Thorn Creek site is shown below (Figure 57).

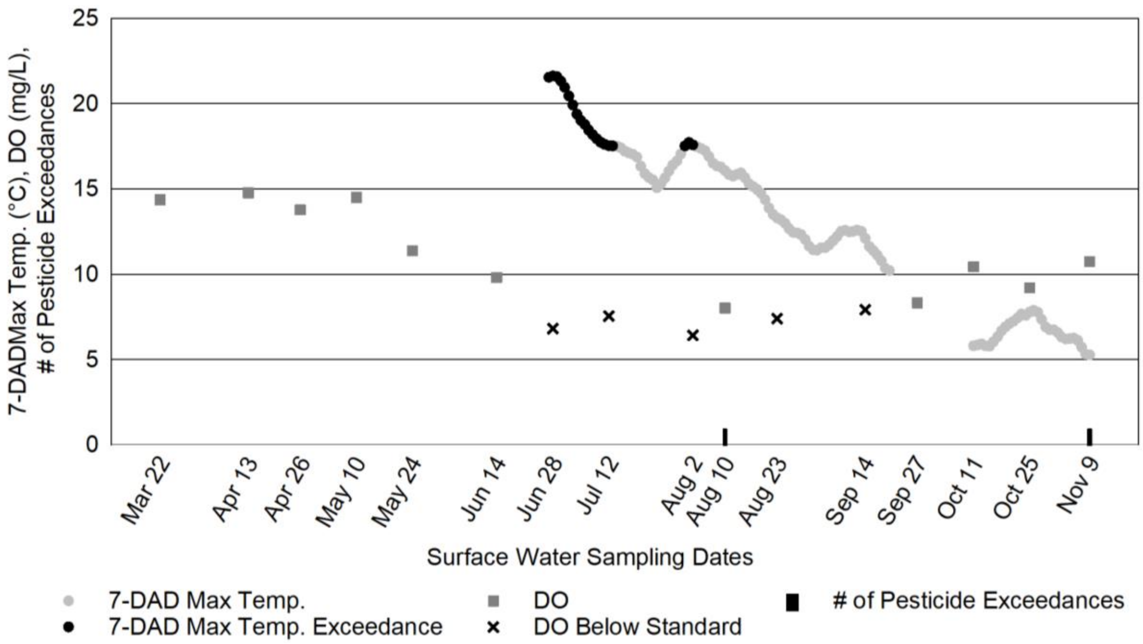


Figure 57 - Thorn Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.41 to 8.43 with an average of 7.83. Over half (69%) of the DO measurements met the state standard, ranging from 6.42 mg/L to 14.77 mg/L with an average of 10.09 mg/L. The 7-DADMax temperatures exceeded the 17.5°C standard on 20 days of the sampling season, primarily from June 27 through July 13.

Although Thorn 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 Thorn 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). NRAS will continue to monitor this drainage because of its representative regional dryland agriculture land use.

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 18 current monitoring sites has distinct watershed and land use characteristics that dictate the pesticides detected. Different sites are sampled for different periods of time (9 to 29 sampling events) and samples from several sites are tested for a subset of pesticides compared to the majority of sites (89 to 173 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 24) provides a useful overview but should be used with caution.

Table 24 – 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		1
Legacy pesticides	5	3	3	178
Degradate	21	18		775
Fungicide	23	16		821
Herbicide	60	46	3	2,355
Insect repellent	1	1		54
Insecticide	59	32	13	734
Synergist	2	2		6
Wood preservative	1	1		4
Total analytes	173	120	19	4,928

There were 120 different analytes detected in 2021 (Table 24). Across 18 monitoring sites, we identified 4,928 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 388 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 388 individual exceedances, 210 (54%) were currently registered pesticides or their associated degradates. The other 178 (46%) were detections of legacy pesticides or their degradates. Approximately half of the exceedances, 257 (66%), occurred at monitoring sites in Central Washington and Palouse region including many of the statewide exceedances of DDT or its degradates (132). Imidacloprid, a neonicotinoid insecticide, accounted for 68 (18%) of the individual pesticide exceedances with 54 of the exceedances found at Western Washington monitoring sites; there was at least one exceedance detected at 14 of the 18 monitoring sites.

Pesticide Detection Summary

Below, statewide detections are summarized by pesticide general use categories. This subsection only presents analytes detected in 2021. Appendix B: 2021 Quality Assurance Summary provides a list of all analytes tested.

Herbicide Detections

Herbicides were the most frequently detected group making up approximately 48% (2,355 detections) of the total pesticide detections. Of the 60 herbicides included in the laboratory analysis, 46 were detected in surface water samples. Table 25 provides a statewide summary of the detected herbicides.

Table 25 – Statewide summary of herbicides with one or more detections in 2021

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	309	167 (54%)		16		0.00251 - 0.0821
Metolachlor	309	149 (48%)		16		0.00176 - 0.361
2,4-D	265	132 (50%)		13		0.0128 - 2.07
Diuron	292	132 (45%)	11	10	3	0.00349 - 2.83
Atrazine	309	128 (41%)		14		0.00266 - 0.125
Imazapyr	292	124 (42%)		10		0.00345 - 3.64
Dichlobenil	309	121 (39%)		11		0.00142 - 0.298
Bromacil	309	115 (37%)		13		0.00284 - 0.129
Hexazinone	309	108 (35%)		13		0.00105 - 0.0846
Pendimethalin	309	104 (34%)		11		0.0021 - 0.0854
Simazine	309	100 (32%)		11		0.00403 - 0.54
Terbacil	309	93 (30%)		8		0.0027 - 0.276
Tebuthiuron	309	92 (30%)		9		0.00356 - 0.0677
Norflurazon	309	89 (29%)		7		0.00172 - 0.0472
Eptam	309	80 (26%)		14		0.00111 - 0.0506
Prometon	309	76 (25%)		10		0.00228 - 0.0191
Dicamba acid	265	61 (23%)		12		0.00929 - 12.6
Glyphosate	60	60 (100%)		4		0.0186 - 26.7
Picloram	265	49 (18%)		9		0.0215 - 0.77
Metribuzin	309	49 (16%)		11		0.00221 - 0.27
Triclopyr acid	265	43 (16%)		7		0.0117 - 1.19
Sulfometuron-methyl	292	34 (12%)		7		0.00238 - 0.0806
Trifluralin	309	25 (8%)		5		0.00232 - 0.00964
Sodium bentazon	265	24 (9%)		6		0.0102 - 0.0881
Indaziflam	292	21 (7%)		5		0.00195 - 0.0261
Chlorpropham	309	17 (6%)		3		0.0011 - 0.0318
Bromoxynil	265	16 (6%)		6		0.0136 - 0.252
Oxadiazon	309	16 (5%)		2		0.00175 - 0.00595
Dithiopyr	309	15 (5%)		5		0.00194 - 0.0146
MCPA	265	14 (5%)		8		0.013 - 1.31
Metsulfuron-methyl	292	14 (5%)	2	4	1	0.00472 - 0.283
Clopyralid	265	13 (5%)		5		0.0254 - 0.71
Mecoprop (MCPP)	265	11 (4%)		5		0.0154 - 0.128
Aminocyclopyrachlor	292	10 (3%)		5		0.0179 - 0.0292
Imazapic	292	10 (3%)		5		0.00615 - 0.013
Chlorsulfuron	292	8 (3%)		2		0.0118 - 0.129
Dacthal (DCPA)	265	7 (3%)		1		0.0201 - 0.0623
Isoxaben	292	6 (2%)		5		0.00225 - 0.00856
Oxyfluorfen	309	6 (2%)		3		0.0335 - 0.05

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)
Napropamide	309	5 (2%)		2		0.0199 - 0.0958
Triallate	309	4 (1%)		2		0.00216 - 0.0159
Flumioxazin	309	2 (1%)		2		0.0496 - 0.0619
Prometryn	309	2 (1%)		2		0.00388 - 0.00812
Glufosinate-ammonium	60	1 (2%)		1		0.0221 - 0.0221
Benfluralin	309	1 (<1%)		1		0.00147 - 0.00147
Pyroxasulfone	292	1 (<1%)	1	1	1	0.312 - 0.312

WSDA considers bolded analytes to be statewide POCs.

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 three monitoring sites.

Sulfentrazone and metolachlor were the most frequently detected herbicides that NRAS annually tests for with 167 and 149 detections, respectively. There were 15 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Diuron, metsulfuron-methyl, and pyroxasulfone were detected above the WSDA assessment criteria, accounting for roughly 4% of the total exceedances in 2021.

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 seven monitoring sites),
  - → Triazine HA (detected at 12 monitoring sites),
  - → Triazine DIA (detected at five monitoring sites),
- Dichlobenil → 2,6-dichlorobenzamide (detected at all 18 monitoring sites),
- Diuron → 1-(3,4-Dichlorophenyl)-3methylurea (detected at nine monitoring sites),
- Glyphosate → Aminomethylphosphoric acid (AMPA) (detected at four of four monitoring sites).

Fungicide Detections

Fungicides were the second most frequently detected group of pesticides making up 821 detections, or 17%, of the total number of detections. Out of 23 fungicides included in the laboratory analysis, 16 were detected in surface water samples. Table 26 provides a statewide summary of the detected fungicides.

Table 26 – Statewide summary of fungicides with one or more detections in 2021

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	309	207 (67%)		17		0.000611 - 0.244
Fludioxonil	309	175 (57%)		9		0.00344 - 0.648
Carbendazim	292	97 (33%)		12		0.00227 - 0.0701
Azoxystrobin	292	77 (26%)		10		0.0019 - 0.106
Propiconazole	292	73 (25%)		10		0.00407 - 0.195

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)
Pyrimethanil	292	64 (22%)		6		0.00217 - 0.0306
Metalaxyl	309	62 (20%)		7		0.00525 - 1.34
Fluopicolide	292	19 (7%)		2		0.00371 - 0.274
Myclobutanil	292	12 (4%)		4		0.00447 - 0.0119
Paclobutrazol	292	9 (3%)		4		0.00278 - 0.0132
Cyprodinil	292	7 (2%)		3		0.00435 - 0.104
Chlorothalonil	309	6 (2%)		6		0.00301 - 0.0248
Difenoconazole	292	5 (2%)		1		0.00982 - 0.0128
Trifloxystrobin	292	4 (1%)		3		0.00228 - 0.0111
Pyraclostrobin	292	2 (1%)		2		0.00467 - 0.00686
Triadimefon	309	2 (1%)		2		0.00414 - 0.00432

Boscalid, fludioxonil, and carbendazim were the most commonly detected fungicides with 207, 175, and 97 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 2021.

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

- Azoxystrobin
- Boscalid
- Carbendazim
- Propiconazole

Insecticide Detections

Current-use insecticides were the third most frequently detected group of pesticides representing approximately 15% (734 detections) of the total pesticide detections. Of the 59 current-use insecticides included in the laboratory analysis, 32 were detected in surface water samples. Table 27 provides a statewide summary of the detected insecticides.

Table 27 – Statewide summary of insecticides with one or more detections in 2021

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	292	111 (38%)		10		0.00204 - 0.234
Chlorpyrifos	309	84 (27%)	81	12	10	0.00176 - 0.113
Imidacloprid	292	75 (26%)	68	14	14	0.00389 - 0.0906
Diazinon	309	53 (17%)	2	16	2	0.00152 - 0.25
Dinotefuran	292	51 (17%)		6		0.00296 - 0.446
Clothianidin	292	49 (17%)	7	7	1	0.0029 - 0.0553
Malathion	309	49 (16%)	7	8	3	0.00215 - 2.28
Flupyradifurone	292	38 (13%)		5		0.00439 - 0.338
Oxamyl	292	35 (12%)		6		0.000845 - 0.0455

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	309	26 (8%)	18	7	6	0.00326 - 0.0236
Carbaryl	292	25 (9%)	1	10	1	0.00236 - 1.39
Acephate	292	24 (8%)		5		0.00349 - 2.61
Dimethoate	309	20 (6%)		7		0.00216 - 0.101
Acetamiprid	292	14 (5%)		4		0.00223 - 0.131
Cyantraniliprole	292	14 (5%)		2		0.0143 - 0.941
Chlorantraniliprole	292	13 (4%)		3		0.0066 - 0.0249
Methoxyfenozide	292	8 (3%)		4		0.00252 - 0.00307
Etoxazole	309	7 (2%)		3		0.00399 - 0.0338
Methiocarb	292	7 (2%)		2		0.00338 - 0.553
Phosmet	309	6 (2%)		6		0.00441 - 0.00528
gamma-Cyhalothrin	309	5 (2%)	5	2	2	0.00189 - 0.0162
Pyriproxyfen	309	4 (1%)	3	3	3	0.00188 - 0.0178
Spirotetramat	292	4 (1%)		2		0.0604 - 4.8
Ethoprop	309	3 (1%)		3		0.00319 - 0.00488
Methomyl	292	2 (1%)		2		0.00217 - 0.00321
Bifenazate	309	1 (<1%)		1		0.12 - 0.12
Bifenthrin	309	1 (<1%)	1	1	1	0.00694 - 0.00694
cis-Permethrin	309	1 (<1%)	1	1	1	0.00521 - 0.00521
Dichlorvos (DDVP)	309	1 (<1%)	1	1	1	0.00549 - 0.00549
Fenbutatin oxide	292	1 (<1%)	1	1	1	0.0565 - 0.0565
Pyridaben	309	1 (<1%)		1		0.00262 - 0.00262
Tetramethrin	309	1 (<1%)		1		0.0462 - 0.0462

WSDA considers bolded analytes to be statewide POCs.

Thiamethoxam, chlorpyrifos, and imidacloprid were the most commonly detected insecticides with 111, 84, and 75 detections, respectively. The neonicotinoids 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:

- Carbaryl
- Chlorpyrifos
- Diazinon
- Imidacloprid
- Thiamethoxam

Detections of current-use insecticides accounted for almost 51% (196 detections) of all exceedances in 2021. All detections of bifenthrin, cis-permethrin, dichlorvos, gamma-cyhalothrin, and fenbutatin oxide were at concentrations above the WSDA assessment criteria. Of the 32 current-use insecticides that NRAS detected, 41% (13 insecticides) had a concentration detected that exceeded WSDA assessment criteria at least once.

The three statewide POCs identified in 2021 were chlorpyrifos, diuron, and imidacloprid. Chlorpyrifos has been a WSDA POC since 2009 and was most often applied on fruit trees. There were 81 exceedances of chlorpyrifos found across eight Central Washington sites and two Western Washington sites. 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 four monitoring sites),
- Fipronil → fipronil sulfide (detected at four monitoring sites),
    - → fipronil sulfone (detected at two monitoring sites),
    - → fipronil disulfinyl (detected at two monitoring sites),
- Malathion → malaoxon (detected at one monitoring site),
- Oxamyl → oxamyl oxime (detected at two monitoring sites),

Degradate and Other Pesticide Detections

This group includes degradates of current-use pesticides as well as several other pesticide-related chemicals. Degradates represented 16% (775 detections) of total detections and pesticide-related chemicals represented 1% (65 detections) of total detections. Of the 21 degrades from current-use chemicals included in the laboratory analysis, 18 were detected in surface water samples. Two synergists tested for were detected. Each antimicrobial, wood preservative, and insect repellent tested for had at least one detection. Table 28 provides a statewide summary of the detected degradates and other pesticide product ingredients.

Table 28 – Statewide summary of degradates and other pesticide products in 2021

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	309	234 (76%)		18		0.00134 - 0.405
Triazine HA	292	158 (54%)		12		0.00106 - 0.047
Triazine DEA	292	89 (30%)		7		0.00203 - 0.014
AMPA	60	59 (98%)		4		0.0238 - 6.13
Tetrahydrophthalimide	309	55 (18%)		9		0.00129 - 0.214
Triazine DIA	292	45 (15%)		5		0.00329 - 0.0518
1-(3,4-Dichlorophenyl)-3-methylurea	292	38 (13%)		9		0.0034 - 0.0566
Oxamyl oxime	292	29 (10%)		2		0.0154 - 0.12
Fipronil sulfide	309	20 (6%)		4		0.00132 - 0.00687
Methamidophos	292	19 (7%)		4		0.00161 - 0.217
Fipronil sulfone	309	8 (3%)		2		0.00298 - 0.0062
Acetochlor ESA	292	5 (2%)		2		0.0278 - 0.0795
4-Nitrophenol	265	4 (2%)		3		0.0314 - 0.0985
Clethodim sulfoxide	292	3 (1%)		1		0.029 - 0.267
Dimethenamid ESA	292	3 (1%)		1		0.0853 - 0.174
Fipronil disulfinyl	309	3 (1%)		2		0.00328 - 0.00725
Malaoxon	292	2 (1%)		1		0.00488 - 0.0168
Clethodim sulfone	292	1 (<1%)		1		0.095 - 0.095
Antimicrobial:						

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)
Triclosan	309	1 (<1%)		1		0.0113 - 0.0113
Insect repellent:						
DEET	309	54 (17%)		14		0.00146 - 0.154
Synergist:						
Piperonyl butoxide	309	5 (2%)		2		0.0086 - 0.0285
MGK264	309	1 (<1%)		1		0.00785 - 0.00785
Wood preservative:						
Pentachlorophenol	265	4 (2%)		2		0.0129 - 0.0189

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 234 detections, followed by triazine HA (degradate of the herbicide atrazine) with 158 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. Clethodim sulfoxide and clethodim sulfone are breakdown products of clethodim, an herbicide, and dimethenamid ESA is a breakdown product of dimethenamid, another herbicide. Clethodim and dimethenamid were not tested for in 2021 due to analytical method compatibility issues.

Other associated pesticide ingredients detected were pentachlorophenol, triclosan, piperonyl butoxide, and MGK264. Pentachlorophenol's main usage is for wood preservation. Also, the insect repellent DEET (N,N-diethyl-m-toluamide), detected 54 times, was found at every monitoring site but four. 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 3% (178 detections) of the total pesticide detections. Three out of five legacy analytes included in the lab analysis were detected. A statewide summary of the legacy analytes is shown below in Table 29.

Table 29 – Statewide summary of legacy pesticides and degradates with one or more detections in 2021

Analyte	# of samples collected	# of detections (% samples)	# of detections above WSDA assessment criteria	# of sites with detections	# of sites with exceeding detections	Concentration range (µg/L)
4,4'-DDD	309	89 (29%)	89	10	10	0.00213 - 0.00761
4,4'-DDE	309	66 (21%)	66	13	13	0.00138 - 0.0378
4,4'-DDT	309	23 (7%)	23	4	4	0.00157 - 0.0129

One DDT degradate, 4,4'-DDD, was the most frequently detected legacy chemical with 89 detections, closely followed by another DDT degradate, 4,4'-DDE, with 66 detections. DDT or an associated breakdown product were found at four of seven Western Washington sites, seven of nine Central Washington sites, and all three Palouse region sites. 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.

The parent compound 4,4’-DDT and its degradates (4,4'-DDE and 4,4'-DDD) accounted for 46% of the total exceedances detected in 2021. Of the 178 combined DDT exceedances, 58 (33%) 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 LC_{50} or EC_{50} 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 LC_{50}, invertebrate EC_{50}, and plant EC_{50} assessment criteria with WSDA’s safety factor for a more conservative approach. If the TU ratio is above or equal to one, there is a higher possibility of lethal or sublethal effects on aquatic life. Of the 309 sampling events analyzed using TUs, there were 96 samples that had a TU above or equal to one. Of the 96 samples, one sample had an exceeding TU using fish criteria, 88 samples had exceeding TUs using invertebrate criteria, and seven samples had exceeding TUs using plant criteria. The TU exceedances occurred at all monitoring sites except Juanita Creek and Touchet River. All 96 samples had exceeding TUs primarily due to an elevated concentration of one or two pesticides. The pesticide that contributed significantly to samples with TUs greater than or equal to one was chlorpyrifos (TU > 1 in 76 samples). This insecticide was found in concentrations above WSDA assessment criteria predominately in the spring and early summer, coinciding with the samples where TU was exceeded. Chlorpyrifos has relatively high toxicity to both fish and invertebrates at low concentrations. For comparison, in 2020, there were only seven sampling events out of 293 analyzed that had a TU above or equal to one. The substantial increase in samples with TUs above or equal to one in 2021 was attributed to a large decrease in the WSDA assessment criteria for chlorpyrifos.

Nutrient Analysis

In 2021, we sampled nutrients at six monitoring sites, two of which were sampled for the first time (Kamiache Creek and Thorn Creek). Table 30 provides a summary of nutrient results at the six 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 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 2021 is the second 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 30 – Summary of 2021 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	29	27 (93%)		0.157	0.442
	Dry Creek	13	10 (77%)		0.014	0.027
	Kamiache Creek	16	9 (56%)		0.015	0.024
	Marion Drain	28	9 (32%)		0.018	0.047
	Sulphur Creek	18	12 (67%)		0.019	0.057
	Thorn Creek	16	13 (81%)		0.015	0.062
Nitrate-nitrite as N	Upper Big Ditch	29	27 (93%)	25	0.39	1.10
	Dry Creek	13	13 (100%)	13	2.50	6.47
	Kamiache Creek	16	16 (100%)	16	5.68	7.02
	Marion Drain	28	28 (100%)	28	1.81	4.70
	Sulphur Creek	18	18 (100%)	18	2.94	7.11
	Thorn Creek	16	16 (100%)	16	5.83	7.34
Total phosphorus as P	Upper Big Ditch	29	29 (100%)	29	0.100	0.175
	Dry Creek	13	13 (100%)	13	0.150	0.294
	Kamiache Creek	16	16 (100%)	16	0.104	0.175
	Marion Drain	28	28 (100%)	28	0.111	0.327
	Sulphur Creek	18	18 (100%)	18	0.165	0.676
	Thorn Creek	15	15 (100%)	15	0.103	0.189
Orthophosphate as P	Upper Big Ditch	29	28 (97%)	N/A	0.014	0.032
	Dry Creek	13	13 (100%)	N/A	0.129	0.240
	Kamiache Creek	16	16 (100%)	N/A	0.096	0.158
	Marion Drain	27	27 (100%)	N/A	0.086	0.292
	Sulphur Creek	17	17 (100%)	N/A	0.106	0.620
	Thorn Creek	16	16 (100%)	N/A	0.100	0.162

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 2022). There were no known orthophosphate criteria to compare to.

Conclusions

Staff collected surface water monitoring data at 18 locations across Western Washington, Central Washington, and the Palouse region in 2021. Water samples were collected from the middle of March into November a total of 316 times. Samples taken from three of the monitoring sites were tested in a lab for 173 pesticide and pesticide-related chemicals, 11 monitoring site were tested for 170 chemicals, one site was tested for 156 chemicals, and two more sites were tested for a subset of 89 chemicals.

- Of 173 pesticides tested for, 120 unique pesticides were detected.
- NRAS detected pesticides in water samples a total of 4,928 times.
- Sulfentrazone, metolachlor, and 2,4-D were the most frequently detected herbicides (167, 149, and 132 times, respectively).
- Thiamethoxam, chlorpyrifos, and imidacloprid were the most frequently detected insecticides (111, 84, and 75 times, respectively).
- Boscalid, fludioxonil, and carbendazim were the most frequently detected fungicides (207, 175, and 97 times, respectively).
- Eight chemicals were detected at more than 50% of sampling events they were tested for. 2,6-dichlorobenzamide (a degradate) was detected at more than 75% of sampling events. Glyphosate and its breakdown product, AMPA, were detected almost 100% of the sampling events at the four monitoring sites they were tested at.

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 388 exceedances total with at least one exceedance at every monitoring site. Approximately 54% of the total exceedances (210 exceedances) were from 16 current-use pesticides. A summary of current-use pesticides with exceedances is below in Table 31. Every detection of six pesticides exceeded WSDA assessment criteria; however, not every detection of the other ten pesticides did. Although the total number of chlorpyrifos detections were similar to those in 2020, there were many more exceedances in 2021 than 2020 because the aquatic life criterion that the detections were compared to was lowered during this time. Detections of legacy pesticides and associated degradates accounted for the remaining 46% (178 exceedances) of the total exceedances. DDT and/or one of its degradates tested for were detected at four Western Washington sites, ranging from one exceeding detection at the Upper Bertrand site to a maximum of 17 exceeding detections at the Lower Big Ditch site. In Central Washington and the Palouse region, DDT and/or one of its degradates was detected at 10 sites; detections ranged from one exceedance at Ahtanum Creek and Thorn Creek to a maximum of 58 exceedances at Brender Creek. Every detection of DDT exceeded WSDA assessment criteria.

Exceedances by current-use pesticide types are as follows.

- Out of 2,355 total herbicide detections, 14 detections exceeded criteria (<1%).
- Out of 821 total fungicide detections, no detection exceeded criteria (0%).
- Out of 734 total insecticide detections, 196 detections exceeded criteria (27%).

Table 31 – Summary of WSDA assessment criteria exceedances from current-use pesticides

Analyte	# of detections	# of detections above assessment criteria	Pesticide general use category
Diuron	132	11 (8%)	Herbicide
Chlorpyrifos	84	81 (96%)	Insecticide
Imidacloprid	75	68 (91%)	Insecticide
Diazinon	53	2 (4%)	Insecticide
Clothianidin	49	7 (14%)	Insecticide
Malathion	49	7 (14%)	Insecticide
Fipronil	26	18 (69%)	Insecticide
Carbaryl	25	1 (4%)	Insecticide
Metsulfuron-methyl	14	2 (14%)	Herbicide
gamma-Cyhalothrin	5	5 (100%)	Insecticide
Pyriproxyfen (Nylar)	4	3 (75%)	Insecticide
Bifenthrin	1	1 (100%)	Insecticide
cis-Permethrin	1	1 (100%)	Insecticide
Dichlorvos (DDVP)	1	1 (100%)	Insecticide
Fenbutatin oxide	1	1 (100%)	Insecticide
Pyroxasulfone	1	1 (100%)	Herbicide

In 2021, monitoring sites commonly contained mixtures of pesticides in samples. All 18 monitoring sites had two or more pesticide detections at every sampling event during the entire field season. The maximum number of detections (41) at a single sampling event occurred on April 27 at the Lower Big Ditch site and on June 15 at the Upper Bertrand 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 17 of the 18 monitoring sites. All sampling events at the six 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, diuron, and imidacloprid. 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 1,197 pesticide active ingredients (including pesticides, synergists, adjuvants, and additives) registered for use at the beginning of 2024 (WSPMRS 2024). Surface water samples in 2021 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 2021 and 2022 sampling seasons. In Central Washington, sampling of Touchet River was discontinued after the 2021 monitoring season due to few pesticide detections exceeding WSDA assessment criteria for several years. Staff sampled the remaining seven Central Washington sites sampled in 2021, in 2022. The seven monitoring sites sampled in Western Washington in 2021 were sampled in 2022 as well. NRAS partnered with the Palouse Conservation District to continue to monitor Dry Creek for a third sampling season and Thorn Creek and Kamiache Creek for a second season.

Out of the 173 analytes tested for in 2021, 153 were tested for in 2022. Table 32 shows the 20 analytes that weren't sampled for. No new analytes for testing were added between the 2021 and 2022 sampling due to budget constraints. Although included in the total analyte count, we only tested for glyphosate, AMPA, and glufosinate-ammonium at the three Palouse-region monitoring sites during 2022.

Table 32 – 2021 analytes removed from testing in 2022

Analytes removed	CAS number	General Use
3,5-Dichlorobenzoic acid	51-36-5	Herbicide degradate
Alachlor	15972-60-8	Herbicide
Benfluralin	1646-87-3	Insecticide degradate
Chlorethoxyfos	1861-40-1	Herbicide
Chlorpyrifos-methyl	54593-83-8	Insecticide
Coumaphos	5598-13-0	Insecticide
Cycloate	56-72-4	Insecticide
Fenbuconazole	1134-23-2	Herbicide
Methidathion	114369-43-6	Fungicide
MGK264	113-48-4	Synergist
Naled	300-76-5	Insecticide
Phenothrin	26002-80-2	Insecticide
Phorate	298-02-2	Insecticide
Prallethrin	23031-36-9	Insecticide
Propoxur	114-26-1	Insecticide
Propyzamide (Pronamide)	23950-58-5	Herbicide
Pyraflufen-ethyl	129630-19-9	Herbicide
Tetrachlorvinphos	961-11-5	Insecticide
Thiacloprid	111988-49-9	Insecticide
Zoxamide	156052-68-5	Fungicide

Similar to the 2021 field season, staff sampled nutrients at Upper Big Ditch, Marion Drain, Sulphur Creek Wasteway, Dry Creek, Thorn Creek and Kamiache Creek monitoring sites in 2022.

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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 33a. 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
    - BrT – Brown trout
    - BS – Bluegill sunfish
    - BT – Brook trout
    - CC – Carp
    - CF – Catfish
    - CI – *Ctenopharyngodon idella* (grass carp)
    - FF – Flagfish
    - FM – Fathead minnow
    - JM – Japanese medaka
    - LT – Lake trout
    - ND – Not described
    - OC – *Oncorhynchus clarkia* (cutthroat trout)
    - RT – Rainbow trout
- Invertebrate:
    - AA – *Aedes albopictus* (mosquito larvae)
    - ACR – Acute to chronic ratio
    - CD – *Chironomus dilutus* (midge)
    - CG – *Chloroperia grammatical* (stonefly)
    - CH – *Caenis horaria* (midge)
    - CL – *Cloeon dipterum* (midge)
    - CP – *Chironomus plumosus*
    - CR – *Chironomus riparius*
    - CT – *Chironomus tentans* (midge)
    - DD – *Ceriodaphnia dubia* (water flea)
    - DM – *Daphnia magna*
    - DP – Daphnia pulex
    - GF – Gammarus fasciatus (scud)
    - GL – Gammarus lacustris (scud)
    - HA – *Hyalella azteca* (amphipod)
    - MATC – Maximum allowed toxic concentration
    - ND – Not described
    - PC – *Pteronarcys californica* (stonefly)
    - SV – *Simulium vittatum* (black fly)
- 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 – *Scendesmus subspicatus* (green algae)

In cases where different organisms were used for acute and chronic toxicity tests, the organism used for the acute test is noted first and the organism used for the chronic test is second. Table 33a contains only chemicals detected in 2021. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2021 Quality Assurance Summary.

Table 33a – WSDA Freshwater assessment criteria (WSDA safety factors applied, µg/L)

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	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]	2040	20400	11800	RT/FM	6250	8025	DM	149.6	LG				
2,6-Dichlorobenzamide[2]	3000	30000	5000	BS/RT	46000	160000	DM	50000	SP				
3,5-Dichlorobenzoic acid													
4,4'-DDD[3]													
4,4'-DDE[3]										0.55	0.0005	0.55	0.0005
4,4'-DDT[3]										0.55	0.0005	0.55	0.0005
4-Nitrophenol[4]	100	1000		RT	1250		DM						
Acephate[5]	20800	208000	2880	RT	275	75	DM	25000	SD				
Acetamiprid[6]	2500	25000	9600	RT/FM	5.25	1.05	CR/ACR	500	LG				
Acetochlor[7]	9.5	95	65	RT	2050	11.05	DM	0.715	SC				
Acetochlor ESA[7]	4500	45000		RT	31250		DM	4950	SC				
Afidopyropen[8]	429.5	4295	150	CC/FM	2225	0.0615	DM	1020	SD				
Alachlor[9]	45	450	93.5	RT	625	55	DM	0.82	SC				
Aminocyclopyrachlor[10]	3000	30000	5500	BS/RT	9925	185	DM	3700	AF				
Aminomethylphosphoric acid (AMPA)[11]	12475	124750		RT	170750		DM						
Atrazine[12]	132.5	1325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin[13]	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Benfluralin[14]	1.7425	17.425	0.95	BS/RT	545	7.75		50	LG				
Bensulide[15]	27.5	275	84.5	RT/FM	145	5.5	DM	70	LG				
Bifenazate[16]	14.5	145		BS	125	75	DM	445	SC				
Bifenthrin[17]	0.00375	0.0375	0.002	RT/ND	0.00012325	0.000025	HA	145	SC				
Boscalid[18]	67.5	675	58		1332.5	395		670					
Bromacil[19]	900	9000	1500	RT	30250	4100	DM	3.4	SC				
Bromoxynil[20]	52.5	525		RT	3977.5		DM						
Captan[21]	0.655	6.55	8.25	BrT/FM	2100	280	DM	160	SS				
Carbaryl[22]	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	170	SC			1.05	1.05

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Carbendazim[23]	0.185	1.85	0.495	CF	27.5	1.55	DM	2290	SD				
Chlorantraniliprole[24]	345	3450	55	RT/RT	4.15	1.51	DM/DM	890	SC				
Chlorethoxyfos													
Chlorothalonil[25]	0.45	4.5	0.385	RT/FM	13.5	0.3	DM	6	NP				
Chlorpropham[26]	75.25	752.5		RT	927.5		DM						
Chlorpyrifos[27]	0.0425	0.425	0.1255	BS/FM	0.00345	0.0025	HA/DM	70		0.0415	0.0205	0.0415	0.0205
Chlorpyrifos-methyl[28]	0.35	3.5			0.0425								
Chlorsulfuron[29]	7500	75000	16000	RT	92500	10000	DM	0.175	LG				
cis-Permethrin[17]	0.01975	0.1975	0.026	BS/BS-ACR	0.00165	0.0021	HA	1.6	LG				
Clethodim sulfone													
Clethodim sulfoxide													
Clopyralid[30]	2575	25750	5000	RT/FM	58250	2350	DM	3450	SC				
Clothianidin[31]	2537.5	25375	4850	RT/FM	5.5	0.025	CR	32000					
Coumaphos[32]	8.5	85	5.85	BS/RT	0.0185	0.01685	GL/GF	83	LG				
Cyantraniliprole[33]	250	2500	5350	CF/RT	5.1	3.28	DM	5000	SD				
Cycloate[34]	112.5	1125	15.5	RT/FM	600	110	DM	30.5	SD				
Cyfluthrin-Total[17]	0.0017	0.017	0.0021	RT	0.00625	0.00006	DM/HA	1	SS				
Cypermethrin-Total[17]	0.00975	0.0975	0.0255	RT/FM	0.00014	0.000025	HA	0.81	LG				
Cyprodinil[35]	54.5	545	115	BS/FM	8	4.1	DM	985	AF				
Dacthal (DCPA)[36]	165	1650		RT	4505		DM						
Deltamethrin[17]	0.00375	0.0375	0.0085	RT/FM	0.00005	0.000013	HA	1.55	NP				
Diazinon[37]	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1850	SC			0.085	0.085
Dicamba acid[38]	700	7000		RT	25000		DM	30.5	AF				
Dichlobenil[2]	123.25	1232.5	165	RT	1550	280	DM	15	LG				
Dichlorprop[39]	2287.5	22875		RT	139500	50000	DM	38.5	NP				
Dichlorvos (DDVP)[39]	2.5	25	2.6	RT	0.0167	0.0029	DP/DM	7000	ND				
Dicofol[40]	1.325	13.25	2.2		35	9.5		2500					
Difenoconazole[41]	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP				
Diflubenzuron[9]	3225	32250	50	BS/FM	0.0007	0.000125	AA/DM	95	LG				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Dimethenamid ESA[42]													
Dimethenamid OA[42]													
Dimethoate[43]	155	1550	215	RT	10.75	0.25	PC	10000	CB				
Dinotefuran[44]	2477.5	24775	3180	CC/RT	242075	47650	DM	48800	SC				
Dithiopyr[45]	11.75	117.5	10	BS/FM	1300	40.5	DM	3.055	LG				
Diuron[46]	33	330	13.2	OC/FM	43.75	0.415	GF	0.065	LG				
Eptam[47]	350	3500	20	BS/FM-ACR	1625	400	DM	700	SC				
ES Fenvalerate[17]	0.00355	0.0355	0.0085	BS/FM	0.000212	0.00001545	HA	2.8	SC				
Ethalfluralin[48]	0.8	8	0.2	BS/RT	15	12	DM	3.65	LG				
Ethoprop[49]	7.5	75	12	RT/FM	11	0.4	DM	4200					
Etoxazole[50]	9.25	92.5	7.5	RT	1.825	0.065	DM	25.95	NP				
Etridiazole[51]	19.25	192.5	50.5	RT/FM	770	185	DM	36	SC				
Fenarimol[52]	22.5	225	90	RT	1700	56.5	DM	50	SC				
Fenbuconazole[53]	17	170	13.5	BS/FM	575	39	DM	205	SC				
Fenbutatin oxide[54]	0.0425	0.425	0.155	RT	7.75	8	DM						
Fenpropathrin[17]	0.055	0.55	0.03	BS/FM	0.0007625	0.00075	HA	31.5	SC				
Fipronil[55]	2.075	20.75	3.3	BS/RT	0.055	0.0055	SV/ACR	38	SS				
Fipronil disulfinyl[55]	0.5	5	0.265	BS/ACR	88.75	20.5	DM/DD	38	SC				
Fipronil sulfide[55]	0.77	7.7	0.415	BS/BS-ACR	25	2.58	DM/ND	38	SS				
Fipronil sulfone[55]	0.625	6.25	0.335	BS/BS-ACR	7.25	0.11	DM/DM	38	SS				
Fludioxonil[56]	11.75	117.5	9	RT/FM	225	7	DM	140	SC				
Flumioxazin[57]	57.5	575	0.255	RT/FM	1375	14	DP/DM	0.245	LG				
Fluopicolide[58]	8.725	87.25	75.5	RT/FM	425	95	DM	1300	SC				
Flupyradifurone													
Fluroxypyr 1-methylheptyl ester[59]	15.75	157.5		BS	150	30.25	DM	28	NP				
gamma-Cyhalothrin[17]	0.000725	0.00725		BS	0.00002	0.000965	HA	0.254	LG				
Glufosinate-ammonium[60]	7800	78000	25000	RT	162750	15500	DM	36	AF				
Glyphosate[11]	1075	10750	12850	BS/FM	13300	24950	CP/DM	5950	LG				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Hexazinone[61]	6850	68500	8500	RT/FM	37900	10000	DM	3.5	SC				
Hexythiazox[62]	3	30		RT		3.05	DM	60	LG				
Imazapic[63]	2500	25000	48000	RT/FM	25000	48000	DM	3.11	LM				
Imazapyr[64]	2500	25000	21550	RT/FM	25000	48550	DM	12	LM				
Imidacloprid[65]	5725	57250	4500	RT	0.1925	0.005	CL/CH						
Indaziflam[66]								0.0305	LG				
Inpyrfluxam[67]	0.775	7.75	2.45	RT/RT-ACR	275	70	DM	365	LG				
Isoxaben[68]	25	250	200	RT	325	345	DM	5	LG				
Linuron[69]	75	750	2.79	RT	30	0.045	DM	1.25	EN				
Malaoxon[70]	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020					0.05
Malathion[70]	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020					0.05
MCPA[71]								85	SC				
Mecoprop (MCPP)[72]	2325	23250		RT	22750	25400	DM	7	SC				
Metalaxyl[73]	3250	32500	4550	RT/FM	7000	600	DM	42500	LG				
Methamidophos[74]	625	6250	86.8	RT	6.5	2.25	DM	25000	SD				
Methidathion[75]	0.055	0.55	3.15	BS/FM	0.75	0.33	DM						
Methiocarb[76]	4.5	45	25	BS	1.375								
Methomyl[77]	12.5	125	28.5	CF/FM	2.2	0.3	DM/MATC						
Methomyl oxime													
Methoxyfenozide[78]	105	1050	265	RT/FM	14.25	1.55	CR	1700	SC				
Metolachlor[79]	80	800	15	BS/FM	5875	1600	DM	4	SC				
Metribuzin[80]	1050	10500	1500	RT	1050	645	DM	4.05					
Metsulfuron-methyl[81]	3750	37500	2250	BS	37500		DM	0.18	LG				
MGK264[82]	35	350	4	RT/ECOSAR Estimate	575	10	DM/ECOSAR Estimate	4	ECOSAR Estimate				
Myclobutanil[83]	60	600	110	BS/BS-ACR	2750	1950	DM	61	SD				
N,N-Diethyl-m-toluamide (DEET)[84]	1875	18750		RT	18750		DM						
Naled[85]	2.3	23	1.7	LT/FM	0.02875	0.005	DP/DM	12	NP				
Napropamide[86]	300	3000	550	BS/RT	6175	550	DM	175	LM				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Norflurazon[87]	202.5	2025	385	RT	3750	500	DM	4.85	SC				
Oryzalin[88]	72	720	110	BS/FM	375	179	DM	6.5	LG				
Oxadiazon[89]	30	300	0.44	RT	600	15	DM	2.6	SC				
Oxamyl[90]	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Oxamyl oxime[90]	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Oxyfluorfen[91]	5	50	0.65	BS/FM	375	6.5	DM	0.165	LG				
Paclobutrazol[92]	397.5	3975	24.5	CI/RT	60	4.5	DM	4	LG				
Pendimethalin[93]	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC				
Pentachloronitrobenzene (PCNB)[94]	2.5	25	6.5		192.5	9							
Pentachlorophenol[95]	0.375	3.75	5.5	RT	23	2.05	DM	25	SC			9.5	7.5
Phenothrin[96]	0.395	3.95	0.55	BS/FM	1.1	0.235	DM						
Phorate[97]	0.0585	0.585	0.17	BS	0.15	0.105	GF/DM	650					
Phosmet[98]	1.75	17.5	0.5	RT/FM	2.16	0.375	DM	70	NP				
Picloram[99]	137.5	1375	275	RT	8600	5900	DM	17450	SC				
Piperonyl butoxide (PBO)[100]	72.5	725	3.9	RT/FM	10.55	15	HA/DM	605	SC				
Prallethrin[101]	0.3	3	1.5	RT	1.55	0.325	DM	0.662	LG				
Prodiamine[102]	0.325	3.25		BS	3.25	0.75	DM						
Prometon[103]	490	4900	3265	RT/RT-ACR	6425	1725	DM	49	SC				
Prometryn[104]	72.75	727.5	310	RT/FM	2425	500	DM	0.52	NP				
Propargite[105]	1.1	11	8	RT/FM	3.5	4.5	DM	9.7	SC				
Propiconazole[106]	21.25	212.5	7.5	RT/FM-ACR	1200	90	DM	10.5	ND				
Propoxur[107]	92.5	925		RT	2.75		DM						
Propyzamide (Pronamide)[108]	265	2650	112	RT/FM	1400	300	DM	380	SC				
Pyraclostrobin[109]	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP				
Pyraflufen-ethyl[110]	2.125	21.25	0.445		20.5	40.5		0.75					
Pyrethrins[17]	0.1275	1.275	0.95	RT/FM	0.19	0.02	HA/CD	52.5	SC				
Pyridaben[111]	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG				
Pyrimethanil[112]	252.5	2525	10	RT	750	500	DM	900	ND				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Pyriproxyfen[113]	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG				
Pyroxasulfone[114]	55	550	1000	RT/FM	1100	950	DM	0.19	SC				
Simazine[115]	160	1600	30	FM	250	20	DM/ACR	3	SC				
Simetryn													
Sodium bentazon[116]	4750	47500	4915	RT/FM	15575	50600	CR/DM	2250	SC				
Spirotetramat[117]	35.25	352.5	267	RT/FM	165	50	CT	180	NP				
Sulfentrazone[118]	2345	23450	1475	BS/RT	15100	100	DM	14.4	SC				
Sulfometuron-methyl[119]	3700	37000		RT	37500	48500	DM	0.225	LG				
Sulfoxaflor[120]	9075	90750	330	BS/FM	100000	25250	DM	40600	NP				
tau-Fluvalinate[121]	0.00875	0.0875	0.032	CC/FM	0.235	0.05	DM						
Tebuthiuron[122]	2650	26500	4650	FM	74250	10900	DM	25	SC				
Tefluthrin[123]	0.0015	0.015	0.002	RT/FM	0.0175	0.004	DM						
Terbacil [124]	1155	11550	600	RT	16250	25	DM	5.5	NP				
Tetrachlorvinphos[125]	13.25	132.5	23.5	BS/FM	0.475	0.0625	DM	1600	SC				
Tetrahydrophthalimide (THPI)[21]	3000	30000		RT	28250		DM	90500	SC				
Tetramethrin[126]	0.0925	0.925		RT									
Thiacloprid[127]	630	6300	459	BS/RT	9.45	0.485	HA/ACR	22500	SC				
Thiamethoxam[128]	2850	28500	10000	BS/RT	8.75	0.37	CR	45100	LM				
Thiram[129]	1.05	10.5	0.55	BS/FM	52.5	10	DM	70	SC				
Tolfenpyrad[130]	0.004075	0.04075	0.094	RT/FM	0.25	0.122	DM	5	SC				
Tralomethrin[131]	0.04	0.4	0.044	RT/FM	0.00975	0.0022	DM						
trans-Permethrin[17]	0.01975	0.1975	0.026	BS/BS-ACR	0.00165	0.0021	HA	1.6	LG				
Triadimefon[132]	102.5	1025	85	RT	400	26	DM	1000	SC				
Triallate[133]	30	300	19	RT	22.75	7	DM	10.5	SC				
Triazine DEA degradate[134]								500					
Triazine DIA degradate[134]	425	4250			31500			1250					
Triazine HA degradate[134]	75	750		RT	1025		DM	5000	AI				
Triclopyr acid[135]	2925	29250	37200	RT/FM	33250	28850	DM	2100	AF				

	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Triclopyr butoxyethyl ester[135]	9	90	13	BS/RT	87.5	85	DM	50	NP				
Triclosan[136]	7.2	72		FM	97.5		DM	0.35	SS				
Trifloxystrobin[137]	0.3575	3.575	2.15	RT	6.325	1.38	DM	18.55	SC				
Trifluralin[138]	0.4625	4.625	0.95		62.75	1.2		10.95					
Zoxamide[139]	3.9	39	1.74	RT	195	19.5	DM	5	SS				

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Appendix B: 2021 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 2021, QA/QC samples were 12% of all the samples collected in the field. There were 213 QC samples in total: 93 field replicates, 66 field blanks, 35 MS/MSD samples and 19 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 at least one pesticide analytical method. In 2021, all pesticide and nutrient 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 solely due to field replicate results in 2021. 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, SSC, 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 2021) and standard deviation are presented in Table 34b.

Table 34b – Mean performance of analytical method reporting limits (LLOQ or MRL) in ng/L

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Method: LCMS-Pesticides; Reporting Limit: LLOQ				
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	1.02E+02	1.47E+01
Afidopyropen	915972-17-7	Insecticide	2.00E+02	0.00E+00
Aminocyclopyrachlor	858956-08-8	Herbicide	1.00E+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	1.44E+01	2.14E+01
Chlorantraniliprole	500008-45-7	Insecticide	5.00E+01	0.00E+00
Chlorsulfuron	64902-72-3	Herbicide	1.00E+02	0.00E+00
Clethodim sulfone	111031-17-5	Degradate	1.00E+02	0.00E+00
Clethodim sulfoxide	111031-14-2	Degradate	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
Dimethenamid ESA	1418095-09-6	Degradate	5.00E+02	0.00E+00
Dimethenamid OA	380412-59-9	Degradate	1.14E+02	6.24E+01
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	3.11E+01	1.23E+01
Fluopicolide	239110-15-7	Fungicide	1.00E+01	0.00E+00
Flupyradifurone	951659-40-8	Insecticide	2.00E+01	0.00E+00
Hexythiazox	78587-05-0	Insecticide	1.00E+01	0.00E+00
Imazapic	104098-48-8	Herbicide	1.00E+02	0.00E+00
Imazapyr	81334-34-1	Herbicide	1.03E+02	3.17E+01
Imidacloprid	138261-41-3	Insecticide	2.00E+01	0.00E+00
Indaziflam	950782-86-2	Herbicide	1.00E+01	0.00E+00
Inpyrfluxam	1352994-67-2	Fungicide	5.00E+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	2.00E+01	0.00E+00
Methiocarb	2032-65-7	Insecticide	2.00E+01	0.00E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Methomyl	16752-77-5	Insecticide	1.00E+01	0.00E+00
Methomyl oxime	13749-94-5	Degradate	1.00E+02	0.00E+00
Methoxyfenozide	161050-58-4	Insecticide	1.00E+01	0.00E+00
Metsulfuron-methyl	74223-64-6	Herbicide	5.11E+01	7.35E+00
Myclobutanil	88671-89-0	Fungicide	2.00E+01	0.00E+00
Oryzalin	19044-88-3	Herbicide	2.44E+02	1.23E+02
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	1.00E+01	0.00E+00
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	2.03E+02	4.49E+01
Sulfometuron-methyl	74222-97-2	Herbicide	2.00E+01	0.00E+00
Sulfoxaflor	946578-00-3	Insecticide	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	3.38E+02	2.35E+02
Tolfenpyrad	129558-76-5	Insecticide	5.00E+01	0.00E+00
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
Method: LCMS-Glyphos; Reporting Limit: LLOQ				
AMPA	1066-51-9	Degradate	1.71E+01	3.78E+01
Glufosinate-ammonium	77182-82-2	Herbicide	4.04E+02	1.04E+03
Glyphosate	1071-83-6	Herbicide	1.91E+01	4.06E+01
Method: GCMS-Herbicides; Reporting Limit: LLOQ				
2,4-D	94-75-7	Herbicide	6.42E+01	5.10E+01
3,5-Dichlorobenzoic acid	51-36-5	Degradate	6.23E+01	4.01E+01
4-Nitrophenol	100-02-7	Degradate	6.23E+01	4.01E+01
Bromoxynil	1689-84-5	Herbicide	6.23E+01	4.01E+01
Clopyralid	1702-17-6	Herbicide	6.23E+01	4.01E+01
Dacthal (DCPA)	1861-32-1	Herbicide	6.23E+01	4.01E+01
Dicamba acid	1918-00-9	Herbicide	6.42E+01	5.12E+01
Dichlorprop	120-36-5	Herbicide	6.23E+01	4.01E+01
MCPA	94-74-6	Herbicide	6.23E+01	4.01E+01
Mecoprop (MCPP)	93-65-2	Herbicide	6.23E+01	4.01E+01
Pentachlorophenol	87-86-5	Wood Preservative	6.23E+01	4.01E+01
Picloram	1918-02-1	Herbicide	3.12E+02	2.01E+02

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Sodium bentazon	25057-89-0	Herbicide	6.23E+01	4.01E+01
Triclopyr acid	55335-06-3	Herbicide	6.23E+01	4.01E+01
Method: GCMS-Pesticides; Reporting Limit: LLOQ				
2,6-Dichlorobenzamide	2008-58-4	Degradate	5.13E+00	6.56E-01
4,4'-DDD	72-54-8	Degradate	5.26E+00	1.67E+00
4,4'-DDE	72-55-9	Degradate	5.40E+00	5.64E-01
4,4'-DDT	50-29-3	Insecticide	9.77E+00	6.11E+00
Acetochlor	34256-82-1	Herbicide	4.99E+00	5.08E-02
Alachlor	15972-60-8	Herbicide	5.29E+00	1.57E+00
Atrazine	1912-24-9	Herbicide	5.23E+00	1.79E+00
Benfluralin	1861-40-1	Herbicide	4.99E+00	5.08E-02
Bifenazate	149877-41-8	Insecticide	6.46E+00	7.99E+00
Bifenthrin	82657-04-3	Insecticide	4.99E+00	5.08E-02
Boscalid	188425-85-6	Fungicide	5.06E+00	4.55E-01
Bromacil	314-40-9	Herbicide	4.99E+00	5.08E-02
Captan	133-06-2	Fungicide	5.95E+00	1.96E+00
Chlorethoxyfos	54593-83-8	Insecticide	9.98E+00	1.08E-01
Chlorothalonil	1897-45-6	Fungicide	4.99E+00	5.08E-02
Chlorpropham	101-21-3	Herbicide	5.50E+00	2.94E+00
Chlorpyrifos	2921-88-2	Insecticide	4.99E+00	5.08E-02
Chlorpyrifos-methyl	5598-13-0	Insecticide	4.99E+00	5.08E-02
cis-Permethrin	54774-45-7	Insecticide	4.99E+00	5.08E-02
Coumaphos	56-72-4	Insecticide	9.31E+00	1.71E+00
Cycloate	1134-23-2	Herbicide	1.50E+01	1.54E-01
Cyfluthrin-Total	68359-37-5	Insecticide	4.99E+00	5.08E-02
Cypermethrin-Total	52315-07-8	Insecticide	4.99E+00	5.08E-02
Deltamethrin	52918-63-5	Insecticide	4.99E+00	5.08E-02
Diazinon	333-41-5	Insecticide	4.99E+00	5.08E-02
Dichlobenil	1194-65-6	Herbicide	5.32E+00	1.89E+00
Dichlorvos (DDVP)	62-73-7	Insecticide	4.99E+00	5.08E-02
Dicofol	115-32-2	Insecticide	2.49E+01	2.54E-01
Dimethoate	60-51-5	Insecticide	4.99E+00	5.08E-02
Dithiopyr	97886-45-8	Herbicide	5.01E+00	1.28E-01
Eptam	759-94-4	Herbicide	4.99E+00	5.08E-02
ES Fenvalerate	51630-58-1	Insecticide	4.99E+00	5.08E-02
Ethalfluralin	55283-68-6	Herbicide	4.99E+00	5.08E-02
Ethoprop	13194-48-4	Insecticide	5.33E+00	1.75E+00
Etoxazole	153233-91-1	Insecticide	1.50E+01	1.54E-01
Etridiazole	2593-15-9	Fungicide	4.99E+00	5.08E-02
Fenarimol	60168-88-9	Fungicide	2.88E+01	1.19E+01
Fenpropathrin	39515-41-8	Insecticide	4.99E+00	5.08E-02
Fipronil	120068-37-3	Insecticide	7.65E+00	2.51E+00
Fipronil disulfinyl	205650-65-3	Degradate	4.99E+00	5.08E-02
Fipronil sulfide	120067-83-6	Degradate	4.99E+00	5.08E-02
Fipronil sulfone	120068-36-2	Degradate	9.98E+00	1.08E-01
Fludioxonil	131341-86-1	Fungicide	5.05E+00	1.08E+00
Flumioxazin	103361-09-7	Herbicide	2.49E+01	2.49E-01

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Fluroxypyr 1-methylheptyl ester	81406-37-3	Herbicide	2.49E+01	2.54E-01
gamma-Cyhalothrin	76703-62-3	Insecticide	4.99E+00	5.08E-02
Hexazinone	51235-04-2	Herbicide	7.84E+00	6.50E+00
Malathion	121-75-5	Insecticide	5.27E+00	5.18E+00
Metalaxyl	57837-19-1	Fungicide	1.01E+01	2.19E+00
Metolachlor	51218-45-2	Herbicide	5.47E+00	2.17E+00
Metribuzin	21087-64-9	Herbicide	4.99E+00	5.08E-02
MGK264	113-48-4	Synergist	4.99E+00	5.08E-02
N,N-Diethyl-m-toluamide	134-62-3	Insect Repellent	4.62E+01	1.82E+02
Naled	300-76-5	Insecticide	4.99E+01	5.08E-01
Napropamide	15299-99-7	Herbicide	4.99E+00	5.08E-02
Norflurazon	27314-13-2	Herbicide	4.99E+00	5.08E-02
Oxadiazon	19666-30-9	Herbicide	4.99E+00	5.08E-02
Oxyfluorfen	42874-03-3	Herbicide	4.99E+01	5.08E-01
Pendimethalin	40487-42-1	Herbicide	4.99E+00	5.08E-02
Pentachloronitrobenzene	82-68-8	Fungicide	4.99E+00	5.08E-02
Phenothrin	26002-80-2	Insecticide	9.98E+00	1.08E-01
Phosmet	732-11-6	Insecticide	4.99E+00	4.93E-02
Piperonyl butoxide (PBO)	51-03-6	Synergist	1.62E+01	9.47E+00
Prallethrin	23031-36-9	Insecticide	4.99E+00	5.08E-02
Prodiamine	29091-21-2	Herbicide	2.49E+01	2.54E-01
Prometon	1610-18-0	Herbicide	4.99E+00	5.08E-02
Prometryn	7287-19-6	Herbicide	9.98E+00	1.08E-01
Propargite	2312-35-8	Insecticide	9.98E+00	1.08E-01
Propyzamide (Pronamide)	23950-58-5	Herbicide	4.99E+00	5.08E-02
Pyraflufen-ethyl	129630-19-9	Herbicide	4.99E+00	5.08E-02
Pyridaben	96489-71-3	Insecticide	4.99E+00	5.08E-02
Pyriproxyfen	95737-68-1	Insecticide	1.10E+01	5.26E+00
Simazine	122-34-9	Herbicide	1.01E+01	2.17E+00
Simetryn	1014-70-6	Herbicide	2.49E+01	2.54E-01
Sulfentrazone	122836-35-5	Herbicide	5.36E+00	1.30E+00
tau-Fluvalinate	102851-06-9	Insecticide	4.99E+00	5.08E-02
Tebuthiuron	34014-18-1	Herbicide	9.98E+00	1.08E-01
Tefluthrin	79538-32-2	Insecticide	4.99E+00	5.08E-02
Terbacil	5902-51-2	Herbicide	4.99E+00	5.08E-02
Tetrachlorvinphos	961-11-5	Insecticide	4.99E+00	5.08E-02
Tetrahydrophthalimide (THPI)	27813-21-4	Degradate	4.99E+00	5.08E-02
Tetramethrin	7696-12-0	Insecticide	4.99E+00	5.08E-02
Tralomethrin	66841-25-6	Insecticide	4.99E+00	5.08E-02
trans-Permethrin	61949-77-7	Insecticide	4.99E+00	5.08E-02
Triadimefon	43121-43-3	Fungicide	4.99E+00	5.08E-02
Triallate	2303-17-5	Herbicide	4.99E+00	5.08E-02
Triclopyr butoxyethyl ester	64700-56-7	Herbicide	9.98E+00	1.08E-01
Triclosan	3380-34-5	Antimicrobial	4.41E+01	2.60E+01
Trifluralin	1582-09-8	Herbicide	9.98E+00	1.08E-01

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
<u>Various Methods; Reporting Limit: MRL</u>				
Specific conductivity			15.0 µmhos/cm	0.00E+00
Suspended sediment concentration			0.981 mg/L	3.95E-02
Total suspended solids			2.04 mg/L	1.41E+00
Ammonia as N	7664-41-7	Nutrient	0.0110 mg/L	5.38E-03
Nitrate-Nitrite as N		Nutrient	0.0959 mg/L	1.89E-01
ortho-Phosphate as P		Nutrient	0.00542 mg/L	9.10E-03
Total phosphorus as P		Nutrient	0.0100 mg/L	5.71E-10

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 35b that are used for sample analysis of pesticides, TSS, SSC, nutrients, and specific conductivity (MEL, 2016).

Table 35b – 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 2021, 5% of pesticide, nutrient, TSS, and SSC samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 263 consistently identified pairs for pesticide analysis, 22 consistently identified pairs for nutrient analysis, 5 consistently identified pairs for TSS analysis, and 12 consistently identified pairs for SSC 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 63 inconsistently identified pairs for pesticide analysis, 2 inconsistently identified pair for nutrients, 1 inconsistently identified pair for TSS, and 1 inconsistently identified pair for SSC.

Of the 173 pesticide analytes tested for, 48% (83 analytes) were detected in field replicates as well as all four nutrients, TSS, and SSC. Table 36b 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 36b.

Table 36b – 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 (%)
Benfluralin	PESTMSQ3	17	0		1	100	100
Chlorantraniliprole	CARBAMQ3DI	17	0		1	100	100
Fipronil	PESTMSQ3	16	0		2	100	100
Glufosinate-ammonium	GLYPHOS	3	0		1	100	100
Myclobutanil	CARBAMQ3DI	17	0		1	100	100
Prometryn	PESTMSQ3	17	0		1	100	100
1-(3,4-Dichlorophenyl)-3-methylurea	CARBAMQ3DI	16	1	31	1	50	95

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 (%)
Clothianidin	CARBAMQ3DI	16	1	5	1	50	95
Fipronil sulfide	PESTMSQ3	16	1	13	1	50	95
Fipronil sulfone	PESTMSQ3	16	1	2	1	50	95
Methoxyfenozide	CARBAMQ3DI	16	1	16	1	50	95
Oxamyl oxime	CARBAMQ3DI	16	1	3	1	50	95
Trifluralin	PESTMSQ3	16	1	1	1	50	95
4,4'-DDE	PESTMSQ3	17	1	7	0	0	90
Aminocyclopyrachlor	CARBAMQ3DI	17	1	12	0	0	90
Clethodim sulfoxide	CARBAMQ3DI	17	1	14	0	0	90
Dacthal (DCPA)	HERBS	16	1	9	0	0	90
Difenoconazole	CARBAMQ3DI	17	1	13	0	0	90
Dimethenamid ESA	CARBAMQ3DI	17	1	13	0	0	90
Imazapic	CARBAMQ3DI	17	1	5	0	0	90
Mecoprop (MCPP)	HERBS	16	1	1	0	0	90
Metsulfuron-methyl	CARBAMQ3DI	17	1	2	0	0	90
Oxadiazon	PESTMSQ3	17	1	2	0	0	90
Oxyfluorfen	PESTMSQ3	17	1	1	0	0	90
Sodium bentazon	HERBS	16	1	6	0	0	90
Spirotetramat	CARBAMQ3DI	17	1	51	0	0	90
MCPA	HERBS	13	2	14	2	50	86
Acephate	CARBAMQ3DI	15	2	2	1	33	80
Bromoxynil	HERBS	14	2	8	1	33	80
Dithiopyr	PESTMSQ3	15	2	2	1	33	80
Picloram	HERBS	14	2	43	1	33	80
Prometon	PESTMSQ3	13	3	9	2	40	75
Simazine	PESTMSQ3	13	3	7	2	40	75
Pendimethalin	PESTMSQ3	11	4	6	3	43	72
Chlorpropham	PESTMSQ3	16	2	15	0	0	68
Indaziflam	CARBAMQ3DI	16	2	14	0	0	68
Methamidophos	CARBAMQ3DI	16	2	4	0	0	68
Methiocarb	CARBAMQ3DI	16	2	10	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 (%)
Metribuzin	PESTMSQ3	16	2	5	0	0	68
N,N-Diethyl-m-toluamide (DEET)	PESTMSQ3	16	2	32	0	0	68
Oxamyl	CARBAMQ3DI	16	2	6	0	0	68
Paclobutrazol	CARBAMQ3DI	16	2	44	0	0	68
Sulfometuron-methyl	CARBAMQ3DI	16	2	4	0	0	68
Triazine DIA degradate	CARBAMQ3DI	16	2	18	0	0	68
Triclopyr acid	HERBS	15	2	3	0	0	68
Aminomethylphosphoric acid (AMPA)	GLYPHOS	0	3	5	1	25	68
Ammonia	NH3	3	3	4	1	25	68
Clopyralid	HERBS	13	3	6	1	25	68
Flupyradifurone	CARBAMQ3DI	14	3	14	1	25	68
Glyphosate	GLYPHOS	0	3	4	1	25	68
Malathion	PESTMSQ3	14	3	3	1	25	68
Propiconazole	CARBAMQ3DI	14	3	8	1	25	68
Diuron	CARBAMQ3DI	10	5	16	3	38	66
Atrazine	PESTMSQ3	11	5	5	2	29	60
Dicamba acid	HERBS	12	4	9	1	20	58
Imidacloprid	CARBAMQ3DI	13	4	9	1	20	58
Norflurazon	PESTMSQ3	13	4	3	1	20	58
Hexazinone	PESTMSQ3	10	6	2	2	25	54
Thiamethoxam	CARBAMQ3DI	10	6	5	2	25	54
Cyantraniliprole	CARBAMQ3DI	15	3	6	0	0	54
Diazinon	PESTMSQ3	15	3	7	0	0	54
Dinotefuran	CARBAMQ3DI	15	3	8	0	0	54
Eptam	PESTMSQ3	15	3	5	0	0	54
Fluopicolide	CARBAMQ3DI	15	3	21	0	0	54
Metalaxyl	PESTMSQ3	15	3	4	0	0	54
Terbacil	PESTMSQ3	12	5	6	1	17	51
Total suspended solids	TSS	0	5	14	1	17	51

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 (%)
Fludioxonil	PESTMSQ3	9	7	6	2	22	49
2,4-D	HERBS	5	9	14	3	25	48
Boscalid	PESTMSQ3	6	9	4	3	25	48
Sulfentrazone	PESTMSQ3	6	9	12	3	25	48
Bromacil	PESTMSQ3	11	6	18	1	14	45
Dichlobenil	PESTMSQ3	11	6	10	1	14	45
4,4'-DDD	PESTMSQ3	10	7	2	1	13	41
Metolachlor	PESTMSQ3	10	7	3	1	13	41
Ortho phosphate	OP	0	7	26	1	13	41
Triazine HA degradate	CARBAMQ3DI	10	7	7	1	13	41
Azoxystrobin	CARBAMQ3DI	13	5	11	0	0	37
Chlorpyrifos	PESTMSQ3	13	5	2	0	0	37
Pyrimethanil	CARBAMQ3DI	13	5	17	0	0	37
Tetrahydrophthalimide (THPI)	PESTMSQ3	13	5	11	0	0	37
Total phosphorus	TP8-H	0	5	1	0	0	37
Triazine DEA degradate	CARBAMQ3DI	13	5	12	0	0	37
Imazapyr	CARBAMQ3DI	8	9	6	1	10	34
Carbendazim	CARBAMQ3DI	12	6	3	0	0	32
Tebuthiuron	PESTMSQ3	12	6	10	0	0	32
Nitrate-Nitrite as N	NO2NO3	0	7	23	0	0	28
Suspended sediment concentration	SSC	0	12	12	1	8	27
2,6-Dichlorobenzamide	PESTMSQ3	5	13	7	0	0	16

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 74% of analytes (66 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 2021 using the second method indicate only one analyte has a low detection variability rather than the 66 analytes estimated through the first method. This analyte was 2,6-dichlorobenzamide, a degradate that was frequently detected throughout the season at all monitoring sites. This analysis shows that there was not a high reproducibility of detections between replicates. Likely, 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 263 consistently identified replicate pairs for pesticides, eight 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 14%. Of the five consistently identified TSS pairs, one had an RPD equal to or greater than the 20% RPD criterion. For SCC analysis, of the 12 consistently identified pairs, 1 pair had an RPD greater than or equal to 20% (RPD criterion) with a mean RPD of 12%. For nutrients analysis, the mean RPD of the consistently identified replicate-paired analytes was 16%. Of the 22 consistently identified nutrient pairs, two had an RPD that was equal to or greater than the 20% RPD criterion. Results for 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, SSC, and TSS field replicates were of acceptable data quality.

The majority of the 67 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 2021, there were 18 detections in the 66 field blank samples collected for nutrients, TSS, SSC, and pesticide analysis (Table 37b). 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 52 sample detections qualified to *U* in 2021 due to field blank detections.

Table 37b – Analyte detections in field blanks

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	Reporting Limit (ng/L)	MDL (ng/L)	Qualifier
4/20	Bertrand Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	1.63	4.98	1.28	J
6/8	Indian Slough	GCMS-Pesticides	Alachlor	2.69	4.95	0.707	J
9/14	Kamiache Creek	GCMS-Pesticides	Atrazine	3.69	5.03	2.16	J

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	Reporting Limit (ng/L)	MDL (ng/L)	Qualifier
3/29	Snipes Creek	GCMS-Pesticides	Boscalid	1.59	5	0.547	J
5/3	Sulphur Creek Wasteway	LCMS-Pesticides	Carbendazim	24.4	10	1.16	
8/23	Marion Drain	GCMS-Pesticides	Chlorpropham	4.45	4.93	0.966	J
3/29	Snipes Creek	GCMS-Pesticides	DEET	2.16	5	1.33	J
4/6	Stemilt Creek	GCMS-Pesticides	DEET	4.27	5	1.33	J
5/4	Brender Creek	GCMS-Pesticides	DEET	20.5	5	1.33	
8/23	Marion Drain	GCMS-Pesticides	DEET	215	4.93	1.31	
8/23	Marion Drain	GCMS-Pesticides	Dichlobenil	3.21	4.93	1.38	J
5/11	Lower Big Ditch	GCMS-Pesticides	Hexazinone	4.16	4.9	1.02	J
7/12	Dry Creek	NO2NO3	Nitrate-Nitrite as N	0.183 mg/L	0.010 mg/L	0.004 mg/L	
9/27	Kamiache Creek	NO2NO3	Nitrate-Nitrite as N	0.057 mg/L	0.01 mg/L	0.004 mg/L	J
11/9	Thorn Creek	NO2NO3	Nitrate-Nitrite as N	0.012 mg/L	0.01 mg/L	0.004 mg/L	
4/20	Upper Big Ditch	OP	Ortho phosphate	0.0098 mg/L	0.003 mg/L	0.0013 mg/L	J
8/2	Kamiache Creek	OP	Ortho phosphate	0.0059 mg/L	0.003 mg/L	0.0013 mg/L	
10/25	Dry Creek	OP	Ortho phosphate	0.0104 mg/L	0.003 mg/L	0.0013 mg/L	J

Matrix Spike/Matrix Spike Duplicate Results

Summary MS/MSD results for each analyte are shown in Table 38b, 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 38b – 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	24	65	135	99	79 - 117	0	0	12	6	0.1 - 15	38
2,4-D	22	34	125	86	67 - 112	0	0	11	10	2 - 19	132
2,6-Dichlorobenzamide	26	60	140	119	71 - 145	0	1	13	4	0.4 - 16	242

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)
3,5-Dichlorobenzoic acid	22	41	125	76	61 - 83	0	0	11	7	0.7 - 26	
4,4'-DDD	26	60	140	112	94 - 132	0	0	13	4	1 - 9	91
4,4'-DDE	26	60	140	90	72 - 104	0	0	13	5	0.2 - 15	66
4,4'-DDT	26	44	140	85	65 - 110	0	0	13	7	0.2 - 16	23
4-Nitrophenol	22	19	186	93	48 - 120	0	0	11	16	2 - 66	4
Acephate	24	65	135	83	64 - 96	1	0	12	6	0.5 - 17	24
Acetamiprid	24	65	168	124	104 - 149	0	0	12	7	1 - 16	15
Acetochlor	26	60	140	119	102 - 136	0	0	13	4	0.02 - 10	
Acetochlor ESA	24	43	163	107	69 - 147	0	0	12	8	0.6 - 16	5
Afidopyropen	24	44	148	98	70 - 126	0	0	12	10	0.8 - 21	
Alachlor	26	60	140	113	98 - 137	0	0	13	3	0.08 - 7	
Aminocyclopyrachlor	24	10	250	165	76 - 313	0	6	12	7	0.8 - 13	17
AMPA	6	50	150	119	108 - 129	0	0	3	3	0.5 - 6	59
Atrazine	26	60	140	102	87 - 120	0	0	13	3	0.03 - 8	136
Azoxystrobin	24	65	159	105	65 - 138	0	0	12	10	3 - 30	77
Benfluralin	26	60	140	108	93 - 123	0	0	13	4	0.3 - 11	1
Bensulide	24	41	144	85	49 - 119	0	0	12	12	0.6 - 47	
Bifenazate	26	10	250	249	155 - 350	0	12	13	6	0.9 - 12	1
Bifenthrin	26	58	140	102	74 - 128	0	0	13	6	0.02 - 16	1
Boscalid	26	60	141	131	96 - 160	0	7	13	4	0.2 - 9	209
Bromacil	26	60	159	143	116 - 172	0	3	13	4	0.2 - 17	122
Bromoxynil	22	51	125	82	69 - 94	0	0	11	7	0.2 - 13	16
Captan	26	12	140	70	10 - 121	2	0	13	6	1 - 19	
Carbaryl	24	65	135	102	74 - 123	0	0	12	6	0.3 - 19	26
Carbendazim	24	65	135	91	68 - 104	0	0	12	7	0.1 - 17	97
Chlorantraniliprole	24	65	142	103	58 - 145	1	1	12	13	0.2 - 35	13
Chlorethoxyfos	26	60	140	103	87 - 116	0	0	13	3	0.2 - 9	
Chlorothalonil	26	60	140	107	88 - 128	0	0	13	4	0.9 - 11	6
Chlorpropham	26	60	140	123	101 - 145	0	2	13	3	0.1 - 8	17
Chlorpyrifos	26	60	140	95	81 - 113	0	0	13	3	0.5 - 11	86
Chlorpyrifos-methyl	26	60	140	100	84 - 120	0	0	13	4	0.2 - 12	

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)
Chlorsulfuron	24	13	182	107	60 - 171	0	0	12	8	2 - 19	8
cis-Permethrin	26	60	140	120	92 - 155	0	6	13	5	0.5 - 13	1
Clethodim sulfone	24	65	135	108	64 - 161	1	3	12	5	0.9 - 15	1
Clethodim sulfoxide	24	65	135	110	67 - 153	0	4	12	8	0.01 - 23	3
Clopyralid	22	22	125	45	19 - 62	2	0	11	13	2 - 31	13
Clothianidin	24	36	135	88	66 - 112	0	0	12	10	1 - 23	49
Coumaphos	26	60	154	146	115 - 172	0	7	13	4	0.05 - 14	
Cyantraniliprole	24	58	144	104	72 - 132	0	0	12	6	1 - 17	14
Cycloate	26	60	151	117	97 - 145	0	0	13	5	0.1 - 18	
Cyfluthrin-Total	26	60	146	133	105 - 161	0	5	13	5	1 - 13	
Cypermethrin-Total	26	60	153	149	112 - 190	0	7	13	6	0.1 - 15	
Cyprodinil	24	65	135	99	70 - 119	0	0	12	7	0.9 - 14	7
Dacthal (DCPA)	22	52	128	89	70 - 104	0	0	11	6	1 - 14	7
Deltamethrin	26	60	147	134	98 - 161	0	5	13	6	0.1 - 17	
Diazinon	26	60	140	111	101 - 123	0	0	13	3	0.8 - 8	53
Dicamba acid	22	48	125	79	63 - 88	0	0	11	7	1 - 20	61
Dichlobenil	26	60	140	99	75 - 120	0	0	13	6	0.4 - 11	121
Dichlorprop	22	54	125	84	71 - 95	0	0	11	7	2 - 14	
Dichlorvos (DDVP)	26	60	157	127	106 - 153	0	0	13	7	0.7 - 15	1
Dicofol	26	60	250	432	247 - 564	0	25	13	6	2 - 14	
Difenoconazole	24	50	135	89	54 - 133	0	0	12	12	3 - 27	5
Diflubenzuron	24	60	144	101	67 - 139	0	0	12	10	1 - 34	1
Dimethenamid ESA	24	65	135	97	68 - 131	0	0	12	9	0.7 - 23	3
Dimethenamid OA	24	65	135	95	66 - 121	0	0	12	7	0.04 - 17	
Dimethoate	26	60	146	127	110 - 139	0	0	13	3	0.7 - 9	20
Dinotefuran	24	65	163	117	96 - 141	0	0	12	6	0.2 - 15	51
Dithiopyr	26	60	140	104	87 - 120	0	0	13	5	0.7 - 14	15
Diuron	24	65	135	104	74 - 122	0	0	12	8	2 - 18	136
Eptam	26	60	140	101	79 - 125	0	0	13	6	1 - 14	80
ES Fenvalerate	26	60	140	121	92 - 148	0	4	13	5	0.9 - 14	
Ethalfluralin	26	60	140	114	95 - 128	0	0	13	5	0.9 - 12	

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)
Ethoprop	26	60	140	134	111 - 144	0	4	13	4	0.4 - 10	3
Etoxazole	26	60	140	126	103 - 153	0	2	13	6	1 - 14	7
Etridiazole	26	60	140	93	80 - 108	0	0	13	5	0.7 - 12	
Fenarimol	26	60	164	148	129 - 174	0	3	13	3	0.004 - 6	
Fenbuconazole	24	56	156	94	53 - 129	1	0	12	11	0.1 - 36	
Fenbutatin oxide	24	23	169	90	39 - 136	0	0	12	11	2 - 32	1
Fenpropathrin	26	60	140	113	76 - 143	0	2	13	8	0.5 - 28	
Fipronil	26	60	152	133	112 - 151	0	0	13	4	0.09 - 11	26
Fipronil disulfinyl	26	60	140	115	96 - 141	0	1	13	4	0.4 - 14	3
Fipronil sulfide	26	60	140	117	102 - 131	0	0	13	3	0.1 - 10	20
Fipronil sulfone	26	60	144	124	107 - 146	0	1	13	4	0.5 - 9	8
Fludioxonil	26	60	146	132	116 - 153	0	3	13	4	0.7 - 11	175
Flumioxazin	26	60	140	111	37 - 161	2	5	13	5	0.2 - 18	2
Fluopicolide	24	58	159	102	52 - 139	1	0	12	10	1 - 30	20
Flupyradifurone	24	65	135	133	81 - 184	0	10	12	6	0.3 - 13	40
Fluroxypyr 1-methylheptyl ester	26	60	156	118	93 - 143	0	0	13	6	0.06 - 20	
gamma-Cyhalothrin	26	60	140	121	91 - 153	0	5	13	6	0.4 - 14	5
Glufosinate-ammonium	6	50	150	120	103 - 135	0	0	3	4	2 - 6	1
Glyphosate	6	50	150	113	102 - 121	0	0	3	2	0.3 - 3	60
Hexazinone	26	60	141	129	107 - 158	0	8	13	5	0.3 - 13	116
Hexythiazox	24	43	135	95	57 - 145	0	1	12	11	0.2 - 25	
Imazapic	24	32	203	138	102 - 216	0	2	12	8	0.7 - 18	11
Imazapyr	24	39	176	138	67 - 277	0	3	12	7	1 - 16	133
Imidacloprid	24	65	135	99	77 - 116	0	0	12	5	0.2 - 22	75
Indaziflam	24	65	135	101	63 - 138	1	1	12	11	2 - 25	21
Inpyrfluxam	24	65	135	100	55 - 131	1	0	12	14	4 - 32	
Isoxaben	24	65	163	106	62 - 134	1	0	12	9	1 - 30	6
Linuron	24	65	135	102	64 - 122	1	0	12	11	1 - 29	
Malaoxon	24	65	138	110	76 - 135	0	0	12	6	0.07 - 15	2
Malathion	26	60	144	128	105 - 152	0	3	13	3	0.2 - 11	49

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)
MCPA	22	43	125	87	66 - 105	0	0	11	8	0.9 - 25	14
Mecoprop (MCPP)	22	52	125	83	71 - 98	0	0	11	8	0.7 - 20	11
Metalaxyl	26	60	140	115	101 - 132	0	0	13	3	0.3 - 9	62
Methamidophos	24	33	135	50	36 - 64	0	0	12	6	0.3 - 13	19
Methidathion	24	59	146	93	65 - 119	0	0	12	12	0.7 - 34	
Methiocarb	24	65	143	104	66 - 142	0	0	12	14	2 - 44	7
Methomyl	24	65	135	104	76 - 120	0	0	12	7	1 - 16	2
Methomyl oxime	24	35	135	61	48 - 75	0	0	12	6	0.1 - 20	
Methoxyfenozide	24	52	176	101	62 - 129	0	0	12	10	2 - 31	8
Metolachlor	26	60	140	108	94 - 131	0	0	13	3	0.2 - 7	150
Metribuzin	26	60	140	89	76 - 113	0	0	13	4	0.5 - 12	49
Metsulfuron-methyl	24	15	192	111	47 - 181	0	0	12	8	0.9 - 19	14
MGK264	26	60	140	107	91 - 131	0	0	13	4	0.07 - 10	1
Myclobutanil	24	65	158	103	54 - 141	1	0	12	11	0.5 - 40	12
N,N-diethyl-m-toluamide	26	60	140	116	100 - 133	0	0	13	3	0.08 - 7	54
Naled	26	43	140	95	72 - 143	0	1	13	6	1 - 12	
Napropamide	26	60	140	122	107 - 145	0	1	13	3	0.2 - 10	5
Norflurazon	26	60	140	128	108 - 148	0	5	13	4	0.7 - 10	96
Oryzalin	24	10	250	112	81 - 180	0	0	12	11	2 - 32	
Oxadiazon	26	60	140	102	93 - 112	0	0	13	3	0.5 - 7	16
Oxamyl	24	65	135	100	74 - 117	0	0	12	7	0.4 - 15	35
Oxamyl oxime	24	37	135	120	92 - 168	0	2	12	7	0.2 - 19	32
Oxyfluorfen	26	60	159	128	105 - 151	0	0	13	6	2 - 13	6
Paclobutrazol	24	65	136	105	83 - 134	0	0	12	8	0.4 - 18	9
Pendimethalin	26	60	140	118	103 - 136	0	0	13	3	0.03 - 7	105
Pentachloronitrobenzene	26	60	140	101	90 - 110	0	0	13	4	0.2 - 8	
Pentachlorophenol	22	47	125	80	72 - 93	0	0	11	4	0.3 - 13	4
Phenothrin	26	17	140	65	55 - 79	0	0	13	7	0.2 - 25	
Phorate	24	20	142	91	64 - 125	0	0	12	13	0.8 - 52	
Phosmet	26	60	141	111	66 - 142	0	1	13	4	0.6 - 10	6
Picloram	22	10	125	36	18 - 53	0	0	11	11	0.2 - 30	49

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)
Piperonyl butoxide (PBO)	26	60	165	128	108 - 146	0	0	13	5	0.7 - 13	5
Prallethrin	26	60	151	129	109 - 147	0	0	13	4	0.09 - 10	
Prodiamine	26	60	148	120	102 - 133	0	0	13	3	0.2 - 9	
Prometon	26	60	140	113	97 - 129	0	0	13	4	0.7 - 10	77
Prometryn	26	60	140	116	94 - 140	0	0	13	4	0.2 - 15	2
Propargite	26	38	145	110	91 - 124	0	0	13	5	0.3 - 14	
Propiconazole	24	49	159	94	57 - 136	0	0	12	12	2 - 29	73
Propoxur	24	65	135	101	73 - 120	0	0	12	8	1 - 21	
Propyzamide	26	60	140	124	110 - 137	0	0	13	3	0.1 - 8	
Pyraclostrobin	24	57	146	99	56 - 128	1	0	12	9	0.04 - 28	2
Pyraflufen-ethyl	26	60	140	116	95 - 142	0	1	13	5	0.9 - 19	
Pyrethrins	24	10	188	109	22 - 358	0	2	12	20	3 - 54	
Pyridaben	26	60	140	136	109 - 165	0	8	13	5	0.3 - 10	1
Pyrimethanil	24	65	135	99	75 - 123	0	0	12	7	0.6 - 12	64
Pyriproxyfen	26	60	140	114	94 - 138	0	0	13	3	0.07 - 7	4
Pyroxasulfone	24	44	163	100	62 - 131	0	0	12	11	0.2 - 28	1
Simazine	26	60	140	100	70 - 117	0	0	13	3	0.05 - 8	100
Simetryn	26	60	140	101	81 - 127	0	0	13	4	0.4 - 17	
Sodium bentazon	22	36	145	83	62 - 97	0	0	11	9	2 - 15	24
Spirotetramat	24	63	164	99	55 - 142	3	0	12	16	0.9 - 43	4
Sulfentrazone	26	60	163	117	63 - 170	0	2	13	9	0.2 - 29	175
Sulfometuron-methyl	24	57	160	113	67 - 160	0	0	12	6	0.5 - 14	35
Sulfoxaflor	24	65	135	107	90 - 142	0	1	12	8	2 - 20	
tau-Fluvalinate	26	60	147	135	103 - 173	0	6	13	6	0.1 - 13	
Tebuthiuron	26	60	156	132	93 - 174	0	2	13	8	0.1 - 25	92
Tefluthrin	26	60	140	97	73 - 108	0	0	13	6	0.8 - 14	
Terbacil	26	10	250	144	87 - 174	0	0	13	4	0.07 - 12	93
Tetrachlorvinphos	26	60	169	134	114 - 156	0	0	13	3	0.05 - 12	
Tetrahydrophthalimide	26	60	150	131	106 - 159	0	3	13	6	0.1 - 13	55
Tetramethrin	26	60	140	135	82 - 168	0	8	13	5	0.9 - 12	1
Thiacloprid	24	65	145	120	89 - 139	0	0	12	8	2 - 20	

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)
Thiamethoxam	24	32	136	92	69 - 113	0	0	12	9	0.04 - 25	111
Thiram	24	10	250	92	22 - 162	0	0	12	6	1 - 13	
Tolfenpyrad	24	65	135	90	40 - 137	2	1	12	12	1 - 32	
Tralomethrin	26	60	147	134	98 - 161	0	5	13	6	0.1 - 17	
trans-Permethrin	26	60	140	120	91 - 149	0	4	13	6	0.5 - 11	
Triadimefon	26	60	140	113	95 - 134	0	0	13	4	0.5 - 13	3
Triallate	26	60	140	101	86 - 118	0	0	13	4	0.9 - 10	4
Triazine DEA degradate	24	64	135	103	74 - 152	0	2	12	6	0.2 - 15	96
Triazine DIA degradate	24	49	146	105	91 - 139	0	0	12	6	0.07 - 17	45
Triazine HA degradate	24	63	141	113	65 - 157	0	4	12	7	0.7 - 19	158
Triclopyr acid	22	43	141	96	61 - 117	0	0	11	7	0.6 - 17	43
Triclopyr butoxyethyl ester	26	60	140	106	93 - 119	0	0	13	4	1 - 9	
Triclosan	26	60	168	145	117 - 176	0	3	13	5	0.5 - 13	1
Trifloxystrobin	24	47	147	95	54 - 133	0	0	12	11	2 - 27	4
Trifluralin	26	60	140	99	87 - 111	0	0	13	4	0.6 - 9	25
Zoxamide	24	59	143	102	62 - 133	0	0	12	10	0.7 - 32	

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

There was a total of 4,248 spiked results (2,124 MS/MSD pairs) from MS and MSD recoveries that were unqualified or *J* qualified. Overall, the mean recovery was 111% with a standard deviation of 38%. 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 (22 recoveries) fell below the control limits for MS/MSD samples,
- 94% of analyte recoveries (4,012 recoveries) were within the control limits for MS/MSD samples,
- 5% of analyte recoveries (214 recoveries) were above the control limits for MS/MSD samples.

RPDs calculated for 2,124 MS/MSD pairs were below the 40% RPD control limit 99% of the time; only seven pairs had RPDs above the control limit. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 6% 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 49% 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.

Method Blanks

MEL uses method blanks to assess the precision of equipment and the potential for internal laboratory contamination. Method 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 method blank detections occur, the sample LLOQ may be increased, and detections may be qualified as estimates.

Table 39b lists the analyte detections that occurred in the method blanks (220 detections). Regular field sample detections corresponding to the method blank samples in the same batch were qualified if the regular sample result was less than 5 times the method blank result. There were two sample detections qualified to *U* in 2021 due to method blank detections.

Table 39b – Analyte detections in method 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	2	0.6	0.327	0.884	5	1.3
4,4'-DDD	GCMS-Pesticides	2	2.2	1.16	3.33	5	0.7
4,4'-DDE	GCMS-Pesticides	11	1.2	0.849	1.28	5	1.4
4,4'-DDT	GCMS-Pesticides	12	3.5	3.14	4.81	5	0.8
AMPA	LCMS-Glyphos	1	13.1	13.1	13.1	7	2.5
Carbaryl	LCMS-Pesticides	3	0.5	0.466	0.549	20	2.2
Carbendazim	LCMS-Pesticides	5	1.7	0.363	6.86	10	1.2
Dichlobenil	GCMS-Pesticides	3	0.7	0.088	1.4	5	1.4
Difenoconazole	LCMS-Pesticides	6	1.8	1.27	2.43	20	4.9
Dithiopyr	GCMS-Pesticides	1	1.1	1.12	1.12	5	1.7
Ethoprop	GCMS-Pesticides	2	2.9	2.87	2.91	5	1.4
Fenarimol	GCMS-Pesticides	36	5.6	1.17	11.1	5	1.1
Fenbutatin oxide	LCMS-Pesticides	19	7.2	3.17	10.8	20	3.0
Glufosinate-ammonium	LCMS-Glyphos	2	624.0	611	637	7	3.4
Glyphosate	LCMS-Glyphos	2	6.2	5.8	6.6	7	2.5
Hexazinone	GCMS-Pesticides	5	4.5	3.68	5.1	5	1.0
Hexythiazox	LCMS-Pesticides	2	1.3	1.05	1.61	10	1.6
Methomyl	LCMS-Pesticides	2	0.3	0.292	0.295	10	0.7
Metolachlor	GCMS-Pesticides	3	2.3	0.847	3.6	5	0.6
N,N-diethyl-m-toluamide	GCMS-Pesticides	28	2.1	0.941	3.6	5	1.3
Paclobutrazol	LCMS-Pesticides	1	0.7	0.678	0.678	10	1.6
Propiconazole	LCMS-Pesticides	11	2.4	0.811	4.37	50	3.5

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)
Pyraclostrobin	LCMS-Pesticides	6	1.0	0.463	2.36	50	2.1
Pyrimethanil	LCMS-Pesticides	3	1.1	0.716	1.8	10	1.8
Pyriproxyfen	GCMS-Pesticides	1	7.7	7.65	7.65	10	1.4
Thiram	LCMS-Pesticides	6	157.3	105	230	200	51.3
Triazine HA degradate	LCMS-Pesticides	16	0.5	0.287	0.785	10	1.1
Triclosan	GCMS-Pesticides	26	11.4	2.64	17.3	11	1.7
Trifloxystrobin	LCMS-Pesticides	3	0.4	0.33	0.423	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 40b presents summary statistics for surrogate recoveries of only field samples and field replicates.

Table 40b – Pesticide surrogates summary

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
Carbamate pesticides:						
Carbaryl C13	LCMS-Pesticides	330	103	100	65	135
Carbendazim-D4	LCMS-Pesticides	330	94	100	65	135
Acid-derivitizable herbicides:						
2,4,6-Tribromophenol	GCMS-Herbicides	298	74	89.9	63	125
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	298	78	98.3	61	125
Nitrogen containing pesticides:						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	351	96	100	50	132
Chlorinated pesticides:						
4,4'-DDE-13C12	GCMS-Pesticides	351	95	100	65	125
Decachlorobiphenyl (DCB)	GCMS-Pesticides	351	76	98.6	28	125
Glyphosate related pesticides:						
AMPA-C13N15	LCMS-Glyphos	63	102	98.4	20	200
Glufosinate-d3	LCMS-Glyphos	68	109	100	20	200
Glyphosate-C13N15	LCMS-Glyphos	60	105	100	20	200

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
Neonicotinoid pesticides:						
Clothianidin-D3	LCMS-Pesticides	330	88	100	41	135
Clothianidin-D3-Neg	LCMS-Pesticides	330	97	96.1	38	156
Difenoconazole-D4	LCMS-Pesticides	330	92	100	25	151
Organophosphate pesticides:						
Chlorpyrifos-D10	GCMS-Pesticides	351	101	100	68	134
Triphenyl phosphate	GCMS-Pesticides	351	129	98.9	66	163
Chlorine and nitrogen containing pesticides:						
Atrazine-D5	GCMS-Pesticides	351	117	98.6	58	151
Trifluralin-D14	GCMS-Pesticides	351	103	100	54	137

In 2021, the overall mean recovery for surrogates was 97% and > 99% of surrogate recoveries were within control limits.

Laboratory Control Samples

Table 41b 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 41b – 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	66	65	135	102	85 - 122	0	0	33	6	1 - 16
2,4-D	72	50	125	79	67 - 108	0	0	36	7	0.2 - 21
2,6-Dichlorobenzamide	74	54	147	125	95 - 156	0	5	37	4	0.2 - 10
3,5-Dichlorobenzoic acid	72	41	125	75	49 - 92	0	0	36	5	0.1 - 16
4,4'-DDD	74	69	151	119	94 - 151	0	0	37	4	0.04 - 15
4,4'-DDE	74	67	133	102	78 - 132	0	0	37	5	0.4 - 18
4,4'-DDT	74	72	152	114	87 - 142	0	0	37	4	0.2 - 16

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* (%)
4-Nitrophenol	72	31	188	89	50 - 117	0	0	36	8	0.2 - 41
Acephate	66	65	135	101	86 - 118	0	0	33	5	0.5 - 13
Acetamiprid	66	65	142	107	86 - 132	0	0	33	6	0.05 - 15
Acetochlor	74	64	152	122	96 - 149	0	0	37	3	0.04 - 12
Acetochlor ESA	66	34	166	102	75 - 138	0	0	33	7	0.3 - 23
Afidopyropen	66	50	151	98	73 - 133	0	0	33	7	0.2 - 18
Alachlor	74	65	154	118	96 - 151	0	0	37	3	0.08 - 15
Aminocyclopyrachlor	66	62	135	105	76 - 142	0	2	33	5	0.2 - 21
AMPA	38	22	193	110	69 - 138	0	0	19	7	2 - 18
Atrazine	74	64	148	110	81 - 142	0	0	37	4	0.2 - 12
Azoxystrobin	66	63	154	104	79 - 128	0	0	33	8	0.3 - 20
Benfluralin	74	59	137	106	81 - 126	0	0	37	4	0.6 - 10
Bensulide	66	52	135	88	57 - 129	0	0	33	12	0.2 - 36
Bifenazate	74	10	250	122	53 - 169	0	0	37	7	0.4 - 23
Bifenthrin	74	57	132	119	80 - 161	0	18	37	5	0.07 - 26
Boscalid	74	59	162	136	111 - 169	0	4	37	4	0.1 - 13
Bromacil	74	72	174	140	117 - 176	0	2	37	4	0.1 - 15
Bromoxynil	72	68	125	81	71 - 93	0	0	36	5	0.7 - 15
Captan	71	10	125	31	3 - 122	14	0	36	33	1 - 200
Carbaryl	66	65	139	106	88 - 123	0	0	33	8	0.7 - 20
Carbendazim	66	65	135	96	83 - 109	0	0	33	6	0.4 - 17
Chlorantraniliprole	66	55	153	100	70 - 129	0	0	33	12	0.2 - 43
Chlorethoxyfos	74	51	140	103	62 - 128	0	0	37	5	0.2 - 22
Chlorothalonil	74	63	145	112	86 - 145	0	0	37	4	0.2 - 16
Chlorpropham	74	64	159	127	100 - 164	0	2	37	4	0.01 - 15
Chlorpyrifos	74	61	141	104	81 - 135	0	0	37	4	0.2 - 14
Chlorpyrifos-methyl	74	55	149	105	82 - 133	0	0	37	4	0.2 - 16
Chlorsulfuron	66	33	142	89	37 - 128	0	0	33	8	0.3 - 23
cis-Permethrin	74	62	140	133	97 - 174	0	28	37	4	0.3 - 21
Clethodim sulfone	66	65	135	92	56 - 124	2	0	33	6	0.3 - 17
Clethodim sulfoxide	66	65	135	98	61 - 140	3	1	33	6	0.1 - 15

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* (%)
Clopyralid	72	13	125	51	20 - 72	0	0	36	13	0.7 - 45
Clothianidin	66	65	135	105	87 - 126	0	0	33	9	0.5 - 17
Coumaphos	74	67	173	146	111 - 181	0	5	37	4	0.004 - 13
Cyantraniliprole	66	55	153	105	76 - 182	0	2	33	7	0.9 - 18
Cycloate	74	59	150	118	84 - 161	0	3	37	5	0.1 - 16
Cyfluthrin-Total	74	60	147	135	108 - 169	0	18	37	4	0.2 - 20
Cypermethrin-Total	74	58	151	145	110 - 186	0	30	37	5	0.2 - 25
Cyprodinil	66	65	135	100	83 - 123	0	0	33	6	0.01 - 14
Dacthal (DCPA)	72	71	132	88	73 - 103	0	0	36	4	0.3 - 13
Deltamethrin	74	60	144	129	97 - 163	0	12	37	5	0.1 - 31
Diazinon	74	60	151	112	80 - 135	0	0	37	4	0.1 - 12
Dicamba acid	72	48	125	76	59 - 92	0	0	36	5	0.3 - 12
Dichlobenil	74	61	139	105	70 - 135	0	0	37	5	0.2 - 30
Dichlorprop	72	57	125	79	69 - 95	0	0	36	5	0.02 - 14
Dichlorvos (DDVP)	74	57	156	117	88 - 160	0	1	37	5	0.006 - 29
Dicofol	74	13	250	584	172 - 1110	0	64	37	6	0.2 - 26
Difenoconazole	66	59	135	91	63 - 123	0	0	33	9	0.06 - 22
Diflubenzuron	66	62	140	98	73 - 132	0	0	33	12	0.4 - 38
Dimethenamid ESA	66	65	135	98	64 - 148	1	4	33	7	0.3 - 27
Dimethenamid OA	66	65	135	99	68 - 125	0	0	33	7	0.1 - 28
Dimethoate	74	54	159	122	96 - 146	0	0	37	3	0.2 - 9
Dinotefuran	66	65	142	102	79 - 122	0	0	33	6	0.4 - 14
Dithiopyr	74	56	140	113	87 - 147	0	2	37	4	0.1 - 14
Diuron	66	65	137	104	83 - 124	0	0	33	6	0.01 - 17
Eptam	74	51	145	108	80 - 149	0	1	37	5	0.2 - 29
ES Fenvalerate	74	56	131	124	94 - 160	0	27	37	4	0.1 - 26
Ethalfluralin	74	58	142	110	81 - 132	0	0	37	4	0.2 - 11
Ethoprop	74	60	159	130	102 - 159	0	0	37	3	0.01 - 11
Etoxazole	74	58	143	133	101 - 160	0	18	37	4	0.6 - 14
Etridiazole	74	66	151	103	74 - 146	0	0	37	5	0 - 30
Fenarimol	74	54	184	147	113 - 187	0	2	37	4	0.01 - 8

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* (%)
Fenbuconazole	66	52	160	94	65 - 124	0	0	33	9	0.1 - 27
Fenbutatin oxide	66	27	143	100	56 - 156	0	2	33	9	0.2 - 23
Fenpropathrin	74	61	135	129	92 - 175	0	26	37	6	0.2 - 24
Fipronil	74	62	158	128	105 - 162	0	1	37	4	0.1 - 13
Fipronil disulfinyl	74	59	150	119	95 - 150	0	0	37	4	0.2 - 14
Fipronil sulfide	74	58	149	117	98 - 139	0	0	37	4	0.2 - 10
Fipronil sulfone	74	60	160	125	102 - 153	0	0	37	4	0.3 - 13
Fludioxonil	74	66	172	138	111 - 170	0	0	37	4	0.07 - 15
Flumioxazin	72	10	125	59	10 - 136	0	3	36	16	0.1 - 97
Fluopicolide	66	57	156	101	65 - 124	0	0	33	9	0.1 - 24
Flupyradifurone	66	65	135	101	77 - 127	0	0	33	6	0.8 - 18
Fluroxypyr 1-methylheptyl ester	74	61	151	122	97 - 157	0	4	37	4	0.2 - 17
gamma-Cyhalothrin	74	55	133	126	88 - 163	0	27	37	5	0.09 - 28
Glufosinate-ammonium	38	62	153	106	60 - 137	1	0	19	6	0.2 - 25
Glyphosate	38	50	143	100	70 - 119	0	0	19	5	0.01 - 33
Hexazinone	74	65	163	142	106 - 188	0	19	37	4	0.04 - 11
Hexythiazox	66	53	139	94	73 - 139	0	0	33	10	0.2 - 47
Imazapic	66	65	135	101	84 - 133	0	0	33	8	0.05 - 24
Imazapyr	66	65	135	100	75 - 121	0	0	33	6	0.2 - 16
Imidacloprid	66	65	135	102	77 - 122	0	0	33	8	0.5 - 22
Indaziflam	66	65	135	103	76 - 131	0	0	33	7	0.06 - 22
Inpyrfluxam	66	65	135	101	72 - 136	0	1	33	13	2 - 51
Isoxaben	66	59	158	104	76 - 125	0	0	33	9	0.3 - 26
Linuron	66	65	138	101	83 - 137	0	0	33	10	0.9 - 27
Malaoxon	66	65	135	106	86 - 133	0	0	33	7	0.2 - 15
Malathion	74	60	155	124	91 - 156	0	1	37	4	0.05 - 16
MCPA	72	53	125	79	67 - 102	0	0	36	5	0.3 - 12
Mecoprop (MCPP)	72	59	125	82	64 - 102	0	0	36	8	0.05 - 33
Metalaxyl	74	68	155	117	93 - 150	0	0	37	3	0.06 - 10
Methamidophos	66	65	135	99	83 - 113	0	0	33	6	0.4 - 15

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* (%)
Methidathion	66	55	153	98	65 - 134	0	0	33	10	0.3 - 31
Methiocarb	66	65	142	108	75 - 137	0	0	33	9	0.3 - 26
Methomyl	66	65	137	105	93 - 118	0	0	33	5	0.8 - 14
Methomyl oxime	66	58	135	97	75 - 115	0	0	33	7	0.4 - 18
Methoxyfenozide	66	59	162	102	67 - 125	0	0	33	11	0.7 - 31
Metolachlor	74	65	153	114	90 - 146	0	0	37	4	0.03 - 11
Metribuzin	74	60	139	92	62 - 127	0	0	37	4	0.005 - 14
Metsulfuron-methyl	66	29	150	89	31 - 127	0	0	33	7	0.07 - 19
MGK264	74	59	145	111	77 - 149	0	4	37	4	0.02 - 15
Myclobutanil	66	63	153	98	74 - 121	0	0	33	10	0.2 - 28
N,N-Diethyl-m-toluamide	74	63	155	120	91 - 154	0	0	37	3	0.03 - 10
Naled	74	39	161	106	51 - 139	0	0	37	5	0.1 - 19
Napropamide	74	56	162	127	105 - 161	0	0	37	3	0.09 - 14
Norflurazon	74	67	158	130	109 - 167	0	4	37	3	0.002 - 10
Oryzalin	66	35	176	109	69 - 218	0	2	33	11	0.2 - 29
Oxadiazon	74	60	147	106	85 - 129	0	0	37	3	0.1 - 10
Oxamyl	66	65	136	105	92 - 119	0	0	33	6	0.4 - 13
Oxamyl oxime	66	51	135	96	62 - 123	0	0	33	7	0.3 - 16
Oxyfluorfen	74	75	167	123	99 - 152	0	0	37	4	0.09 - 15
Paclobutrazol	66	65	140	100	79 - 121	0	0	33	8	0.6 - 22
Pendimethalin	74	69	149	119	96 - 143	0	0	37	4	0.4 - 14
Pentachloronitrobenzene	74	63	139	101	69 - 122	0	0	37	5	0.4 - 21
Pentachlorophenol	72	52	125	75	53 - 90	0	0	36	6	0.2 - 24
Phenothrin	74	24	125	63	38 - 129	0	1	37	11	0.6 - 38
Phorate	66	33	136	93	59 - 143	0	2	33	10	2 - 32
Phosmet	74	10	132	83	4 - 133	2	1	37	10	0.2 - 60
Picloram	72	10	125	28	9 - 72	1	0	36	35	1 - 122
Piperonyl butoxide (PBO)	74	55	164	126	103 - 157	0	0	37	3	0.2 - 11
Prallethrin	74	49	154	116	94 - 148	0	0	37	4	0.2 - 17
Prodiamine	74	61	150	120	98 - 143	0	0	37	6	0.1 - 19
Prometon	74	62	152	118	89 - 149	0	0	37	3	0.07 - 9

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* (%)
Prometryn	74	64	152	119	94 - 157	0	1	37	4	0.3 - 15
Propargite	74	38	145	114	89 - 152	0	2	37	4	0.05 - 18
Propiconazole	66	48	156	94	68 - 118	0	0	33	10	0.9 - 31
Propoxur	66	65	135	107	89 - 126	0	0	33	6	0.2 - 17
Propyzamide (Pronamide)	74	64	156	122	91 - 156	0	0	37	4	0.01 - 12
Pyraclostrobin	66	39	166	100	73 - 130	0	0	33	9	1 - 22
Pyraflufen-ethyl	74	59	158	124	86 - 168	0	5	37	4	0.02 - 16
Pyrethrins	66	10	187	149	41 - 466	0	12	33	12	1 - 30
Pyridaben	74	61	145	141	112 - 180	0	29	37	4	0.3 - 18
Pyrimethanil	66	65	139	103	82 - 138	0	0	33	6	0.007 - 19
Pyriproxyfen	74	62	147	125	91 - 161	0	10	37	3	0.6 - 9
Pyroxasulfone	66	44	164	98	79 - 128	0	0	33	12	1 - 46
Simazine	74	64	150	110	83 - 148	0	0	37	4	0.1 - 13
Simetryn	74	61	145	107	80 - 144	0	0	37	3	0.001 - 13
Sodium bentazon	72	72	138	87	69 - 101	1	0	36	5	0.05 - 25
Spirotetramat	68	41	161	94	57 - 154	0	0	34	15	0.04 - 38
Sulfentrazone	74	10	137	60	13 - 135	0	0	37	25	2 - 72
Sulfometuron-methyl	66	58	141	99	58 - 135	0	0	33	7	0.6 - 18
Sulfoxaflor	66	65	135	102	81 - 125	0	0	33	7	0.07 - 18
tau-Fluvalinate	74	59	143	132	99 - 171	0	22	37	6	0.1 - 32
Tebuthiuron	74	38	185	130	88 - 173	0	0	37	4	0.05 - 14
Tefluthrin	74	56	125	97	71 - 122	0	0	37	5	0.2 - 15
Terbacil	74	71	175	140	114 - 168	0	0	37	4	0.05 - 10
Tetrachlorvinphos	74	69	173	131	106 - 165	0	0	37	4	0.4 - 17
Tetrahydrophthalimide (THPI)	74	43	125	109	80 - 148	0	10	37	4	0.5 - 16
Tetramethrin	74	20	128	105	13 - 157	2	14	37	7	0.08 - 32
Thiacloprid	66	65	137	108	86 - 135	0	0	33	6	0.1 - 15
Thiamethoxam	66	52	162	104	75 - 123	0	0	33	8	0.09 - 22
Thiram	66	10	205	108	55 - 183	0	0	33	7	0.05 - 34
Tolfenpyrad	66	65	135	93	59 - 117	1	0	33	11	1 - 32
Tralomethrin	74	61	143	129	96 - 163	0	14	37	6	0.2 - 31

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* (%)
trans-Permethrin	74	62	140	131	96 - 174	0	23	37	5	0.1 - 25
Triadimefon	74	65	158	117	91 - 156	0	0	37	4	0.06 - 13
Triallate	74	50	144	103	74 - 125	0	0	37	4	0.4 - 14
Triazine DEA degradate	66	65	137	106	76 - 137	0	0	33	6	0.2 - 13
Triazine DIA degradate	66	62	140	105	81 - 135	0	0	33	6	0.05 - 14
Triazine HA degradate	66	65	135	108	87 - 143	0	2	33	6	0.3 - 14
Triclopyr acid	72	67	133	92	79 - 112	0	0	36	5	0.1 - 13
Triclopyr butoxyethyl ester	74	57	155	110	78 - 134	0	0	37	4	0.04 - 13
Triclosan	74	44	178	125	87 - 166	0	0	37	6	0.05 - 23
Trifloxystrobin	66	62	135	97	75 - 125	0	0	33	10	0.9 - 26
Trifluralin	74	57	139	102	73 - 125	0	0	37	4	0.2 - 13
Zoxamide	66	65	139	99	77 - 127	0	0	33	9	0.3 - 26

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

There was a total of 12,127 spiked results from LCS and LCSD recoveries that were unqualified or *J* qualified and five spiked results that were *U* qualified. Overall, the mean recovery was 110% with a standard deviation of 48%. The percentage of analyte recoveries from LCS/LCSD samples that were above, below, or fell within the laboratory control limits are as follows:

- < 1% of analyte recoveries (28 recoveries) fell below the control limits for LCS/LCSD samples,
- 96% of analyte recoveries (11,606 recoveries) were within the control limits for LCS/LCSD samples,
- 4% of analyte recoveries (493 recoveries) were above the control limits for LCS/LCSD samples.

RPDs calculated for 6,064 LCS/LCSD pairs were below the 40% RPD control limit 99% of the time; only 41 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 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 64% with a standard deviation of 32%.

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

Unlike the pesticide analytes assessed with LCS/LCSD, the analytes and parameters in Table 42b 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 42b – 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	41	80	120	102	96 - 106
Nitrate-Nitrite	40	80	120	99.1	96 - 102
ortho-Phosphate	63	80	120	98.8	94 - 107
Specific conductivity	9	95	105	100	100 - 102
Suspended sediment concentration	33	90	110	99.1	98 - 101
Total phosphorus	26	80	120	97	92 - 105
Total suspended solids	11	80	120	96	92 - 100

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 2021). 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 6% 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 on 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 and a few times at random for the Palouse monitoring sites.

Field Data Collection Performance

Quality control results for two different conventional water quality parameter replicates are shown below in Table 43b. Precision of the specific conductivity and streamflow replicates was gauged by relative percent difference (RPD). Data that did not meet measurement quality objectives (MQOs) were qualified. Streamflow replicates were measured at least once at every site that staff took flow at except Dry Creek. Specific conductivity replicates were collected at every site once on average.

Table 43b – Quality control results for conventional water qualiter parameter replicates

Replicate parameter	MQO	Western Washington		Central Washington		Palouse	
		Mean	Maximum	Mean	Maximum	Mean	Maximum
Specific conductivity (field meter vs. laboratory)	10% RPD	2% RPD	3% RPD	2% RPD	3% RPD	2% RPD	2% RPD
Streamflow	10% RPD	5% RPD	21% RPD	4% RPD	17% RPD	6% RPD	10% RPD

Of the total 19 conductivity replicates taken, one specific conductivity replicate that was at Indian Slough was considered an outlier and excluded from this analysis (43% RPD). Indian Slough's specific conductivity can vary thousands of µS/cm within a 2 ft. water depth since it is at a tide gate.

Out of the 57 streamflow replicate comparisons, eight did not meet MQOs. Results for streamflow measurements and their replicates were not qualified as a result of the replicate analysis because RPD has limited effectiveness in assessing variability at low levels (Mathieu, 2006). Some variability could have been due to active rain event during flow measurement. All replicates that did not meet the MQO were under 5 cfs.

Field Meter Performance

Table 44b describes measurement quality objectives for field meter post-checks as described in the 2023 WSDA QAPP (Nickleson et al. 2023). The 2023 MQOs were used because they were updated from the 2021 WSDA QAPP.

Table 44b – Measurement quality objectives for YSI ProDSS post-checks

Parameter	Units	Accept	Qualify	Reject	Resolution
Water temperature	°C	± 0.2	N/A	> ± 0.2	0.1
pH	standard units	± 0.15	> ± 0.15 and ≤ ± 0.20	> ± 0.20	0.01
Conductivity*	µS/cm	≤ 5% RPD	> ± 5% and ≤ ± 15% RPD	> ± 15% RPD	0.1
DO	mg/L	≤ ± 0.05	> ± 0.05 and ≤ ± 0.10	> ± 0.10	0.01

*Criteria expressed as a percentage of readings; for example, buffer or post-calibration value = 1,000 µS/cm and post-check YSI = 987.2 µS/cm; {|1,000 - 987.2| / [(1,000 + 987.2)/2]} * 100 = 1.29% 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:

- Palouse YSI meter pH post-check failed MQOs the week of May 10.
  - The 10.0 pH calibration millivolts were outside of the acceptable range. There were no field pH values that were greater than pH 10, so none were requalified.
- Palouse YSI meter DO post-check failed MQOs the week of June 28.
  - The three field DO readings were requalified and not used in the technical report analysis.
- Palouse YSI meter pH post-check failed MQOs the week of July 12.
  - The 4.0 pH calibration milivolts were outside of the acceptable range. There were no field pH values that were less than pH 4, so none were requalified.

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, 2021, the Central and Westside NRAS surface water monitoring teams and the Palouse Conservation District monitoring team conducted a field audit to compare 2021 sampling procedures. Each team calibrated their YSI ProDSS meter on 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. 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 45b. Westside teams had two ProDSS meters but only one OTT MF Pro flow meter. The Westside 1 ProDSS was used for the field season by the Westside staff and the Westside 2 was a backup.

Table 45b - Conventional water quality parameters and flow data from field audit

Westside 1	6.2	7.89	172.5	12.33	103.1	48.46
Westside 2	6.1	7.86	173.7	12.47	103.9	
Central	6.2	7.87	174.0	12.33	103.2	46.78
Palouse	6.3	8.03	171.3	12.71	106.2	45.88
All 3	±0.2° C	1% RSD	1% RSD	±0.4 mg/L	1% RSD	3% 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). 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. Only the Palouse team was unable to post-check their YSI field meter. The Westside and Central team's YSI meters post-check passed MQOs found in Table 44b.

Quality Assurance Summary References

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