



Washington
State Department of
Agriculture

Ambient Monitoring for Pesticides in Washington State Surface Water

2023 Technical Report

February 2025

Washington State Department of Agriculture
Natural Resources and Agricultural Sciences

Derek I. Sandison, Director

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Publication AGR2-2502-009 (N/2/25))

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Acknowledgments

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

- The Washington State Department of Ecology Manchester Environmental Laboratory staff for their care and attention to detail in every step of the process: method development, sample transport, logging, extraction, analysis, quality assurance and quality control, and data reporting. Without their work, this project would not be possible.
- WSDA Natural Resources and Agricultural Sciences staff for their sampling assistance.
- Yakama Nation: Joe Herrea, Daniele Squeochs
- WSDA Pesticide Compliance: Timothy Stein, Scot Nielson, Chris Sutherland, and David Bryson
- Roza-Sunnyside Board of Joint Control: Forrest Chapin
- Chelan County Natural Resource Department: Mike Kaputa
- The many private landowners who allow us to access our monitoring sites through their property.

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Executive Summary

Washington State Department of Agriculture (WSDA) has been gathering monitoring data since 2003 in an ongoing effort to assess the frequency and concentration of pesticides 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 2023, WSDA's Natural Resources and Agricultural Sciences team (NRAS) collected surface water samples weekly or biweekly from March 20 to November 28 at 17 monitoring sites. Staff selected sites of potential pesticide contamination and poor water quality conditions based on land with high pesticide usage or historic pesticide detections. Sites were located in Benton, Chelan, Clark, King, Skagit, Whatcom, Whitman, and Yakima counties with watershed areas ranging from 2,000 acres to over 100,000 acres. Land use within each watershed varied between commercial, residential, urban, and agricultural uses that included tree-fruit, berries, wheat, corn, grass hay, and potato production. The samples were analyzed by Manchester Environmental Laboratory (MEL) in Port Orchard, Washington.

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 2023 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 state and national water quality standards such as the EPA Aquatic Life Benchmarks (ALB) (EPA 2024a). 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 bifenthrin, chlorpyrifos, diuron, gamma-cyhalothrin, and imidacloprid for 2023.

This report summarizes activities and data from the 17 separate sites selected for the 2023 ambient surface water monitoring season. Below is a brief overview of the findings.

There were 325 surface water sampling events between March 20 and November 28.

Out of 153 analytes (pesticide active ingredients and degradates) tested for, there were 111 unique pesticides detected.

There were 4,386 positively identified pesticide detections.

Out of 325 sampling events, mixtures of two or more pesticides were detected at 317 of them.

Sulfentrazone was the most frequently detected herbicide (210 times), boscalid was the most frequently detected fungicide (224 times), and thiamethoxam was the most frequently detected insecticide (84 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 (239 times). Detections of this analyte occurred at over 74% of sampling events.

There were 262 unique pesticide detections with concentrations exceeding WSDA assessment criteria (6% of total detections), approaching levels that could adversely affect aquatic life.

- Legacy pesticides and their breakdown products accounted for 163 of the exceedances (62% of total exceedances). The chemicals include:
 - 4,4'-DDD (80 exceedances),
 - 4,4'-DDE (52 exceedances),
 - 4,4'-DDT (31 exceedances).

- Current-use pesticides accounted for 99 of the exceedances (38% of total exceedances). The chemicals include:
 - bifenthrin (7 exceedances),
 - carbendazim (1 exceedance),
 - chlorpyrifos (1 exceedances),
 - cis-permethrin (1 exceedances),
 - clothianidin (19 exceedances),
 - diazinon (2 exceedances),
 - diuron (11 exceedances),
 - fenpropathrin (1 exceedance)
 - fipronil (7 exceedances),
 - flumioxacin (1 exceedance),
 - gamma-cyhalothrin (5 exceedances),
 - imidacloprid (31 exceedances),
 - malathion (8 exceedances),
 - pyridaben (1 exceedance),
 - pyriproxyfen (1 exceedances),
 - tolfenpyrad (1 exceedances),
- One degradate of a pesticide accounted for one of the exceedances (<1% of total exceedances).
 - malaoxon (1 detections).

Of the 262 detections that exceeded WSDA assessment criteria, many (75% or 197 detections) also exceeded state, national, or toxicity study criteria that WSDA assessment criteria was derived from. Current-use pesticides accounted for 32% (63 detections) of those exceedances of assessment criteria without the WSDA safety factor (See Table 2). All seven detections of bifenthrin exceeded the acute and chronic invertebrate EPA Aquatic Life Benchmarks; four of those exceeded the chronic fish benchmarks. Gamma-Cyhalothrin, found at four of the monitoring sites, exceeded the acute invertebrate EPA ALB five times out of a total of five detections with two of those detections also exceeding the chronic invertebrate EPA ALB. Another insecticide detected frequently, imidacloprid, exceeded the chronic invertebrate EPA ALB 30 times out of 31 detections and was found at 7 of the 17 monitoring sites. The exceedances of these pesticides can be attributed to three characteristics; low laboratory method detection levels, low toxicity criteria, and common usage across the state. Other pesticide detected less often that still exceeded state, national, or toxicity study criteria included chlorpyrifos, clothianidin, diazinon, diuron, fenpropathrin, fipronil, malathion, malaoxon, permethrin, and pyriproxyfen. Legacy insecticide DDT and its associated degradates accounted for the remaining 68% (134 detections) of the total detected exceedances of state or national standards.

NRAS also collected samples for suspended sediment concentration analysis and measured the water quality parameters of dissolved oxygen, pH, conductivity, water temperature, and streamflow in the field during 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 2024a). At least one conventional water quality parameter did not meet state water quality standards on one or more occasions at 16 of the 17 monitoring sites.

Nutrient samples were collected at eight monitoring sites. There was at least one exceedance of an Environmental Protection Agency (EPA) Ambient Water Quality Criteria Recommendation (EPA 2000a, EPA 2000b) for nutrients at each sampling event at these eight 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 2020). 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. The program also provides 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

The Washington State Department of Agriculture has authority as a state lead agency to regulate the distribution 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 (Chapter 15.58 RCW, 1971) and Washington Pesticide Application Act (Chapter 17.21 RCW, 1971).

Since 2003, WSDA has received funding from the Washington State Legislature and the U.S. Environmental Protection Agency (EPA) to administer a comprehensive program to assess the frequency and biological significance of pesticides detected in Washington state surface waters. To make that evaluation, WSDA's Natural Resources 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 2023.
- 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 outreach and education with an emphasis on pesticides of concern.

NRAS conducted ambient surface water monitoring for pesticides in 2023 in March through November throughout the state. During the first year of monitoring (2003), NRAS sampled nine monitoring sites in agricultural and urban areas. By 2023, the program has expanded to 17 monitoring sites, including two of the nine original sites. WSDA has monitored surface water in 25 unique watersheds since the start of the program.

NRAS sent water samples to the Manchester Environmental Lab (MEL) for analysis of pesticide and pesticide-related chemicals such as insecticides, herbicides, fungicides, an antimicrobial, a wood preservative, an insect repellent, degradates and synergists. In 2023, NRAS tested for 153 analytes, with 111 confirmed chemicals detected in surface water samples. Between the 2022 and 2023 monitoring seasons, no analytes were taken off or added the testing list. The list of chemicals to be analyzed may change from year to year because of new use restrictions, changes in pesticide registration, analytical cost, or lack of detections in surface water.

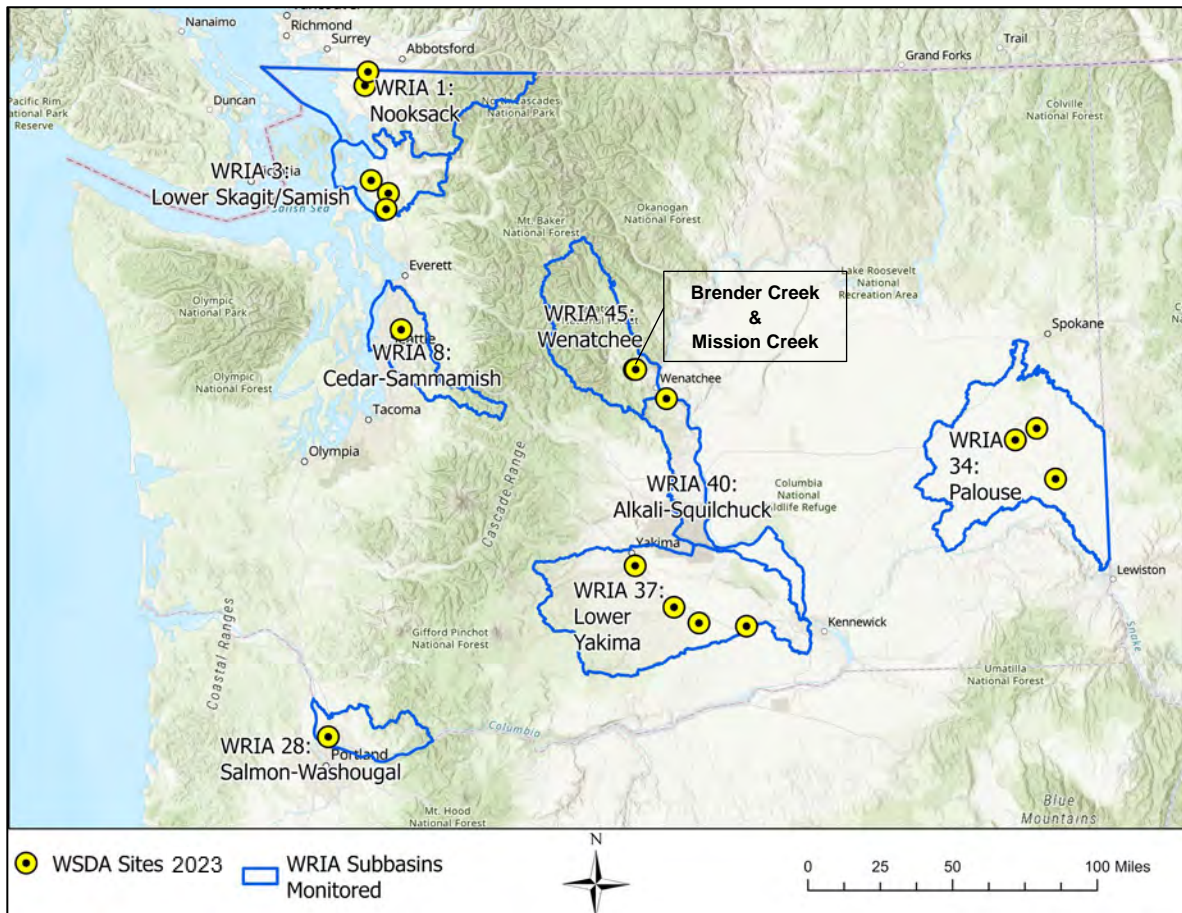
We compare the surface water data to internal assessment criteria that are derived by applying a safety factor to state and national water quality standards and toxicity study criteria to be protective of aquatic life. Persistent contamination of surface waters with pesticides or pesticide-related chemicals can prompt the implementation of adaptive management techniques. 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 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 2024d). Figure 1 shows the boundaries of the 8 subbasins that NRAS sampled in 2023, identified by their WRIA codes and corresponding subbasin names.

Figure 1 – Subbasins monitored in Washington state in 2023



All eight 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 six 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 November. Staff collected surface water samples at 17 monitoring sites across the state, which MEL analyzed for suspended sediment concentration (SSC) and 153 pesticide active ingredients and pesticide-related products. Additionally, MEL analyzed nutrients for eight monitoring sites. The nutrients sampled were total phosphorus, orthophosphate, ammonia as N, and nitrate-nitrite as N. Due to equipment malfunctions at MEL, some ammonia as N and nitrate-nitrite as N samples were analyzed by OnSite Environmental Inc. in Redmond, Washington at the beginning of the sampling season. The sampling schedule and analytes tested were 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 (Nickleson et al. 2024).

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 2024). Before delivery to MEL, staff labeled and preserved all samples according to the Quality Assurance Project Plan (Nickelson et al. 2024).

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 2023) 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 2022). Mission Creek and Lower Bertrand Creek 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). Flow meters are calibrated at the beginning of every sampling week as described in the OTT MF Pro Basic User Manual (OTT 2018). We obtained streamflow data for the remaining five sites from gauging stations managed by other agencies. The gauging stations provided 15-minute streamflow measurements throughout the sampling season. NRAS used the recorded streamflow closest to the actual sampling start time. Details of those gauging stations are listed below.

- 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)

The 2023 field data quality results are summarized in Appendix B of this report.

Laboratory Analyses

MEL analyzed the surface water grab samples for pesticides, SSC, nutrients, and specific conductivity. Additionally, OnSite Environmental Lab analyzed ammonia as N and nitrate-nitrite as N samples on behalf of MEL when their equipment malfunctioned. Table 1 provides a summary of the extraction and analytical methods used by the labs.

Table 1 – Summary of laboratory methods

Analytical method	Extraction method reference*	Analytical method reference*	Instrument
GCMS-Pesticides	SW3535A	SW8270E	GC/MS/MS
GCMS-Herbicides (Derivatizable acid herbicides)	SW3535A	SW8270E	GC/MS
LCMS-Glyphos	SW3535A	SW8321BM	LC/MS/MS
LCMS-Pesticides	n/a	SW8321BM	LC/MS/MS
SSC	n/a	ASTM D3977B	Gravimetric
Specific Conductivity	n/a	APHA SM2510B	Electrode
Nitrate+Nitrite-N	n/a	APHA SM4500N03I	Lachat
Nitrate+Nitrite-N ¹	n/a	US EPA 353.2	Lachat
Ammonia-N (NH ₃)	n/a	APHA SM4500NH3H	Lachat
Ammonia-N (NH ₃) ¹	n/a	APHA SM4500NH3D	Lachat
Phosphate, Ortho- (OP)	n/a	APHA SM4500PG	Lachat
Phosphorus, Total	n/a	APHA SM4500PH	Lachat

*Analytical methods refer to EPA SW 846, unless otherwise noted.

¹Analytical method used by OnSite Environmental Lab

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 utilizes the analysis of quality control (QC) samples in comparison to measurement quality objectives to determine data quality. 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 2023, 10% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2023 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 Measurement Quality Control

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 seven 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 the corresponding YSI ProDSS meter measurement. In 2023, all but three streamflow measurement and their paired replicate measurements were below the measurement quality objective of 10% RPD. In addition, all but one specific conductivity measurements and their paired replicate samples were below the measurement quality objective of 10% RPD.

Accuracy of the YSI meter was assessed based on the difference between the meter value and the criterion. Two out of 86 instances of the temperature calibration resulted in a failure (greater than a 0.2°C difference), and one out of 87 instances of the temperature post check resulted in a failure (greater than a 0.2°C difference). Four out of 97 instances of the dissolved oxygen (DO) post check resulted in a failure (greater than a 0.10 mg/L difference). One DO post check differed by greater than 0.20 mg/L, and all temperature post checks and calibrations were within a 0.3°C difference.

Field Replicates

Field replicate samples were collected 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 replicates were counted as consistent non-detect pairs and are described in Table 35b in Appendix B of this report. The highest concentration of the positively detected sample or field replicate was selected for comparison to WSDA assessment criteria, regardless of 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 nine of the 239 consistently identified replicate pairs detected for pesticide, nutrient, and SSC analysis exceeded an RPD criterion (40% RPD for pesticides; 20% RPD for nutrients and SSC). The results were not qualified for the nine 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. Even so, all pesticide, nutrient, and SSC 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.

Blanks

Field and method blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were 22 detections in field blanks and 179 detections in method blanks. Detections in field blanks included analytes such as 2,6-dichlorobenzamide, acetochlor, ammonia, chlorpropham, DEET, dichlobenil, glyphosate, imazapic, inpyrfluxam, and ortho phosphate. Detections in method blanks included analytes such as 2,6-dichlorobenzamide, DDT, dichlobenil, ethoprop, fenarimol, fenbutatin oxide, fenvalerate, fipronil fulfide, gamma-cyhalothrin, hexazinone, metolachlor, DEET, permethrin, phosmet, prometryn, pyridaben, pyriproxyfen (Nylar), simetryn, tefluthrin, thiram, triadimefon, triclosan, trifloxystrobin. The origin of these detections was unknown. There were 50 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 (>98%) of surrogate recoveries fell within the control limits established by MEL in 2023. 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. Duplicate spikes are used 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 93.02% 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.

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 96.87% 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 2023b), and Washington State Water Quality Standards for Surface Waters (WAC 2024a). A 0.5x safety factor is applied to all 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 determine effects using monitoring 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. Quantifying mixture effects with the variety and magnitude of concentrations found in this monitoring effort is beyond the scope of this program. In addition, toxicity values such as those used for pesticide registration are determined using exposure over times from between hours to weeks. NRAS collects weekly or biweekly discrete grab samples that cannot be used to determine the exposure duration. It is recognized that the measured instantaneous concentrations may or may not be maintaining for a duration consistent with the exposure time used to derive assessment criteria. 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 2023a).

Researchers calculate acute toxicity by exposing a sensitive (representative) species at a susceptible life stage to a range of pesticide concentrations to determine potential negative effects. The LC₅₀ (concentration causing death to 50% of the organisms, in the case of fish) or EC₅₀ (concentration causing immobility or growth reduction to 50% of the organisms, in the case of invertebrates or plants) is calculated. The test duration is 96 hours for fish and aquatic plants and 48 hours for invertebrates.

Chronic toxicity tests normally use either reproductive effects or effects to offspring as the measured effect. Researchers use chronic toxicity study values to derive a pesticide's No Observable Adverse Effects

Concentration (NOAEC). The concentration signifies the highest concentration in the toxicity test not showing a statistically significant difference from the control. The chronic toxicity test is longer than the 96-hour acute test (28 days for fish, 21 days for invertebrates) to simulate the type of exposure that would result from a persistent chemical or the effect of repeated applications.

NRAS uses an increased safety factor to signal the potential impacts to endangered species. Researchers commonly use rainbow trout as a surrogate fish species to assess the potential risk of a pesticide to salmonids. As a result, the WSDA assessment criteria for endangered species (in this case, typically salmonids) is 1/20th of the most sensitive LC₅₀ for fish.

National Recommended Water Quality Criteria

EPA's National Recommended Water Quality Criteria (NRWQC) includes a list of approximately 150 pollutants with criteria to protect aquatic life and human health (EPA 2024b). Acute and chronic toxicity data from pesticide registration toxicity studies provide the pesticide criteria in the NRWQC. NRAS used the 2023 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 2024a). 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. The term ‘exceedance’ throughout this report is used to describe pesticide concentrations above WSDA assessment criteria and not concentrations above the unaltered water quality standards.

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 (POCs) 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 2023, 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 2023, five watershed POCs were found in seven or more of the 17 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 a 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 2024b), 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 2023 was freshwater 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 (°C), highest allowable	DO (mg/L), lowest 1-day minimum	pH
Char Spawning and Rearing	12.0	10	6.5 – 8.5
Core Summer Salmonid Habitat	16.0	10	6.5 – 8.5
Salmonid Spawning, Rearing, & Migration	17.5	10	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). Three NRAS monitoring sites in 2023 had an additional temperature standard within the reaches of creek that encompassed the sites. The Upper Bertrand and Ahtanum Creek sites had a 7-DADMax temperature standard of less than 13°C between February 15 and June 15. 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. WSDA utilizes these numeric standards for conventional parameters to qualitatively account for any compounding impacts to aquatic life when co-occurring pesticide detections.

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 ($\text{NO}_2 + \text{NO}_3$) 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	Ahtanum Creek, Dry Creek, Kamiache Creek, Marion Drain, Snipes Creek, Sulphur Creek	NO ₂ + NO ₃	0.072
		Wasteway, Thorn Creek	TP	0.030

The ammonia detections were compared to the Water Quality Standards for Surface Waters of The State of Washington (WAC 2024c). 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 2023 except for Dry Creek, Kamiache Creek, and Thorn Creek were considered salmonid present waterway as per the State Water Quality Standards.

For salmonids present:

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

For salmonids absent:

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

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

Monitoring Site Results

In 2023, NRAS monitored 17 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 but not limited to the local and regional meteorology, pest pressure, and sampling schedule.

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 2023 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 present below reportable sample quantitation limits. Concentrations are presented in $\mu\text{g/L}$, rounded to the thousandth place.

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

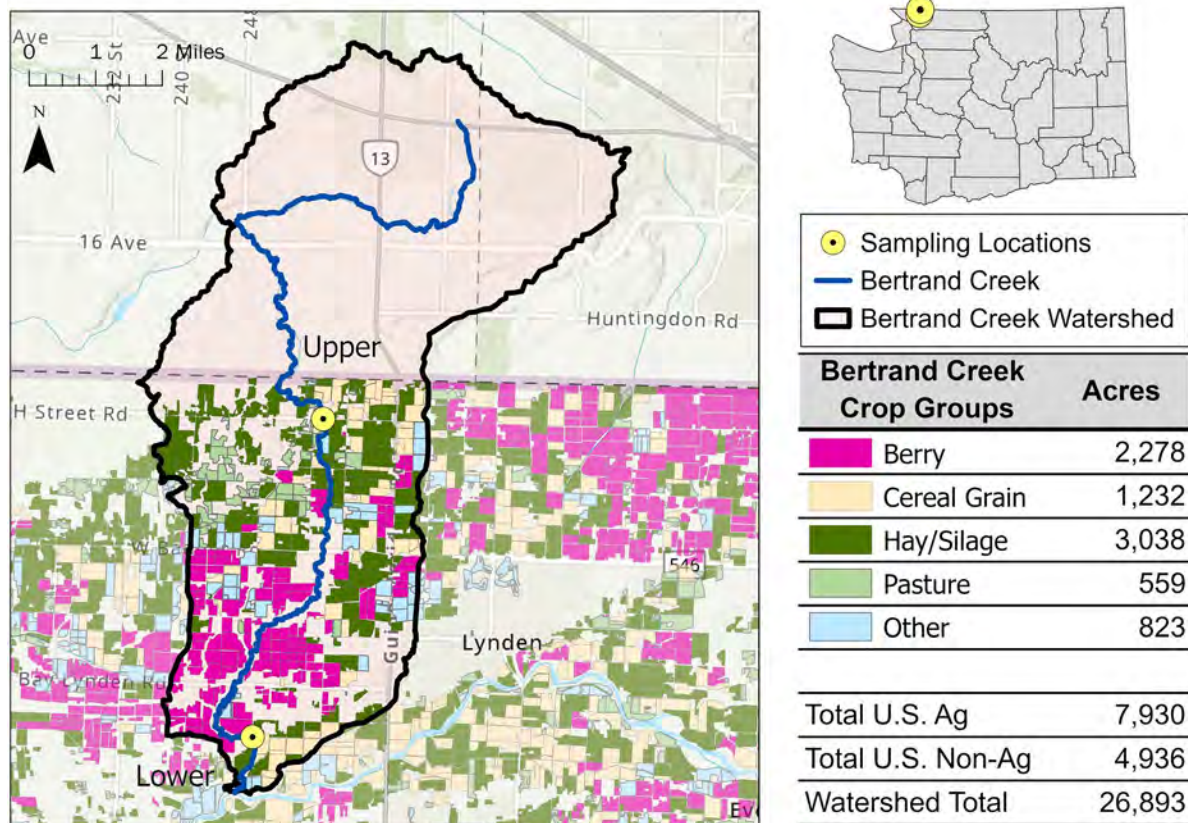


Figure 2 – Map of Bertrand Creek and its drainage area with associated sampling locations and crop groups identified

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



Figure 3 – Upper Bertrand Creek site upstream view

Bertrand Creek water drains into the Nooksack River subbasin, known for its endangered salmon runs. Precipitation events and irrigation influence streamflow in Bertrand Creek. Washington Department of Fish and Wildlife (WDFW) has documented the presence of coho, fall Chinook, fall chum, pink, and sockeye salmon, as well as bull trout, cutthroat trout, and winter steelhead within the reaches of creek that encompass both Bertrand sites (WDFW 2024). Staff have frequently observed juvenile fish of unknown



Figure 4 – Lower Bertrand Creek site upstream view

species and freshwater lamprey at the Upper Bertrand Creek monitoring site. In addition, the presence of invasive New Zealand mud snails has been confirmed in Upper Bertrand mid-sampling season.

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, pastures, and potatoes. The ‘Other’ crop group category consists mostly of fallow fields and 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 Upper Bertrand Creek in 2023.

- There were 341 total pesticide detections in Upper Bertrand Creek from five different use categories: 20 types of herbicides, 9 insecticides, 6 fungicides, 5 degradates, and 1 insect repellent.
- Of the total pesticide detections in Upper Bertrand Creek, 11 were above WSDA’s assessment criteria (Table 6).
- The Upper Bertrand Creek watershed POCs were bifenthrin, chlorpyrifos, diuron, and imidacloprid. Below, each POC detected is compared to toxicity test reference values.
- The two detections of bifenthrin exceeded the invertebrate LC₅₀ (0.000493 µg/L) and invertebrate NOAEC (0.00005 µg/L).
 - The detection on April 11 also approached the fish NOAEC (0.004 µg/L).
 - The detection on April 17 also exceeded the fish NOAEC (0.004 µg/L).
- All nine detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- The two detections of chlorpyrifos did not exceed any reference values in 2023, however, the insecticide was still considered a watershed POC because of detections that have exceeded criteria in recent years at this site.
- There were no detections of diuron at this site in 2023, however, it was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Upper Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2023 monitoring season and a visual comparison to the WSDA assessment criteria (Table 6). 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^{1,2}

Month		Mar	Apr				May					Jun				Jul				Sep			Oct				Nov
Day of the Month	Use*	28	4	11	17	25	1	8	15	23	30	5	12	21	26	5	10	17		11	18	25	2	9	16	23	30
2,4-D	H				0.138	0.051	0.045	0.623	0.039	0.033												0.466					
2,6-Dichlorobenzamide	D	0.166	0.175	0.137	0.183	0.167	0.140	0.183	0.159	0.176	0.151	0.116	0.236	0.171	0.134	0.101	0.108	0.079	0.044	0.035	0.029	0.091	0.061	0.131	0.144	0.138	0.282
2-Hydroxyatrazine	D					0.011	0.009	0.007	0.011	0.015	0.014	0.016	0.031	0.028		0.021			0.015		0.014		0.016		0.013	0.024	
Acephate	I						0.196	0.419		0.011												0.534	0.039	0.309			
Atrazine	H			0.010						0.010											0.006						
Azoxystrobin	F							0.007																			
Bifenthrin	I			0.003	0.007																						
Boscalid	F	0.070	0.064	0.104	0.116	0.132	0.065	0.079	0.067	0.123	0.090	0.061	0.085	0.072	0.050	0.046	0.056	0.050	0.029	0.027	0.027	0.033	0.026	0.035	0.053	0.040	0.142
Bromacil	H																						0.017				
Carbendazim	F							0.007																			
Chlorothalonil (Daconil)	F				0.017	0.002																					
Chlorpyrifos	I																				0.002						0.002
Deisopropyl atrazine	D										0.032	0.082	0.048														
Diazinon	I					0.003		0.003		0.004																	
Dicamba	H			0.004	0.021	0.005		0.005		0.008																	0.061
Dichlobenil	H	0.027	0.030	0.026	0.078	0.045	0.020	0.027	0.017	0.015	✗	0.005	0.013	0.013	0.009	0.004	0.004	0.003				0.007	0.002	0.006	0.018	0.017	0.109
Eptam	H							0.002		0.003																	
Flumioxazin	H				0.026	0.052					✗	✗	✗	✗	✗	✗	✗	✗									
Flupyradifurone	I	0.026	0.025	0.030	0.041	0.043	0.028	0.038	0.019	0.022	0.019	0.015	0.029	0.023	0.044	0.030	0.024	0.020				0.027	0.012		0.062	0.042	0.152
Hexazinone	H									0.001			0.002										0.002				
Imidacloprid	I	0.033	0.029	0.031	0.027	0.021	0.022	0.034	0.016																		0.062
Malathion	I																0.004	0.005									
MCPA	H			0.048		0.072		0.114																			
MCPP	H		0.020		0.130	0.052		0.050																			0.039
Metalaxyl	F	0.011	0.014	0.025	0.159	0.184	0.049	0.036	0.024	0.017		0.036	0.019	0.015	0.014	0.010	0.011					0.044	0.024	0.034	0.023	0.018	0.071
Methamidophos	D					0.025	0.048	0.012														0.074	0.009	0.066			
Metolachlor	H	0.016	0.114	0.188	0.340	0.434	0.043	0.020	0.012	0.008	0.005	0.003	0.006	0.004	0.004	0.002	0.002	0.002	0.001	0.001	0.001			0.004	0.012	0.014	0.036
Metribuzin	H			0.003	0.069	0.018	0.011	0.024	0.005	0.004																	0.003
N,N-Diethyl-m-toluamide (DEET)	IR																								0.011	0.010	0.016
Napropamide	H			0.111	0.217	0.085	0.011	0.009						0.016											0.005	0.005	0.022
Oxadiazon	H		0.002	0.003																							
Oxamyl	I																								0.005	0.002	0.005
Propiconazole	F		0.019	0.058	0.093	0.065	0.013	0.012	0.007																		
Simazine	H	0.015	0.015	0.011	0.421	0.252	0.030	0.153	0.060	0.039	0.361	0.528	0.269	0.135	0.087	0.064	0.063	0.047	0.012	0.009	0.007	0.053	0.021	0.029	0.028	0.031	0.033
Sulfentrazone	H	0.005	0.005		0.005	0.004	0.006	0.006	0.007	0.009	0.008	0.006	0.011	0.009	0.006							0.004		0.007	0.006		
Tebuthiuron	H																										0.004
Terbacil	H	0.014	0.015	0.010	0.008	0.011	0.015	0.015	0.021	0.017	0.017	0.009	0.037	0.019	0.011							0.045	0.011	0.088	0.028	0.019	0.030
Tetrahydrophthalimide	D	0.029	0.011	0.008	0.005		0.026	0.018		0.003	0.002		0.004	0.003				0.003			0.006				0.002	0.010	
Thiamethoxam	I			0.005					0.016	0.035	0.010		0.013														
Triclopyr	H																					0.257					
Triclopyr butoxyethyl ester	H																					0.023					
Suspended sediment concentration		3	2	4	15	10	4	3	4	2	2	2	2	6	1	2	2	4	3	2	3	2	3	2	1	4	
Streamflow (cubic ft/sec)		35.3	32.2	59.3	-	91.5	21.4	18.2	8.2	7.5	4.0	2.9	4.6	5.7	2.8	1.9	1.3	0.6	0.9	1.4	3.6	2.1	1.9	4.2	4.9	4.1	48.6
Precipitation (total in/week)†		0.79	0.61	1.11	0.74	1.29	0.39	2.84	0.13	1.72	0.00	0.00	1.40	1.00	0.43	0.00	0.00	0.00	0.00	0.00	0.88	1.19	0.44	1.66	1.49	0.60	9.32

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

 Current-use exceedance Detection No criteria

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

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

Below is a brief overview of the pesticide findings in Lower Bertrand Creek in 2023.

- There were 528 total pesticide detections in Lower Bertrand Creek from six different use categories: 19 types of herbicides, 9 insecticides, 7 fungicides, 3 legacies, 8 degradates, and 1 insect repellent.
- Of the total pesticide detections in Lower Bertrand Creek, 28 were above WSDA's assessment criteria. (Table 7)
 - The two detections of 4,4'-DDD, a legacy degradate of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - The single detections of 4,4'-DDE, a legacy degradates of DDT, and 4,4'-DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - Of the eight detections of carbendazim, one detection exceeded the Endangered Species level of Concern (0.37 µg/L).
- Of the four detections of malaoxon, one detection exceeded the invertebrate LC₅₀ (0.098 µg/L), invertebrate NOAEC (0.06 µg/L), and NRWQC chronic criteria (0.1 µg/L). It also approached the Endanger Species of Concern (0.205 µg/L).

The Lower Bertrand Creek watershed POCs were bifenthrin, diazinon, gamma-cyhalothrin, imidacloprid, malathion, and permethrin. Below, each POC detected is compared to toxicity test reference values.

- The two detections of bifenthrin approached the fish NOAEC (0.004 µg/L). They also exceeded the invertebrate LC₅₀ (0.000493 µg/L) and invertebrate NOAEC (0.00005 µg/L).
- The 14 detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the 12 detections of malathion, six detections approached or exceeded the invertebrate LC₅₀ (0.098 µg/L) and invertebrate NOAEC (0.06 µg/L).
 - The detections on April 4 and April 11 also approached NRWQC chronic criteria (0.1 µg/L).
 - The detection on April 25 and May 15 also exceeded NRWQC chronic criteria (0.1 µg/L).
- All detections of diazinon in 2023 did not exceed any assessment criteria, but the insecticide was still classified as a watershed POC because of detections that have exceeded criteria in recent years at this site.
- There were no detections of gamma-cyhalothrin or permethrin at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.

The Lower Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2023 monitoring season and a visual comparison to the WSDA assessment criteria. (Table 7). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 7 – Lower Bertrand pesticide calendar, µg/L^{3, 4}

Month		Mar					Apr					May					Jun					Jul				Sep			Oct				Nov				
Day of the Month	Use*	28	4	11	17	25	1	8	15	23	30	5	12	21	26	5	10	17	11	18	25	2	9	16		23	30	6	14								
2,4-D	H				0.062	0.053	0.062	0.069																													
2,6-Dichlorobenzamide	D	0.151	0.164	0.136	0.145	0.174	0.131	0.146	0.130	0.132	0.120	0.129	0.113	0.114	0.128	0.120	0.145	0.150	0.127	0.129	0.119	0.125	0.147	0.115	0.164	0.155	0.283	0.200									
2-Hydroxyatrazine	D				0.008	0.015	0.011				0.010	0.014		0.015	0.016		0.015	0.016				0.010		0.015		0.023	0.026										
4,4'-DDD	L			<0.001	0.001																																
4,4'-DDE	L				0.002																																
4,4'-DDT	L				0.002																																
Acephate	I						0.214															0.081	0.030														
Atrazine	H	0.005	0.005	0.010						0.005												0.005	0.005														
Bifenthrin	I			0.004	0.003																																
Boscalid	F	0.064	0.060	0.094	0.106	0.115	0.062	0.057	0.038	0.046	0.035	0.029	0.032	0.036	0.032	0.025	0.031	0.029	0.024	0.030	0.035	0.028	0.028	0.023	0.046	0.031	0.123	0.102									
Bromacil	H	0.007	0.008				0.010	0.010	0.014	0.016	0.017	0.024	0.017	0.017	0.017	0.025	0.029	0.040	0.021	0.022	0.018	0.018	0.021	0.016	0.013	0.012											
Carbendazim	F					0.422	0.061	0.031	0.019	0.010	0.010	0.009	0.007																								
Chlorothalonil (Daconil)	F	0.004			0.006	0.002	0.002																														
Diazinon	I				0.023	0.005	0.004	0.003	0.025	0.012	0.010	0.004	0.005	0.002	0.002																						
Dicamba	H				0.007	0.006	X	0.007																				0.062									
Dichlobenil	H	0.018	0.029	0.025	0.033	0.048	0.013	0.014	0.009	0.006	X	0.003	0.003	0.002	0.004	0.002	0.002	0.002				0.002	0.002		0.015	0.016	0.144	0.138									
Dinotefuran	I	0.016	0.010	0.013	0.185	0.167	0.083		0.024																												
Diuron	H													0.026																							
Eptam	H						0.002	0.002	0.002	0.003	0.002		0.003	0.002																							
Fipronil sulfide	D						0.001																														
Fipronil sulfone	D						0.002																														
Fludioxonil	F													0.006	0.005	0.007	0.006	0.008			0.005	0.005															
Flupyradifurone	I	0.018	0.018	0.030	0.031	0.033	0.014				0.011				0.021										0.045	0.023	0.147	0.081									
Hexazinone	H	0.001					0.002		0.003	0.003			0.003	0.003			0.004						0.004					0.005	0.005	0.004							
Imazapyr	H																							0.004		0.003		0.011	0.008								
Imidacloprid	I	0.024	0.022	0.024	0.019	0.016	0.015	0.022	0.011																			0.031	0.018	0.028		0.040					
Malaoxon	D		0.005	0.005		0.164				0.018																					0.050	0.033					
Malathion	I	0.011	0.058	0.085	0.040	0.124	0.006	0.036	0.126							0.008	0.006	0.006														0.009					
MCPA	H		0.095	0.077	0.093	0.144	X	0.094																							0.132						
MCPP	H	0.027		0.038	0.046	0.049	X	0.048																							0.041						
Metalaxyl	F	0.052	0.051	0.050	0.404	0.328	0.092	0.079	0.094	0.079	0.089	0.108	0.079	0.081	0.081	0.095	0.111	0.113	0.103	0.100	0.096	0.103	0.104	0.094	0.075	0.070	0.102	0.059									
Methamidophos	D						0.030	0.020														0.012															
Metolachlor	H	0.018	0.053	0.275	0.129	0.253	0.039	0.019	0.016	0.014	0.012	0.014	0.010	0.013	0.011	0.014	0.017	0.015	0.017	0.019	0.021	0.018	0.018	0.018	0.019	0.020	0.045	0.018									
Metribuzin	H			0.003	0.037	0.027	0.010	0.011	0.004																						0.003						
N,N-Diethyl-m-toluamide (DEET)	IR		X		0.009																				0.010	0.011	0.015	0.011									
Napropamide	H			0.090	0.149	0.082	0.009	0.007																							0.005	0.004	0.017	0.011			
Norflurazon	H	0.002								0.002		0.003	0.003			0.004	0.005	0.006	0.003	0.005	0.005	0.004	0.004	0.003	0.002	0.002											
Oxamyl	I	0.049	0.041	0.027	0.060	0.021	0.059		0.123	0.110	0.149	0.199	0.123	0.141	0.169	0.227	0.238	0.290	0.249	0.288	0.194	0.220	0.114	0.165	0.123	0.146	0.030	0.024									
Oxamyl oxime	D	0.052							0.120	0.067	0.071	0.142	0.081	0.081	0.100	0.147	0.191	0.197	0.095	0.099		0.113	0.067	0.084	0.064												
Propiconazole	F			0.043	0.042	0.051		0.008																													
Pyrimethanil	F											0.009																									
Simazine	H	0.012	0.012	0.020	0.184	0.385	0.033	0.144	0.034	0.015	0.082	0.126	0.111	0.070	0.040	0.022	0.025	0.019	0.005	0.005	0.013	0.019	0.014	0.010	0.028	0.021	0.036	0.029									
Sulfentrazone	H	0.034	0.039	0.025	0.022	0.023	0.044	0.043	0.059	0.062	0.051	0.081	0.060	0.072	0.069	0.079	0.095	0.104	0.080	0.108	0.084	0.084	0.090	0.083	0.063	0.070	0.021	0.013									
Tebuthiuron	H	0.004		0.004				0.006				0.007	0.005					0.007			0.008	0.007	0.007	0.007	0.006	0.005		0.006									
Terbacil	H	0.008	0.013	0.007	0.012	0.008	0.009	0.008	0.006	0.005					0.006																0.008	0.008	0.006	0.026	0.014	0.040	0.045
Tetrahydrophthalimide	D	0.057	0.019	0.004	0.092	0.071	0.029	0.006	0.006	0.014	0.009	0.011	0.015	0.030	0.007	0.013	0.012	0.022	0.017	0.019	0.029	0.021	0.019	0.016	0.010	0.019	0.020	0.012									
Thiamethoxam	I	0.015	0.015	0.011	0.010	0.011	0.025	0.022	0.034	0.051	0.049	0.045	0.037	0.045	0.039	0.049	0.046	0.053	0.042	0.039	0.039	0.053	0.060	0.051	0.013	0.022	0.006										
Suspended Sediment Concentration		3	3	7	30	17	5	4	4	3	2	2	2	3	2	2	1	1	1																		
Streamflow (cubic ft/sec)		63.3	57.0	108.0	194.0	164.0	46.7	37.5	35.7	17.6	13.0	9.1	14.3	16.2	11.0	6.5	5.4	4.2	5.6	4.7	8.5	7.8	17.5	10.1	12.0	10.9	78.1	81.0									
Precipitation (total in/week)†		0.79	0.61	1.11	0.74	1.29	0.39	2.84	0.13	1.72	0.00	0.00	1.40	1.00	0.43	0.00	0.00	0.00	0.00	0.00	0.88	1.19	0.44	1.66	1.49	0.60	9.32	0.06									

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

- Below is a brief overview comparison between the two sites in Bertrand Creek.
- NRAS tested for 150 unique pesticides in Upper and Lower Bertrand Creek.
- Pesticides were detected at each sampling event.
- Up to 25 pesticides were detected within one sample in Upper Bertrand, and up to 29 pesticides were detected within one sample Lower Bertrand.
- There were 34 pesticides that were detected at least once in both the Upper and Lower Bertrand Creek sites throughout the sampling season. Conversely, seven pesticides were found only at the upper site and 13 pesticides were found only at the lower site.

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. In Upper Bertrand Creek, pesticide exceedances coincided with water quality measurements that did not meet the state standards at four of the 26 site visits (15%). In Lower Bertrand Creek, pesticide exceedances coincided with water quality measurements that did not meet the state standards at seven of the 27 site visits (26%). Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in Figure 6 are shown below.

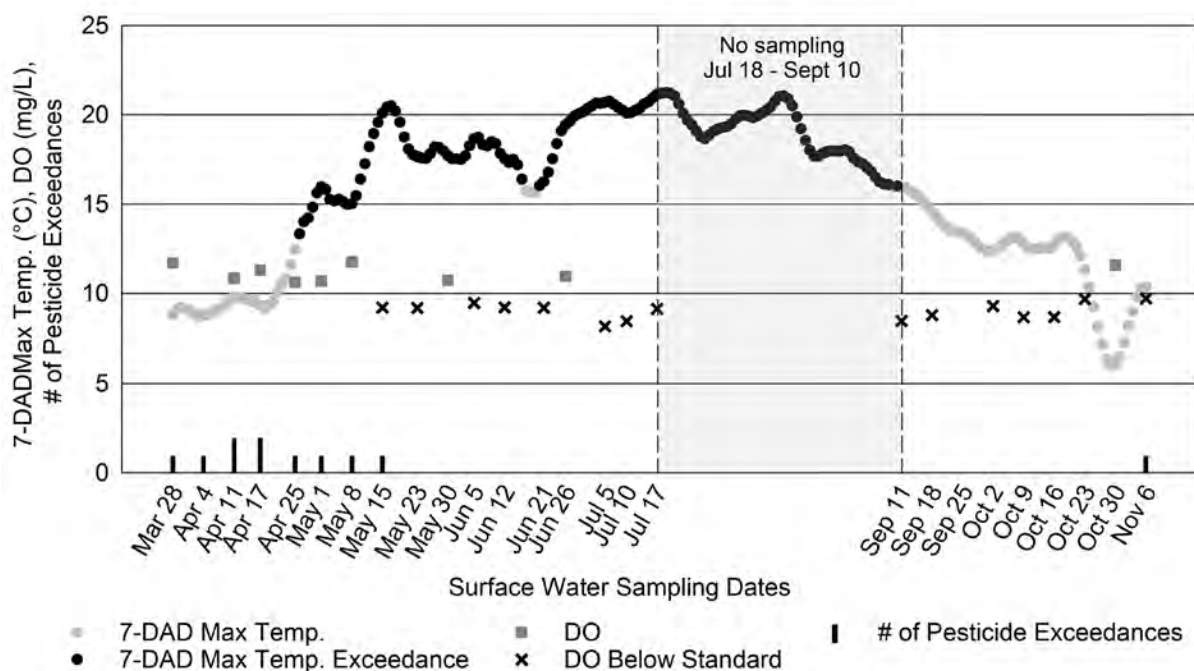


Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 7.23 to 8.11 with an average of 7.23. DO measurements ranged from 8.16 mg/L to 11.77 mg/L with an average of 9.82 mg/L. More than half (63%) of the DO measurements did not meet the state standard, with 15 measurements falling below 10 mg/L. Two of the DO measurements that did not meet the state water quality standard coincided with one pesticide exceedance.

Upper Bertrand Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods of the sampling season. From February 15 through June 15, the 7-DADMax temperature should remain below 13 °C, while June 16 through the end of the sampling

season should remain below 16 °C (Ecology 2011; WAC 2024b). The 7-DADMax temperature exceeded the standard on 134 days, primarily from April 26 through September 8. Pesticide exceedances coincided with 7-DADMax temperature exceedances at three site visits.

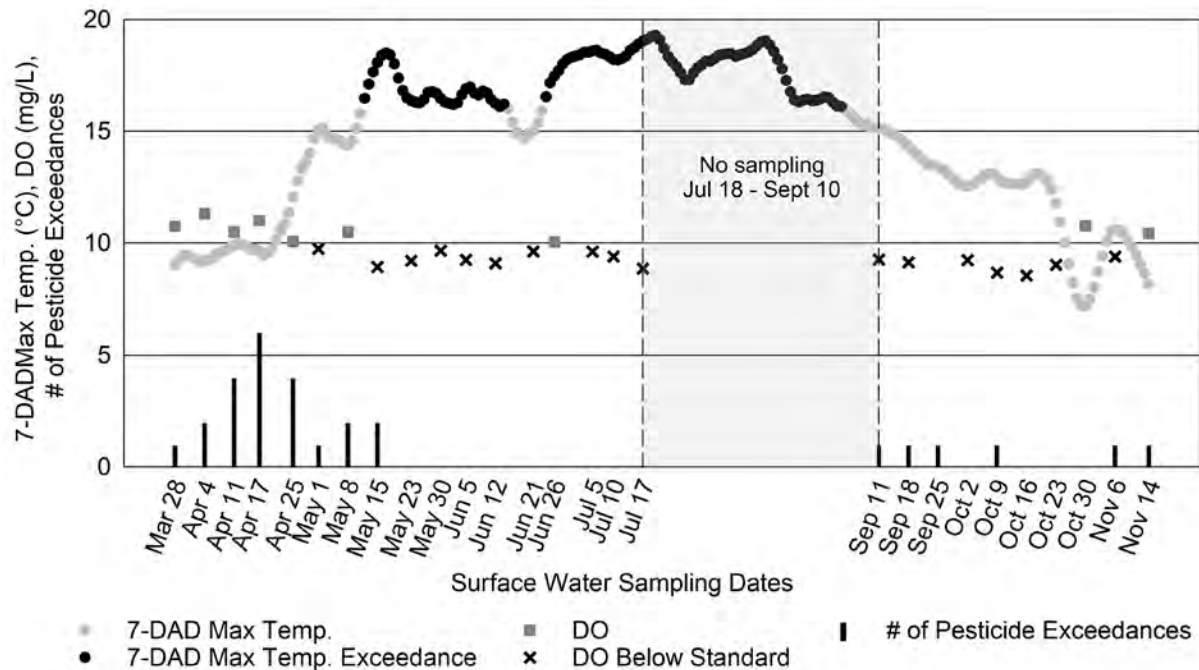


Figure 6 – Lower Bertrand Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.13 to 7.58 with an average of 7.35. DO measurements ranged from 8.54 mg/L to 11.31 mg/L with an average of 9.69 mg/L. More than half (65%) of the DO measurements did not meet the state water quality standard, with 17 measurements falling below 10 mg/L. Six of the DO measurements that did not meet the state water quality standard coincided with one or two pesticide exceedances. The 7-DADMax temperature exceeded the standard of 16 °C on 105 days throughout the sampling season, from May 15 through September 2. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit.

Bertrand Creek has been designated as a freshwater body that provides a core summer habitat for salmonids by the WAC (WAC 2024d). NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Upper Big Ditch

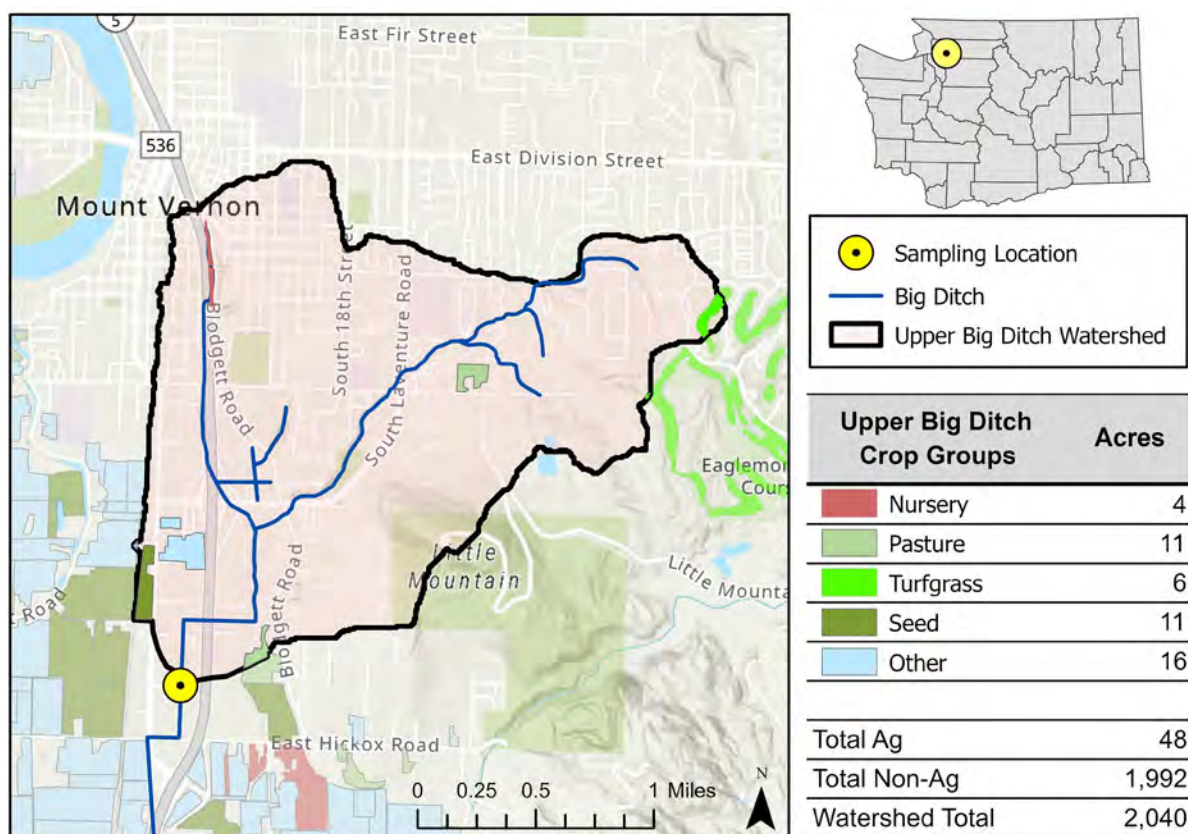


Figure 7 – Map of Upper Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2007, NRAS started monitoring the Upper Big Ditch in Skagit County. The entire Big Ditch watershed drains a mixture of non-agricultural and agricultural land. The upper monitoring site is located just upstream from the bridge crossing at Eleanor Lane in Mt. Vernon (latitude: 48.3882°, longitude: -122.3330°) (Figure 7, Figure 8).

Water from the Big Ditch drains into Puget Sound. WDFW has documented the presence of coho, fall Chinook, fall chum, and pink salmon, as well as cutthroat trout and winter steelhead trout within the reach of ditch that encompasses the monitoring site (WDFW 2024). A culvert that impeded fish passage upstream of the Upper Big Ditch monitoring site was removed in the fall of 2020. Coho salmon 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. Towards the end of the sampling season, flows became almost stagnant due to dense aquatic vegetation. The water sampling method was adapted based on flow conditions, using single, double, or triple-point sampling where the highest velocity water was flowing 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



Figure 8 – Upper Big Ditch upstream view

monitors have nursery or greenhouse crop groups as their main agricultural commodity. The 'Other' crop group category includes of fallow fields and other assorted small acreage crops (Figure 7).

Below is a brief overview of the pesticide findings in Upper Big Ditch in 2023.

- NRAS tested for 150 unique pesticides in Upper Big Ditch.
- There were 349 total pesticide detections from six different use categories: 26 types of herbicides, 6 insecticides, 8 fungicides, 6 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 21 sampling events.
- Up to 27 pesticides were detected at the same time.
- Of the total pesticide detections, one was above WSDA's assessment criteria (Table 8).

The Upper Big Ditch watershed POCs were bifenthrin and chlorpyrifos. Below, each POC detected is compared to toxicity test reference values.

- The single detection of bifenthrin exceeded the fish NOAEC (0.004 µg/L), invertebrate LC₅₀ (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- There were no detections of chlorpyrifos at this site in 2023, however, it was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Upper Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{5, 6}

Month		Apr				May					Jun					Oct					Nov		
Day of the Month	Use*	4	11	18	25	2	9	16	23	30	6	13	20	27		3	10	17	24	31	7	14	28
2,4-D	H		0.069	0.069	0.079	0.049	0.054		0.108			0.039	0.083			0.148	0.330	0.527	0.050		0.070	0.061	
2,6-Dichlorobenzamide	D	0.215	0.239	0.234	0.268	0.192	0.227	0.139	0.141	0.114	0.102	0.110	0.088	0.091		0.083	0.093	0.205	0.091	0.116	0.158	0.242	0.130
2-Hydroxyatrazine	D					0.007		0.009	0.012	0.012	0.024	0.022		0.026		0.026	0.035	0.014	0.026	0.020		0.013	0.022
4-Nitrophenol	D		0.085					0.070					0.167								0.106		
Atrazine	H		0.003										0.002			0.004		0.006	0.004				
Azoxystrobin	F														0.002								
Bifenthrin	I		0.007													0.002							
Boscalid	F	0.004	0.021	0.004	0.004	0.004	0.004	0.005	0.003	0.002	0.002	0.002	0.016		0.013	0.010	0.007	0.003	0.003	0.015	0.006	0.002	
Bromacil	H															0.005					0.006		
Carbendazim	F											0.005					0.013			0.022			
Chlorothalonil (Daconil)	F		0.003										0.003										
Chlorpropham	H		0.002																				
Diazinon	I						0.001																
Dicamba	H		0.007	0.005	0.015	0.008	0.007		0.023									0.011					
Dichlobenil	H	0.009	0.039	0.021	0.027	0.005	0.010		0.005		0.002	0.003	0.004	0.002	0.003	0.002	0.011	0.001	0.003	0.010	0.010	0.003	
Dimethoate	I							0.004															
Dinotefuran	I	0.088	0.016	0.058	0.064	0.095	0.094	0.118	0.057	0.034	0.022	0.045	0.081	0.032				0.009			0.037	0.017	0.037
Dithiopyr	H	0.003	0.006	0.004	0.004	0.002	0.003											0.002			0.003	0.004	
Diuron	H		0.007												0.015	0.006	0.019			0.016	0.012		
Eptam	H					0.007	0.002	0.006	0.003	0.002	0.003	0.003	0.002	0.002					0.005	0.003	0.001		
Fipronil	I		0.002															0.002					
Fipronil sulfide	D																	0.001					
Fipronil sulfone	D																	0.002					
Fludioxonil	F	0.014	0.038	0.015	0.011	0.011	0.012	0.012	0.007	0.006	0.006	0.006	0.034	0.005	0.032	0.024	0.012	0.012	0.007	0.036	0.010	0.006	
Flupyradifurone	I	0.012			0.010	0.010	0.012	0.012															
Hexazinone	H																	0.002			0.004		
Imazapic	H	0.007	0.029	0.018	0.014																	0.013	
Imazapyr	H	0.021	0.038	0.026	0.031	0.021	0.031	0.025	0.023	0.039	0.044	0.047	0.020	0.028	0.013	0.016	0.019	0.018	0.037	0.024	0.103	0.021	
Indaziflam	H		0.005				0.002	0.002															
Inpyrfluxam	F									0.013													
MCPP	H			0.037	0.034																		
Metolachlor	H		0.002	0.001			0.002	0.005	0.006			0.004	0.016	0.001				0.003	0.002	0.001	0.003	0.002	
Metribuzin	H														0.003						0.006		
N,N-Diethyl-m-toluidide (DEET)	IR		0.013	0.008				0.028	0.016				0.019		0.018	0.016	0.037	0.011	0.011	0.016	0.041	0.010	
Napropamide	H																					0.005	
Pendimethalin	H																	0.010	0.003		0.003		
Pentachlorophenol	WP		0.013															0.021			0.011		
Picloram	H			0.081	0.080	0.140	0.126	0.216	0.122	0.214	0.203	0.197	0.119	0.111	0.077	0.174			0.155	0.092			
Prometon	H	0.007	0.006	0.006	0.008	0.006	0.007	0.006	0.006	0.005	0.006	0.005	0.004	0.006	0.006	0.006	0.030	0.008	0.009	0.007	0.009	0.007	
Propiconazole	F		0.017	0.006									0.009										
Simazine	H			0.035														0.006					
Sulfentrazone	H	0.003		0.004	0.005	0.003	0.004											0.009				0.003	
Tebuthiuron	H	0.025		0.014	0.015	0.025	0.024	0.037	0.041	0.036	0.053	0.045	0.032	0.050	0.056	0.066	0.007	0.066	0.077		0.024	0.070	
Tetrahydrophthalimide	D							0.002					0.005		0.003	0.001	0.003				0.002		
Treflan (Trifluralin)	H	0.002	0.002												0.003	0.001	0.003						
Triadimefon	F																			0.002			
Triclopyr	H		0.382	0.125	0.069		0.161		0.049			0.038	0.067	0.021	0.037		0.191			0.098	0.184		
Triclopyr butoxyethyl ester	H		0.002																				
Suspended sediment concentration		4	55	6	4	5	8	9	7	7	6	6	4	4	13	3	8	5	3	37	3	3	
Streamflow (cubic ft/sec)		2.8	13.1	4.1	4.1	1.9	2.9	1.4	1.2	1.1	0.8	0.8	0.9	0.6	0.5	0.8	1.6	0.3	0.3	3.4	1.7	0.7	
Precipitation (total in/week)†		0.07	0.44	0.56	0.63	0.03	0.58	0.00	0.05	0.00	0.00	0.50	0.12	0.12	0.29	0.06	0.99	0.31	0.87	1.24	1.22	0.18	

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

Current-use exceedance Detection No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, 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. There were no pesticide exceedances that coincided with water quality measurement that did not meet the state standards. Water quality at the Upper Big Ditch site is shown below (Figure 9).

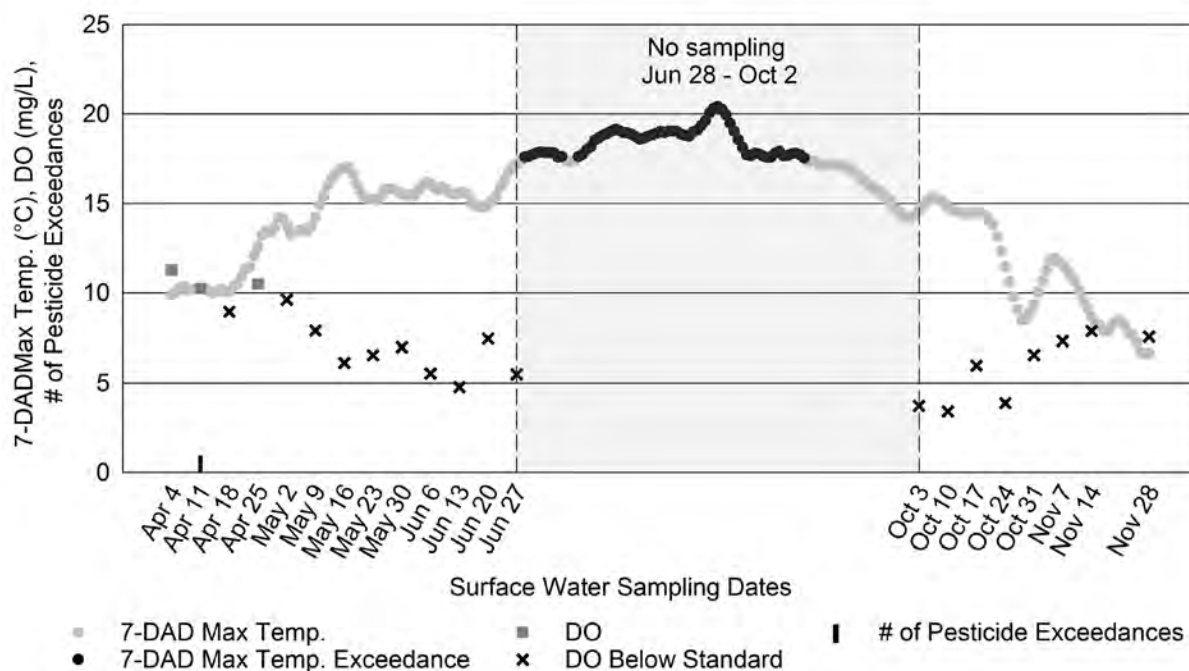


Figure 9 – Upper Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 6.89 to 7.31 with an average of 7.05. DO measurements ranged from 3.41 mg/L to 11.28 mg/L with an average of 7.03 mg/L. More than three-quarters (86%) of the DO measurements did not meet the state water quality standard, with 18 measurements falling below 10 mg/L. Upper Big Ditch consistently recorded the lowest DO measurement among all monitoring sites, consistent with data from the previous five years. The 7-DADMax temperature exceeded the standard of 17.5°C on 66 days throughout the sampling season, occurring intermittently from June 29 through September 5.

Upper Big Ditch has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2024d). Flow in the ditch towards the end of summer was slowed substantially due to constriction from aquatic vegetation. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs.

Lower Big Ditch

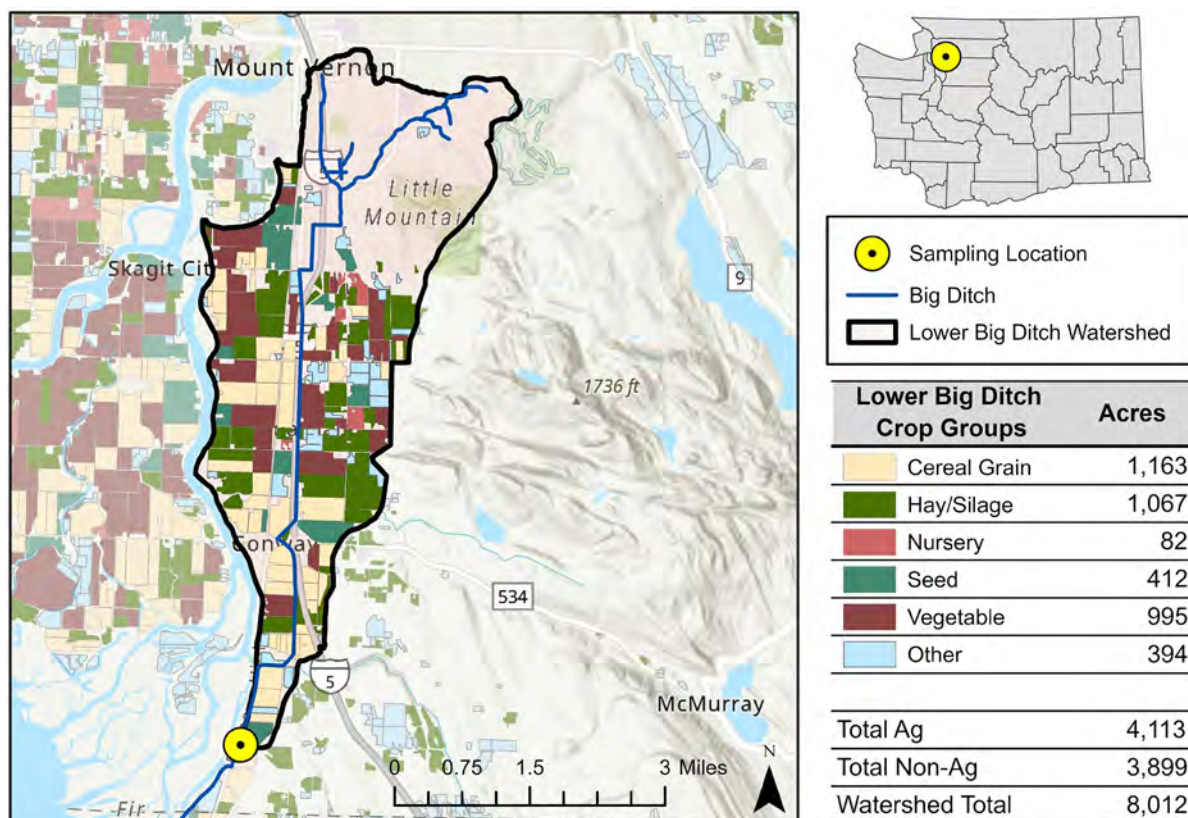


Figure 10 – Map of Lower Big Ditch and its drainage area with associated sampling location and crop groups identified

In 2006, NRAS started sampling the Lower Big Ditch monitoring site in Skagit County. The entire Big Ditch watershed drains a mixture of non-agricultural and agricultural land. Currently, the lower monitoring site is located just upstream from the bridge crossing at Milltown Road near Mt. Vernon (latitude: 48.3085°, longitude: -122.3474°) (Figure 10, Figure 11).

NRAS 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 coho, fall Chinook, fall chum, kokanee, and pink salmon, as well as cutthroat trout, rainbow trout and winter steelhead trout within the reach of ditch that encompasses the monitoring site (WDFW 2024).



Figure 11 – Lower Big Ditch upstream view

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 grass hay, potatoes, field corn, barley, and grass seed. The ‘Other’ crop group category consists mostly of pastures, fallow fields, and wildlife feed (Figure 10).

Below is a brief overview of the pesticide findings in Lower Big Ditch in 2023.

- NRAS tested for 150 unique pesticides in Lower Big Ditch.
- There were 283 total pesticide detections from six different use categories: 24 types of herbicides, 4 insecticides, 6 fungicides, 2 legacies, 6 degradates, and 1 insect repellent.
- Pesticides were detected at all 15 sampling events.
- Up to 34 pesticides were detected at the same time.
- Of the total pesticide detections, 16 were above WSDA's assessment criteria (Table 9).
 - All detections of 4,4'-DDD and 4,4'-DDE, legacy degradates of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Lower Big Ditch watershed POCs were bifenthrin, fipronil, and imidacloprid. Below, each POC detected is compared to toxicity test reference values.

- Of the nine detections of fipronil, three approached the invertebrate NOAEC and one exceeded the invertebrate NOAEC (0.011 µg/L).
- The single detection of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- There were no detections of bifenthrin at this site in 2023, however, it was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{7, 8}

Month		Mar	Apr					May					Jun				Jul
Day of the Month	Use*	27	3	10	18	24	2	9	16	22	31	6	13	20	27	3	
2,4-D	H	0.034	0.045	0.052	0.136	0.139	0.049	0.067	0.033	0.321							
2,6-Dichlorobenzamide	D	0.171	0.157	0.142	0.156	0.170	0.135	0.090	0.047	0.026	0.003	0.023	0.009	0.002	0.014	0.002	
2-Hydroxyatrazine	D	0.048	0.043	0.035	0.044	0.088	0.050	0.041	0.023	0.021	0.006	0.050	0.032		0.045	0.027	
4,4'-DDD	L	0.002		0.001	<0.001	0.003	0.001	0.001	<0.001				<0.001			<0.001	
4,4'-DDE	L	0.003				0.003											
Atrazine	H						0.003	0.003									
Azoxystrobin	F	0.011	0.008		0.029	0.051	0.014	0.029	0.010	0.022	0.008						
Bentazon	H	0.055	0.053	0.064	0.261	0.235	0.058	0.134	0.011	0.007	0.059						
Boscalid	F	0.003	0.003	0.003	0.004	0.005	0.003	0.002	0.002			0.002	0.002		0.002		
Chlorpropham	H	0.001	0.003	0.002	0.001	0.003	0.001										
Diazinon	I							0.003									
Dicamba	H	0.013			0.013	0.053	0.007	0.015									
Dichlobenil	H	0.011		0.005	0.013	0.033	0.003								0.002		
Difenoconazole	F										0.015						
Dinotefuran	I	0.020	0.017	0.021	0.019	0.023	0.025	0.012									
Dithiopyr	H	0.002			0.002	0.002											
Diuron	H	0.017			0.012	0.025		0.012	0.004								
Eptam	H	0.007	0.007	0.009	0.008	0.005	0.013	0.005	0.011	0.004		0.005	0.006	0.003	0.003	0.006	
Fipronil	I	0.008	0.002	0.002	0.006	0.007	0.002	0.003		0.028		0.003					
Fipronil disulfinyl	D									0.004		0.002					
Fipronil sulfide	D	0.006	0.006	0.006	0.005	0.006	0.005	0.004	0.003	0.004	0.001	0.002	0.002	0.001	0.002	0.001	
Fipronil sulfone	D	0.008	0.004	0.004	0.006	0.008	0.004	0.003	0.002	0.005		0.003	0.002		0.002		
Fludioxonil	F	0.028	0.028	0.036	0.043	0.046	0.041	0.026	0.019	0.011	0.004	0.012	0.010	0.005	0.010	0.008	
Flumioxazin	H					0.016											
Hexazinone	H			0.002			0.002										
Imazapyr	H	0.028	0.026	0.028	0.031	0.029	0.027	0.016	0.011			0.011	0.004			0.007	
Imidacloprid	I					0.013											
Indaziflam	H				0.004	0.008											
Inpyrfluxam	F													0.109			
MCPA	H							0.227									
MCPP	H					0.040		0.031									
Metalaxyl	F	0.033	0.021	0.017	0.035	0.042	0.015	0.019									
Metolachlor	H	0.197	0.093	0.094	0.108	0.452	0.168	0.088	0.046	0.036	0.002	0.012	0.005	0.001	0.002	0.001	
Metribuzin	H	0.015	0.013	0.005	0.012	0.020	0.006	0.007									
N,N-Diethyl-m-toluamide (DEET)	IR			0.007		0.012		0.012								0.010	
Norflurazon	H	0.001															
Picloram	H			0.075			0.058										
Prometon	H	0.005	0.004	0.004	0.004	0.005	0.004	0.003	0.002								
Simazine	H	0.089	0.011	0.006	0.013	0.016	0.004										
Sulfentrazone	H	0.160	0.072	0.062	0.071	0.137	0.064	0.045	0.021	0.011		0.005			0.005		
Tebuthiuron	H	0.017	0.023	0.023	0.018	0.018	0.024	0.013	0.014	0.008		0.013			0.008		
Tetrahydrophthalimide	D				0.043	0.137		0.002									
Triclopyr	H		0.054	0.055	0.124	0.105		0.066									
Suspended sediment concentration		55	19	23	14	104	17	24	11	8	4	4	5	3	5	28	
Streamflow (cubic ft/sec)		-	16.4	8.4	10.3	49.4	12.7	35.3	7.7	15.2	12.9	5.9	6.1	6.7	4.3	6.1	
Precipitation (total in/week)†		1.13	0.07	0.23	0.56	0.51	0.03	0.58	0.00	0.00	0.00	0.00	0.50	0.12	0.12	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. The "X" signifies data rejected by failing laboratory 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: Mt. Vernon (latitude: 48.44°, longitude: -122.39°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 10 of the 15 site visits (67%). Water quality at the Lower Big Ditch site is shown below (Figure 12).

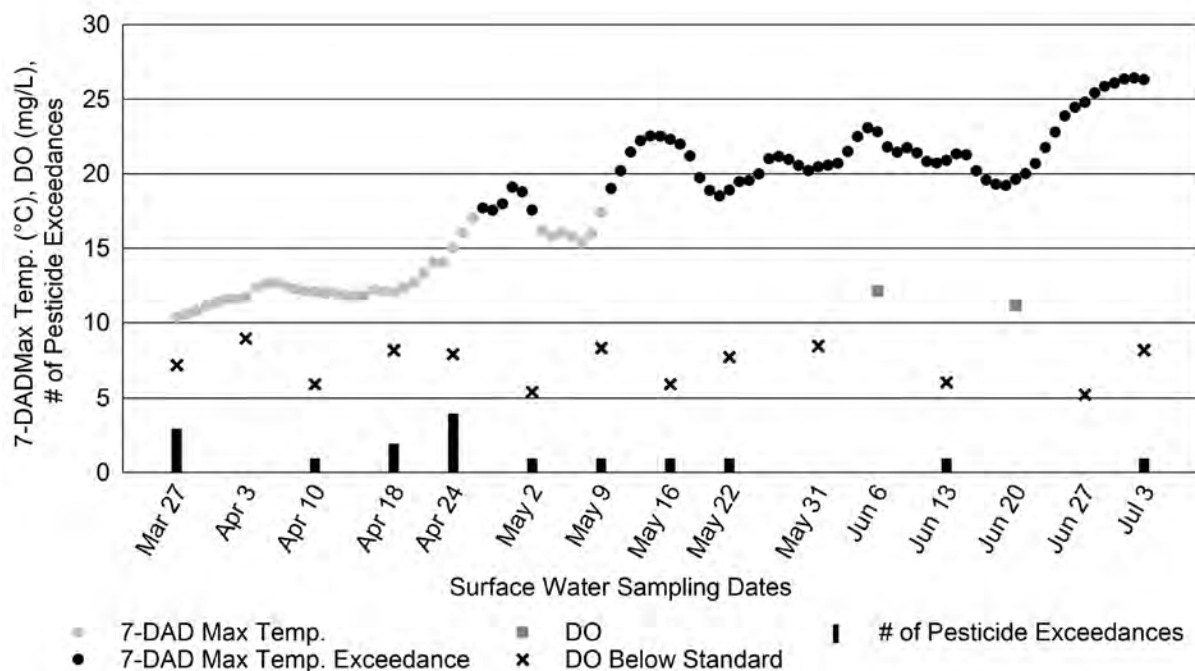


Figure 12 – Lower Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 6.92 to 8.20 with an average of 7.26. DO measurements ranged from 5.23 mg/L to 12.15 mg/L with an average of 7.79 mg/L. More than three-quarters (87%) of these measurements did not meet the state water quality standard, with 13 measurements falling below 10 mg/L. Ten of the DO measurements that did not meet the standard coincided with one, two, three, or four pesticide exceedances. DO variability can be attributed to the effects of tidal fluctuations. The 7-DADMax temperature exceeded the standard of 17.5°C on 61 days throughout the sampling season, occurring intermittently from April 27 through July 3. Pesticide exceedances coincided with 7-DADMax temperature exceedances at five site visits.

Lower Big Ditch is not only considered a habitat for salmonid spawning, rearing, and migration, but is also used as a corridor for migrating waterfowl (WAC 2024d). WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

Burnt Bridge Creek

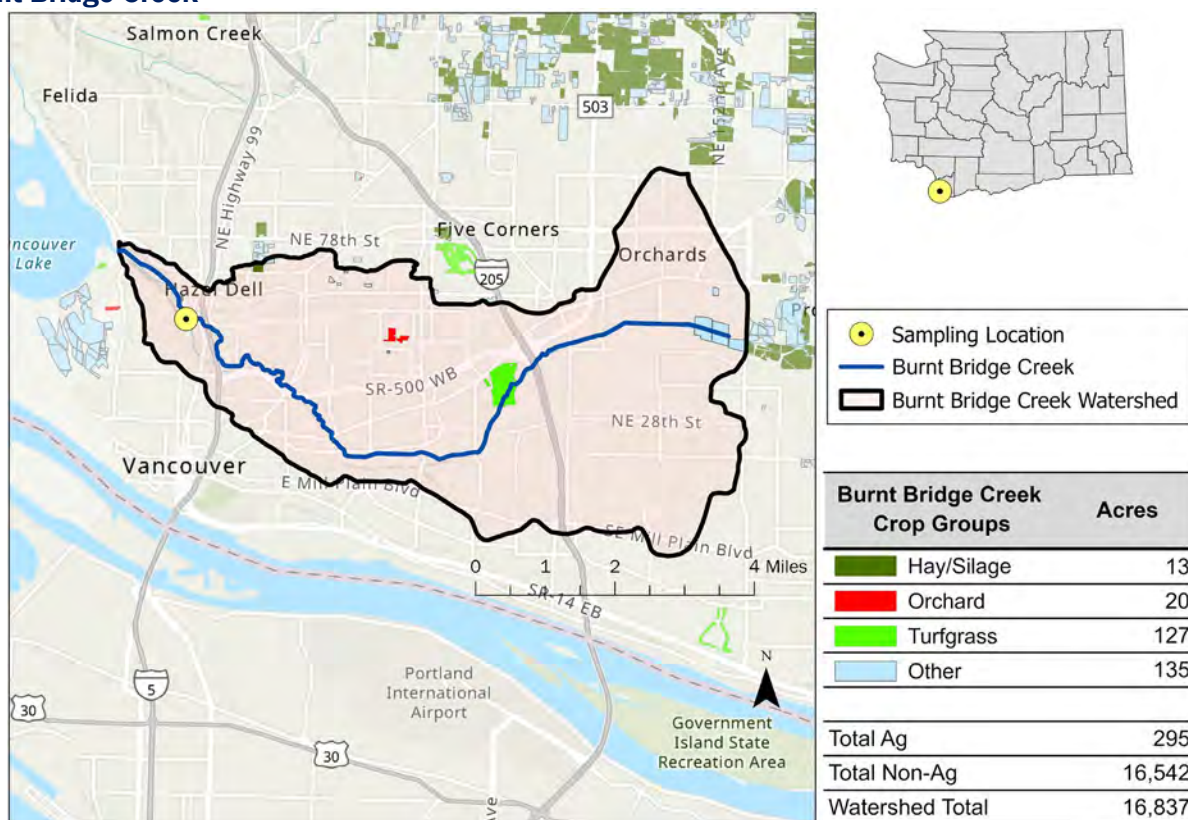


Figure 13 – Map of Burnt Bridge Creek and its drainage area with associated sampling location and crop groups identified

In 2017, NRAS started sampling the Burnt Bridge watershed in Clark County. The monitoring site selected on Burnt Bridge Creek is located approximately 10 meters downstream from the bridge crossing at Alki Road (latitude: 45.6614°, longitude: -122.6720°) (Figure 13, Figure 14). Roughly 10 miles of Burnt Bridge Creek flows through the center of Vancouver, Washington. The watershed is highly impacted by residential, commercial, and industrial development (Figure 13). The ‘Other’ crop group category includes mostly land used for conservation purposes. This site was one of two urban sites monitored in 2023.

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 coho and fall Chinook salmon, as well as rainbow trout and winter steelhead trout within the Burnt Bridge watershed (WDFW 2024). Staff observed fish of unknown species at this site.

Below is a brief overview of the pesticide findings in Burnt Bridge Creek in 2023.

- NRAS tested for 150 unique pesticides in Burnt Bridge Creek.

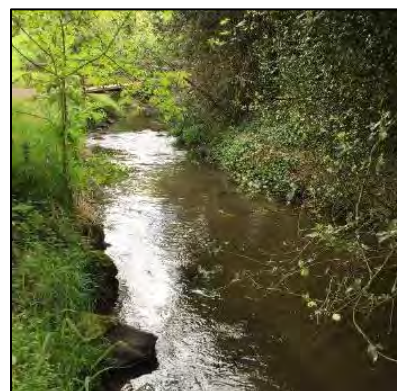


Figure 14 – Burnt Bridge Creek upstream view

- There were 285 total pesticide detections from eight different use categories: 27 types of herbicides, 6 insecticides, 5 fungicides, 3 legacies, 6 degradates, 1 insect repellent, 1 synergist, and 1 wood preservative.
- Pesticides were detected at all 19 sampling events.
- Up to 37 pesticides were detected at the same time.
- Of the total pesticide detections, 23 were above WSDA's assessment criteria (Table 10).
 - Of all the detections of 4,4'DDD, a legacy degradate of DDT, nine exceeded NRWQC and WAC chronic criteria, while three approached the criteria (both 0.001 µg/L).
 - All detections of 4,4'-DDE and 4,4'-DDT, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Burnt Bridge Creek watershed POCs were bifenthrin, diuron, fipronil, flumioxazin, and gamma-cyhalothrin. Below, each POC detected is compared to toxicity test reference values.

- The single bifenthrin detection exceeded the fish NOAEC (0.004 µg/L), invertebrate LC₅₀ (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- Of the five diuron detections, two detections exceeded the invertebrate NOAEC (0.83 µg/L), plant EC₅₀ (0.13 µg/L).
 - The detection on September 26 was an unusually high compared to diuron detections in the past three years and occurred soon after a rain event. This detection also approached the fish NOAEC (26.4 µg/L).
- Of the seven fipronil detections, two approached or exceeded the invertebrate NOAEC (0.011 µg/L).
- Of the two flumioxazin detections, one approached the fish NOAEC (0.51 µg/L) and plant EC₅₀ (0.49 µg/L).
- The single detection of gamma-cyhalothrin exceeded the invertebrate LC₅₀ (0.00008 µg/L), invertebrate NOAEC (0.00193 µg/L).

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{9, 10}

Month		Apr			May					Jun			Jul		Aug		Sep				Oct
Day of the Month	Use*	12	19	26	3	10	17	24	31	7	14	28	12		14	28	5	12	19	26	11
1-(3,4-Dichlorophenyl)-3-methylurea	D																			1.270	0.125
2,4-D	H	0.062	0.114	0.045		0.047	0.029									0.028				0.151	0.220
2,6-Dichlorobenzamide	D	0.159	0.190	0.200	0.195	0.210	0.179	0.198	0.179	0.212	0.205	0.189	0.246		0.267	0.300	0.237	0.240	0.225	0.256	0.409
4,4'-DDD	L	0.002	0.001	0.001	0.001	0.001	0.001	0.001	<0.001	0.001	<0.001									<0.001	0.002
4,4'-DDE	L	0.002	0.001																		0.002
4,4'-DDT	L																				0.001
4-Nitrophenol	D	0.100																		0.151	0.134
Atrazine	H	0.163		0.006	0.005	0.005	0.005	0.003	0.003	0.003	0.003	0.003	0.006		0.004	0.005	0.006	0.006	0.005		0.005
Bifenthrin	I																				0.003
Boscalid	F	0.001	0.002												0.001					0.003	0.003
Bromacil	H										0.003				0.008	0.008		0.004		0.019	
Carbendazim	F																			0.015	0.013
Chlorothalonil (Daconil)	F	0.001																			
Chlorpropham	H	0.004	0.002																		
Chlorpyrifos	I		0.001																	0.002	
Dicamba	H	0.007																		0.031	0.017
Dichlobenil	H	0.037	0.019	0.009	0.007	0.017	0.013	0.005	X	0.005	0.003	0.009	0.005		0.004	0.004	0.011	0.006		0.046	0.270
Dinotefuran	I	0.008																			
Dithiopyr	H	0.007	0.007	0.003	0.002	0.003	0.002	0.002	0.002						0.005		0.002			0.004	0.006
Diuron	H	0.015					0.005										0.008			21.70	2.650
Eptam	H					0.002	0.002			0.002										0.004	0.002
Ethoprop	I		0.004																	0.015	0.026
Fipronil	I	0.004	0.002		0.002	0.005									0.005					0.007	0.013
Fipronil disulfenyl	D																			0.002	0.003
Fipronil sulfide	D	0.001																		0.001	
Fipronil sulfone	D	0.003	0.002	0.002		0.003	0.002								0.006					0.004	0.007
Flumioxazin	H																			0.162	0.325
gamma-Cyhalothrin	I																				0.002
Hexazinone	H														0.004					0.005	
Imazapic	H	0.014																			0.022
Imazapyr	H	0.009	0.008	0.013	0.021	0.022	0.025	0.023	0.022	0.032	0.034	0.028	0.026		0.028	0.022	0.014	0.024	0.021	0.077	0.011
Inpyrfluxam	F																			0.013	
Isoxaben	H	0.004	0.005																		0.005
MCPA	H																			0.072	
MCPP	H																			0.032	
Metolachlor	H	0.002	0.005			0.001											0.002	0.001		0.017	0.015
Metribuzin	H																			0.004	
N,N-Diethyl-m-toluamide (DEET)	IR	0.012	0.016			0.041					0.011				0.448	0.022		X		0.091	0.143
Oxadiazon	H																				0.008
Pendimethalin	H	0.042	0.015	0.005	0.003	0.004	0.011	0.003	0.003	0.002	0.004	0.002	0.002				0.004			0.014	0.082
Pentachlorophenol	WP	0.018																		0.021	0.037
Piperonyl butoxide (PBO)	Sy																			0.009	0.009
Proflumicarb	H		0.018																		
Prometon	H		0.003												0.003					0.005	0.003
Propiconazole	F	0.215	0.173	0.048	0.021	0.019	0.018	0.016	0.013	0.015	0.017										0.041
Simazine	H	0.053	0.121	0.013	0.005	0.007	0.009						0.006			0.011	0.008	0.007	0.005	0.076	0.122
Sulfentrazone	H	0.006	0.003	0.005	0.004	0.005	0.007	0.006		0.006		0.006			0.007	0.009	0.004	0.003	0.004	0.019	0.012
Tebuthiuron	H					0.004	0.006									0.005	0.005			0.069	0.037
Treflan (Trifluralin)	H	0.003	0.004	0.003		0.002	0.002	0.002												0.009	0.010
Triclopyr	H	0.113	0.107	0.064	0.059	0.077	0.051			0.043						0.023				0.197	0.558
Suspended sediment concentration		45	15	13	10	10	10	9	9	8	8	8	7		5	3	4	5	4	12	95
Streamflow (cubic ft/sec)		-	32.1	21.6	15.4	14.9	11.6	9.5	8.2	7.2	6.3	4.9	4.6		3.7	2.9	3.8	3.4	3.7	9.5	28.2
Precipitation (total in/week)†		0.00	0.00	0.51	0.00	0.91	0.09	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.16	0.84	0.00	0.00	1.00	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. The "X" signifies data rejected by failing laboratory quality assurance performance measures.

 Current-use exceedance
 DDT/degrade exceedance
 Detection
 No criteria

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

† Washington State University AgWeatherNet station: Vancouver (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 five of the 19 site visits (26%). Water quality at the Burnt Bridge Creek site is shown below (Figure 15).

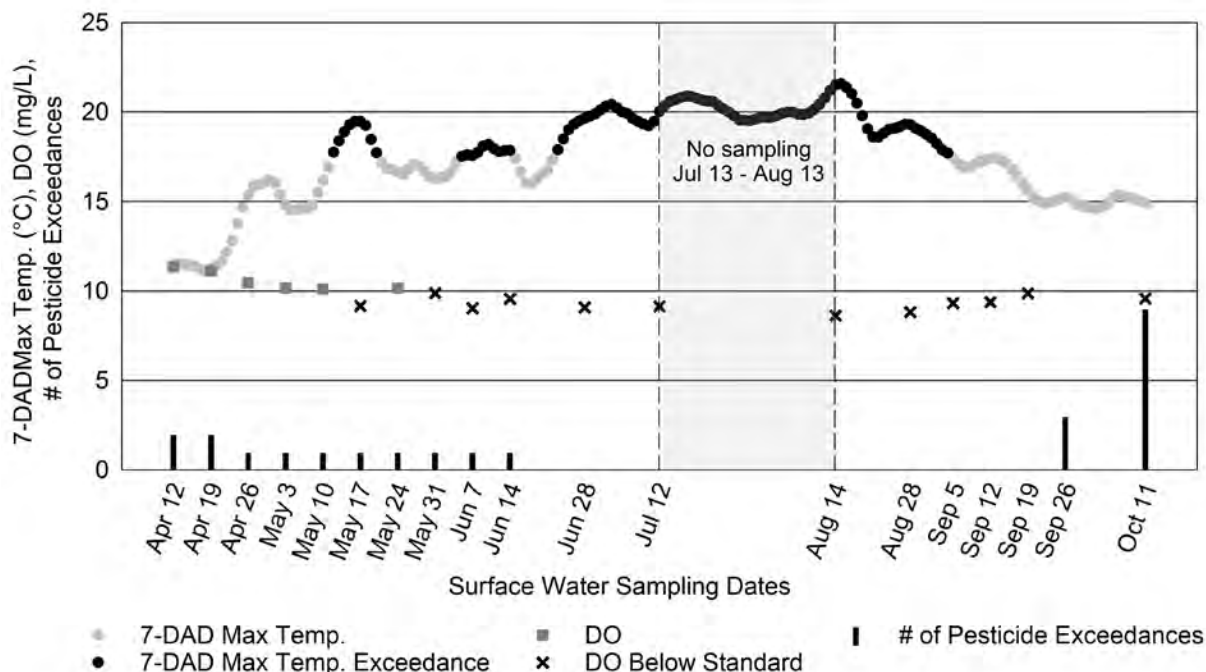


Figure 15 – Burnt Bridge Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.42 to 8.09 with an average of 7.93. DO measurements ranged from 8.62 mg/L to 11.36 mg/L with an average of 9.71 mg/L. More than half (67%) of the DO measurements did not meet the state water quality standard, with 12 measurements falling below 10 mg/L. Five of the DO measurements that did not meet the standard coincided with one or nine pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 93 days throughout the sampling season, occurring intermittently from May 12 through September 4. Pesticide exceedances coincided with 7-DADMax temperature exceedances at three site visits.

Burnt Bridge Creek has been designated as a freshwater habitat for salmonid spawning, rearing, and migration (WAC 2024d). Historically, this urban creek has been one of the least healthy streams in Clark County, often exceeding the total maximum daily loads for DO and temperature in certain reaches of the creek above WSDA's 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 such as diuron.

Indian Slough

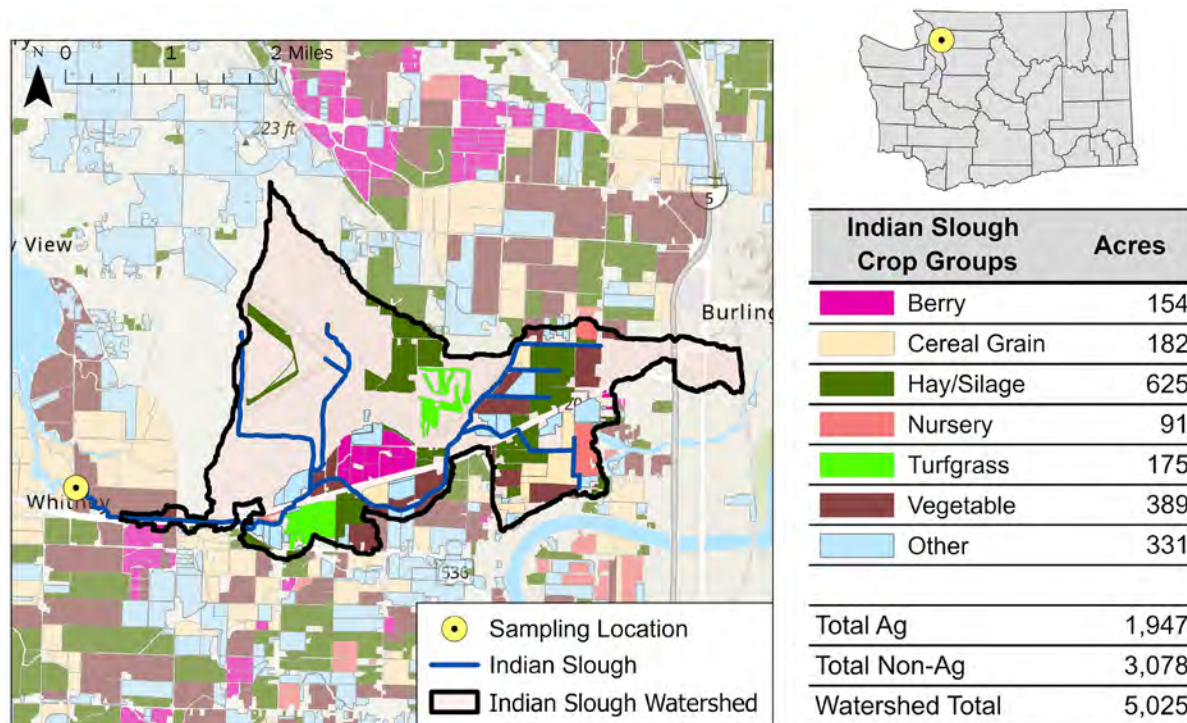


Figure 16 – Map of Indian Slough and its drainage area with associated sampling location and crop groups identified

In 2006, NRAS started sampling the Indian Slough watershed, 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: 48.4506°, longitude: -122.4650°) (Figure 16, Figure 17).

Indian Slough water drains directly into Puget Sound. Agricultural irrigation and precipitation events generally influence streamflow in the slough. WDFW has documented the presence of coho, fall Chinook, fall chum, and pink salmon, as well as winter steelhead trout within the reach of slough that encompasses the Indian Slough site (WDFW 2024). 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.

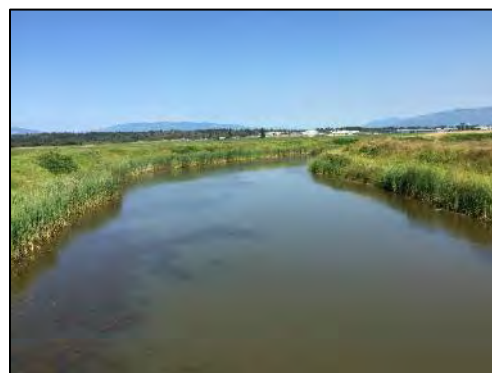


Figure 17 – Indian Slough upstream view

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 grass hay, potatoes, blueberries, wheat, and brassicas. The 'Other' crop group category consists mostly of fallow fields, pastures, 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 2023.

- NRAS tested for 150 unique pesticides in Indian Slough.
- There were 380 total pesticide detections from six different use categories: 24 types of herbicides, 3 insecticides, 9 fungicides, 1 legacy, and 6 degradates.
- Pesticides were detected at all 17 sampling events.
- Up to 32 pesticides were detected at the same time.
- Of the total pesticide detections, 10 were above WSDA's assessment criteria (Table 11).
 - All the detections of 4,4'-DDD, a legacy degradate of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Indian Slough watershed POCs were diuron, fipronil, and imidacloprid. Below, each POC detected is compared to toxicity test reference values.

- All detections of diuron and fipronil did not exceed any assessment criteria at this site in 2023, however, they were still considered watershed POCs because of detections that have exceeded criteria in recent years.
- There were no detections of imidacloprid at this site in 2023, however, it was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Indian Slough monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{11, 12}

Month		Mar	Apr					May					Jun				Jul		
Day of the Month	Use*	27	3	10	18	24	2	9	16	22	31	6	13	20	27	3	11	18	
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.005	0.009													
2,4-D	H				0.077	0.124		0.243	0.054	0.051		0.090	0.039		0.072				
2,6-Dichlorobenzamide	D	0.149	0.121	0.140	0.152	0.146	0.122	0.146	0.116	0.083	0.090	0.077	0.058	0.055	0.090	0.058	0.027	0.022	
2-Hydroxyatrazine	D	0.015	0.011	0.016	0.011	0.068	0.017	0.018	0.021	0.024	0.026	0.048	0.043	0.046	0.047	0.054	0.040	0.070	
4,4'-DDD	L	0.001		<0.001	0.001	0.001		<0.001	<0.001	<0.001		0.001	<0.001			<0.001			
Atrazine	H					0.003							0.002						
Azoxystrobin	F	0.026	0.187	0.139	0.067	0.106	0.119	0.173	0.059	0.025	0.014	0.014	0.035	0.015	0.011	0.013	0.012		
Bentazon	H	0.036	0.042	0.059	0.051	0.049	0.049		0.022	0.016	0.012	0.013			0.010				
Boscalid	F	0.036	0.014	0.012	0.012	0.010	0.012	0.016	0.013	0.011	0.013	0.013	0.012	0.010	0.012	0.012	0.009	0.009	
Bromacil	H	0.010	0.013	0.010	0.010	0.012	0.010	0.010	0.011	0.006	0.010	0.013	0.008	0.007	0.011	0.009			
Carbendazim	F	0.034	0.009		0.177	0.015					0.006								
Chlorantraniliprole	I	0.016																	
Chlorpropham	H	0.013	0.084	0.092	0.056	0.117	0.041	0.073	0.026	0.003				0.002					
Dicamba	H				0.010			0.119	0.004										
Dichlobenil	H	0.024	0.009	0.006	0.077	0.035	0.009	0.013	✗	0.002	✗	0.002	0.002	0.002	0.003				
Difenoconazole	F		0.010																
Diuron	H	0.011	0.006		0.010	0.011			0.005		0.004								
Eptam	H		0.002	0.002	0.002	0.021	0.011	0.007	0.014	0.008	0.005	0.004	0.004	0.003	0.005	0.004			
Fipronil	I	0.004	0.002	0.002	0.003	0.002		0.002											
Fipronil sulfide	D	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001		0.002		0.001	
Fipronil sulfone	D	0.003			0.002	0.002		0.002	0.002			0.002	0.002			0.003			
Fludioxonil	F	0.041	0.164	0.085	0.052	0.073	0.074	0.131	0.073	0.055	0.029	0.027	0.026	0.031	0.013	0.020	0.031	0.038	
Flumioxazin	H					0.038			✗	✗	✗	✗	✗	✗				✗	
Hexazinone	H	0.011	0.013	0.012	0.015	0.011	0.018	0.015	0.017	0.014	0.015	0.014	0.011	0.011	0.014	0.014	0.006		
Imazapyr	H	0.708	1.860	2.130	3.940	5.430	2.000	3.400	0.536	0.099	0.062	0.072	1.020	0.838	0.341	0.198	0.046	0.066	
Indaziflam	H				0.009	0.016			0.003										
Inpyrfluxam	F										0.090			✗					
Metalaxyl	F	0.021	0.011		0.018	0.020			0.008										
Metolachlor	H	0.011	0.006	0.004	0.005	0.006	0.005	0.012	0.004	0.007	0.010	0.016	0.021	0.006	0.007	0.004	0.003	0.003	
Metribuzin	H	0.003										0.006	0.006						
Norflurazon	H	0.079	0.015	0.009	0.024	0.016	0.005	0.006		0.005	0.005		0.016	0.004	0.004	0.004			
Prometon	H	0.005	0.004		0.028	0.006		0.002							0.009	0.004			
Propiconazole	F	0.059	0.011		0.030	0.052	0.017	0.018	0.027	0.011	0.015	0.013	0.033		0.017	0.021		0.010	
Pyrimethanil	F														0.017				
Simazine	H	0.062	0.016	0.010	0.007														
Sulfentrazone	H	0.047	0.041	0.038	0.039	0.036	0.051	0.042	0.041	0.122	0.045	0.029	0.063	0.028	0.035	0.032	0.012	0.012	
Sulfometuron-methyl	H							0.012											
Tebuthiuron	H	0.043	0.055	0.057	0.036	0.034	0.054	0.049	0.058	0.050	0.052	0.062	0.044	0.033	0.050	0.042	0.029	0.033	
Terbacil	H		0.017	0.015			0.012	0.011	0.014	0.016	0.013	0.014	0.011	0.010	0.012	0.008			
Tetrahydrophthalimide	D						0.001				0.023		0.003						
Thiamethoxam	I	0.016	0.011	0.011	0.013	0.010			0.013	0.009	0.011		0.010						
Treflan (Trifluralin)	H	0.002																	
Triclopyr	H				0.045	0.094	0.034	0.057							0.021				
Suspended sediment concentration		9	10	13	7	9	9	11	16	17	8	11	8	38	8	4	30	36	
Streamflow (cubic ft/sec)		33.9	25.8	22.8	40.8	53.6	4.5	19.0	31.0	9.5	17.7	8.4	16.1	2.9	7.5	4.8	18.4	1.1	
Precipitation (total in/week)†		1.13	0.07	0.23	0.56	0.51	0.03	0.58	0.00	0.00	0.00	0.00	0.50	0.12	0.12	0.00	0.00	0.00	

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

DDT/degrade exceedance Detection No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, 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 10 of the 17 site visits (59%). Water quality at the Indian Slough site is shown below (Figure 18 and Figure 19).

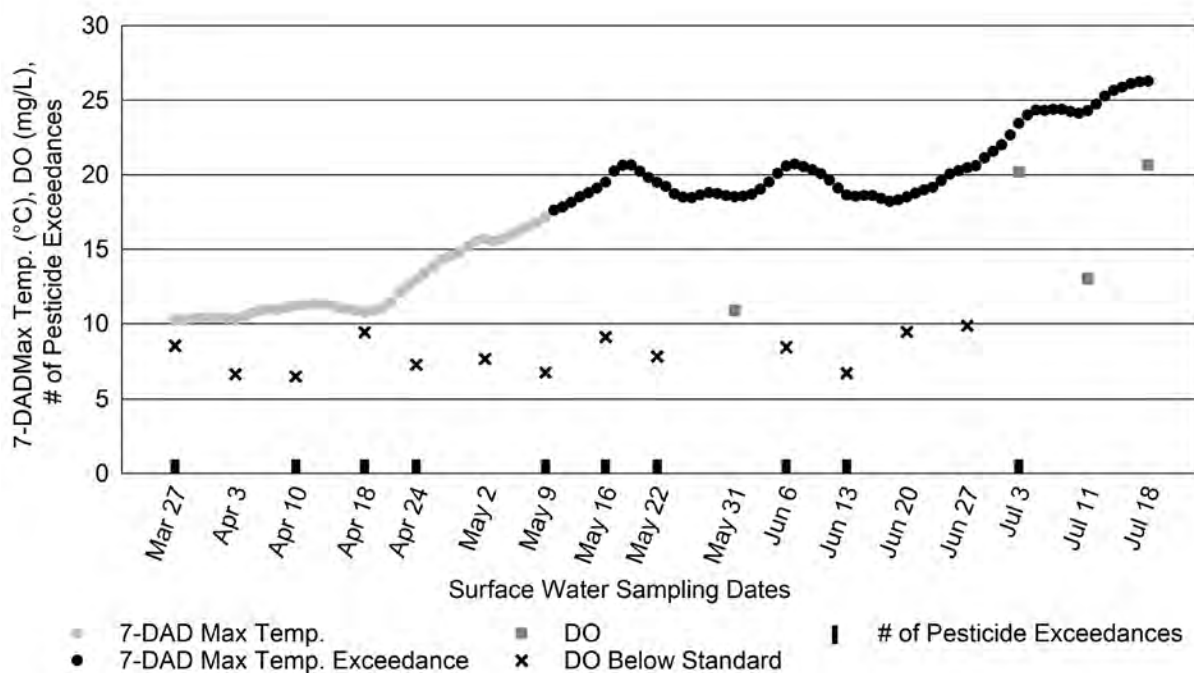


Figure 18 – Indian Slough water quality measurements and exceedances of assessment criteria

DO measurements ranged from 6.51 mg/L to 20.67 mg/L with an average of 9.95 mg/L. More than three-quarters (76%) of the DO measurements did not meet the state water quality standard, with 13 measurements falling below 10 mg/L. Nine of the DO measurements that did not meet the state water quality standard coincided with one pesticide exceedance. The 7-DADMax temperature exceeded the standard of 17.5°C on 70 days throughout the sampling season, from May 10 through July 18. Pesticide exceedances coincided with 7-DADMax temperature exceedances at five site visits.

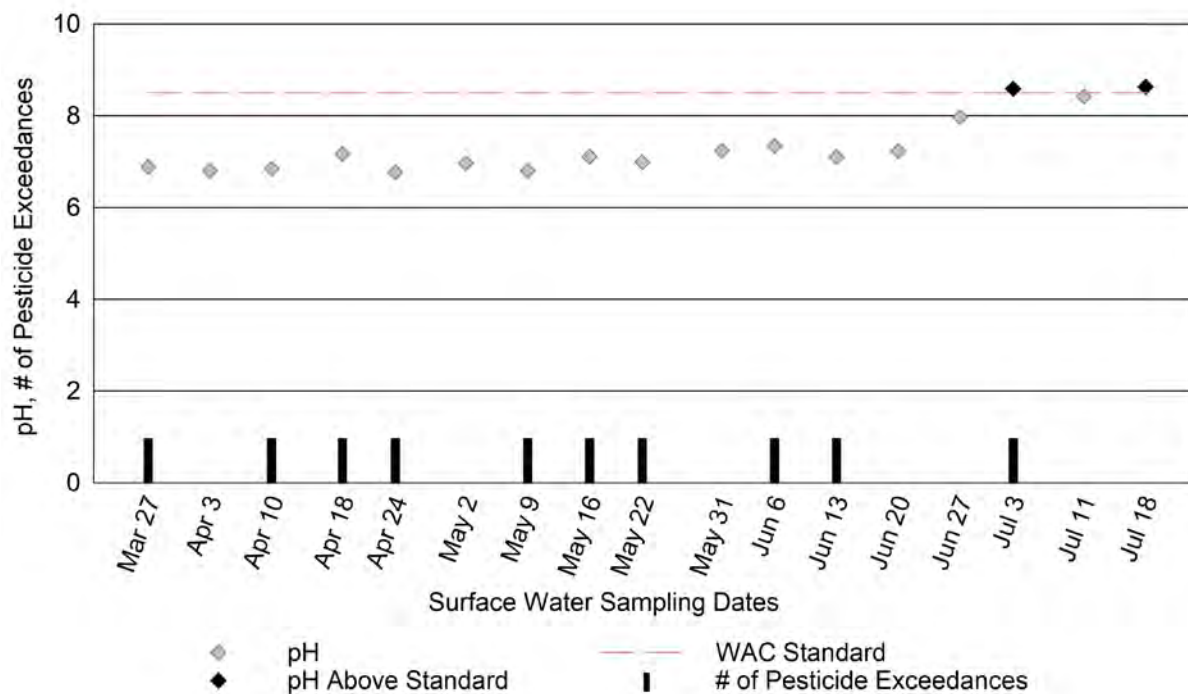


Figure 19 – Indian Slough pH measurements and exceedances of assessment criteria

The pH measurements ranged from 6.77 to 8.63 with an average of 7.34. Less than a quarter (12%) of these measurements exceeded the state water quality standard; two measurements were above 8.50. One of the pH exceedances coincided with one pesticide exceedance (Figure 19). Pesticide exceedance overlapped with both pH and 7-DADMax temperature exceedances on July 3rd.

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 a habitat for salmonid spawning, rearing, and migration, but is also used as a corridor by migrating waterfowl (WAC 2024d). NRAS will continue to monitor this drainage because of its representative regional land use.

Juanita Creek

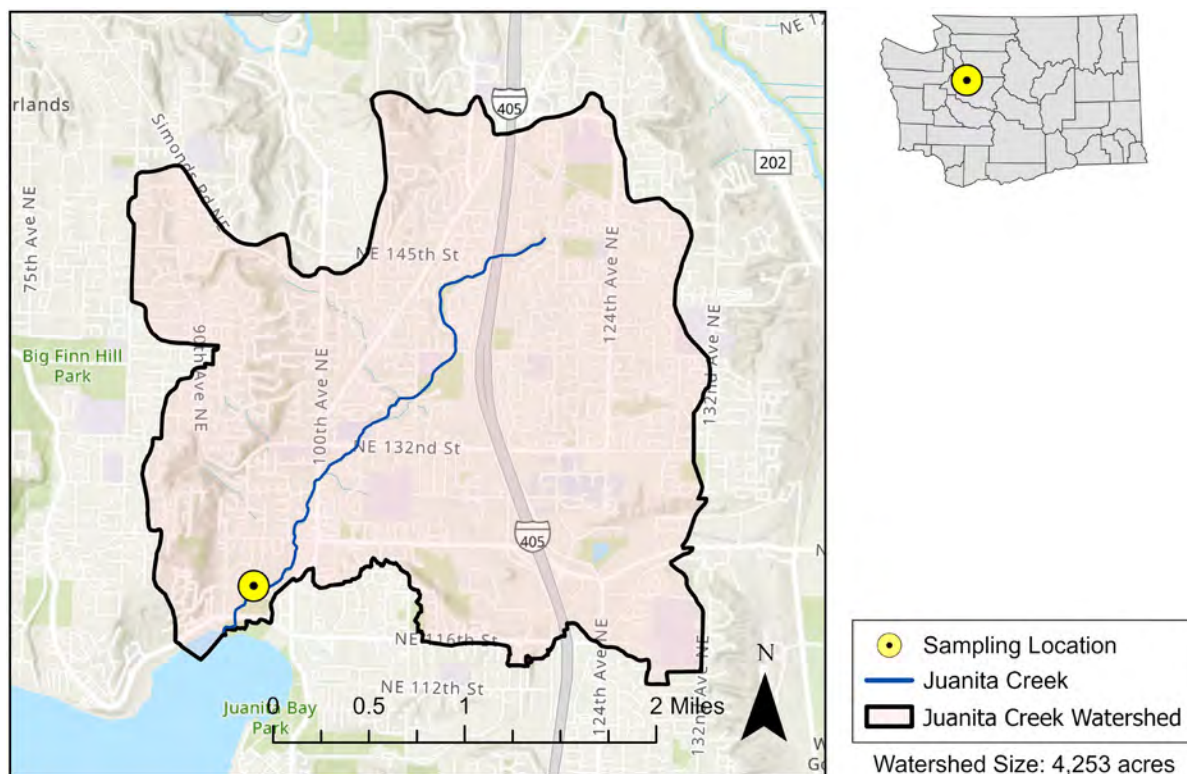


Figure 20 – Map of Juanita Creek and its drainage area with associated sampling location and crop groups identified

In 2020, NRAS started monitoring the Juanita watershed in King County. Juanita Creek flows roughly 5 miles through Kirkland, Washington. The Juanita monitoring site is located just downstream of an open-bottom culvert where an ephemeral tributary also drains alongside NE 120th Street (latitude: 47.7077°, longitude: -122.2148°). Within the Juanita drainage area, the land use is predominantly residential (Figure 20, Figure 21). This site was one of two urban sites NRAS monitored in 2023.

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 coho, fall Chinook, and sockeye salmon, as well as cutthroat trout and winter steelhead trout within the reach of creek that encompasses the monitoring site (WDFW 2024). 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 2023.

- NRAS tested for 150 unique pesticides in Juanita Creek.

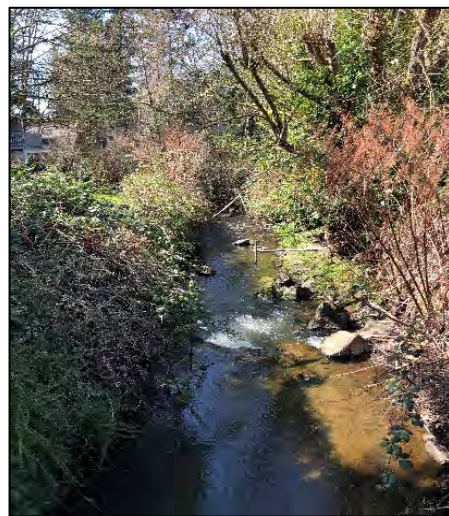


Figure 21 – Juanita Creek downstream view

- There were 189 total pesticide detections from eight different use categories: 20 types of herbicides, 3 insecticides, 4 fungicides, 1 legacy, 7 degradates, 1 antimicrobial, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 14 sampling events.
- Up to 26 pesticides were detected at the same time.
- Of the total pesticide detections, two were above WSDA's assessment criteria (Table 12).
 - The single detection of 4,4'-DDD, a legacy degradate of DDT, approached NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Juanita Creek watershed POCs were diuron and fipronil. Below, each POC detected is compared to toxicity test reference values.

- Of the six detections of fipronil, one detection exceeded the invertebrate NOAEC (0.011 µg/L).
- All detections of diuron did not exceed any assessment criteria at this site in 2023, however, the herbicide was still considered a watershed POC because of detections that have exceeded criteria in recent years.

The Juanita Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{13, 14}

Month		Mar	Apr	May	Jun		Aug	Sep	Oct						
Day of the Month	Use*	27	10	24	8	23	5	21	7	21	5	18	2	17	30
2,4-D	H		0.049	0.051		0.057		0.031	0.175			0.041			
2,6-Dichlorobenzamide	D	0.260	0.210	0.260	0.277	0.297	0.274	0.258	0.325	0.288	0.259	0.278	0.260	0.236	0.273
2-Hydroxyatrazine	D			0.005				0.027			0.022		0.029	0.031	0.017
4,4'-DDD	L				<0.001										
4-Nitrophenol	D								0.248			0.082			
Aminocyclopyrachlor	H	0.227													
Atrazine	H	0.004		0.003	0.003				0.003	0.003	0.004	0.004	0.004	0.004	
Boscalid	F	<0.001	0.003			0.002			0.005				0.001	0.001	0.001
Bromacil	H		0.011												
Carbendazim	F		0.008						0.023					0.010	
Dicamba	H								0.013			0.013			
Dichlobenil	H	0.012	0.025	0.020	0.022	0.010	0.005	0.011	0.020	0.002	0.009	0.009	0.016	0.022	0.006
Dithiopyr	H	0.002	0.008	0.004	0.002			0.002	0.006				0.002	0.003	
Diuron	H		0.013	0.007					0.022				0.008	0.012	
Eptam	H														0.002
Ethoprop	I								0.002						
Fipronil	I	0.002	0.004	0.003					0.048				0.003	0.003	
Fipronil disulfenyl	D								0.002					0.002	
Fipronil sulfide	D	0.001	0.002	0.002	0.001	0.001		0.001	0.003	0.001			0.002	0.002	0.001
Fipronil sulfone	D		0.003	0.002	0.002			0.002	0.009				0.003	0.004	
Fludioxonil	F								0.005						
Hexazinone	H		0.002			0.002								0.002	
Imazapyr	H	0.014	0.010	0.079	0.056	0.023	0.015	0.044	0.025				0.047	0.052	0.024
MCPP	H								0.029						
N,N-Diethyl-m-toluamide (DEET)	IR		0.020	0.013				0.072	0.210			0.030	0.015	0.021	
Norflurazon	H					0.004									
Phosmet (Imidan)	I		0.002											0.004	
Piperonyl butoxide (PBO)	Sy								0.026					0.005	
Prometon	H	0.005	0.006	0.005	0.004	0.005	0.003	0.004		0.006	0.005	0.005	0.004	0.005	0.005
Prometryn	H					0.009			0.003					0.002	0.001
Simetryn	H					0.016									0.021
Sulfentrazone	H	0.002	0.005	0.004	0.004	0.008	0.005	0.008	0.089			0.010	0.005		
Tebuthiuron	H	0.009	0.008	0.008		0.009		0.009	0.017	0.005	0.008	0.007	0.010	0.015	0.009
Tetrahydrophthalimide	D									0.002					
Treflan (Trifluralin)	H	0.002	0.002											0.009	
Triadimefon	F		0.003			0.004			0.008						0.003
Triclopyr	H			0.043	0.043	0.039			0.091						
Triclosan	A								0.046						
Suspended sediment concentration		2	9	3	3	3	2	9	9	3	7	2	4	4	1
Streamflow (cubic ft/sec)		7.1	22.9	10.8	4.9	2.7	1.9	3.8	3.6	1.9	2.5	2.4	2.9	6.1	1.7
Precipitation (total in/week)†		1.10	1.47	0.83	0.75	0.23	0.00	0.96	0.00	0.00	0.28	0.03	3.92	1.51	0.80

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

 Current-use exceedance DDT/degrade exceedance Detection No criteria

* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, L: Legacy; 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 one of the 14 site visits (7%). Water quality at the Juanita Creek site is shown below (Figure 22).

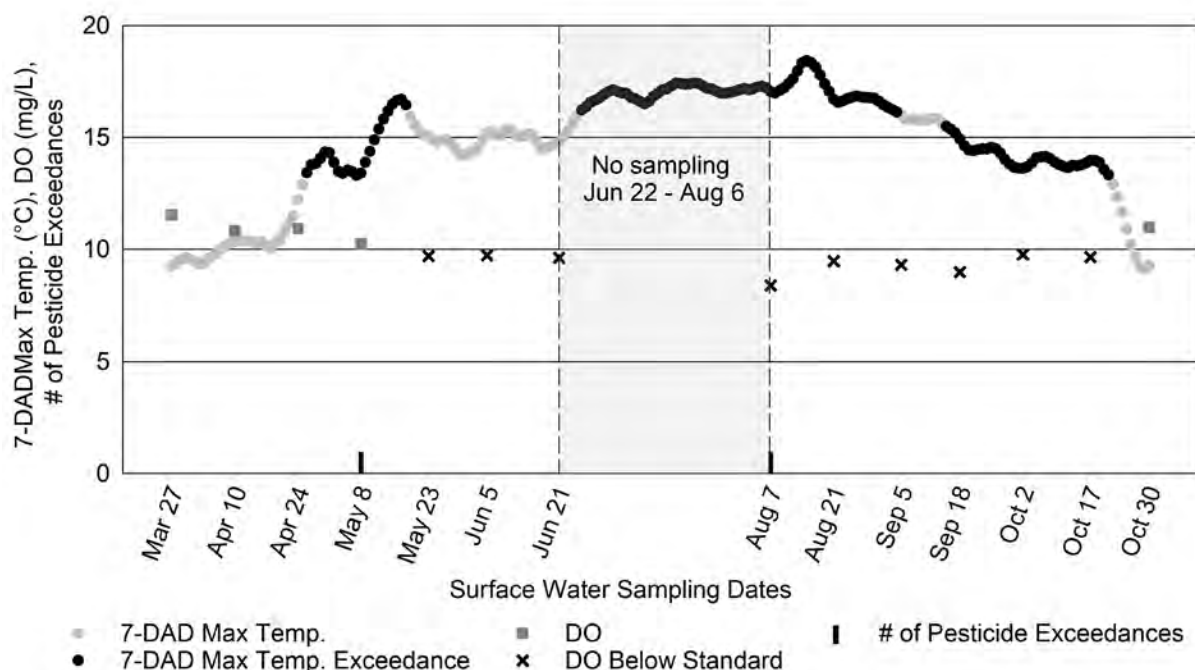


Figure 22 – Juanita Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.11 to 7.59 with an average of 7.46. DO measurements ranged from 8.38 mg/L to 11.55 mg/L with an average of 9.94 mg/L. Almost three-quarters (64%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L. One of the DO measurements that did not meet the standard coincided with one pesticide exceedance.

Juanita Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods of the sampling season. From September 15 through May 15, the 7-DADMax temperature should remain below 13°C, while May 16 through September 14 should remain below 16°C (Ecology 2011; WAC 2024b). The 7-DADMax temperature exceeded the standard on 131 days, occurring intermittently from April 26 through October 21. Pesticide exceedances coincided with 7-DADMax temperature exceedances at two site visits.

Juanita Creek has been designated as a freshwater body that provides a core summer habitat for salmonids by the WAC (WAC 2024d). NRAS has decided to discontinue sampling at this drainage starting 2024. The decision was made due to a combination of low pesticide detection frequency and exceedances.

Central Region

Ahtanum Creek

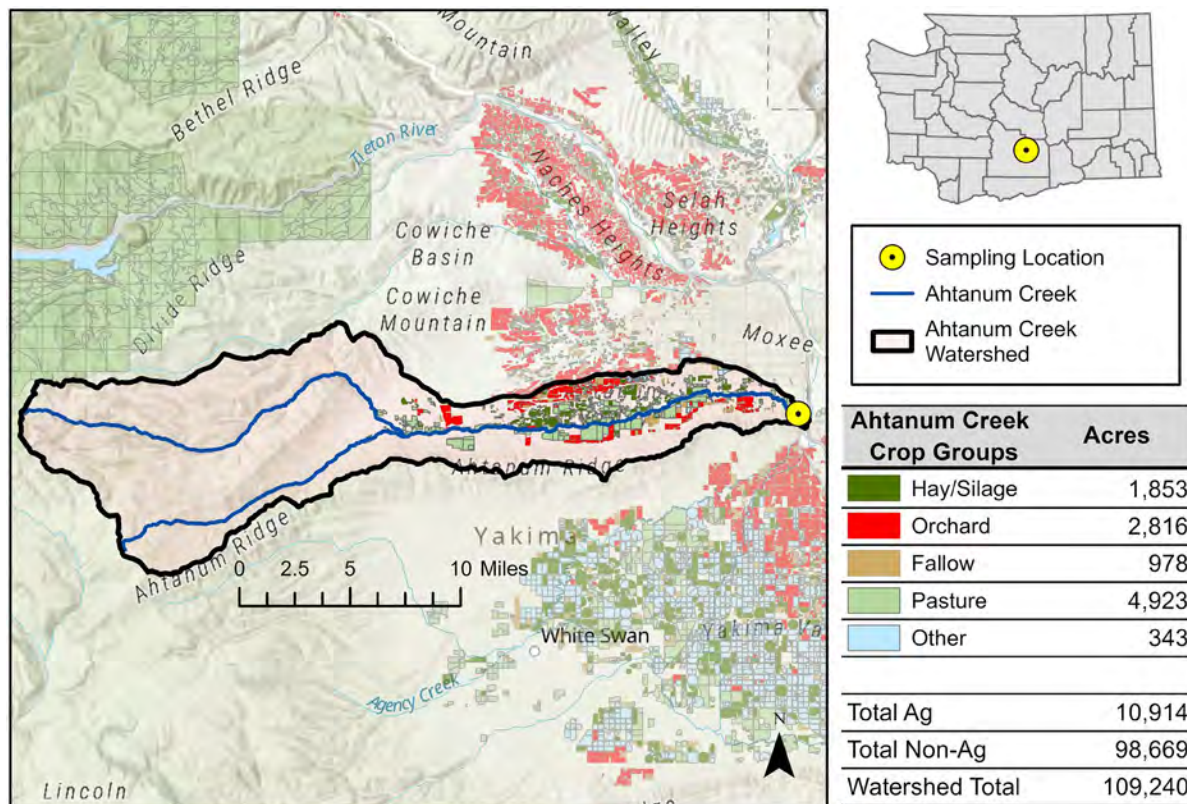


Figure 23 – Map of Ahtanum Creek and its drainage area with associated sampling location and crop groups identified

In 2021, NRAS started monitoring the Ahtanum watershed in Yakima County. 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 23, Figure 24). WSDA selected this watershed for its diverse agricultural land uses and large watershed drainage area. WDFW has documented the presence of coho and spring Chinook salmon, as well as bull trout, rainbow trout, and summer steelhead trout within the Ahtanum Creek watershed (WDFW 2024). 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 features low, flat-lying terrain, where the majority of agricultural activities take place.

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 from the creek is utilized for irrigating surrounding crops. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. Land use within the Ahtanum Creek drainage area predominantly consists of pastures, apples, and grass hay. The 'Other' crop group category includes a golf course, hops, oats, and other assorted small acreage crops (Figure 23).



Figure 24 – Ahtanum Creek downstream view

Below is a brief overview of pesticide findings in Ahtanum Creek in 2023.

- NRAS tested for 150 unique pesticides in Ahtanum Creek.
- There were 24 total pesticide detections from five different use categories: 4 types of herbicides, 2 insecticides, 2 fungicides, 1 degradate, and 1 insect repellent.
- Pesticides were detected in 12 out of 14 sampling events.
- Up to six pesticides were detected at the same time.
- The Ahtanum Creek watershed POCs were chlorpyrifos and gamma-cyhalothrin. Below, each POC detected is compared to toxicity test reference values.
- There were no detections of chlorpyrifos and gamma-cyhalothrin at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.

The Ahtanum Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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^{15, 16}

Month		Mar	Apr	May	Jun	Jul	Aug	Sep							
Day of the Month	Use*	27	10	24	8	22	5	20	5	17	31	14	28	11	26
2,6-Dichlorobenzamide	D				0.003	0.002	0.002	0.002	0.003		0.003	0.003	0.003		0.002
Boscalid	F				0.002										0.002
Bromacil	H				0.005										
Diazinon	I	0.002		0.007											
Malathion	I			0.005											
Metolachlor	H				<0.001										
N,N-Diethyl-m-toluamide (DEET)	IR								0.013						
Pendimethalin	H		0.003												
Sulfentrazone	H		0.007	0.004	0.006		0.005	0.006							
Triadimefon	F				0.002										
Suspended Sediment Concentration		10	111	51	83	66	25	15	14	5	4	3	6	3	6
Streamflow (cubic ft/sec)		91.5	133.0	115.0	354.0	348.0	109.0	38.4	19.7	13.1	11.8	8.5	13.1	11.3	21.9
Precipitation (total in/week)†		0.16	0.41	0.25	0.01	0.03	0.00	0.04	0.00	0.17	0.00	0.00	0.25	0.04	0.18

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

 Detection

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

† 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. Water quality at the Ahtanum Creek site is shown below (Figure 25).

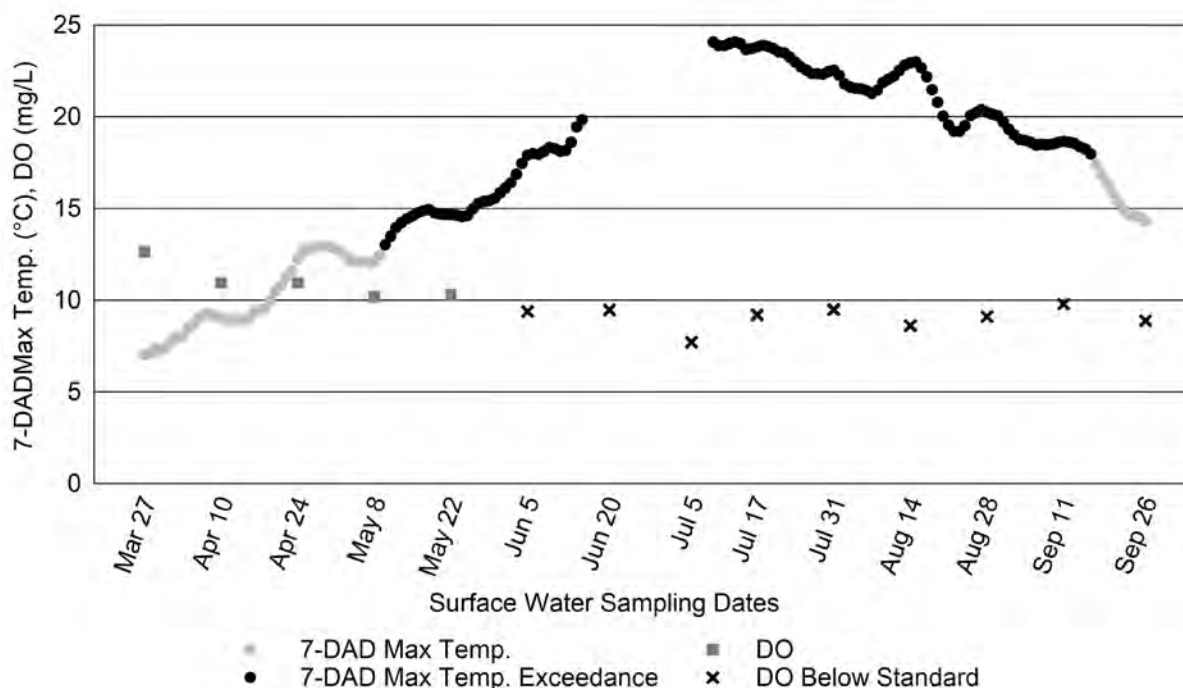


Figure 25 – Ahtanum Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.11 to 8.07, with an average of 7.68. DO measurements ranged from 7.71 mg/L to 12.64 mg/L with an average of 9.76 mg/L. More than half (64%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L.

Ahtanum Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods of the sampling season. From February 15 through June 15, the 7-DADMax temperature should remain below 13°C, while June 16 through the end of the sampling season should remain below 17.5°C (Ecology 2011; WAC 2024b). The 7-DADMax temperature exceeded the standard of 13°C on 37 days from May 10 through June 15 and exceeded the standard of 17.5°C on 71 days throughout the sampling season, from July 8 through September 16. Data is unavailable for the period from June 15 through July 3rd because the temperature sensor went missing. Temperature sensors may be taken by visitors to the stream or displaced by high flow events. This sampling site is in close proximity to a park and the sensor went missing during a period in which there were no high flow events, so it is suspected that the sensor was found and removed.

Ahtanum Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2024d). NRAS has decided to discontinue sampling at this drainage starting in 2024. The decision was made due to a combination of low pesticide detection frequency and exceedances.

Brender Creek

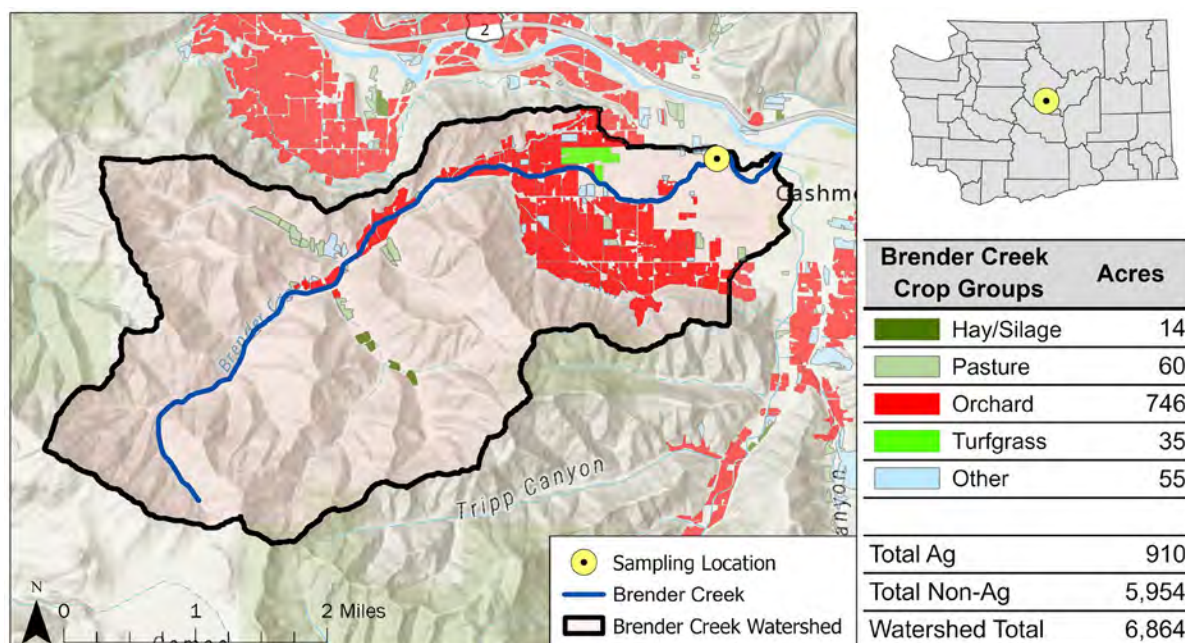


Figure 26 - Map of Brender Creek and its drainage area with associated sampling location and crop groups identified

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

The Brender site is located in Cashmere, on the upstream side of the culvert at Evergreen Drive (latitude: 47.5211°, longitude: -120.4863°) (Figure 26, Figure 27). 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, rainbow trout, and summer steelhead within the lower reaches of the creek (WDFW 2024).



Figure 27 - Brender Creek upstream view

The watershed terrain in the upper three-quarters is mountainous with a transition into low-lying, flat terrain in the bottom quarter where tree fruit crops are plentiful. Agricultural land use is predominately pears, apples, pastures, and cherries. The 'Other' crop group category mostly consists of fallow fields and other assorted small acreage crops (Figure 26).

Below is a brief overview of the pesticide findings in Brender Creek in 2023.

- NRAS tested for 137 unique pesticides in Brender Creek.
- There were 261 total pesticide detections from six different use categories: 11 types of herbicides, 15 insecticides, 3 fungicides, 4 legacies, 1 degradate, and 1 insect repellent.
- Pesticides were detected at all 25 sampling events.
- Up to 19 pesticides were detected at the same time.

- Of the total pesticide detections, 81 were above WSDA's assessment criteria (Table 14).
 - DDT and its degradates account for 74 of these exceedances. The 25 detections of 4,4'-DDD, 25 detections of 4,4'-DDE, and 24 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Brender Creek watershed POCs were carbaryl, chlorpyrifos, fenpropathrin, gamma-cyhalothrin, imidacloprid, malathion, and tolfenpyrad. Below, each POC detected is compared to toxicity test reference values.

- The single detection of fenpropathrin exceeded the invertebrate LC₅₀ (0.00305 µg/L) and invertebrate NOAEC (0.0015 µg/L).
- The two detections of gamma-cyhalothrin approached or exceeded the invertebrate NOAEC (0.00193 µg/L) and also exceeded the invertebrate LC₅₀ (0.00008 µg/L).
- The two detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the nine detections of malathion, one approached the invertebrate LC₅₀ (0.098 µg/L) and invertebrate NOAEC (0.06 µg/L).
- The two detections of chlorpyrifos did not exceed any assessment criteria at this site in 2023, however, this insecticide was still considered a watershed POC because of detections that have exceeded criteria in recent years.
- There were no detections of carbaryl at the site in 2023, however, carbaryl was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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, 1 degradate, and 1 wood preservative removed from testing at this site as a result of infrequent historic detections.

Table 14 – Brender Creek pesticide calendar, µg/L ^{17, 18}

Month		Mar			Apr			May					Jun				Jul				Aug					Sep
Day of the Month	Use*	21	28	4	11	18	25	2	9	16	23	30	6	13	20	27	5	11	18	25	1	8	15	21	29	5
2,6-Dichlorobenzamide	D	0.008	0.007	0.006				0.005	0.005		0.004	0.005	0.004		0.004	0.005	0.004	0.005	0.006	0.005	0.005	0.007	0.007	0.007	0.007	0.006
4,4'-DDD	L	0.002	0.003	0.004	0.011	0.004	0.003	0.008	0.010	0.008	0.003	0.005	0.003	0.006	0.006	0.005	0.005	0.012	0.009	0.011	0.005	0.007	0.004	0.010	0.009	0.004
4,4'-DDE	L	0.008	0.011	0.017	0.031	0.009	0.009	0.027	0.034	0.029	0.019	0.018	0.015	0.031	0.024	0.026	0.022	0.051	0.035	0.062	0.027	0.033	0.017	0.049	0.040	0.023
4,4'-DDT	L	0.002	0.002	0.004	0.003	0.002	0.002	0.006	0.008	0.007	0.008	0.004	0.005	0.012	0.007	0.009	0.005	0.011	0.009	0.019	0.009	0.018		0.014	0.008	0.007
Acetamiprid	I						0.011	0.014		0.012		0.015	0.016												0.008	
Atrazine	H																			0.004						
Bifenazate	I																0.031			0.019						
Boscalid	F	0.023	0.018	0.016	0.036	0.013	0.013	0.023	0.013	0.011	0.008	0.009	0.022	0.005	0.007	0.004	0.005	0.008	0.004	0.005	0.003	0.015	0.014	0.007	0.006	0.003
Bromacil	H	0.006	0.007	0.009	0.006	0.010	0.014	0.007	0.006	0.007	0.007	0.008	0.007	0.005			0.005		0.005	0.005			0.013		0.006	0.005
Carbendazim	F																							0.019	0.032	0.017
Chlorpyrifos	I							0.002		0.001																
Diazinon	I				0.033	0.002	0.004	0.005																		
Dichlobenil	H	0.002	0.002																							
Etoxazole	I												0.028	0.028	0.029	0.026	0.024	0.004	0.010	0.003		0.008				
Fenarimol	L																			0.004						
Fenbutatin oxide	I																		0.007							
Fenpropathrin	I																	0.006								
gamma-Cyhalothrin	I				0.001																	0.002				
Hexazinone	H							0.007			0.002									0.001						
Imidacloprid	I								0.067										0.027							
Kelthane	I																			0.019						
Malathion	I	0.003	0.035	0.009	0.022	0.006	0.003	0.007	0.005					0.005												
Metolachlor	H																			<0.001						
N,N-Diethyl-m-toluamide (DEET)	IR																0.016		0.045					0.010		
Norflurazon	H	0.014	0.013	0.012	0.009	0.009	0.010	0.007	0.006	0.006	0.006	0.009	0.006	0.009	0.006	0.006	0.010	0.008	0.017	0.010	0.007	0.015	0.023	0.010	0.010	0.006
Pendimethalin	H				0.003			0.005	0.003	0.006	0.003	0.003	0.003	0.007	0.006	0.004	0.003	0.007		0.005				0.004	0.003	
Prometryn	H																			0.003						
Pyridaben	I																	0.001				0.002				
Pyriproxyfen	I				0.002																					
Simazine	H	0.007											0.007	0.004	0.010	0.004	0.017	0.009	0.007	0.006		0.005		0.009	0.009	
Sulfentrazone	H						0.004	0.003		0.005			0.005			0.005			0.003	0.003						
Thiamethoxam	I													0.012			0.058	0.019	0.005							
Tolfenpyrad	I													0.014												
Treflan (Trifluralin)	H				0.002																					
Triadimefon	F																			0.002						
Suspended sediment concentration		5	11	18	49	10	8	34	43	37	24	25	22	54	35	41	38	106	59	115	30	53	15	59	49	26
Streamflow (cubic ft/sec)		0.8	1.0	0.9	2.4	2.3	1.4	4.3	5.5	4.6	2.7	-	2.0	4.9	-	3.9	-	4.7	4.6	3.1	3.7	6.5	1.9	-	5.0	-
Precipitation (total in/week)†		0.09	0.00	0.02	0.35	0.04	0.09	0.09	0.09	0.03	0.02	0.04	0.00	0.18	0.00	0.00	0.00	0.15	0.00	0.00	0.00	1.04	0.00	0.00	0.00	0.48

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. The "X" signifies data rejected by failing laboratory 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: 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 13 of the 25 site visits (52%). Water quality at the Brender site is shown below (Figure 28).

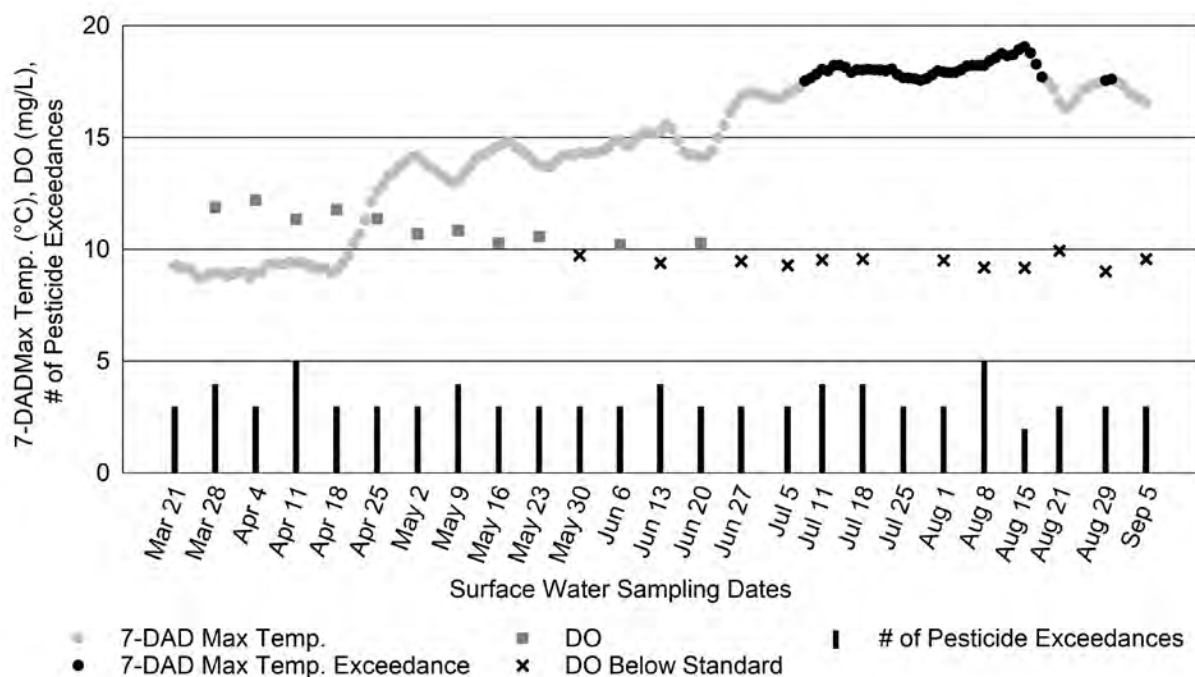


Figure 28 – Brender Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.55 to 8.37 with an average of 8.00. DO measurements ranged from 9.01 mg/L to 12.20 mg/L with an average of 10.21 mg/L. More than half (52%) of the DO measurements did not meet the state water quality standard, with 12 measurements falling below 10 mg/L. All 12 of the DO measurements that did not meet the standard coincided with two, three, four, or five pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 44 days throughout the sampling season, occurring intermittently from July 8 through August 30. Pesticide exceedances coincided with 7-DADMax temperature exceedances at seven site visits.

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 2024d). 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

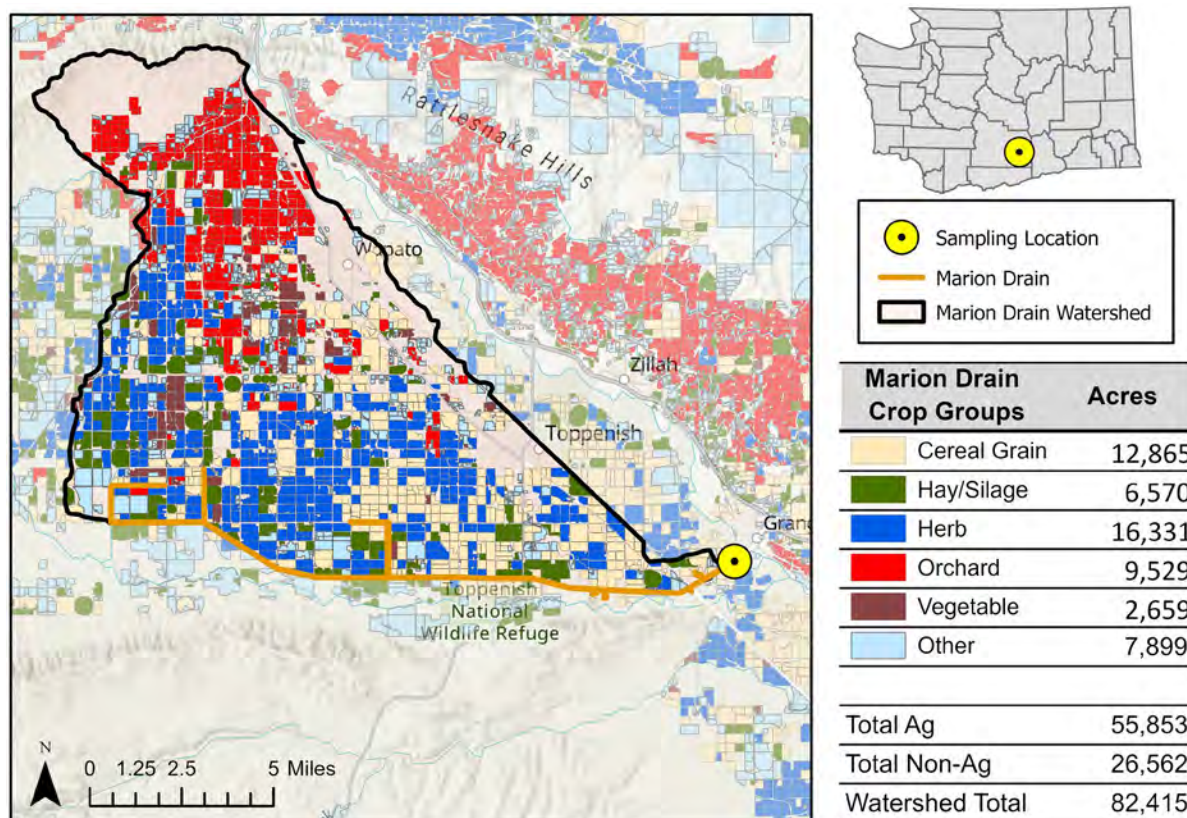


Figure 29 – Map of Marion Drain and its drainage area with associated sampling location and crop groups identified

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

Marion Drain flows directly into the Yakima River. Melting snowpack, precipitation events, groundwater, and irrigation generally influence flows in the stream. There is often heavy aquatic vegetation growing in the streambed of this site. WDFW and the Yakama Nation have documented coho and fall Chinook salmon, as well as rainbow trout and summer steelhead trout within the Marion Drain watershed (WDFW 2024).

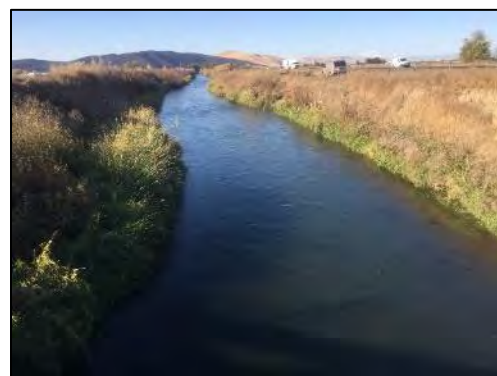


Figure 30 – Marion Drain upstream view

The Marion Drain watershed has a 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, alfalfa, mint, and wheat. The 'Other' crop group category consists of nurseries and other assorted small acreage crops (Figure 29).

Below is a brief overview of the pesticide findings in Marion Drain in 2023.

- NRAS tested for 150 unique pesticides in Marion Drain.
- There were 524 total pesticide detections from six different use categories: 23 types of herbicides, 10 insecticides, 6 fungicides, 1 legacy, 5 degradates, and 1 insect repellent.
- Pesticides were detected at all 32 sampling events.
- Up to 25 pesticides were detected at the same time.
- Of the total pesticide detections, 23 were above WSDA's assessment criteria (Table 15).
 - All three detections of 4,4'-DDD approached NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Marion Drain watershed POCs were bifenthrin, chlorpyrifos, clothianidin, and gamma-cyhalothrin. Below, each POC detected is compared to toxicity test reference values.

- Of the two detections of chlorpyrifos, one approached invertebrate LC₅₀ (0.0138 µg/L) and exceeded the invertebrate NOAEC (0.005 µg/L).
- Of the 30 detections of clothianidin, 17 approached the invertebrate NOAEC and two exceeded the invertebrate NOAEC (0.05 µg/L).
- There were no detections of bifenthrin or gamma-cyhalothrin at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.
- The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 monitoring season and a visual comparison to the WSDA assessment criteria (Table 15). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 15 – Marion Drain pesticide calendar, µg/L ^{19, 20}

Month		Mar			Apr			May					Jun				Jul		Aug				Sep				Oct					Nov		
Day of the Month	Use*	20	27	3	10	17	24	1	8	15	22	30	5	12	20	26	5	31	7	14	21	28	5	11	18	26	2	9	16	23	30	6	13	
2,4-D	H					0.046		0.069	0.060	0.045	0.062	0.036	0.054	0.047	0.036	0.055	0.050	0.051	0.069	0.036	0.055	0.056	0.036	0.030		0.035								
2,6-Dichlorobenzamide	D							0.001	0.002		0.002	0.002	0.002		0.002		0.001	0.001	0.002		0.002	0.002	0.002		0.002		0.003	0.002	0.001	-	0.002	0.002		
2-Hydroxyatrazine	D											0.006		0.013	0.019	0.021	0.016	0.023																
4,4'-DDD	L				<0.001	<0.001				<0.001																								
Acephate	I										0.162	0.197	0.086	0.036	0.023		0.013	0.038	0.183	0.248											-			
Aminocyclopyrachlor	H																															2.690		
Atrazine	H	0.008	0.008	0.010	0.004	0.005	0.005		0.025	0.018	0.012	0.011	0.013	0.008	0.012	0.009	0.009	0.010	0.009	0.008	0.007	0.008	0.009	0.008	0.008	0.009	0.008	0.009	0.010	-	0.010	0.009	0.010	
Azoxystrobin	F								0.009	0.011	0.010							0.007	0.012															
Bentazon	H									0.020	0.008		0.013	0.022	0.009	0.023	0.015	0.133	0.204	0.072	0.046	0.047	0.045	0.046	0.094	0.067	0.053	0.070	0.062	0.051	0.044	0.045	0.047	
Boscalid	F		<0.001		0.003	0.004	0.003	0.003	0.004	0.005	0.003	0.004	0.006	0.004	0.004	0.005	0.006	0.004	0.009	0.006	0.006	0.006	0.004	0.004	0.005	0.004	0.005	0.004	0.003	-	0.002	0.002	0.002	
Bromacil	H				0.007	0.014	0.009	0.019	0.017	0.019	0.010	0.007	0.009	0.006	0.005		0.004	0.007	0.011		0.007	0.009			0.009	0.005	0.006	0.004		-				
Bromoxynil	H								0.040	0.028	0.025																							
Chlorantraniliprole	I	0.015	0.015								0.014	0.014	0.015	0.014			0.013	0.017	0.020	0.018	0.036	0.019		0.028	0.029	0.025	0.022	0.022	0.030		0.021	0.024	0.026	
Chlorpropham	H															0.001															-			
Chlorpyrifos	I				0.011	0.001																									-			
Clothianidin	I	0.036	0.034	0.035	0.010	0.011	0.009		0.010	0.013	0.015	0.017	0.019	0.018	0.030	0.028	0.026	0.029	0.033	0.022		0.042	0.042	0.028	0.028	0.038	0.043	0.065	0.086	0.026	0.035	0.024	0.027	
Desethylatrazine	D	0.007	0.008	0.007																									0.008		0.007	0.007	0.007	
Diazinon	I				0.005	0.009	0.004	0.001										0.031	0.007	0.006	0.005	0.002								-	0.007	0.007	0.007	
Dicamba	H							0.005	0.005	0.005	0.018			0.010	0.009	0.015	0.010	0.012	0.051		0.025			0.011							-			
Dichlobenil	H				0.002	0.001									0.010	0.009	0.015	0.010	0.012	0.051		0.025			0.011					-				
Dimethoate	I								0.005	0.004					0.004																-			
Diuron	H				0.007	0.016	0.005	0.025	0.014	0.013	0.009	0.005	0.005	0.006																				
Eptam	H									0.003	0.002		0.002	0.003	0.004	0.002	0.002														-			
Ethoprop	I				0.002											0.002															-			
Fipronil sulfide	D					0.001																									-			
Fludioxonil	F				0.041	0.071	0.048	0.031	0.017	0.015	0.016	0.024	0.033	0.024	0.011	0.013	0.009	0.021	0.025	0.018	0.021	0.028	0.018	0.016	0.010	0.013	0.013	0.016	0.004	-				
Hexazinone	H							0.003		0.002	0.002				0.002															0.002	-	0.002		
Metalaxyl	F																	0.006													-			
Methamidophos	D											0.015	0.009	0.005					0.018	0.013														
Methoxyfenozide	I																			0.042	0.022	0.005		0.013	0.057	0.022	0.024	0.017	0.004					
Metolachlor	H					0.001					0.002	0.001	0.001	0.001	0.006	0.007	0.004	0.003	0.005	0.002		0.002	0.002	0.001	0.001	0.002					-			
Metribuzin	H					0.002			0.008		0.005																					-		
N,N-Diethyl-m-toluamide (DEET)	IR												0.021																		-			
Norflurazon	H	0.004	0.003	0.003	0.003	0.003	0.002	0.002		0.002		0.002						0.002	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.005	-	0.005	0.004	0.005	
Oxamyl	I										0.002			0.005	0.004							0.007			0.009	0.005								
Pendimethalin	H	0.003	0.015	0.013	0.018	0.009	0.007	0.011	0.044	0.041	0.045	0.025	0.031	0.020	0.007	0.007	0.005	0.006	0.005	0.004	0.005	0.004	0.002		0.003	0.002	0.003	0.003		-				
Prometon	H																			0.003		0.003	0.004						0.002	-				
Prometryn	H					0.002																									-			
Propiconazole	F											0.025	0.012																					
Pyrimethanil	F				0.007	0.020	0.013							0.011				0.009				0.014			0.015			0.022	0.006					
Simazine	H	0.009	0.009	0.012		0.008	0.005	0.033	0.030	0.024	0.016	0.013	0.009	0.006	0.013	0.006	0.005	0.008	0.009	0.009	0.010	0.012	0.006	0.007	0.007	0.007	0.007	0.006	0.008	-	0.010	0.010	0.011	
Sulfentrazone	H			0.006			0.005	0.004	0.014	0.037	0.032	0.005	0.012	0.006	0.013	0.010	0.009	0.009	0.037	0.029	0.015	0.015	0.010	0.010	0.015	0.016	0.018	0.021	0.021	-	0.021	0.019		
Terbacil	H								0.123	0.288	0.171	0.145	0.119	0.098	0.064	0.086	0.065	0.126	0.193	0.092	0.053	0.116	0.042	0.568	0.854	0.973	0.374	0.446	0.025	-	0.007	0.007	0.007	
Thiamethoxam	I	0.013	0.013	0.012						0.005		0.006	0.019	0.006	0.008		0.006	0.008			0.283	0.017	0.019	0.015	0.019	0.025	0.027	0.035	0.051	0.017	0.023	0.013	0.013	
Treflan (Trifluralin)	H				0.002				0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002														-				
Triclopyr	H										0.032																							
Suspended sediment concentration		19	17	16	78	81	34	23	17	6	53	7	5	6	2	4	3	4	3	3	3	16	12	2	2	1	8	4	16	12	12	13	11	
Streamflow (cubic ft/sec)		159.8	151.0	142.2	-	-	-	77.6	105.7	52.8	110.5	-	31.8	33.2	-	22.2	-	25.8	29.6	22.8	-	94.8	-	37.8	29.0	34.5	-	73.2	-	203.4	197.1	-	-	
Precipitation (total in/week)†		0.00	0.07	0.07	0.13	0.76	0.06	0.00	0.04	0.00	0.11	0.00	0.00	0.15	0.01	0.01	0.00	0.00	0.18	0.00	0.00	0.14	0.05	0.00	0.00	0.11	0.18	0.02	0.13	0.00	0.13	0.35	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. The "X" signifies data rejected by failing laboratory 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: 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 16 of the 32 site visits (50%). Water quality at the Marion Drain site is shown below (Figure 31 and Figure 32).

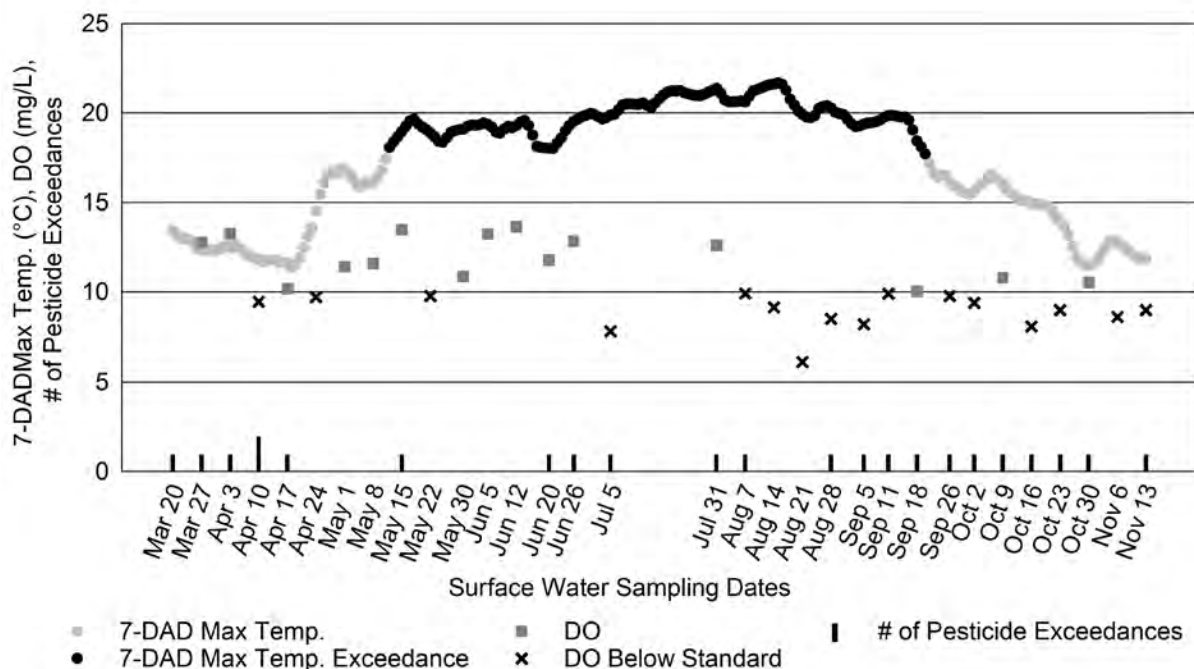


Figure 31 – Marion Drain water quality measurements and exceedances of assessment criteria

DO measurements ranged from 6.12 mg/L to 13.64 mg/L with an average of 10.36 mg/L. More than half (52%) of the DO measurements did not meet the state water quality standard, with 16 measurements falling below 10 mg/L. Eleven of the DO measurements that did not meet the standard coincided with one or two pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 132 days throughout the sampling season, from May 12 through September 20. Pesticide exceedances coincided with 7-DADMax temperature exceedances at 10 site visits.

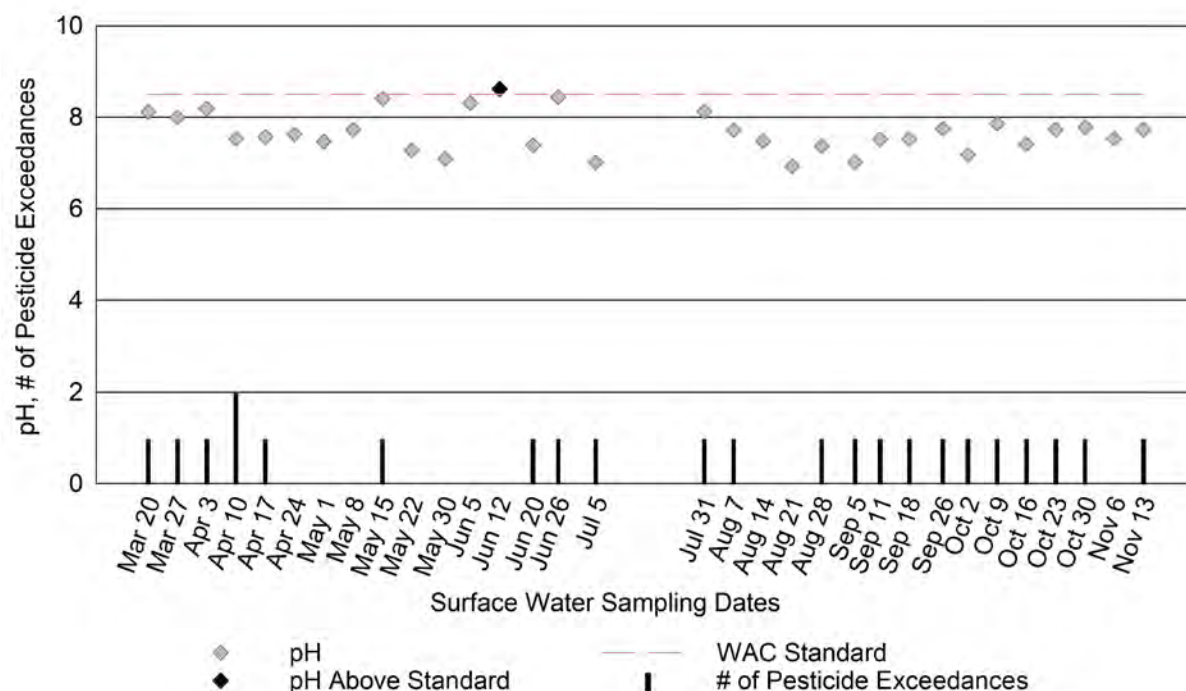


Figure 32 – Marion Drain pH measurements and exceedances of assessment criteria

The pH measurements ranged from 6.93 to 8.62 with an average of 7.67. Less than a quarter (3%) of these measurements exceeded the state water quality standard; one measurement was above 8.50 (Figure 32).

Marion Drain has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2024d). Staff at the site frequently observed juvenile fish of an unknown species. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Mission Creek

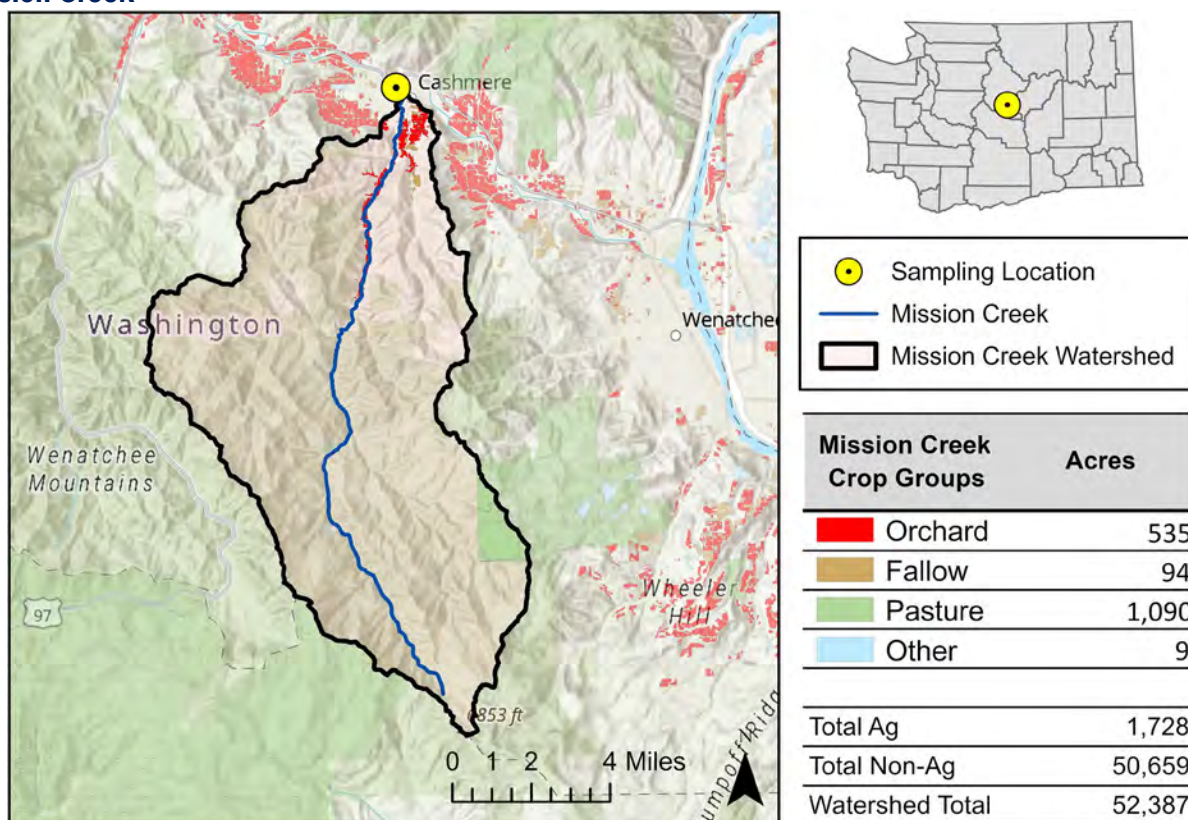


Figure 33 – Map of Mission Creek and its drainage area with associated sampling location and crop groups identified

In 2007, NRAS started monitoring the Mission Creek watershed in Chelan County. The site is located in Cashmere, approximately 10 meters downstream from the bridge crossing of Sunset Highway where the Department of Ecology manages a stream gauging station (latitude: 47.5212°, longitude: -120.4760°) (Figure 33, Figure 34). 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 (Figure 33).

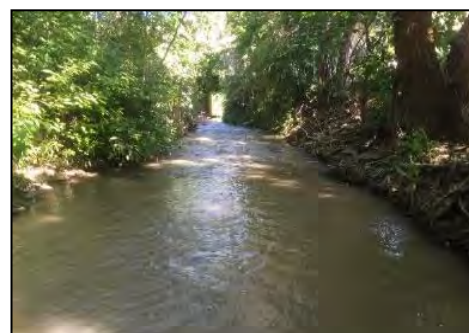


Figure 34 – Mission Creek downstream view

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 salmon, as well as rainbow and summer steelhead trout (WDFW 2024). Staff at the site frequently observed juvenile fish of unknown species.

Below is a brief overview of the pesticide findings in Mission Creek in 2023.

- NRAS tested for 137 unique pesticides.
- There were 52 total pesticide detections from five different use categories: 5 types of herbicides, 4 insecticides, 1 fungicide, 3 legacies, and 1 degradate.
- Pesticides were detected at all 12 sampling events.

- Up to 10 pesticides were detected at the same time.
- Of the total pesticide detections, 15 were above WSDA's assessment criteria (Table 16).
 - DDT and its degradates account for 14 of these exceedances. Two detections of 4,4'-DDD, six detections of 4,4'-DDE, and three detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - The 4,4'-DDD detections on April 18, May 9, and May 30 approached NRWQC and WAC chronic criteria.
 - The single detection of pyridaben approached the invertebrate NOAEC (0.044 µg/L) and exceeded the Endangered Species Level of Concern (0.036 µg/L)

The Mission Creek watershed POCs were chlorpyrifos, gamma-cyhalothrin, malathion, pyriproxyfen and tolfenpyrad. Below, each POC detected is compared to toxicity test reference values.

- The four detections of malathion and two detections of pyriproxyfen did not exceed any assessment criteria at this site in 2023, however, these insecticides were still considered watershed POCs because of detections that have exceeded criteria in recent years.
- There were no detections of chlorpyrifos, gamma-cyhalothrin, or tolfenpyrad at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.
- The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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. There were 11 herbicides, 1 degradate, and 1 wood preservative removed from testing at this site as a result of infrequent historic detections.

Table 16 – Mission Creek pesticide calendar, µg/L ^{21, 22}

Month		Mar		Apr				May				Jun	
Day of the Month	Use*	21	28	4	11	18	25	2	9	16	23	30	6
2,6-Dichlorobenzamide	D			0.003	X	X		0.003	0.002	X	0.004	0.003	0.003
4,4'-DDD	L				0.002	<0.001		0.003	<0.001			<0.001	
4,4'-DDE	L	0.002			0.007		0.001	0.010	0.002			0.002	
4,4'-DDT	L				0.001			0.013	0.001				
Boscalid	F				0.002			0.003					0.004
Diazinon	I						0.002						
Eptam	H									0.002			
Hexazinone	H	0.002	0.003		0.005	0.007	0.010	0.022	0.009	0.005	0.005		
Malathion	I		0.003	0.003	0.013	0.017							
Metribuzin	H							0.003					
Norflurazon	H		0.001	0.002				0.002				0.002	0.003
Pendimethalin	H	0.003				0.002		0.002				0.003	0.200
Pyridaben	I							0.041					
Pyriproxyfen	I				0.007	0.003							
Suspended sediment concentration		95	33	20	280	47	121	648	121	74	27	167	55
Streamflow (cubic ft/sec)		37.0	40.7	39.1	122.0	74.8	101.0	-	105.0	85.8	61.4	29.9	22.2
Precipitation (total in/week)†		0.09	0.00	0.02	0.35	0.04	0.09	0.09	0.09	0.03	0.02	0.04	0.00

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

Current-use exceedance DDT/degradate exceedance Detection

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

† 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. 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 35).

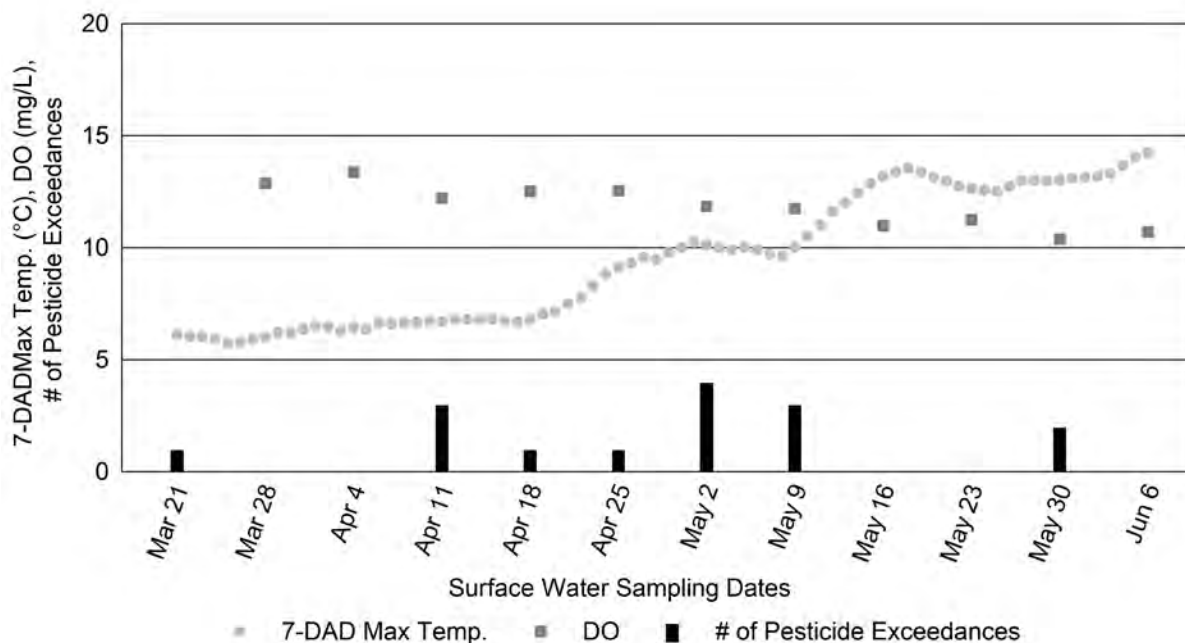


Figure 35 – Mission Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.84 to 8.44 with an average of 8.17. All DO measurements met the state water quality standard, ranging from 10.38 mg/L to 13.38 mg/L with an average of 11.86 mg/L. The 7-DADMax temperatures met the state water quality standard during the sampled period, consistently below 17.5°C.

Mission Creek provides a habitat for salmonid spawning, rearing, and migration (WAC 2024d). 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 malathion.

Snipes Creek

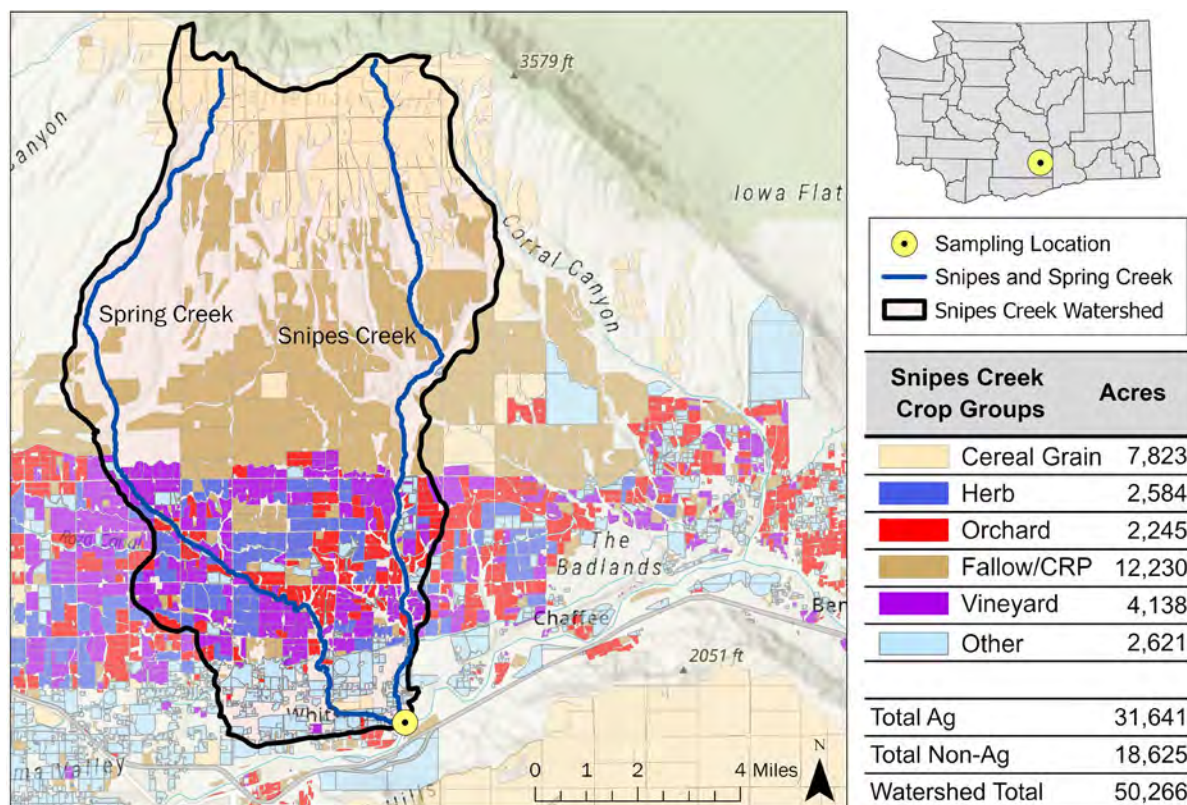


Figure 36 – Map of Snipes Creek and its drainage area with associated sampling location and crop groups identified

In 2016, NRAS started monitoring the Snipes Creek watershed in Benton County. A monitoring site within the Snipes Creek watershed on Spring Creek was sampled from 2003 to 2015. NRAS moved the monitoring site downstream in order to incorporate a larger watershed capture area. Currently, the site is located near Prosser, approximately 20 meters downstream from the confluence of Spring Creek and Snipes Creek (latitude: 46.2332°, longitude: -119.6774°) (Figure 36, Figure 37).

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 coho, fall Chinook, and spring Chinook salmon, as well as rainbow trout and summer steelhead trout within the reach of creek that encompasses the monitoring site (WDFW 2024). 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, flat-lying terrain where crop diversity increases substantially. The agricultural land use in Snipes Creek watershed is predominantly wheat, hops, wine and



Figure 37 – Snipes Creek upstream view with average streamflow

juice grapes, and apples. The 'Other' crop group category consists of hay, blueberries, nurseries, and other assorted small acreage crops (Figure 36).

Below is a brief overview of pesticide findings in Snipes Creek in 2023.

- NRAS tested for 150 unique pesticides in Snipes Creek.
- There were 289 total pesticide detections from five different use categories: 18 types of herbicides, 8 insecticides, 7 fungicides, 2 legacies, and 3 degradates.
- Pesticides were detected at all 21 sampling events.
- Up to 22 pesticides were detected at the same time.
- Of the total pesticide detections, 15 were above WSDA's assessment criteria (Table 17).
 - The four detections of 4,4'-DDD and four detections of 4,4'-DDE, legacy degradates of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Snipes Creek watershed POCs were chlorpyrifos, diazinon, diuron, fenvalerate, gamma-cyhalothrin, imidacloprid, and permethrin. Below, each POC detected is compared to toxicity test reference values.

- Of the 13 detections of diazinon, one approached the invertebrate LC₅₀ (0.21 µg/L).
- Of the 14 detections of diuron, four approached or exceeded the plant EC₅₀ (0.13 µg/L).
 - The detection on April 3 also approached the invertebrate NOAEC (0.83 µg/L).
- The two detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- There was no detection of chlorpyrifos, fenvalerate, gamma-cyhalothrin, or permethrin at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 ^{23, 24}

Month		Mar			Apr				May					Jun				Jul			Aug		Sep
Day of the Month	Use*	20	27	3	10	17	24	1	8	15	22	30	5	12	20	26	5	17	31	14	28	11	
1-(3,4-Dichlorophenyl)-3-methylurea	D		0.008	0.015		0.008	0.006		0.006	0.007		0.010											
2,4-D	H				0.045	0.067	0.052	0.049	0.077	0.144	0.051	0.089	0.177	0.063	0.097	0.141	0.052	0.047	0.072	0.046	0.034		
2,6-Dichlorobenzamide	D	0.021		0.005			0.006	0.005	0.004		0.005	0.004	0.005		0.005	0.006	0.007	0.023	0.004	0.006	0.006	0.013	
4,4'-DDD	L	<0.001							<0.001	<0.001							<0.001						
4,4'-DDE	L		0.001						0.002	0.002	0.002												
Atrazine	H	0.012	0.005	0.005	0.004	0.003	0.004	0.003	0.006	0.007	0.004	0.003	0.004	0.003	0.003	0.004	0.004	0.009	0.005	0.006	0.004	0.006	
Boscalid	F	0.003	0.007	0.005	0.003	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.006	0.006	0.005	0.006	0.009	0.007	0.004	0.005	0.005	0.004	
Bromacil	H	0.002	0.006	0.009	0.006	0.005	0.005	0.005	0.022	0.004	0.003			0.004	0.004		0.005	0.015	0.007	0.008			
Carbaryl	I									0.024													
Chlorantraniliprole	I	0.015									0.013							0.014					
Chlorothalonil (Daconil)	F																0.002						
Desethylatrazine	D	0.015																					
Diazinon	I		0.003	0.022	0.038	0.021	0.011	0.006	0.003				0.004	0.002				0.003	0.064	0.006	0.004		
Dicamba	H								0.011	0.009	0.010	0.011				0.008	0.007		0.008				
Dichlobenil	H	0.002	0.002		0.004	0.002		0.002															
Dimethoate	I								0.007	0.007					0.006	0.004							
Diuron	H		0.158	0.448	0.029	0.048	0.074	0.048	0.028	0.074	0.045	0.035	0.010	0.016	0.012	0.009							
Eptam	H				0.002				0.002	0.004	0.002	0.004	0.002	0.004	0.002	0.002							
Etiozazole	I															0.025							
Fludioxonil	F	0.012	0.033	0.028	0.026	0.015	0.030	0.017	0.006	0.013	0.012	0.013	0.025	0.018	0.031	0.033	0.023	0.039	0.049	0.044	0.035	0.014	
Hexazinone	H	0.001								0.002	0.002												
Imazapyr	H											0.004											
Imidacloprid	I												0.028	0.011									
Inpyrfluxam	F																			0.015			
Metalaxyl	F									0.038				0.006	0.007								
Methoxyfenozide	I	0.004																					
Metolachlor	H					<0.001			0.001	0.004	0.002	0.003	0.004	0.004	0.001	0.001	0.001	0.001	<0.001	<0.001		0.001	
Metribuzin	H								0.006	0.003	0.004												
Norflurazon	H	0.012	0.004	0.011	0.004	0.032	0.004	0.004	0.006	0.008	0.007	0.005	0.005	0.006	0.004	0.004	0.004	0.006	0.003	0.004	0.003	0.005	
Oxamyl	I										0.011												
Pendimethalin	H	0.004	0.028	0.049	0.038	0.035	0.015	0.011	0.014	0.009	0.009	0.008	0.004	0.004	0.003	0.003	0.003			0.015	0.016	0.005	
Pyrimethanil	F	0.006	0.017		0.008	0.012	0.010						0.015	0.010	0.011	0.017			0.017		0.025		
Simazine	H	0.007																0.006			0.007		
Sulfentrazone	H	0.003		0.003				0.004	0.007	0.008			0.005	0.005	0.005	0.005		0.008		0.011		0.004	
Terbacil	H				0.014																	0.007	
Treflan (Trifluralin)	H	0.002																					
Triclopyr	H								0.053	0.016	0.029	0.024											
Trifloxystrobin	F						0.005			0.003													
Suspended sediment concentration		2	56	19	19	22	26	37	52	57	88	36	26	60	76	51	25	5	15	20	19	6	
Streamflow (cubic ft/sec)		2.3	-	-	-	-	72.1	67.0	71.5	39.0	62.2	-	40.2	68.0	-	-	-	10.8	39.3	56.4	82.5	25.0	
Precipitation (total in/week)†		0.05	0.04	0.05	0.29	0.55	0.11	0.00	0.15	0.00	0.09	0.02	0.00	0.20	0.00	0.00	0.00	0.13	0.00	0.02	0.08	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. The "X" signifies data rejected by failing laboratory quality assurance performance measures.

Current-use exceedance
 DDT/degradate exceedance
 Detection
 No criteria

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

† Washington State University AgWeatherNet station: Roza.2, (latitude: 46.29°, longitude: -119.73°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at nine of the 21 site visits (43%). Water quality at the Snipes Creek site is shown below (Figure 38 and Figure 39).

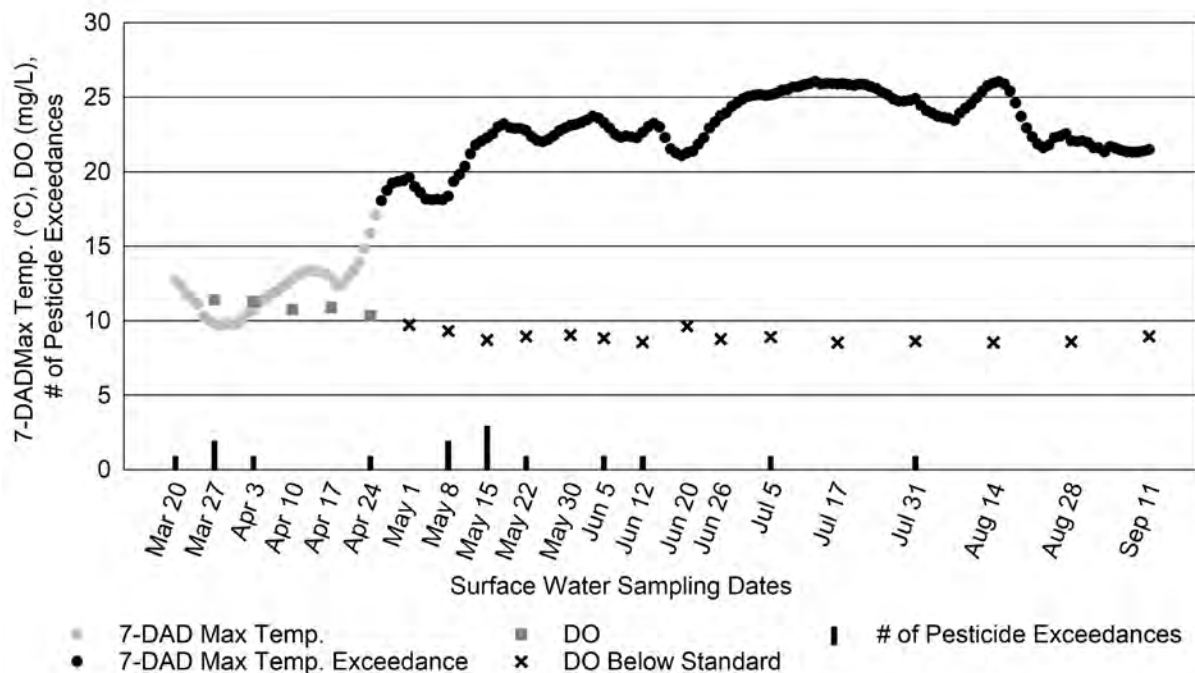


Figure 38 – Snipes Creek water quality measurements and exceedances of assessment criteria

DO measurements ranged from 8.53 mg/L to 11.41 mg/L with an average of 9.41 mg/L. Three-quarters (75%) of the DO measurements did not meet the state water quality standard, with 15 measurements falling below 10 mg/L. Seven of the DO measurements that did not meet the standard coincided with one, two, or three pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5 °C on 139 days throughout the sampling season, from April 26 through September 11. The DO measurements that did not meet the standard and 7-DADMax temperature exceedances at the same seven site visits coincided with one, two, or three pesticide exceedances.

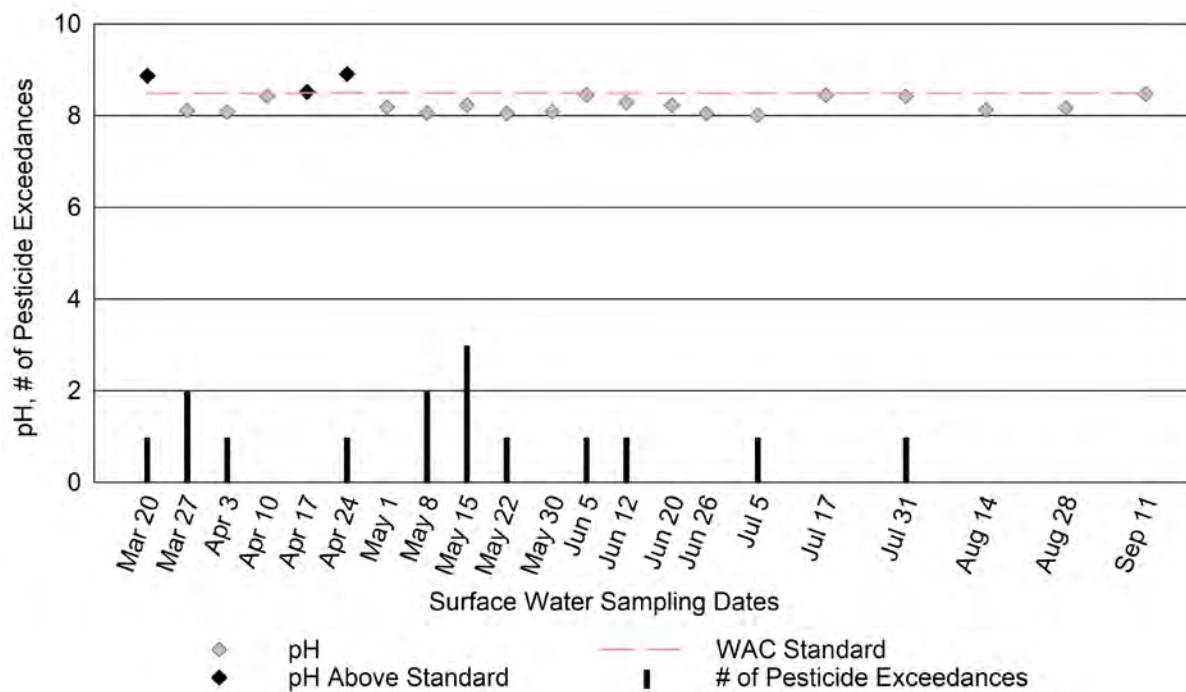


Figure 39 – Snipes Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 8.01 to 8.91 with an average of 8.30. Almost a quarter (14%) of these measurements exceeded the state water quality standard; three measurements were above 8.50. Two of the pH exceedances coincided with one pesticide exceedance (Figure 39).

Snipes Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2024d). 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 diuron and imidacloprid.

Stemilt Creek

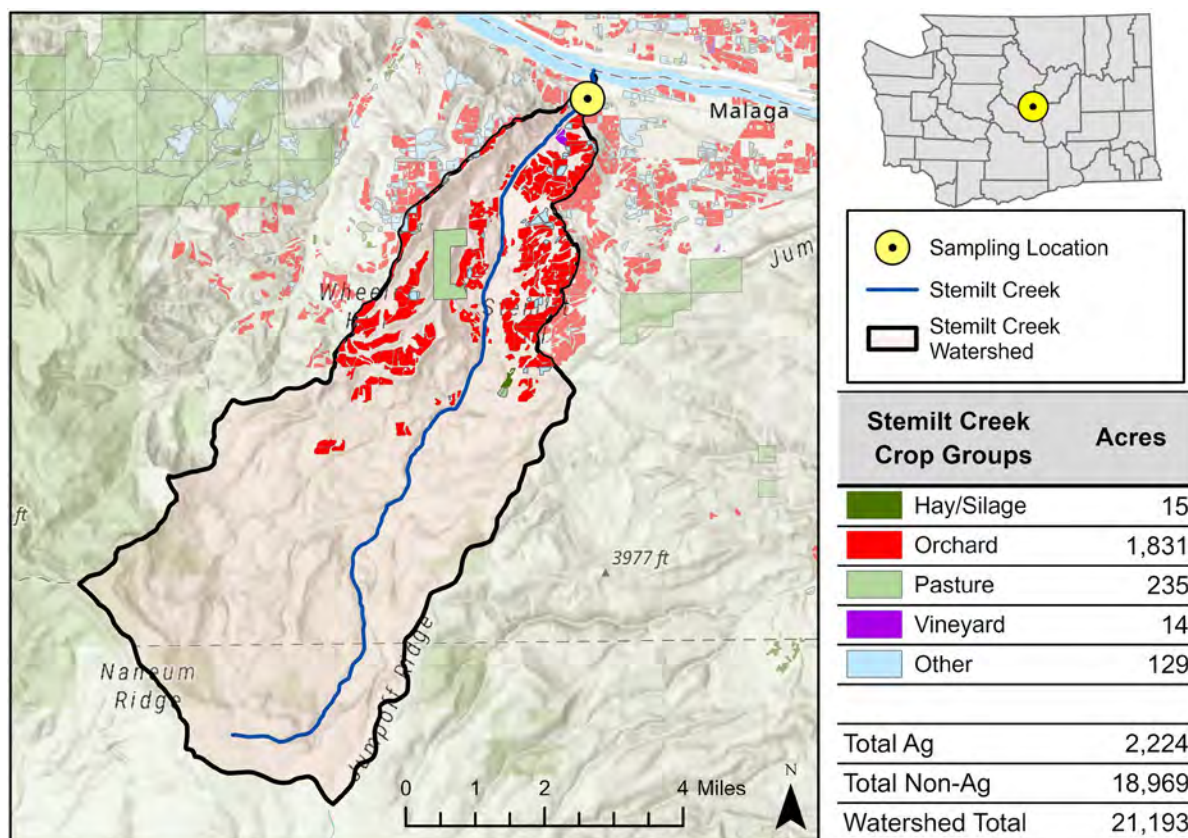


Figure 40 – Map of Stemilt Creek and its drainage area with associated sampling location and crop groups identified

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 40, Figure 41). 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, rainbow trout, and summer steelhead trout (WDFW 2024). 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 a rearing habitat for salmon.

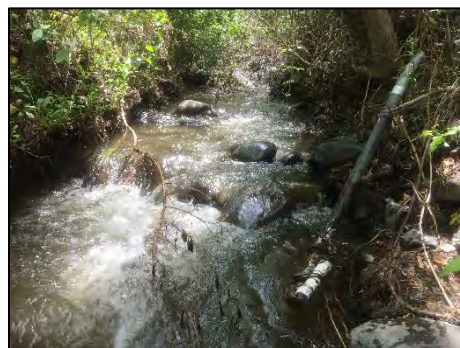


Figure 41 – Stemilt Creek upstream view

The watershed that contains the 12-mile-long Stemilt Creek has mountainous terrain. WSDA selected the watershed to be representative of agricultural practices used in tree fruit cultivation in Central Washington. The agricultural land use is predominately tree fruit production of cherries, apples, and pears. The 'Other' crop group category consists of fallow fields, nurseries, and other assorted small acreage crops (Figure 40).

Below is a brief overview of pesticide findings in Stemilt Creek in 2023.

- NRAS tested for 137 unique pesticides in Stemilt Creek.

- There were 44 total pesticide detections from five different use categories: 4 types of herbicides, 3 insecticides, 2 fungicides, 2 legacies, and 2 degradates.
- Pesticides were detected at all seven sampling events.
- Up to nine pesticides were detected at the same time.
- Of the total pesticide detections, seven were above WSDA's assessment criteria (Table 18).
 - The three detections of 4,4'-DDD and single detection of 4,4'-DDT, legacy degradates of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
 - The single detection of pyriproxyfen exceeded the invertebrate NOAEC (0.015 µg/L).

The Stemilt Creek watershed-specific POCs were chlorpyrifos, diazinon, and malathion. Below, each POC detected is compared to toxicity test reference values.

- Of the five detections of diazinon, one approached the invertebrate LC₅₀ (0.21 µg/L), invertebrate NOAEC (0.17 µg/L), and the NRWQC acute and chronic criteria (both 0.17 µg/L).
- Of the four detections of malathion, one exceeded the invertebrate LC₅₀ (0.098 µg/L), invertebrate NOAEC (0.06 µg/L), and NRWQC chronic criteria (0.1 µg/L). The detection also approached the fish LC₅₀ (4.1 µg/L).
- There were no detections of chlorpyrifos at this site in 2023, however, this insecticide was still classified as a watershed POC because of detections that have exceeded criteria in recent years.

The Stemilt Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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. There were 11 herbicides, 1 degradate, and 1 wood preservative removed from testing at this site as a result of infrequent historic detections.

Table 18 – Stemilt Creek pesticide calendar, µg/L ^{25, 26}

Month		Mar		Apr				May
Day of the Month	Use*	21	28	4	11	18	25	2
2,6-Dichlorobenzamide	D	0.046	0.044	0.039	0.024	0.017	0.013	0.006
4,4'-DDD	L				0.001	<0.001		0.001
4,4'-DDT	L					<0.001		
Boscalid	F	0.007	0.009	0.008	0.017	0.006	0.005	0.005
Diazinon	I			0.003	0.002	0.003	0.167	0.009
Dichlobenil	H	0.002						0.001
Hexazinone	H							0.002
Malaoxon	D						0.004	
Malathion	I			0.004	0.005		2.900	0.006
Metalaxyl	F	0.054	0.033	0.019	0.014			
Pendimethalin	H				0.003			0.003
Pyriproxyfen	I						0.041	
Sulfentrazone	H	X	0.008	0.006	0.008	0.003	0.008	0.005
Suspended sediment concentration		6	3	13	48	7	16	66
Streamflow (cubic ft/sec)		5.1	2.8	6.9	19.8	8.8	12.2	-
Precipitation (total in/week)†		0.14	0.01	0.00	0.63	0.02	0.14	0.10

The "-" signifies a sample or measurement that was not collected or could not be analyzed. The "X" signifies data rejected by failing laboratory 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: 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. There were no pesticide exceedances that coincided with water quality measurement that did not meet the state standards. Water quality at the Stemilt Creek site is shown below (Figure 42).

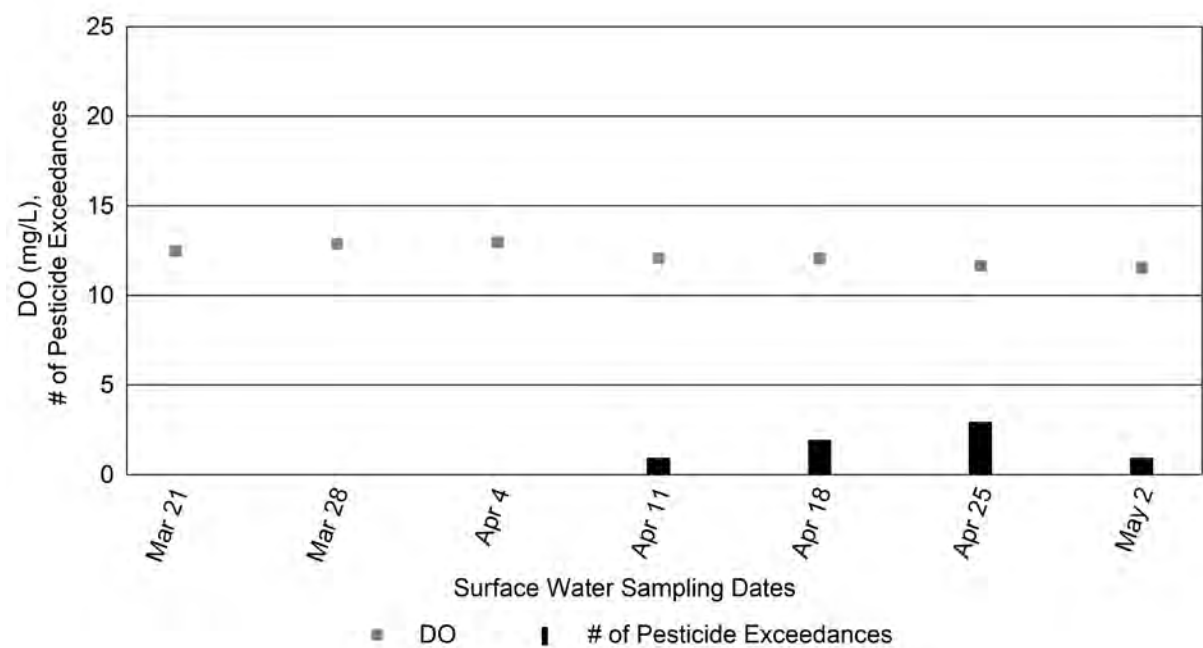


Figure 42 – Stemilt Creek water quality measurements and exceedances of assessment criteria

All DO measurements met the state water quality standard, ranging from 11.55 mg/L to 12.97 mg/L with an average of 12.20 mg/L.

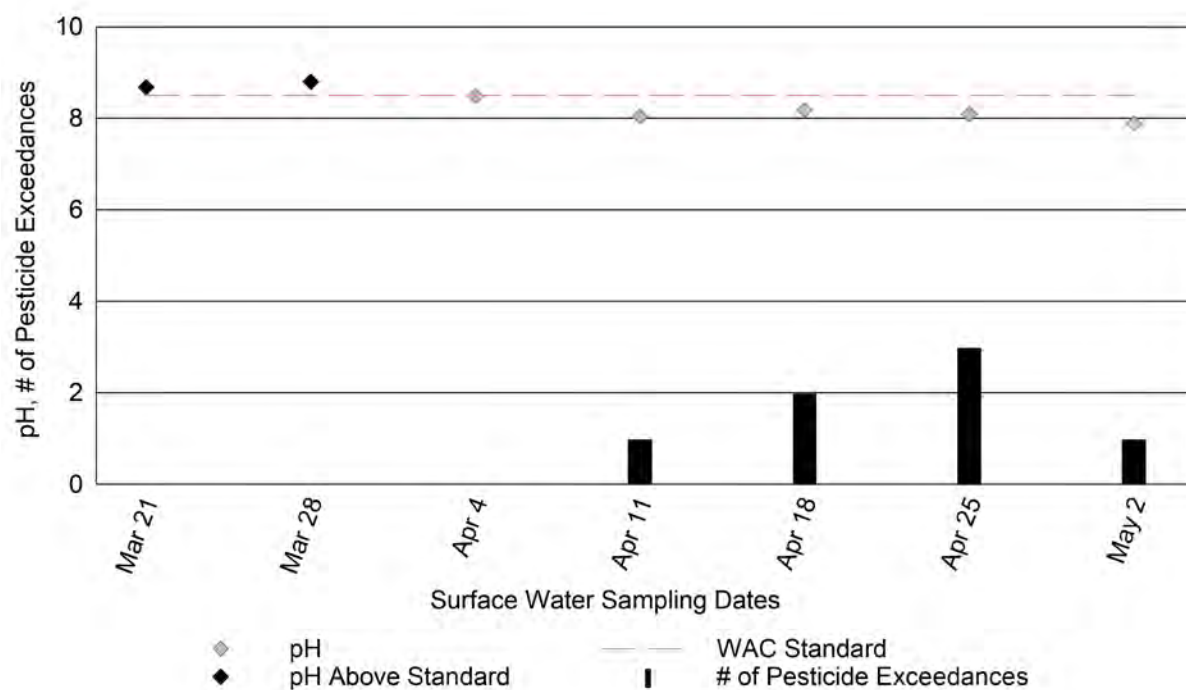


Figure 43 – Stemilt Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.89 to 8.80 with an average of 8.31. More than a quarter (29%) of these measurements exceeded the state water quality standard; two measurements were above 8.50.

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 2024d). 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 diazinon and malathion.

Sulphur Creek Wasteway

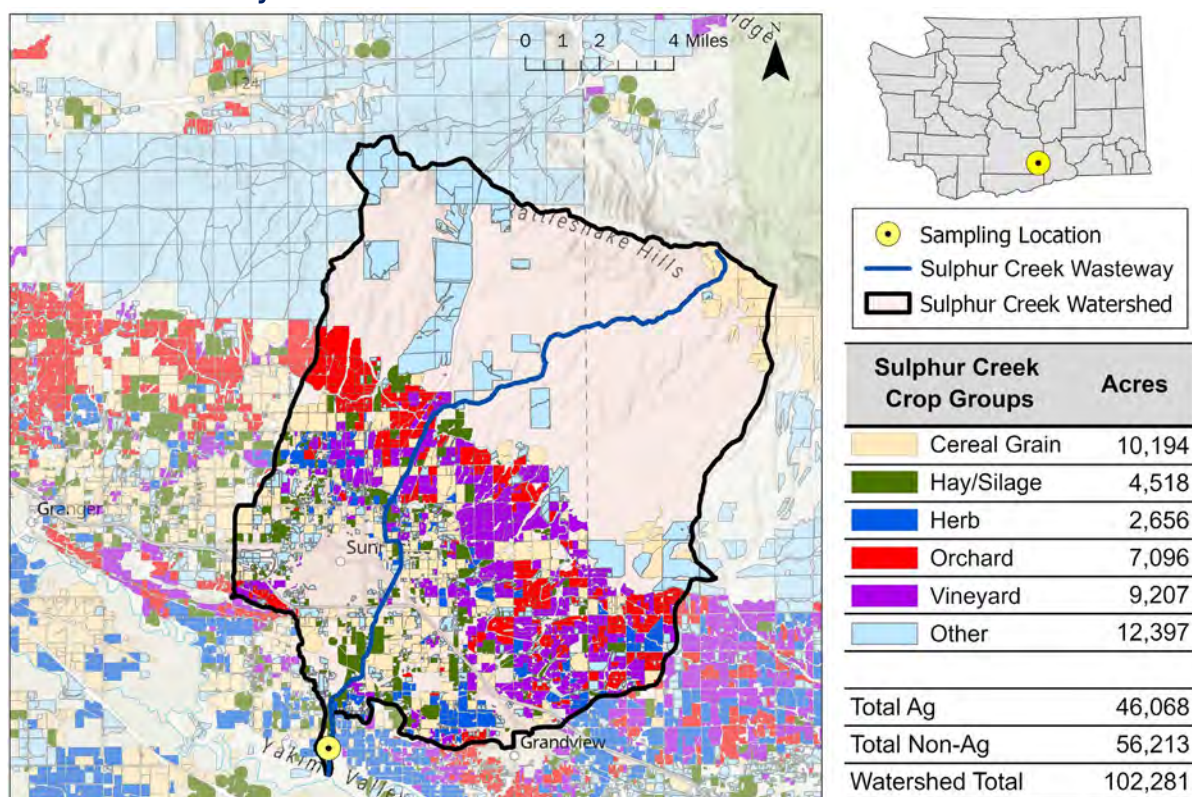


Figure 44 – Map of Sulphur Creek Wasteway and its drainage area with associated sampling location and crop groups identified

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: -120.0202°) (Figure 44, Figure 45).

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 coho, fall Chinook, and spring Chinook salmon, as well as rainbow trout and summer steelhead trout within the reach of wasteway that encompasses the monitoring site downstream of the fish barrier near the Holaday Road crossing (WDFW 2024). 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, wine and juice grapes, apples, and alfalfa hay. The 'Other' crop group category consists of pastures, vegetables, grass, nurseries, and other assorted small acreage crops (Figure 44).



Figure 45 – Sulphur Creek Wasteway downstream view

Below is a brief overview of pesticide findings in Sulphur Creek Wasteway in 2023.

- NRAS tested for 150 unique pesticides in Sulphur Creek Wasteway.
- There were 341 total pesticide detections from seven different use categories: 24 types of herbicides, 11 insecticides, 5 fungicides, 2 legacies, 5 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 18 sampling events.
- Up to 30 pesticides were detected at the same time.
- Of the total pesticide detections, 22 were above WSDA's assessment criteria (Table 19).
 - The four detections of 4,4'-DDD and 11 detections of 4,4'-DDE, legacy degradates of DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The Sulphur Creek Wasteway watershed-specific POCs were bifenthrin, chlorpyrifos, diuron, gamma-cyhalothrin, imidacloprid, and permethrin. Below, each POC detection is compared to toxicity test reference values.

- Of the 14 detections of diuron, five detections approached or exceeded the plant EC₅₀ (0.13 µg/L).
- The single detection of gamma-cyhalothrin exceeded the invertebrate LC₅₀ (0.00008 µg/L). It also approached the invertebrate 0.00193 µg/L.
- The single detection of cis-permethrin, an isomer of permethrin, exceeded the invertebrate NOAEC (0.0042 µg/L) and the invertebrate LC₅₀ (0.0066 µg/L).
- There were no detections of bifenthrin, chlorpyrifos, and imidacloprid at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years.

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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. No samples were collected at Sulphur Creek Wasteway between June 13 and August 27th due to historically low detection frequencies during that time.

Table 19 – Sulphur Creek Wasteway pesticide calendar, µg/L ^{27, 28}

Month		Mar			Apr			May						Jun			Aug		Sep		
Day of the Month	Use*	20	27	3	10	17	24	1	8	15	22	30	5	12	28		5	11	18	26	
1-(3,4-Dichlorophenyl)-3-methylurea	D					0.004		0.005		0.012	0.014	0.007	0.005		⚡						
2,4-D	H				0.049	0.045	0.094	0.084	0.077	0.102	1.110	0.156	0.156	0.096		0.066	0.045	0.043	0.049	0.060	
2,6-Dichlorobenzamide	D	0.020	0.007	0.006	0.002	0.002	0.006	0.008	0.007	0.002	0.008	0.009	0.008		0.010	0.008	0.002	0.010	0.008		
2-Hydroxyatrazine	D												0.008		0.018	0.020					
4,4'-DDD	L				<0.001					0.001	0.002	<0.001									
4,4'-DDE	L	0.001	0.002		0.002	0.001	0.002	0.002	0.002	0.004	0.010	0.002		0.002							
4-Nitrophenol	D										0.049										
Acetamiprid	I							0.012							⚡						
Atrazine	H	0.010	0.005	0.005	0.004	0.005	0.004	0.004	0.010	0.007	0.006	0.022	0.019	0.009		0.007	0.007	0.007	0.007	0.006	
Bentazon	H	0.044								0.011	0.010	0.015	0.015	0.011	0.029	0.032	0.034	0.040	0.043		
Boscalid	F	0.003	0.003	0.003	0.002	0.002	0.003	0.003	0.003	0.003	0.004	0.004	0.004	0.004	0.010	0.008	0.005	0.006	0.006		
Bromacil	H	0.049	0.016	0.014	0.012	0.021	0.013	0.015	0.018	0.017	0.015	0.017	0.017	0.010	0.018	0.013	0.016	0.016	0.016		
Bromoxynil	H										0.027										
Carbaryl	I								0.031	0.169					⚡						
Carbendazim	F	0.011																		0.013	
Chlorantraniliprole	I											0.014									
Chlorpropham	H													0.001	⚡						
cis-Permethrin	I												0.007								
Clopyralid	H										0.019										
Clothianidin	I														0.014	0.012					
Desethylatrazine	D	0.010											0.006								
Diazinon	I		0.002	0.014	0.036	0.014	0.006	0.003	0.002		0.003	0.008	0.015	0.004	0.003	0.001					
Dicamba	H						0.005	0.009	0.011	0.032	0.032	0.011	0.017	0.015	0.010	0.016	0.015	0.012	0.008		
Dichlobenil	H	0.002			0.003																
Dimethoate	I								0.004	0.014		0.004	0.004	0.008	⚡						
Diuron	H	0.009	0.024	0.107	0.046	0.044	0.073	0.076	0.045	0.138	0.115	0.027	0.021	0.016		0.012					
Eptam	H	0.001			0.002			0.002	0.114	0.015	0.003	0.010	0.004	0.005							
Fludioxonil	F		0.015	0.039	0.021	0.011	0.028	0.011	0.007	0.008	0.009	0.014	0.015	0.021	0.031	0.020	0.013	0.017	0.023		
gamma-Cyhalothrin	I											0.002			⚡						
Hexazinone	H	0.009	0.002		0.003			0.003		0.003	0.003			0.004		0.008		0.006	0.005	0.005	
Imazapyr	H	0.028				0.007	0.004		0.009	0.007	0.005	0.009	0.013	0.008				0.009	0.008		
Malathion	I			0.014							0.006										
Metolachlor	H								0.011		0.005	0.002	0.002	0.002	0.003	0.001	0.001	0.001			
Metribuzin	H							0.004	0.003	0.014	0.017	0.015	0.022	0.003							
N,N-Diethyl-m-toluamide (DEET)	IR										0.017	0.017	0.028								
Norflurazon	H	0.008	0.002	0.003	0.003	0.004	0.003	0.005	0.004	0.004	0.004	0.005	0.004	0.003	0.005	0.004	0.004	0.004	0.004		
Oxamyl	I										0.005										
Pendimethalin	H	0.006	0.020	0.010	0.013	0.024	0.021	0.051	0.022	0.057	0.080	0.024	0.013	0.008	0.003	0.004	0.007	0.004	0.005		
Pentachlorophenol	WP							0.007	0.007												
Prometon	H	0.002													0.003						
Pyrimethanil	F			0.015		0.009	0.017						0.011	0.011	0.017	0.012			0.016		
Simazine	H	0.008													0.008						
Sulfentrazone	H	0.003	0.003	0.007		0.007	0.007	0.007	0.012	0.013	0.013	0.017	0.014	0.008	0.015	0.015	0.012	0.013	0.019		
tau-Fluvalinate	I											0.002									
Tebuthiuron	H	0.006																			
Terbacil	H	0.038	0.028	0.012	0.021	0.034	0.025	0.082	0.030	0.055	0.021	0.056	0.033	0.020	0.024	0.021	0.034	0.041	0.035		
Treflan (Trifluralin)	H							0.002		0.003	0.003		0.002								
Triclopyr	H									0.025	0.049										
Trifloxystrobin	F						0.002								⚡						
Suspended sediment concentration		6	43	49	33	33	70	37	27	73	524	14	6	25		10	12	7	8	9	
Streamflow (cubic ft/sec)		54.7	173.3	241.2	147.3	136.7	181.2	117.0	108.2	111.2	128.3	86.9	91.8	158.2	171.4	181.2	162.0	165.7	179.2		
Precipitation (total in/week)†		0.01	0.07	0.00	0.15	0.46	0.11	0.00	0.07	0.00	0.45	0.00	0.00	0.04	0.07	0.07	0.00	0.00	0.04		

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

Current-use exceedance DDT/degrade 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: 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 eight of the 18 site visits (44%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 46).

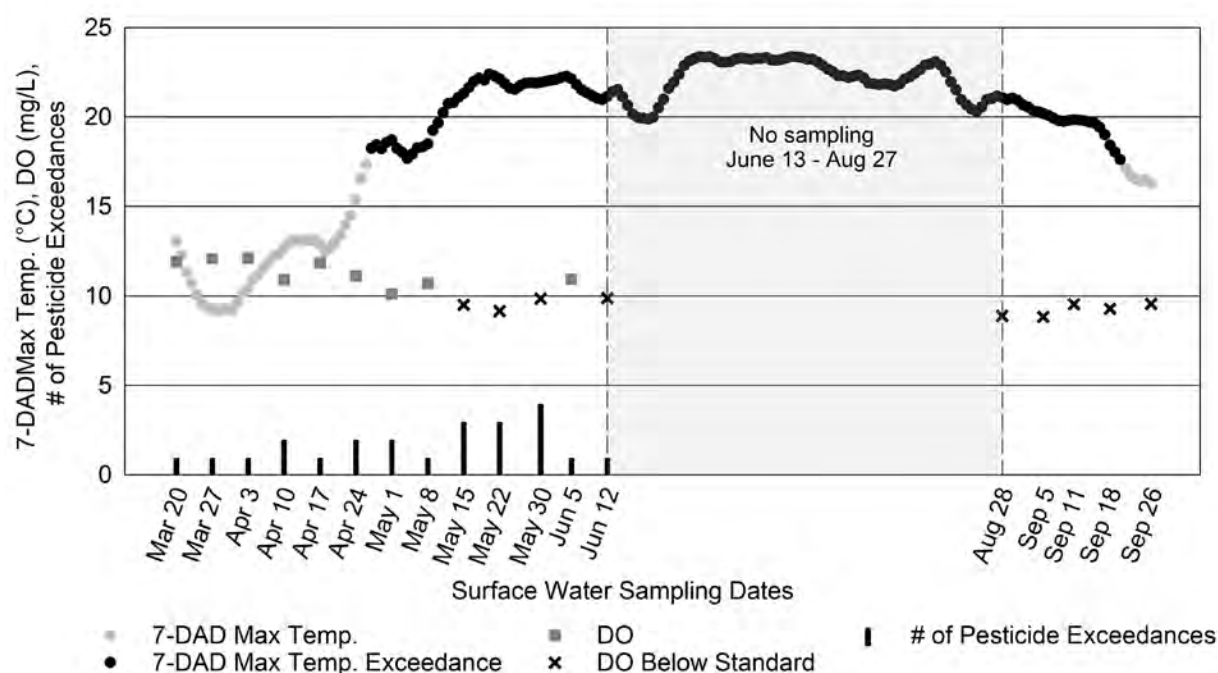


Figure 46 – Sulphur Creek Wasteway water quality measurements and exceedances of assessment criteria

DO measurements ranged from 8.83 mg/L to 12.11 mg/L with an average of 10.25 mg/L. Half (53%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L. Four of the DO measurements that did not meet the standard coincided with one, three, or four pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 147 days throughout the sampling season, occurring from April 27 through September 20. Pesticide exceedances coincided with 7-DADMax temperature exceedances at seven site visits.

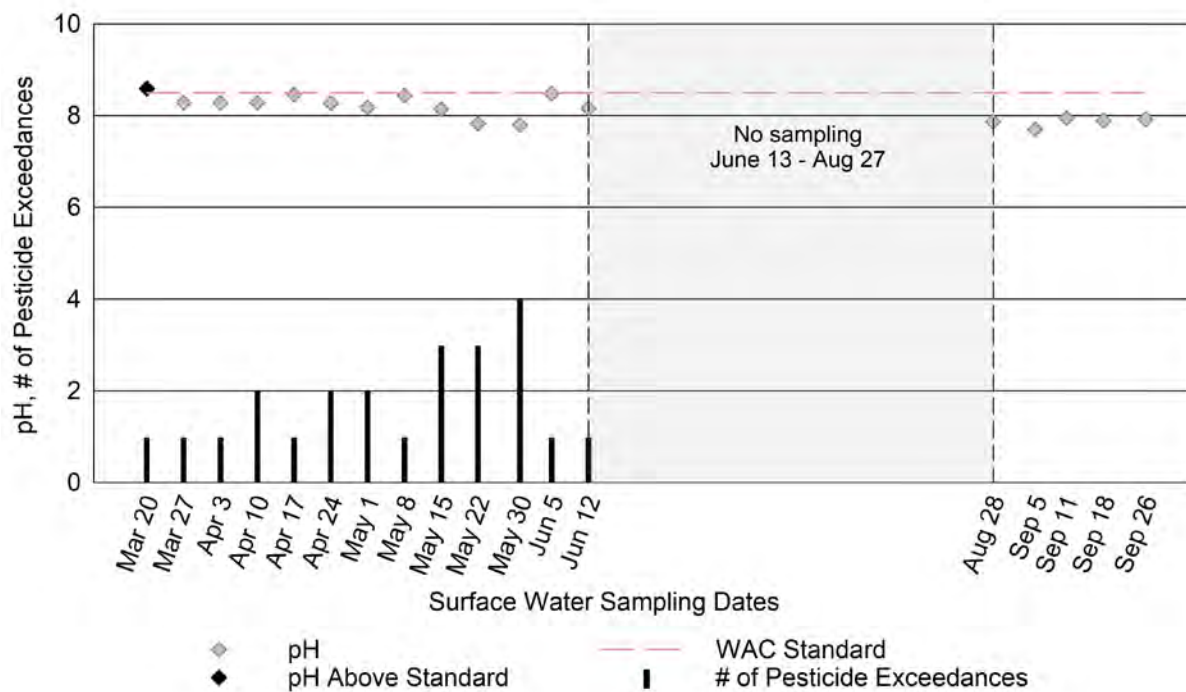


Figure 47 – Sulphur Creek Wasteway pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.70 to 8.59 with an average of 8.14. The measurement on March 20 exceeded the state water quality standard of 8.50 and coincided with one pesticide exceedance (Figure 47).

Sulphur Creek Wasteway provides habitat for salmonid spawning, rearing, and migration (WAC 2024d). 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.

Palouse Region

Dry Creek

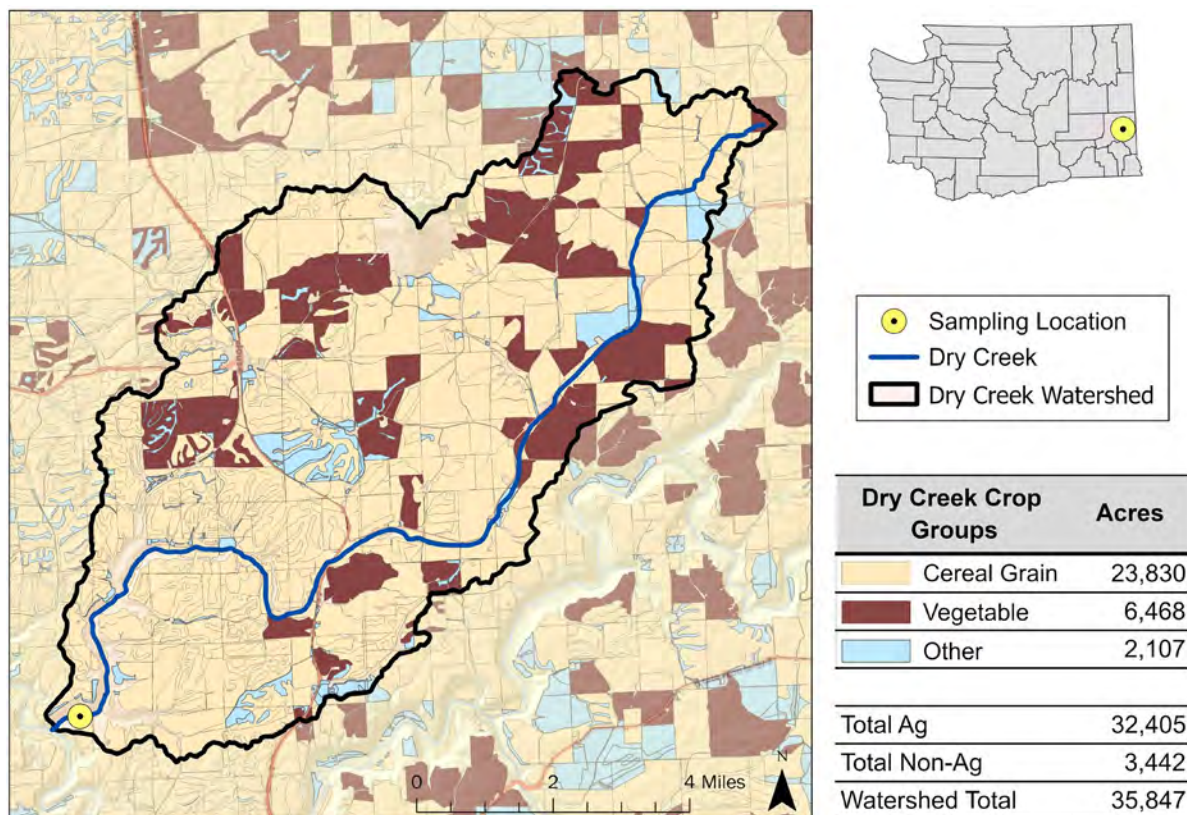


Figure 48 – Map of Dry Creek and its drainage area with associated sampling location and crop groups identified

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 third 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 48, Figure 49).

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. Palouse Falls prevents salmon from migrating further into the Palouse River Watershed and, by 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.

The watershed features low-lying, flat terrain with rolling hills, and the majority of the creek is ditched and straightened in between agricultural fields. The agricultural land use is predominately wheat, legumes, and barley. The 'Other' crop group category consists of oilseed, pastures, fallow fields, and other assorted small acreage crops (Figure 48).



Figure 49 – Dry Creek upstream view

NRAS tested for three additional analytes at this site in 2023 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were AMPA (a glyphosate breakdown product), glyphosate, 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 which summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Dry Creek in 2023.

- NRAS tested for 153 unique pesticides in Dry Creek.
- There were 259 total pesticide detections from four different use categories: 24 types of herbicides, 3 insecticides, 5 fungicides, and 4 degradates.
- Pesticides were detected at all 22 sampling events.
- Up to 20 pesticides were detected at the same time.
- Of the total pesticide detections, two were above WSDA's assessment criteria (Table 20).
- The Dry Creek watershed POCs were bifenthrin, gamma-cyhalothrin, imidacloprid, linuron, metsulfuron-methyl, and pyroxasulfone. Below, each POC is compared to toxicity test reference values.
- The single detection of bifenthrin exceeded the fish NOAEC (0.004 µg/L), invertebrate LC₅₀ (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- The single detection of gamma-cyhalothrin exceeded the invertebrate LC₅₀ (0.00008 µg/L).
- There were no detections of imidacloprid, linuron, metsulfuron-methyl, or pyroxasulfone at this site in 2023, however, they were still classified as watershed POCs because of detections that have exceeded criteria in recent years at the site.

The Dry Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 monitoring season and a visual comparison to the WSDA assessment criteria (Table 20).

The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 20 – Dry Creek pesticide calendar, µg/L^{29, 30}

Month		Mar	Apr					May					Jun				Jul					Aug		
Day of the Month	Use*	27	4	10	18	24	2	8	16	22	30	5	15	21	27	5	11	17	25	31	8	14	21	
2,4-D	H									0.061	0.040	0.083	0.040		0.065		0.040	0.108		0.037			0.033	
2,6-Dichlorobenzamide	D		0.002					0.002								-								
Aminomethylphosphoric acid (AMPA)	D	0.657	1.090	0.649	0.684	0.658	0.743	1.090	1.060	1.210	0.885	0.926	0.732	0.637	0.547	-	0.473	0.464	0.410	0.443	0.379	0.369	0.344	
Atrazine	H		0.006													-	0.004	0.004	0.004					
Azoxystrobin	F		0.015		0.006	0.008		0.023	0.019		0.011		0.013	0.012	0.009	-								
Bentazon	H	0.047	0.049	0.056	0.059	0.055	0.055	0.062	0.030	0.025	2.210	0.116	0.237	0.047	0.036	0.007								
Bifenthrin	I				0.007											-								
Boscalid	F															-					0.001			
Bromacil	H		0.005													-								
Bromoxynil	H						0.032	0.128	0.029	0.061	0.040		0.040											
Clethodim sulfone	D										0.064					-								
Clethodim sulfoxide	D										1.080		0.327			-								
Clopyralid	H	0.059	0.077	0.037	0.037	0.052	0.044	0.099	0.045	0.024	0.025	0.027	0.153		0.022									
Dicamba	H		0.007						0.021			0.024		0.009	0.015									
Eptam	H				0.002					0.002						-								
Ethalfuralin (Sonalan)	H				0.002											-								
Fluroxypyr-meptyl	H								0.011							-								
gamma-Cyhalothrin	I					<0.001										-								
Glyphosate	H	0.152	0.493	0.146	0.400	0.439	0.192	0.550	0.553	0.372	0.203	0.291	0.132	0.107	0.089	-	0.085	0.066	0.053	0.055	0.060	0.063	0.047	
Imazapic	H				0.018											-								
Imazapyr	H											0.004	0.004			-								
Indaziflam	H							0.010								-								
MCPA	H		0.054				0.059	0.262			0.072													
Metalaxyl	F		0.012					0.009								-								
Metolachlor	H	0.001	0.015	0.001	0.001	<div></div>		0.002		0.002	0.001	0.001	0.005	0.002	0.001	-	0.001	<0.001	<0.001	<0.001	<0.001	0.001		
Metribuzin	H	0.021	0.054	0.019	0.020	0.065	0.110	0.217	0.047	0.036	0.018	0.009	0.009	0.008	0.005	-	0.005	0.005	0.005	0.005	0.003		0.004	
Pendimethalin	H	0.004	0.025	0.005	0.005	0.003	0.004	0.005	0.005	0.003	0.003					-			0.002					
Picloram	H													0.053										
Prometon	H	0.004	0.004	0.003	0.003	0.003	0.003	0.003	0.004	0.003	0.003	0.004	0.003	0.003	0.003	-		0.003	0.004	0.003	0.004	0.003	0.004	
Propiconazole	F	0.015	0.026	0.011	0.011		0.016	0.082	0.023		0.024	0.018	0.015		0.008	-								
Pyraclostrobin	F				0.008											-								
Sulfentrazone	H	<div></div>	0.049	0.003	0.030	0.134	0.044	0.303	0.049	0.035	0.018	0.021	0.023	0.021	0.018	-	0.020	0.020	0.022	0.018	0.048	0.044	0.020	
Tebuthiuron	H	0.008	0.011	0.010	0.007		0.009	0.012			0.007		0.006			-	0.008	0.008	0.009	0.008	0.007	0.006	0.009	
Thiamethoxam	I	0.011	0.036	0.011	0.011	0.010		0.025			0.007	0.005				-								
Triallate	H	0.007	0.011	0.006	0.003	0.004	0.006	0.008	0.002							-								
Triclopyr	H										0.031													
Suspended sediment concentration		14	52	9	7	6	9	17	26	36	38	23	11	7	10	-	10	12	5	8	6	5	10	
Streamflow (cubic ft/sec)		10.4	17.4	11.4	11.5	9.0	7.1	6.8	4.8	3.6	2.5	1.7	1.2	1.1	0.8	0.5	0.3	0.2	0.3	0.2	0.3	0.3	0.2	
Precipitation (total in/week)†		0.12	0.36	0.10	0.64	0.32	0.00	0.74	0.06	0.00	0.02	0.00	1.00	0.04	0.04	0.00	0.03	0.03	0.00	0.00	0.02	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. The "X" signifies data rejected by failing laboratory quality assurance performance measures.

 Current-use exceedance  Detection  No criteria

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

† 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 one of the 22 site visits (5%). Water quality at the Dry Creek site is shown below (Figure 50). Temperature measurements are unavailable from May 8th through May 16th due to the sensor being lost.

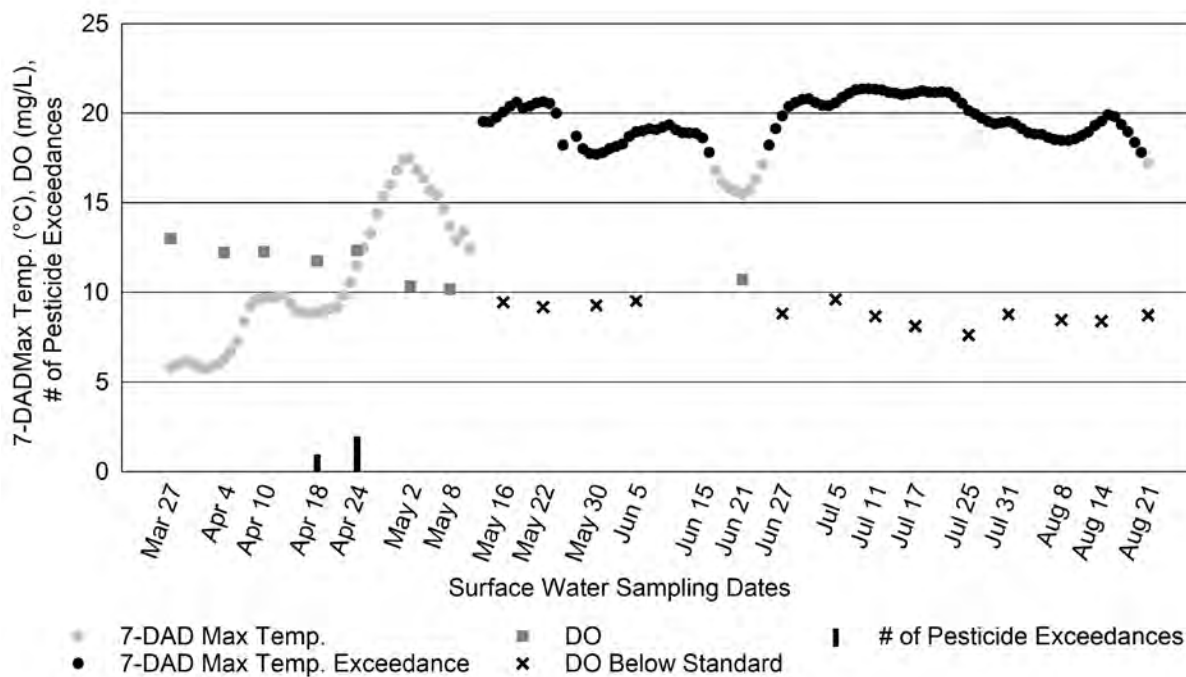


Figure 50 – Dry Creek water quality measurements and exceedances of assessment criteria

DO measurements ranged from 7.61 mg/L to 13.01 mg/L with an average of 9.88 mg/L. More than half (62%) of the DO measurements did not meet the state water quality standard, with 13 measurements falling below 10 mg/L. The 7-DADMax temperature exceeded the standard of 17.5°C on 91 days throughout the sampling season, occurring intermittently from May 13 through August 20.

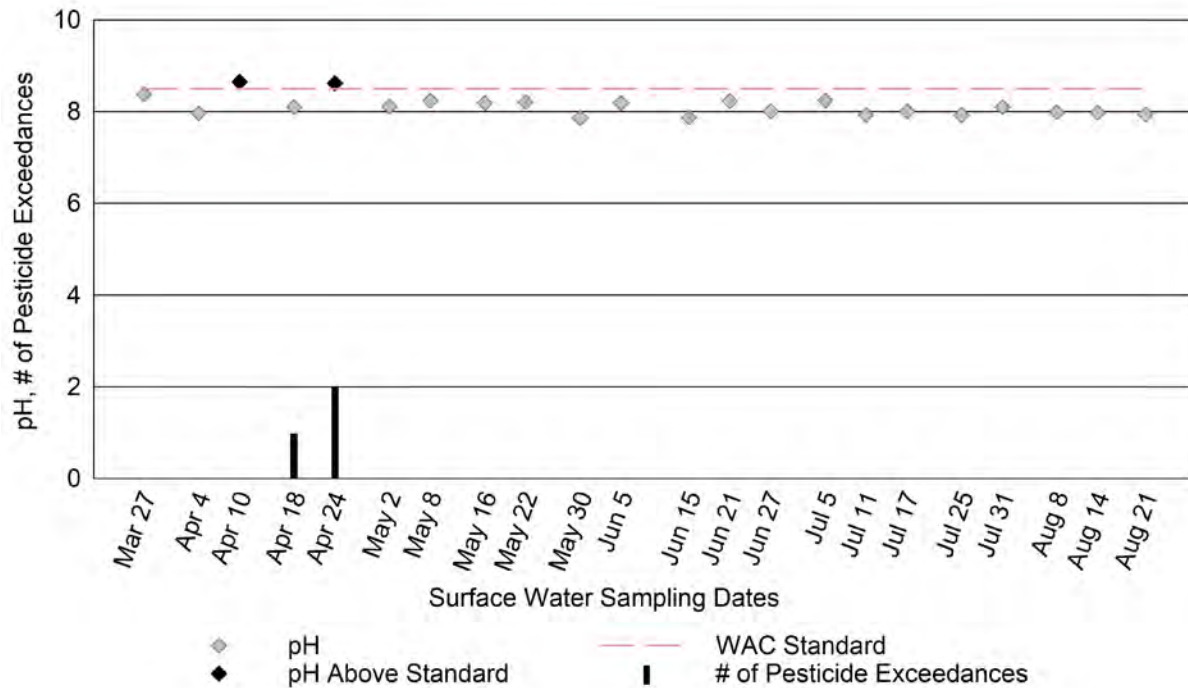


Figure 51 – Dry Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.86 to 8.65 with an average of 8.12. Less than a quarter (9%) of these measurements exceeded the state water quality standard; two measurements were above 8.50. One of the pH exceedances coincided with two pesticide exceedances (Figure 51).

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 2024d). 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

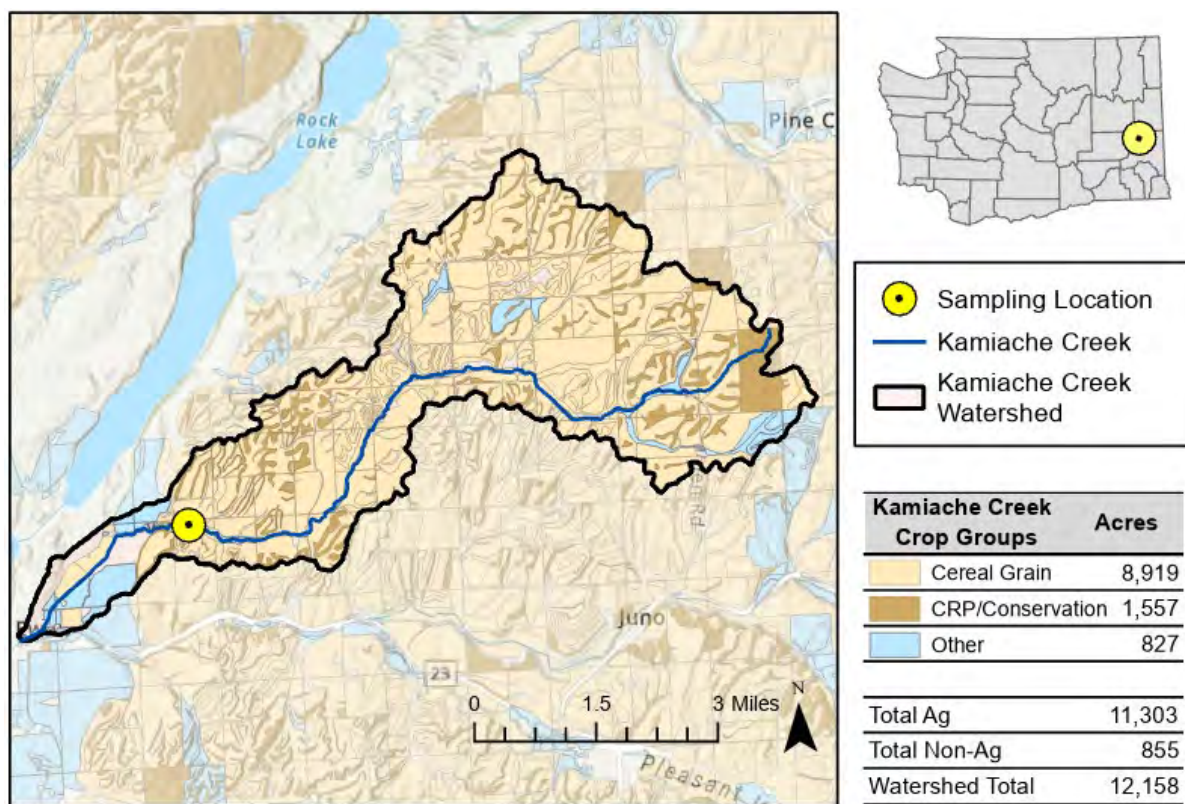


Figure 52 - Map of Kamiache Creek and its drainage area with associated sampling location and crop groups identified

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Kamiache Creek in Whitman County, for a third sampling season, during the 2023 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).

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. Palouse Falls prevents 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. The 'Other' crop group category consists of oilseed, pastures, alfalfa, barley, and idle fallow fields (Figure 52). There were efforts between 2016 and 2021 by a regional



Figure 53 - A colleague measuring streamflow in Kamiache Creek

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 2022, many farms were still managed with these conservation techniques.

NRAS tested for three additional analytes at this site in 2023 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were AMPA (a glyphosate breakdown product), glyphosate, 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 which summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Kamiache Creek in 2023.

- NRAS tested for 153 unique pesticides in Kamiache Creek.
- There were 106 total pesticide detections from seven different use categories: 15 types of herbicides, 3 insecticides, 3 fungicides, 1 legacy, 3 degradates, 1 antimicrobial, and 1 wood preservative.
- Pesticides were detected at all 18 sampling events.
- Up to 13 pesticides were detected at the same time.
- Of the total pesticide detections, three were above WSDA's assessment criteria (Table 21).
 - The single detection of 4,4'-DDD, a legacy degradate of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

The singular Statewide POC detected in Kamiache Creek was imidacloprid. Below, the POC detections are compared to toxicity test reference values.

- The two detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).

The Kamiache Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 – Kamiache Creek pesticide calendar, µg/L ^{31, 32}

Month		Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov									
Day of the Month	Use*	27	10	24	8	22	5	20	5	17	31	8	14	28	11	25	9	23	6
2,4-D	H	0.029			0.061	0.031					0.074	0.702	0.173	0.038	0.035	0.038	0.038		0.110
2,6-Dichlorobenzamide	D																	0.002	0.001
2-Hydroxyatrazine	D			0.147					-										
4,4'-DDD	L		0.001																
Aminomethylphosphoric acid (AMPA)	D	0.246	0.189	0.327	0.541	0.222	0.208	0.151	0.153	0.807	1.290	1.230	0.779	0.374	0.211	0.124	0.127	0.095	0.847
Atrazine	H																0.004		
Azoxystrobin	F			0.006	0.012				-										
Boscalid	F		0.002									0.003	0.001						0.001
Bromoxynil	H				0.036		0.055	0.025				0.072	0.031						0.030
Clopyralid	H				0.409														
Dicamba	H			0.020	0.009	0.007					0.054	0.498	0.108	0.015		0.007	0.009		0.092
Dimethoate	I				0.005														
Eptam	H			0.002	0.002	0.003	0.002												
Glyphosate	H	0.110	0.119	0.682	0.308	0.166	0.162	0.104	0.097	1.070	0.739	1.810	0.430	0.207	0.127	0.124	0.095	0.074	0.516
Hexazinone	H		0.001																
Imazapic	H						0.012		-										
Imidacloprid	I					0.022			-										0.026
MCPA	H				1.070		0.065					0.049	0.616						
Metribuzin	H	0.003	0.004	0.009	0.022	0.003													0.003
Norflurazon	H		0.002																
Pentachlorophenol	WP		0.006		0.009	0.004													0.032
Phosmet (Imidan)	I		0.002																
Prometryn	H		0.002																
Propiconazole	F						0.018		-										
Terbacil	H																0.006		
Triallate	H			0.022	0.005														
Triclosan	A								0.006										
Suspended sediment concentration		2	5	5	12	5	8	4	7	13	90	44	4	2	4	2	2	2	3
Streamflow (cubic ft/sec)		1.4	1.5	1.5	1.2	0.6	0.4	0.3	0.2	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.2	0.3	0.4
Precipitation (total in/week)†		0.06	0.25	0.25	0.60	0.00	0.00	0.00	0.05	0.09	0.01	0.14	0.00	0.24	0.00	0.41	0.05	0.01	1.15

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

Current-use exceedance DDT/degradate exceedance Detection

* (A: Antimicrobial, D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, L: Legacy, WP: Wood preservative)

† 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 two of the 18 site visits (11%). Water quality at the Kamiache Creek site is shown below (Figure 54).

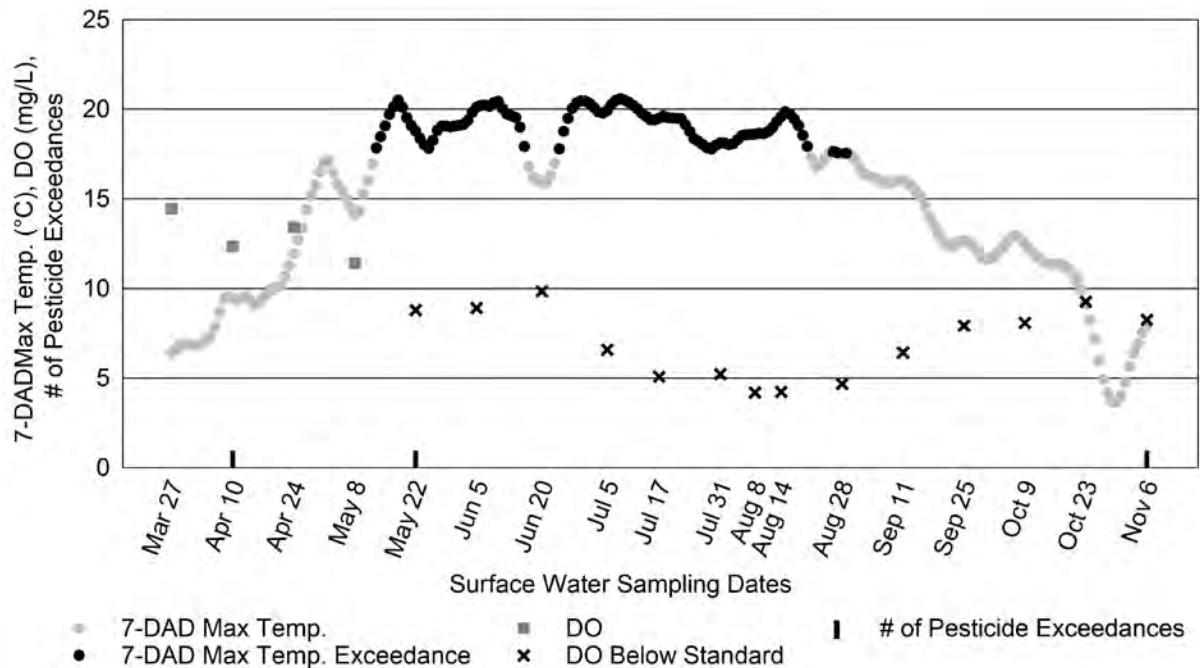


Figure 54 – Kamiache Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.58 to 8.46 with an average of 7.97. DO measurements ranged from 4.19 mg/L to 14.45 mg/L with an average of 8.28 mg/L. More than three-quarters (78%) of the DO measurements did not meet the state water quality standard, with 14 measurements falling below 10 mg/L. Two of the DO measurements that did not meet the standard coincided with one pesticide exceedance. The 7-DADMax temperature exceeded the standard of 17.5°C on 96 days throughout the sampling season, occurring intermittently from May 13 through September 29. Pesticide exceedances coincided with 7-DADMax temperature exceedances 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 2024d). Staff observed small, unknown fish during the sampling season. NRAS has decided to discontinue sampling at this drainage starting 2024. The decision was made due to a combination of low pesticide detection frequency and exceedances, as well as funding limitations.

Thorn Creek

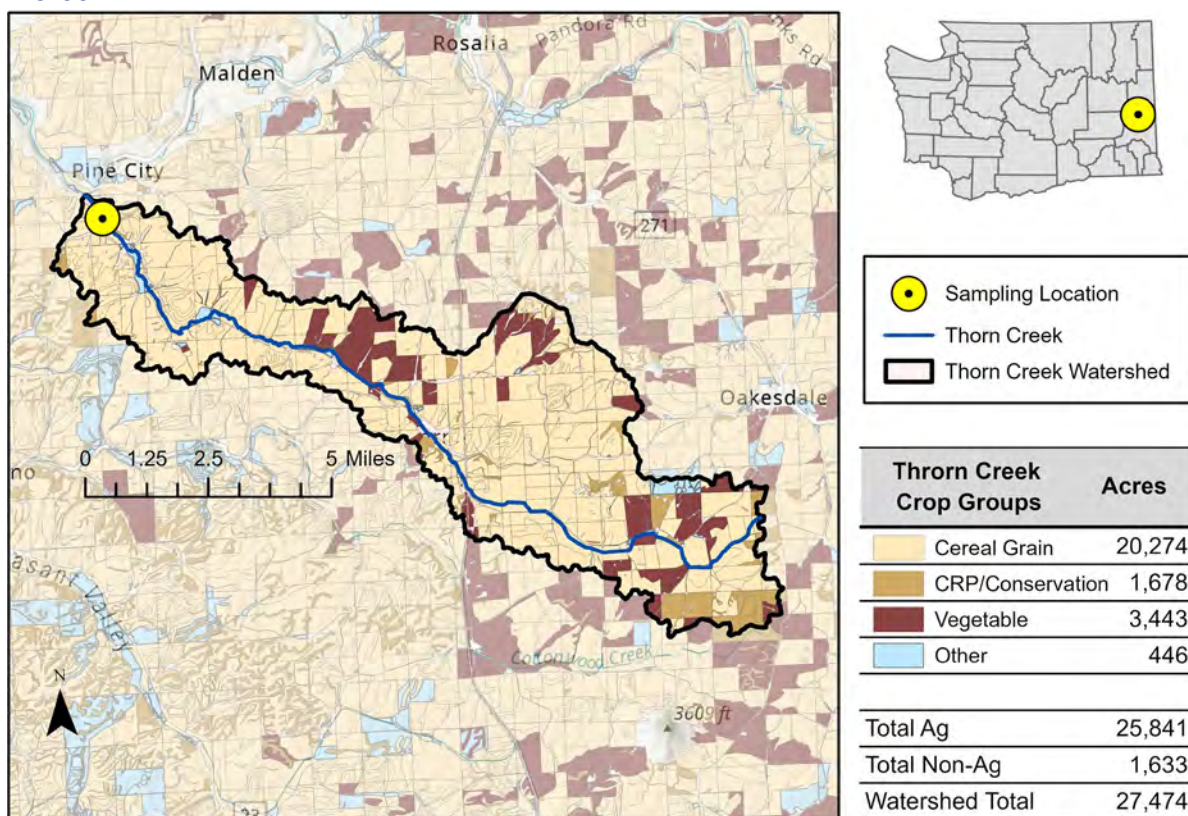


Figure 55 – Map of Thorn Creek and its drainage area with associated sampling location and crop groups identified

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Thorn Creek in Whitman County, for a third sampling season, during the 2023 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: 47.1885°, 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. 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, legumes, and barley. The 'Other' crop group category consists of hay, 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 2023 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were AMPA (a glyphosate breakdown product), glyphosate, 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 2023.

- NRAS tested for 153 unique pesticides in Thorn Creek.
- There were 131 total pesticide detections from five different use categories: 17 types of herbicides, 3 insecticides, 4 fungicides, 2 legacies, and 2 degradates.
- Pesticides were detected at all 17 sampling events.
- Up to 13 pesticides were detected at the same time.
- Of the total pesticide detections, three were above WSDA's assessment criteria (Table 22).
 - The detections of 4,4'-DDD and 4,4'-DDT, legacy degradates of DDT, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

Statewide POCs detected in Thorn Creek were gamma-cyhalothrin and imidacloprid. Below, the POC detections are compared to toxicity test reference values.

- The single detection of imidacloprid approached the invertebrate NOAEC (0.01 µg/L).
- There were no detections of gamma-cyhalothrin at this site in 2023, however, this insecticide was still classified as a watershed POC because of detections that have exceeded criteria in recent years at the site.

The Thorn Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2023 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 – Thorn Creek pesticide calendar, µg/L ^{33,34}

Month		Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Day of the Month	Use*	27	10 24	8 22	5 20	5 17 31	14 28	11 25	9 23	13
2,4-D	H				0.033		0.060			
2,6-Dichlorobenzamide	D			0.002	0.001	0.002		0.001		0.002
4,4'-DDD	L									0.003
4,4'-DDT	L									0.002
Aminomethylphosphoric acid (AMPA)	D	0.405	0.328 0.439	0.544 0.655	2.260 1.350	0.595 0.450	0.330 0.314 0.241	0.258 0.305	0.186 0.160	0.573
Atrazine	H	0.004							0.004	
Azoxystrobin	F	0.008	0.009			-				
Boscalid	F						<0.001			
Bromacil	H	0.008	0.010 0.009	0.008 0.007	0.008 0.006		0.005			0.006
Bromoxynil	H			0.075 0.022	0.023	0.029				0.039
Clopyralid	H	0.049	0.031	0.129 0.040	0.028	0.022				
Dicamba	H			0.007 0.046	0.228 0.260	0.010				0.029
Dichlobenil	H	0.003								
Dimethoate	I					0.007				
Eptam	H		0.002	0.002 0.003	0.002					
Glyphosate	H	0.079	0.051 0.273	0.159 0.163	0.220 0.301	0.141 0.145	0.105 0.098 0.075	0.138 0.363	0.120 0.109	0.205
Hexazinone	H		0.001							
Imidacloprid	I	0.008				-				
MCPA	H			0.119	0.067	0.069				
Metalaxyl	F			0.008 0.008					0.009	0.023
Metribuzin	H	0.003	0.004 0.004	0.193 0.011	0.005					
Picloram	H				0.100 0.078					
Prometon	H	0.002					0.003			
Propiconazole	F	0.010				-				
Sulfentrazone	H		0.005 0.011	0.055 0.011	0.010 0.008	0.008 0.009	0.008 0.021	0.009 0.006	0.007 0.008	0.006
Tebuthiuron	H	0.005	0.004	0.006						
Thiamethoxam	I		0.004	0.033		0.008	- 0.011	0.011	0.019	0.025 0.012
Triallate	H		0.002							0.044
Suspended sediment concentration		11	7 6	12 14	10 9	5 7 6	8 3	7 3	4 1	30
Streamflow (cubic ft/sec)		7.4	7.9 6.2	4.8 2.4	1.2 0.8	0.5 0.3	0.3 0.3	0.2 0.2	0.3 0.3	0.4 -
Precipitation (total in/week)†		0.06	0.25 0.25	0.60 0.00	0.00 0.00	0.05 0.09	0.01 0.00	0.24 0.00	0.41 0.05	0.01 0.35

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

Current-use exceedance
 DDT/degrade exceedance
 Detection

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, 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 one of the 17 site visits (6%). Due to the loss of samples on November 6, water samples were recollected on November 13. However, water quality measurements were not taken during this resampling event. Water quality at the Thorn Creek site is shown below (Figure 57).

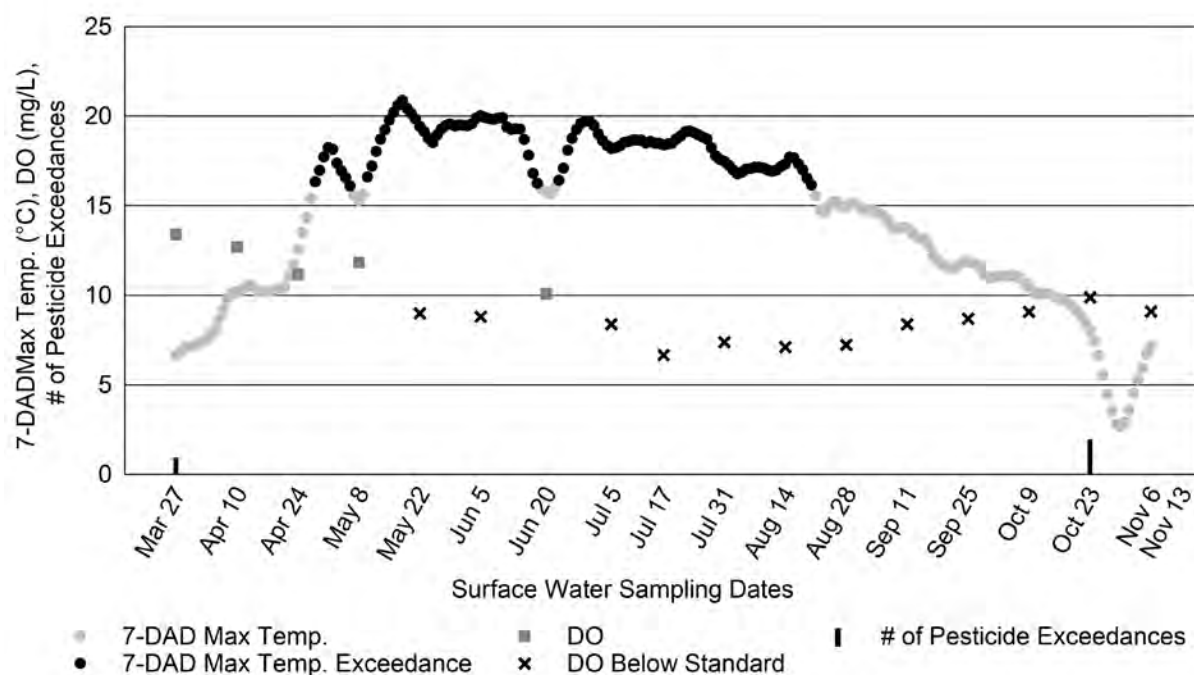


Figure 57 – Thorn Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.45 to 8.36 with an average of 7.79. DO measurements ranged from 6.66 mg/L to 13.39 mg/L with an average of 9.34 mg/L. Almost three-quarters (71%) of the DO measurements did not meet the state water quality standard, with 12 measurements falling below 10 mg/L. One of the DO measurements that did not meet the standard coincided with two pesticide exceedances. The 7-DADMax temperature exceeded the standard of 16°C on 108 days throughout the sampling season, occurring intermittently from April 28 through August 20.

Thorn Creek has been designated as a freshwater body that provides a core summer habitat for salmonids by the WAC (WAC 2024d). NRAS has decided to discontinue sampling at this drainage starting 2024. The decision was made due to a combination of low pesticide detection frequency and exceedances, as well as funding limitations.

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 17 current monitoring sites has distinct watershed and land use characteristics that dictate the pesticides detected. Different sites are sampled for different periods of time (7 to 32 sampling events) and samples from several sites are tested for a subset of pesticides compared to the majority of sites (137 to 153 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 23) provides a useful overview to describe common themes in the dataset regarding pesticide occurrence in this study but should not be used to describe Washington streams collectively. This summary is not applicable to streams outside of this study.

Table 23 – 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		2
Degradate	20	16	1	606
Fungicide	21	13	1	606
Herbicide	55	44	2	2430
Insect repellent	1	1		47
Insecticide	48	30	13	515
Legacy pesticides	5	4	3	164
Synergist	1	1		4
Wood preservative	1	1		12
Total analytes	153	111	20	4386

There were 111 different analytes detected in 2023 (Table 23). Across 17 monitoring sites, we identified 4,386 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 262 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 262 individual exceedances, 99 (38%) were currently registered pesticides or their associated degradates. The other 163 (62%) were detections of legacy pesticides or their degradates. Over half of the exceedances, 171 (65%), occurred at monitoring sites in Central Washington and the Palouse region including many of the statewide exceedances of DDT or its degradates (121). Imidacloprid, a neonicotinoid insecticide, accounted for 31 (12%) of the individual pesticide exceedances with 24 of the exceedances found at Western Washington monitoring sites; there was at least one exceedance detected at seven of the total 17 monitoring sites.

Pesticide Detection Summary

Below, statewide detections are summarized by pesticide general use categories. This subsection only presents analytes detected in 2023. Appendix B: 2023 Quality Assurance Summary provides a list of all analytes tested.

Herbicide Detections

Herbicides were the most frequently detected group making up approximately 55% (2,430 detections) of the total pesticide detections. Of the 55 herbicides included in the laboratory analysis, 44 were detected in surface water samples. Table 24 provides a statewide summary of the detected herbicides.

Table 24 – Statewide summary of herbicides with one or more detections in 2023

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Sulfentrazone	293	210 (72%)		15		0.00246 - 0.303
Metolachlor	323	160 (50%)		12		0.000666 - 0.452
2,4-D	281	130 (46%)		13		0.0275 - 1.11
Bromacil	323	130 (40%)		13		0.00242 - 0.0494
Dichlobenil	323	126 (39%)		13		0.00144 - 0.27
Simazine	322	125 (39%)		10		0.00378 - 0.528
Norflurazon	323	124 (38%)		10		0.00131 - 0.0788
Atrazine	323	120 (37%)		14		0.00221 - 0.163
Pendimethalin	323	115 (36%)		10		0.00211 - 0.2
Tebuthiuron	323	99 (31%)		10		0.00371 - 0.0772
Imazapyr	319	95 (30%)		9		0.00394 - 5.43
Terbacil	320	94 (29%)		7		0.00469 - 0.973
Eptam	323	91 (28%)		14		0.00114 - 0.114
Dicamba acid	280	83 (30%)		13		0.00421 - 0.498
Prometon	323	81 (25%)		9		0.0022 - 0.0299
Hexazinone	323	75 (23%)		15		0.0011 - 0.0217
Metribuzin	323	74 (23%)		13		0.00244 - 0.217
Bentazon	280	70 (25%)		5		0.00688 - 2.21
Diuron	320	66 (21%)	11	9	3	0.00401 - 21.7
Glyphosate	56	56 (100%)		3		0.0473 - 1.81
Triclopyr acid	280	45 (16%)		10		0.0162 - 0.558
Dithiopyr	323	32 (10%)		4		0.00171 - 0.008
Trifluralin	323	30 (9%)		8		0.00134 - 0.0103
MCPA	280	22 (8%)		7		0.0476 - 1.07
Bromoxynil	280	21 (8%)		5		0.0225 - 0.128
Chlorpropham	323	21 (7%)		6		0.00108 - 0.117
Clopyralid	280	21 (8%)		4		0.0187 - 0.409
Picloram	280	20 (7%)		4		0.0529 - 0.216
Napropamide	323	19 (6%)		3		0.00445 - 0.217
Mecoprop (MCP)	280	17 (6%)		6		0.0202 - 0.13
Triallate	323	11 (3%)		3		0.00211 - 0.0218
Imazapic	322	9 (3%)		4		0.0072 - 0.0294
Indaziflam	322	9 (3%)		4		0.00181 - 0.016

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Prometryn	323	7 (2%)		4		0.0014 - 0.00898
Flumioxazin	239	6 (3%)	1	4	1	0.0158 - 0.325
Isoxaben	322	3 (1%)		1		0.0041 - 0.00469
Oxadiazon	323	3 (1%)		2		0.00227 - 0.00801
Aminocyclopyrachlor	322	2 (1%)		2		0.227 - 2.69
Simetryn	323	2 (1%)		1		0.0158 - 0.0209
Triclopyr butoxyethyl ester	323	2 (1%)		2		0.00182 - 0.0227
Ethalfuralin	323	1 (<1%)		1		0.0024
Fluroxypyr 1-methylheptyl ester	323	1 (<1%)		1		0.0112
Prodiamine	323	1 (<1%)		1		0.0184
Sulfometuron-methyl	322	1 (<1%)		1		0.012

WSDA considers bolded analytes to be statewide POCs.

The variability in the 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, AMPA (a glyphosate breakdown product), and glufosinate-ammonium were only tested at three sites. 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 210 and 160 detections, respectively. There were 18 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Diuron and flumioxazin were detected above the WSDA assessment criteria, accounting for roughly 5% of the total exceedances in 2023. Diuron was the only herbicide statewide POC. Diuron can be used on a variety of crops such as alfalfa, berries, grass seed, ornamentals, and pasture and non-agricultural uses such as rights-of-way and around buildings. This state-restricted use chemical can be transported off-target via drift or runoff and can contaminate groundwater. Diuron has been found in Washington state groundwater.

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 → 2-hydroxyatrazine (detected at nine monitoring sites),
- → deisopropyl atrazine (detected at one monitoring site),
- → desethyl atrazine (detected at three monitoring sites),
- Dichlobenil → 2,6-dichlorobenzamide (detected at all 17 monitoring sites),
- Diuron → 1-(3,4-Dichlorophenyl)-3methylurea (detected at four monitoring sites),
- Glyphosate → aminomethylphosphoric acid (AMPA) (detected at all three monitoring sites where glyphosate was tested).

Fungicide Detections

Fungicides and degradates tied as the second and third most frequently detected groups of pesticides. Fungicides represented approximately 14% (606 detections) of the total number of detections. Out of 21 fungicides included in the laboratory analysis, 13 were detected in surface water samples. Table 25 provides a statewide summary of the detected fungicides.

Table 25 – Statewide summary of fungicides with one or more detections in 2023

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Boscalid	323	224 (69%)		17		0.000827 - 0.142
Fludioxonil	323	124 (38%)		8		0.00379 - 0.164
Metalaxyl	323	74 (23%)		9		0.00594 - 0.404
Propiconazole	322	54 (17%)		9		0.00585 - 0.215
Azoxystrobin	322	45 (14%)		8		0.00212 - 0.187
Pyrimethanil	322	30 (9%)		5		0.00605 - 0.0251
Carbendazim	322	27 (8%)	1	8	1	0.00451 - 0.422
Chlorothalonil	323	10 (3%)		5		0.00146 - 0.0172
Triadimefon	323	7 (2%)		4		0.00179 - 0.00758
Inpyrfluxam	322	5 (2%)		5		0.0128 - 0.109
Trifloxystrobin	322	3 (1%)		2		0.00237 - 0.00466
Difenoconazole	322	2 (1%)		2		0.0102 - 0.0151
Pyraclostrobin	322	1 (<1%)		1		0.00752

Boscalid and fludioxonil were the most commonly detected fungicides with 224 and 124 detections, respectively. Boscalid and fludioxonil have been among the most commonly detected fungicides each year since 2015. Carbendazim was the only fungicide detected above the WSDA assessment criteria.

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

- Boscalid
- Metalaxyl
- Propiconazole

Insecticide Detections

Current-use insecticides were the fourth most frequently detected group of pesticides representing approximately 12% (515 detections) of the total pesticide detections. Of the 48 current-use insecticides included in the laboratory analysis, 30 were detected in surface water samples. Table 26 provides a statewide summary of the detected insecticides.

Table 26 – Statewide summary of insecticides with one or more detections in 2023

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Thiamethoxam	322	84 (26%)		7		0.00427 - 0.283
Diazinon	323	63 (20%)	2	11	2	0.00139 - 0.167
Flupyradifurone	322	39 (12%)		3		0.00989 - 0.152
Oxamyl	322	37 (11%)		5		0.00187 - 0.29
Malathion	322	34 (11%)	8	7	3	0.00261 - 2.9
Clothianidin	322	32 (10%)	19	2	1	0.00943 - 0.0859
Dinotefuran	322	32 (10%)		4		0.00785 - 0.185
Imidacloprid	322	31 (10%)	31	7	7	0.00824 - 0.0668
Fipronil	323	30 (9%)	7	5	3	0.00168 - 0.0475
Chlorantraniliprole	322	26 (8%)		4		0.0126 - 0.0359
Acephate	322	18 (6%)		3		0.011 - 0.534
Dimethoate	323	15 (5%)		6		0.00352 - 0.0136
Etoxazole	323	10 (3%)		2		0.00297 - 0.029
Methoxyfenozide	322	10 (3%)		2		0.00409 - 0.0571
Chlorpyrifos	323	8 (2%)	1	4	1	0.00126 - 0.0114
Acetamiprid	322	7 (2%)		2		0.0083 - 0.0162
Bifenthrin	323	7 (2%)	7	5	5	0.00261 - 0.00704
Ethoprop	323	6 (2%)		3		0.00184 - 0.0264
gamma-Cyhalothrin	323	5 (2%)	5	4	4	0.000902 - 0.00215
Pyriproxyfen (Nylar)	323	4 (1%)	1	3	1	0.00216 - 0.0405
Carbaryl	322	3 (1%)		2		0.024 - 0.169
Phosmet	300	3 (1%)		2		0.00196 - 0.00393
Pyridaben	323	3 (1%)	1	2	1	0.00137 - 0.0409
Bifenazate	323	2 (1%)		1		0.0191 - 0.0314
cis-Permethrin	323	1 (<1%)	1	1	1	0.00682
Dicofol	323	1 (<1%)		1		0.0189
Fenbutatin oxide	322	1 (<1%)		1		0.0073
Fenpropathrin	323	1 (<1%)	1	1	1	0.0065
tau-Fluvalinate	323	1 (<1%)		1		0.00196
Tolfenpyrad	322	1 (<1%)	1	1	1	0.0136

WSDA considers bolded analytes to be statewide POCs.

Thiamethoxam and diazinon were the most commonly detected insecticides with 84 and 63 detections, respectively. The neonicotinoids thiamethoxam and imidacloprid have been among the most commonly detected insecticides every year since 2015. Diazinon was detected at more than 50% of the monitoring sites throughout the sampling season.

Current-use insecticides accounted for almost 32% (85 detections) of all exceedances in 2023. All detections of bifenthrin, cis-permethrin, fenpropathrin, gamma-cyhalothrin, imidacloprid, and tolfenpyrad were at concentrations above the WSDA assessment criteria. Of the 30 current-use insecticides that NRAS

detected, 43% (13 insecticides) had a concentration detected that exceeded WSDA assessment criteria at least once.

The four statewide insecticide POCs identified in 2023 were bifenthrin, chlorpyrifos, gamma-cyhalothrin, and imidacloprid. This is the second year bifenthrin has been identified as a statewide POC. It can be applied on crops like berries, corn, legumes, potatoes, and brassicas, and can also be used by homeowners in residential areas. Bifenthrin has extremely low solubility in water. Contamination is likely from bifenthrin bound to the sediment in runoff. There were seven exceedances of bifenthrin found across four Western Washington sites and one Palouse site – the same number of exceedances detected in 2022. Similarly to bifenthrin, this is the second year gamma-cyhalothrin has been identified as a statewide POC. It is used on crops like cereal grains, potatoes, pears, and some vegetables. There were five exceedances of gamma-cyhalothrin across one Western Washington site, two Central Washington sites, and one Palouse site – fewer than the 14 exceedances in 2022. Both bifenthrin and gamma-cyhalothrin are pyrethroids.

Chlorpyrifos, an organophosphate, has been a statewide POC since 2009. It was most often applied on fruit trees until the beginning of 2022 when the EPA revoked the residue tolerances for food and feed uses of the chemical. This change effectively eliminated the most common usages. There was one exceedance of chlorpyrifos found at one Central Washington site in 2023 – significantly fewer exceedances than in previous years (e.g. 81 in 2021 and seven in 2022). Imidacloprid, a neonicotinoid, has been a POC since 2017. This insecticide can be applied to over 250 commercial crop types, including as a seed treatment, and has residential uses. It is unclear to us whether the detections of imidacloprid which exceeded WSDA criteria were a result of agricultural or residential applications. There were 31 exceedances of imidacloprid across three Western Washington sites, two Central Washington sites, and two Palouse sites – fewer than the 49 exceedances in 2022.

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 three monitoring sites),
- Fipronil → fipronil disulfenyl (detected at three monitoring sites),
- → fipronil sulfide (detected at seven monitoring sites),
- → fipronil sulfone (detected at six monitoring sites),
- Malathion → malaoxon (detected at two monitoring sites),
- Oxamyl → oxamyl oxime (detected at one monitoring site).

Degradate and Other Pesticide Detections

This group includes degradates of current-use pesticides as well as several other pesticide-related chemicals. Degradates represented 14% (606 detections) of total detections and pesticide-related chemicals represented less than 2% (65 detections) of total detections. Of the 20 degradates from current-use chemicals included in the laboratory analysis, 16 were detected in surface water samples. Each antimicrobial, insect repellent, synergist, and wood preservative tested for had at least one detection. Table 27 provides a statewide summary of the detected degradates and other pesticide product ingredients.

Table 27 – Statewide summary of degradates and other pesticide products in 2023

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Degradates:						
2,6-Dichlorobenzamide	323	239 (74%)		17		0.00131 - 0.409
2-Hydroxyatrazine	322	89 (28%)		9		0.00548 - 0.147
Aminomethylphosphoric acid (AMPA)	56	56 (100%)		3		0.0948 - 2.26

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
Tetrahydrophthalimide (THPI)	323	54 (17%)		6		0.00125 - 0.137
Fipronil sulfide	323	46 (14%)		7		0.00107 - 0.00641
Fipronil sulfone	323	37 (11%)		6		0.00216 - 0.0092
1-(3,4-Dichlorophenyl)-3-methylurea	322	17 (5%)		4		0.00431 - 1.27
Oxamyl oxime	322	17 (5%)		1		0.0519 - 0.197
Methamidophos	322	14 (4%)		3		0.00517 - 0.0741
4-Nitrophenol	280	10 (4%)		4		0.0489 - 0.248
Desethyl atrazine	322	10 (3%)		3		0.00569 - 0.0155
Fipronil disulfinyl	323	6 (2%)		3		0.0017 - 0.0043
Malaoxon	322	5 (2%)	1	2	1	0.0041 - 0.164
Deisopropyl atrazine	322	3 (1%)		1		0.0323 - 0.0817
Clethodim sulfoxide	322	2 (1%)		1		0.327 - 1.08
Clethodim sulfone	322	1 (<1%)		1		0.064
Antimicrobial: Triclosan	323	2 (1%)		2		0.00641 - 0.0461
Insect repellent: DEET	323	47 (15%)		10		0.00705 - 0.448
Synergist: Piperonyl butoxide (PBO)	323	4 (1%)		2		0.00477 - 0.026
Wood preservative: Pentachlorophenol	280	12 (4%)		4		0.00435 - 0.0367

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 239 detections, followed by 2-hydroxyatrazine (a degradate of the herbicide atrazine) with 89 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 tetrahydrophthalimide and 4-nitrophenol. Tetrahydrophthalimide is the main breakdown product of the fungicide captan and 4-nitrophenol is a breakdown product of several natural and synthetic products. Clethodim sulfone and clethodim sulfoxide are breakdown products of clethodim, an herbicide. Clethodim is not included in the list of analytes due to its poor performance with this analytical method.

Other associated pesticide ingredients detected were pentachlorophenol, piperonyl butoxide, and triclosan. Pentachlorophenol's main usage is for wood preservation. Also, the insect repellent DEET (N,N-diethyl-m-toluamide), detected 47 times, was found at 10 out of 17 monitoring sites. 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 canceled. Detected legacy pesticides and associated degradates accounted for 4% (164 detections) of the total pesticide detections. Four out of five legacy analytes included in the lab analysis were detected. A statewide summary of the legacy analytes is shown below in Table 28.

Table 28 – Statewide summary of legacy pesticides and degradates with one or more detections in 2023

Analyte	Samples collected (n)	Detections (n) (% samples)	Detections above WSDA assessment criteria (n)	Sites with detections (n)	Sites with exceeding detections (n)	Concentration range (µg/L)
4,4'-DDD	323	80 (25%)	80	13	13	0.000726 - 0.0123
4,4'-DDE	323	52 (16%)	52	7	7	0.00139 - 0.0618
4,4'-DDT	323	31 (10%)	31	6	6	0.000986 - 0.0189
Fenarimol	323	1 (<1%)		1		0.00409

One DDT degradate, 4,4'-DDD, was the most frequently detected legacy chemical with 80 detections, followed by another DDT degradate, 4,4'-DDE, with 52 detections. DDT or associated breakdown products were found at five of seven Western Washington sites, all six Central Washington sites, and two of 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'-DDD and 4,4'-DDE) accounted for 61% of the total exceedances detected in 2023. Of the 163 combined DDT exceedances, 74 (45%) 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 assessment criteria. Then, each of those ratios is summed to obtain an estimated TU for the whole sample. In this report, NRAS analyzed TU using the fish LC₅₀, invertebrate EC₅₀, and plant EC₅₀ assessment criteria with WSDA's safety factor for a more conservative approach. If the TU ratio is above or equal to one, there is a higher possibility of lethal or sublethal effects on aquatic life.

Of the 325 sampling events analyzed using TUs, there were 35 instances that had a TU above or equal to one. There were 3 instances where more than one type of criteria had a TU ≥ 1 . Of the 35 instances, one sample had a TU ≥ 1 using fish criteria, 22 samples exceeded a TU ≥ 1 using invertebrate criteria, and 12 samples exceeded a TU ≥ 1 using plant criteria. There was a TU ≥ 1 at 11 out of 17 monitoring sites. Of the 35 instances where TUs ≥ 1 , two instances involved situations where individual pesticides each had a TU below 1, but their combined effects resulted in a total TU exceeding 1 (Table 29). The pesticides that contributed significantly to samples with TUs ≥ 1 were bifenthrin (6 events), diuron (11 events), gamma-cyhalothrin (5 events), and malathion (6 events). The chemicals were found in concentrations above WSDA assessment criteria predominately in the spring and early summer, coinciding with the samples where TU was exceeded.

Table 29 – Instances of toxic units ≥ 1 where individual detected analyte had a toxic unit below 1

Sampling date	Monitoring site	Criteria type	Analyte	Toxic unit value
4/24	Indian Slough	WSDA plant criteria	Diuron	0.166
			Flumioxazin	0.156
			Imazapyr	0.453
			Indaziflam	0.525
			Other 25 analytes	< 0.01
9/26	Burnt Bridge Creek	WSDA invertebrate criteria	Chlorpyrifos	0.516
			Diuron	0.496
			Fipronil	0.121
			Other 31 analytes	< 0.01

Nutrient Analysis

In 2023, nutrients were sampled at eight monitoring sites. Table 30 provides a summary of nutrient results at the eight sites. The results in Table 30 do not include samples that were rejected by laboratory or field QC processes. 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). The relationships described above are more evident with multiple years of data to assess. Since 2023 is the fourth 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 2023 nutrient sampling results

Nutrient	Monitoring site	Samples analyzed (n)	Detections (n) (% samples)	Detections exceeding criteria (n)	Median (mg/L)	Maximum (mg/L)
Ammonia as N	Ahtanum Creek	14	10 (71%)		0.033	0.063
	Upper Big Ditch	21	20 (95%)		0.157	0.344
	Dry Creek	20	16 (80%)		0.032	0.100
	Kamiache Creek	18	11 (61%)		0.031	0.110
	Marion Drain	31	21 (68%)		0.026	0.132
	Snipes Creek	20	13 (65%)		0.043	0.081
	Sulphur Creek	18	10 (56%)		0.053	0.264
	Thorn Creek	16	12 (75%)		0.041	0.113
Nitrate-Nitrite as N	Ahtanum Creek	14	14 (100%)	14	0.233	1.600
	Upper Big Ditch	21	21 (100%)	21	0.427	0.657
	Dry Creek	22	22 (100%)	22	2.765	7.700
	Kamiache Creek	18	18 (100%)	18	4.615	5.620
	Marion Drain	32	32 (100%)	32	2.125	6.880
	Snipes Creek	21	21 (100%)	21	0.467	4.000
	Sulphur Creek	18	18 (100%)	18	4.615	15.000
	Thorn Creek	17	17 (100%)	17	5.400	9.830
Ortho phosphate as P	Ahtanum Creek	14	14 (100%)		0.071	0.102
	Upper Big Ditch	21	21 (100%)		0.038	0.053
	Dry Creek	18	18 (100%)		0.112	0.168
	Kamiache Creek	17	16 (94%)		0.071	0.183
	Marion Drain	32	32 (100%)		0.091	0.284
	Snipes Creek	21	21 (100%)		0.037	0.061
	Sulphur Creek	18	18 (100%)		0.389	1.880
	Thorn Creek	16	16 (100%)		0.095	0.154
Total phosphorus as P	Ahtanum Creek	14	14 (100%)	14	0.093	0.143
	Upper Big Ditch	21	21 (100%)	21	0.089	0.132
	Dry Creek	21	21 (100%)	21	0.151	0.216
	Kamiache Creek	18	18 (100%)	18	0.087	0.198
	Marion Drain	32	32 (100%)	32	0.121	0.297
	Snipes Creek	21	21 (100%)	21	0.068	0.154
	Sulphur Creek	18	18 (100%)	18	0.382	1.760
	Thorn Creek	17	17 (100%)	17	0.109	0.175

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 2024c). There were no known orthophosphate criteria to compare to.

Conclusions

Staff collected surface water monitoring data at 17 locations across Western Washington, Central Washington, and the Palouse region in 2023. Water samples were collected from March 20 to November 28 a total of 325 times. Samples taken from three of the monitoring sites were tested in a lab for 153 pesticide and pesticide-related chemicals, 11 sites were tested for 150 chemicals, and three more sites were tested for a subset of 137 chemicals.

Of 153 pesticides tested for, 111 unique pesticides were detected.

NRAS detected pesticides in water samples a total of 4,386 times.

Sulfentrazone and metolachlor were the most frequently detected herbicides (210 and 160 times, respectively).

Thiamethoxam and diazinon were the most frequently detected insecticides (84 and 63 respectively).

Boscalid and fludioxonil were the most frequently detected fungicides (224 and 124 times, respectively).

Five chemicals were detected at more than 50% of sampling events they were tested for. 2,6-dichlorobenzamide (a degradate) was detected at more than 74% of sampling events. Glyphosate and its breakdown product AMPA were detected in 100% of the sampling events at the three monitoring sites where they were tested.

In order to assess the effects of pesticide exposure to aquatic life and endangered species, we compared detected pesticide concentrations to WSDA assessment criteria. There were 262 exceedances total with at least one exceedance at every monitoring site, except Ahtanum Creek. Approximately 38% of the total exceedances (99 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 eleven pesticides did. One detection of malaoxon, a breakdown product of malathion, exceeded criteria as well. Detections of legacy pesticides and associated degradates accounted for the remaining 62% (163 exceedances) of the total exceedances. Every detection of DDT and its degradates exceeded WSDA assessment criteria. Detections and exceedances were relatively plentiful at Burnt Bridge Creek and Brender Creek with 15 and 74 exceedances, respectively.

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

Analyte	Detections (n)	Detections above WSDA assessment criteria (n) (% samples)	Pesticide general use category
Diuron	66	11 (17%)	Herbicide
Diazinon	63	2 (3%)	Insecticide
Malathion	34	8 (24%)	Insecticide
Clothianidin	32	19 (59%)	Insecticide
Imidacloprid	31	31 (100%)	Insecticide
Fipronil	30	7 (23%)	Insecticide
Carbendazim	27	1 (4%)	Fungicide
Chlorpyrifos	8	1 (13%)	Insecticide
Bifenthrin	7	7 (100%)	Insecticide
Flumioxazin	6	1 (17%)	Herbicide
gamma-Cyhalothrin	5	5 (100%)	Insecticide
Pyriproxyfen (Nylar)	4	1 (25%)	Insecticide
Pyridaben	3	1 (33%)	Insecticide
cis-Permethrin	1	1 (100%)	Insecticide
Fenpropathrin	1	1 (100%)	Insecticide
Tolfenpyrad	1	1 (100%)	Insecticide

In 2023, monitoring sites commonly contained mixtures of pesticides in samples. Approximately 97% of sampling events had two or more pesticide detections during the field season. The maximum number of detections (37) at a single sampling event occurred twice, both at the Burnt Bridge Site on September 26 and October 11. 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 16 of the 17 monitoring sites. All sampling events at the eight 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 reduces 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 2024 statewide POCs were the herbicide diuron and the insecticides bifenthrin, chlorpyrifos, gamma-cyhalothrin, 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.

According to Lenora Jones of WSDA's Registration Services, Washington state had approximately 946 pesticide active ingredients registered for use at the end of 2024 (L. Jones. Personal communication. December 20, 2024). Surface water samples in 2023 were tested for roughly 16% of the total registered pesticide active ingredients. NRAS selects pesticides annually to test 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, analytical performance 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 higher toxicity towards aquatic invertebrates. Meanwhile, herbicides and fungicides are often less toxic to fish and invertebrates but more toxic to aquatic plants. However, indirect effects to ESA-listed species are considered in the federal pesticide registration process and are therefore accounted for in our assessment of pesticides in surface water. Invertebrates are the main food source of juvenile salmonids, and those invertebrates rely on aquatic plants to sustain their populations. Impairment to any organism, food webs and ecosystem functions are considered indirect effects to ESA-listed species. Pesticide monitoring in Washington waterways is essential for understanding the fate and transport of pesticides. WSDA POCs should be given additional prioritization for management by WSDA and partners minimize off target movement. Beginning in 2023, best management practices that have historically been used to reduce nutrient and sediment loading to adjacent natural resources are being included on pesticide labels for the mitigation of pesticide off-target movement. The fate and transport pathways of nutrients and sediments are similar to pesticides. WSDA will work to account for currently implemented best management practices where pesticide mitigation effectiveness is not well understood and work to quantify the effectiveness of practices not yet considered in the pesticide registration process. WSDA will continue 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

Very few changes occurred between the 2022 and 2023 sampling seasons. All 17 monitoring sites sampled in 2022 were sampled in 2023. NRAS partnered with the Palouse Conservation District again to monitor Dry Creek for a fourth sampling season and Thorn Creek and Kamiache Creek for a third season. In addition, all 153 analytes tested for in 2022 were tested for in 2023. No new analytes for testing were added between the 2022 and 2023 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 in 2023. Similar to the 2021 and 2022 field seasons, staff sampled nutrients at Ahtanum Creek, Upper Big Ditch, Marion Drain, Snipes Creek, Sulphur Creek Wasteway, Dry Creek, Thorn Creek, and Kamiache Creek monitoring sites in 2023.

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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 32a. 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
 - BS – Bluegill sunfish
 - BT – Brook trout
 - CC – Carp
 - CF – Catfish
 - FF – Flagfish
 - FM – Fathead minnow
 - JM – Japanese medaka
 - ND – Not described
 - OC – *Oncorhynchus clarkia* (cutthroat trout)
 - RT – *Oncorhynchus mykiss* (rainbow trout)
- Invertebrate:
 - ACR – Acute to chronic ratio
 - CG – *Chloroperia grammical* (stonefly)
 - CH – *Caenis horaria* (mayfly)
 - CL – *Cloeon dipterum* (mayfly)
 - CP – *Chironomus plumosus* (midge)
 - CR – *Chironomus riparius* (midge)
 - DD – *Ceriodaphnia dubia* (water flea)
 - DM – *Daphnia magna* (water flea)
 - DP – *Daphnia pulex*
 - GF – *Gammarus fasciatus* (scud)
 - HA – *Hyalella azteca* (amphipod)
 - 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)
 - LG – *Lemna gibba* (duckweed)
 - LM – *Lemna minor*
 - ND – Not described
 - NP – *Navicula pelliculosa*
 - OL – *Oscillatoria lutea* (blue-green algae)
 - SC – *Pseudokirchneriella subcapitata*
 - SD – *Skeletonema costatum* (diatom)
 - SP – *Scenedesmus pannonicus*
 - SS – *Scenedesmus subspicatus* (green algae)

In cases where different organisms were used for acute and chronic toxicity tests, the organism used for the acute test is noted first and the organism used for the chronic test is second. Table 32a contains only chemicals detected in 2023. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2023 Quality Assurance Summary.

Table 32a – WSDA Freshwater assessment criteria (WSDA safety factors applied, µg/L)

Pesticide	<u>Fish</u>				<u>Invertebrate</u>			<u>Aquatic Plant</u>		<u>WAC</u>		<u>NRWQC</u>	
	Endangered Species	Acute	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				
2-Hydroxyatrazine ³	75	750		RT	1025		DM	5000	AI				
4,4'-DDD ⁴										0.55	0.0005	0.55	0.0005
4,4'-DDE ⁴										0.55	0.0005	0.55	0.0005
4,4'-DDT ⁴										0.55	0.0005	0.55	0.0005
4-Nitrophenol ⁵	100	1000		RT	1250		DM						
Acephate ⁶	20800	208000	2880	RT	275	75	DM	25000	SD				
Acetamiprid ⁷	2500	25000	9600	RT/FM	5.25	1.05	CR/ACR	500	LG				
Aminocyclopyrachlor ⁸	3000	30000	5500	BS/RT	9925	185	DM	3700	AF				
Aminomethylphosphoric acid (AMPA) ⁹	12475	124750		RT	170750		DM						
Atrazine ¹⁰	132.5	1325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin ¹¹	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Bentazon ¹²	4750	47500	4915	RT/FM	15575	50600	CR/DM	2250	SC				
Bifenazate ¹³	14.5	145		BS	125	75	DM	445	SC				
Bifenthrin ¹⁴	0.00375	0.0375	0.002	RT/ND	0.00012325	0.000025	HA	145	SC				
Boscalid ¹⁵	67.5	675	58		1332.5	395		670					
Bromacil ¹⁶	900	9000	1500	RT	30250	4100	DM	3.4	SC				
Bromoxynil ¹⁷	52.5	525		RT	3977.5		DM						
Carbaryl ¹⁸	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	170	SC			1.05	1.05
Carbendazim ¹⁹	0.185	1.85	0.495	CF	27.5	1.55	DM	2290	SD				
Chlorantraniliprole ²⁰	345	3450	55	RT/RT	4.15	1.51	DM/DM	890	SC				
Chlorothalonil ²¹	0.45	4.5	0.385	RT/FM	13.5	0.3	DM	6	NP				
Chlorpropham ²²	75.25	752.5		RT	927.5		DM						
Chlorpyrifos ²³	0.0425	0.425	0.1255	BS/FM	0.00345	0.0025	HA/DM	70		0.0415	0.0205	0.0415	0.0205
cis-Permethrin ²⁴	0.01975	0.1975	0.026	BS/BS-ACR	0.00165	0.0021	HA	1.6	LG				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Clethodim sulfone													
Clethodim sulfoxide													
Clopyralid ²⁵	2575	25750	5000	RT/FM	58250	2350	DM	3450	SC				
Clothianidin ²⁶	2537.5	25375	4850	RT/FM	5.5	0.025	CR	32000					
Deisopropyl atrazine ³	425	4250			31500			1250					
Desethyl atrazine ³								500					
Diazinon ²⁷	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1850	SC			0.085	0.085
Dicamba acid ²⁸	700	7000	4950	RT/FM	25000	21000	DM	30.5	AF				
Dichlobenil ²	123.25	1232.5	165	RT	1550	280	DM	15	LG				
Dicofol ²⁹	1.325	13.25	2.2		35	9.5		2500					
Difenoconazole ³⁰	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP				
Dimethoate ³¹	155	1550	215	RT	10.75	0.25	PC	10000	AF				
Dinotefuran ³²	2477.5	24775	3180	CC/RT	242075	47650	DM	48800	SC				
Dithiopyr ³³	11.75	117.5	10	BS/FM	1300	40.5	DM	3.055	LG				
Diuron ³⁴	33	330	13.2	OC/FM	43.75	0.415	GF	0.065	LG				
Eptam ³⁵	350	3500	20	BS/FM-ACR	1625	400	DM	700	SC				
Ethalfuralin ³⁶	0.8	8	0.2	BS/RT	15	12	DM	3.65	LG				
Ethoprop ³⁷	7.5	75	12	RT/FM	11	0.4	DM	4200					
Etoxazole ³⁸	9.25	92.5	7.5	RT	1.825	0.065	DM	25.95	NP				
Fenarimol ³⁹	22.5	225	90	RT	1700	56.5	DM	50	SC				
Fenbutatin oxide ⁴⁰	0.0425	0.425	0.155	RT	7.75	8	DM						
Fenpropathrin ⁴¹	0.055	0.55	0.03	BS/FM	0.0007625	0.00075	HA	31.5	SC				
Fipronil ⁴²	2.075	20.75	3.3	BS/RT	0.055	0.0055	SV/ACR	38	SS				
Fipronil disulfenyl ⁴²	0.5	5	0.265	BS/ACR	88.75	20.5	DM/DD	38	SC				
Fipronil sulfide ⁴²	0.77	7.7	0.415	BS/BS-ACR	25	2.58	DM/ND	38	SS				
Fipronil sulfone ⁴²	0.625	6.25	0.335	BS/BS-ACR	7.25	0.11	DM/DM	38	SS				
Fludioxonil ⁴³	11.75	117.5	9	RT/FM	225	7	DM	140	SC				
Flumioxazin ⁴⁴	57.5	575	0.255	RT/FM	1375	14	DP/DM	0.245	LG				
Flupyradifurone													

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Fluroxypyr 1-methylheptyl ester ⁴⁵	15.75	157.5		BS	150	30.25	DM	28	NP				
gamma-Cyhalothrin ⁴⁶	0.000725	0.00725		BS	0.00002	0.000965	HA	0.254	LG				
Glyphosate ⁹	1075	10750	12850	BS/FM	13300	24950	CP/DM	5950	LG				
Hexazinone ⁴⁷	6850	68500	8500	RT/FM	37900	10000	DM	3.5	SC				
Imazapic ⁴⁸	2500	25000	48000	RT/FM	25000	48000	DM	3.11	LM				
Imazapyr ⁴⁹	2500	25000	21550	RT/FM	25000	48550	DM	12	LM				
Imidacloprid ⁵⁰	5725	57250	4500	RT	0.1925	0.005	CL/CH						
Indaziflam ⁵¹								0.0305	LG				
Inpyrfluxam ⁵²	0.775	7.75	2.45	RT/RT-ACR	275	70	DM	365	LG				
Isoxaben ⁵³	25	250	200	RT	325	345	DM	5	LG				
Malaoxon ⁵⁴	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020				0.05	
Malathion ⁵⁴	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020				0.05	
MCPA ⁵⁵								85	SC				
Mecoprop (MCP) ⁵⁶	2325	23250		RT	22750	25400	DM	7	SC				
Metalaxyl ⁵⁷	3250	32500	4550	RT/FM	7000	600	DM	42500	LG				
Methamidophos ⁵⁸	625	6250	86.8	RT	6.5	2.25	DM	25000	SD				
Methoxyfenozide ⁵⁹	105	1050	265	RT/FM	14.25	1.55	CR	1700	SC				
Metolachlor ⁶⁰	80	800	15	BS/FM	5875	1600	DM	4	SC				
Metribuzin ⁶¹	1050	10500	1500	RT	1050	645	DM	4.05					
N,N-Diethyl-m-toluamide (DEET) ⁶²	1875	18750		RT	18750		DM						
Napropamide ⁶³	300	3000	550	BS/RT	6175	550	DM	175	LM				
Norflurazon ⁶⁴	202.5	2025	385	RT	3750	500	DM	3.015	NP				
Oxadiazon ⁶⁵	30	300	0.44	RT	600	15	DM	2.6	SC				
Oxamyl ⁶⁶	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Oxamyl oxime ⁶⁶	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Pendimethalin ⁶⁷	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC				
Pentachlorophenol ⁶⁸	0.375	3.75	5.5	RT	23	2.05	DM	25	SC			9.5	7.5
Phosmet ⁶⁹	1.75	17.5	0.5	RT/FM	2.16	0.375	DM	70	NP				

Pesticide	<u>Fish</u>				<u>Invertebrate</u>			<u>Aquatic Plant</u>		<u>WAC</u>		<u>NRWQC</u>	
	Endangered Species	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Picloram ⁷⁰	137.5	1375	275	RT	8600	5900	DM	17450	SC				
Piperonyl butoxide (PBO) ⁷¹	72.5	725	3.9	RT/FM	10.55	15	HA/DM	605	SC				
Prodiamine ⁷²	0.325	3.25		BS	3.25	0.75	DM						
Prometon ⁷³	490	4900	3265	RT/RT-ACR	6425	1725	DM	49	SC				
Prometryn ⁷⁴	72.75	727.5	310	RT/FM	2425	500	DM	0.52	NP				
Propiconazole ⁷⁵	21.25	212.5	7.5	RT/FM-ACR	1200	90	DM	10.5	ND				
Pyraclostrobin ⁷⁶	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP				
Pyridaben ⁷⁷	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG				
Pyrimethanil ⁷⁸	252.5	2525	10	RT	750	500	DM	900	ND				
Pyriproxyfen (Nylar) ⁷⁹	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG				
Simazine ⁸⁰	160	1600	30	FM	250	20	DM/ACR	3	SC				
Simetryn													
Sulfentrazone ⁸¹	2345	23450	1475	BS/RT	15100	100	DM	14.4	SC				
Sulfometuron-methyl ⁸²	3700	37000		RT	37500	48500	DM	0.225	LG				
tau-Fluvalinate ⁸³	0.00875	0.0875	0.032	CC/FM	0.235	0.05	DM						
Tebuthiuron ⁸⁴	2650	26500	4650	FM	74250	10900	DM	25	SC				
Terbacil ⁸⁵	1155	11550	600	RT	16250	25	DM	5.5	NP				
Tetrahydrophthalimide (THPI) ⁸⁶	3000	30000		RT	28250		DM	90500	SC				
Thiamethoxam ⁸⁷	2850	28500	10000	BS/RT	8.75	0.37	CR	45100	LM				
Tolfenpyrad ⁸⁸	0.004075	0.04075	0.094	RT/FM	0.25	0.122	DM	5	SC				
Triadimefon ⁸⁹	102.5	1025	20.5	RT	400	26	DM	550	LG				
Triallate ⁹⁰	30	300	19	RT	22.75	7	DM	10.5	SC				
Triclopyr acid ⁹¹	2925	29250	37200	RT/FM	33250	28850	DM	2100	AF				
Triclopyr butoxyethyl ester ⁹¹	9	90	13	BS/RT	87.5	85	DM	50	NP				
Triclosan ⁹²	7.2	72		FM	97.5		DM	0.35	SS				
Trifloxystrobin ⁹³	0.3575	3.575	2.15	RT	6.325	1.38	DM	18.55	SC				
Trifluralin ⁹⁴	0.4625	4.625	0.95		62.75	1.2		10.95					

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Appendix B: 2023 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 2023, QA/QC samples were 10% of all the samples collected in the field. There were 199 QC samples in total: 94 field replicates, 73 field blanks, 32 MS/MSD samples, and 17 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 2023, all pesticide and nutrient analytes tested for during the season were used to spike MS/MSDs and LCS/LCSDs. 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 2023. 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, 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 2023) and standard deviation are presented in Table 33b.

Table 33b – Mean performance of analytical method reporting limits (LLOQ or MRL) in ng/L

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
<u>Method: LCMS-Pesticides; Reporting Limit: LLOQ</u>				
1-(3,4-Dichlorophenyl)-3-methylurea	3567-62-2	Degradate	1.00E+01	0.00E+00
2-Hydroxyatrazine	2163-68-0	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	1.26E+02	4.37E+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	1.00E+01	0.00E+00
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
Deisopropyl Atrazine	1007-28-9	Degradate	1.00E+01	0.00E+00
Desethylatrazine	6190-65-4	Degradate	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	1.05E+02	2.25E+01
Dinotefuran	165252-70-0	Insecticide	2.00E+01	0.00E+00
Diuron	330-54-1	Herbicide	1.03E+01	4.89E+00
Fenbutatin oxide	13356-08-6	Insecticide	2.64E+01	2.17E+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	3.11E+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	6.41E+01	2.90E+01
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
Methiocarb	2032-65-7	Insecticide	2.00E+01	0.00E+00
Methomyl	16752-77-5	Insecticide	1.00E+01	0.00E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
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	5.00E+01	0.00E+00
Myclobutanil	88671-89-0	Fungicide	2.00E+01	0.00E+00
Oryzalin	19044-88-3	Herbicide	3.97E+02	1.43E+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
Propiconazole	60207-90-1	Fungicide	5.00E+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	5.00E+02	0.00E+00
Spirotetramat	203313-25-1	Insecticide	2.00E+02	0.00E+00
Sulfometuron methyl	74222-97-2	Herbicide	2.00E+01	0.00E+00
Sulfoxaflor	946578-00-3	Insecticide	2.00E+01	0.00E+00
Thiamethoxam	153719-23-4	Insecticide	2.00E+01	0.00E+00
Thiram	137-26-8	Fungicide	2.24E+02	8.13E+01
Tolfenpyrad	129558-76-5	Insecticide	5.00E+01	0.00E+00
Trifloxystrobin	141517-21-7	Fungicide	2.00E+01	0.00E+00

Method: LCMS-Glyphos; Reporting Limit: LLOQ

AMPA	1066-51-9	Degradate	2.15E+01	7.81E+00
Glufosinate-ammonium	77182-82-2	Herbicide	6.45E+00	1.53E-01
Glyphosate	1071-83-6	Herbicide	7.74E+00	4.82E+00

Method: GCMS-Herbicides; Reporting Limit: LLOQ

2,4-D	94-75-7	Herbicide	6.06E+01	9.25E-01
4-Nitrophenol	100-02-7	Degradate	6.06E+01	9.26E-01
Bentazon	25057-89-0	Herbicide	6.06E+01	9.26E-01
Bromoxynil	1689-84-5	Herbicide	6.06E+01	9.26E-01
Clopyralid	1702-17-6	Herbicide	6.06E+01	9.26E-01
Dacthal	1861-32-1	Herbicide	6.06E+01	9.26E-01
Dicamba	1918-00-9	Herbicide	6.06E+01	9.26E-01
Dichlorprop	120-36-5	Herbicide	6.06E+01	9.26E-01
MCPA	94-74-6	Herbicide	6.06E+01	9.26E-01
MCPP	93-65-2	Herbicide	6.06E+01	9.26E-01
Pentachlorophenol	87-86-5	Wood Preservative	6.06E+01	9.26E-01
Picloram	1918-02-1	Herbicide	3.03E+02	4.57E+00
Triclopyr	55335-06-3	Herbicide	6.06E+01	9.26E-01

Method: GCMS-Pesticides; Reporting Limit: LLOQ

2,6-Dichlorobenzamide	2008-58-4	Degradate	6.26E+00	2.87E+00
4,4'-DDD	72-54-8	Degradate	5.05E+00	7.32E-02

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
4,4'-DDE	72-55-9	Degradate	5.05E+00	7.32E-02
4,4'-DDT	50-29-3	Insecticide	5.05E+00	7.32E-02
Acetochlor	34256-82-1	Herbicide	2.73E+01	7.26E+01
Atrazine	1912-24-9	Herbicide	5.05E+00	7.32E-02
Bifenazate	149877-41-8	Insecticide	5.46E+00	1.40E+00
Bifenthrin	82657-04-3	Insecticide	5.05E+00	7.32E-02
Boscalid	188425-85-6	Fungicide	5.05E+00	7.32E-02
Bromacil	314-40-9	Herbicide	5.05E+00	7.32E-02
Captan	133-06-2	Fungicide	5.63E+00	1.62E+00
Chlorothalonil	1897-45-6	Fungicide	5.05E+00	7.32E-02
Chlorpropham	101-21-3	Herbicide	5.24E+00	8.76E-01
Chlorpyrifos	2921-88-2	Insecticide	5.05E+00	7.32E-02
cis-Permethrin	54774-45-7	Insecticide	5.05E+00	7.32E-02
Cyfluthrin	68359-37-5	Insecticide	5.46E+00	1.40E+00
Cypermethrin	52315-07-8	Insecticide	5.46E+00	1.40E+00
Deltamethrin	52918-63-5	Insecticide	5.05E+00	7.32E-02
Diazinon	333-41-5	Insecticide	5.05E+00	7.32E-02
Dichlobenil	1194-65-6	Herbicide	5.52E+00	1.99E+00
Dichlorvos (DDVP)	62-73-7	Insecticide	5.05E+00	7.32E-02
Kelthane	115-32-2	Insecticide	2.52E+01	3.56E-01
Dimethoate	60-51-5	Insecticide	5.05E+00	7.32E-02
Dithiopyr	97886-45-8	Herbicide	5.05E+00	7.32E-02
Eptam	759-94-4	Herbicide	5.05E+00	7.32E-02
Ethalfuralin (Sonalan)	55283-68-6	Herbicide	5.05E+00	7.32E-02
Ethoprop	13194-48-4	Insecticide	5.05E+00	7.33E-02
Etoazole	153233-91-1	Insecticide	1.84E+01	4.72E+00
Etridiazole	2593-15-9	Fungicide	5.05E+00	7.32E-02
Fenarimol	60168-88-9	Fungicide	5.05E+00	7.32E-02
Fenpropathrin	39515-41-8	Insecticide	5.05E+00	7.32E-02
Fenvalerate	51630-58-1	Insecticide	5.05E+00	7.32E-02
Fipronil	120068-37-3	Insecticide	5.05E+00	7.32E-02
Fipronil Desulfinyl	205650-65-3	Degradate	5.05E+00	7.32E-02
Fipronil Sulfide	120067-83-6	Degradate	5.05E+00	7.32E-02
Fipronil Sulfone	120068-36-2	Degradate	1.01E+01	1.43E-01
Fludioxonil	131341-86-1	Fungicide	5.05E+00	7.32E-02
Flumioxazin	103361-09-7	Herbicide	2.53E+01	3.69E-01
Fluroxypyr-meptyl	81406-37-3	Herbicide	2.52E+01	3.56E-01
Gamma-cyhalothrin	76703-62-3	Insecticide	5.05E+00	7.32E-02
Hexazinone	51235-04-2	Herbicide	5.05E+00	7.32E-02
Malathion	121-75-5	Insecticide	5.19E+00	2.56E+00
Metalaxyl	57837-19-1	Fungicide	1.08E+01	3.12E+00
Metolachlor	51218-45-2	Herbicide	5.05E+00	7.32E-02
Metribuzin	21087-64-9	Herbicide	5.05E+00	7.32E-02
N,N-Diethyl-m-toluamide	134-62-3	Insect Repellent	6.24E+01	1.38E+02
Napropamide	15299-99-7	Herbicide	5.05E+00	7.32E-02
Norflurazon	27314-13-2	Herbicide	5.05E+00	7.32E-02

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Oxadiazon	19666-30-9	Herbicide	5.05E+00	7.32E-02
Oxyfluorfen	42874-03-3	Herbicide	5.05E+01	7.32E-01
Pendimethalin	40487-42-1	Herbicide	5.05E+00	7.32E-02
Pentachloronitrobenzene	82-68-8	Fungicide	5.05E+00	7.32E-02
Imidan	732-11-6	Insecticide	5.05E+00	7.30E-02
Piperonyl Butoxide (PBO)	51-03-6	Synergist	5.05E+00	7.32E-02
Prodiamine	29091-21-2	Herbicide	2.52E+01	3.56E-01
Prometon	1610-18-0	Herbicide	5.05E+00	7.32E-02
Prometryn	7287-19-6	Herbicide	1.01E+01	1.43E-01
Propargite	2312-35-8	Insecticide	1.01E+01	1.43E-01
Pyridaben	96489-71-3	Insecticide	5.05E+00	7.32E-02
Pyriproxyfen	95737-68-1	Insecticide	1.01E+01	1.43E-01
Simazine	122-34-9	Herbicide	1.02E+01	2.23E+00
Simetryn	1014-70-6	Herbicide	2.52E+01	3.56E-01
Sulfentrazone	122836-35-5	Herbicide	5.29E+00	1.09E+00
Tau-fluvalinate	102851-06-9	Insecticide	5.24E+00	9.78E-01
Tebuthiuron	34014-18-1	Herbicide	1.01E+01	1.43E-01
Tefluthrin	79538-32-2	Insecticide	5.05E+00	7.32E-02
Terbacil	5902-51-2	Herbicide	5.45E+00	2.15E+00
Tetrahydrophthalimide	27813-21-4	Degradate	5.05E+00	7.32E-02
Tetramethrin	7696-12-0	Insecticide	5.05E+00	7.32E-02
Tralomethrin	66841-25-6	Insecticide	5.05E+00	7.32E-02
trans-Permethrin	61949-77-7	Insecticide	5.05E+00	7.32E-02
Triadimefon	43121-43-3	Fungicide	5.05E+00	7.32E-02
Triallate	2303-17-5	Herbicide	5.05E+00	7.32E-02
Triclopyr-butoxyl	64700-56-7	Herbicide	1.01E+01	1.43E-01
Triclosan	3380-34-5	Antimicrobial	1.01E+01	1.43E-01
Trifluralin	1582-09-8	Herbicide	1.01E+01	1.43E-01
Various Methods; Reporting Limit: MRL				
Specific Conductivity			1.50E+01	0.00E+00
Suspended Sediment Concentration			9.92E-01	2.76E-02
Ammonia	7664-41-7	Nutrient	1.67E-02	3.02E-02
Ammonia	7664-41-7	Nutrient	5.00E-02	1.03E-05
Nitrate-Nitrite as N		Nutrient	6.96E-02	1.73E-01
Nitrate-Nitrite as N		Nutrient	1.05E-01	7.98E-02
Ortho-Phosphate		Nutrient	1.15E-02	4.78E-02
Total Phosphorus		Nutrient	1.11E-02	9.82E-03

Data qualifiers describe the level of confidence associated with the data points. Laboratory data was qualified according to the National Functional Guidelines for Organic Superfund Methods Data Review (EPA 2020a) and National Functional Guidelines for Inorganic Superfund Methods Data Review (EPA 2020b), 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 34b that are used for sample analysis of pesticides, SSC, nutrients, and specific conductivity (MEL 2016).

Table 34b – 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 2023, approximately 5% of pesticide, nutrient, and SSC samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 199 consistently identified pairs for pesticide analysis, 25 consistently identified pairs for nutrient analysis, and 15 consistently identified pairs for SSC analysis. Consistently identified pairs are those where the analytes were detected 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. There were only 38 inconsistently identified pairs for pesticide analysis, no inconsistently identified pairs for nutrients, and no inconsistently identified pairs for SSC.

All of the 153 pesticide analytes tested for were detected in field replicates as well as all four nutrients and SSC. Table 35b 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 86 analytes without replicate detections and, therefore, are not found in Table 35b.

Table 35b – 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 (%)
Acephate	LCMS-Pesticides	16	0		1	100
Chlorothalonil (Daconil)	GCMS-Pesticides	15	0		1	100
Desethylatrazine	LCMS-Pesticides	16	0		1	100
Triadimefon	GCMS-Pesticides	15	0		1	100
Dithiopyr	GCMS-Pesticides	14	1	1	1	50
Fipronil Sulfide	GCMS-Pesticides	12	2	1	2	50
Malathion	GCMS-Pesticides	15	1	6	1	50
Pyrimethanil	LCMS-Pesticides	15	1	3	1	50
Simazine	GCMS-Pesticides	13	2	2	2	50
Terbacil	GCMS-Pesticides	13	3	17	3	50

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Flupyradifurone	LCMS-Pesticides	14	2	7	1	33
Imazapyr	LCMS-Pesticides	11	6	10	3	33
Indaziflam	LCMS-Pesticides	14	2	9	1	33
2,4-D	GCMS-Herbicides	7	6	5	2	25
2-Hydroxyatrazine	LCMS-Pesticides	13	3	6	1	25
Bromoxynil	GCMS-Herbicides	11	3	2	1	25
Diuron	LCMS-Pesticides	15	3	6	1	25
Fipronil Sulfone	GCMS-Pesticides	12	3	8	1	25
Boscalid	GCMS-Pesticides	3	10	6	3	23
Atrazine	GCMS-Pesticides	11	4	8	1	20
Metribuzin	GCMS-Pesticides	11	4	2	1	20
Norflurazon	GCMS-Pesticides	11	4	5	1	20
Pendimethalin	GCMS-Pesticides	11	4	28	1	20
Hexazinone	GCMS-Pesticides	10	5	10	1	17
Prometon	GCMS-Pesticides	10	5	10	1	17
Bromacil	GCMS-Pesticides	9	6	6	1	14
Metolachlor	GCMS-Pesticides	8	7	7	1	13
2,6-Dichlorobenzamide	GCMS-Pesticides	5	10	14	1	9
Sulfentrazone	GCMS-Pesticides	5	10	11	1	9
1-(3,4-Dichlorophenyl)-3-methylurea	LCMS-Pesticides	16	1	7	0	0
4,4'-DDD	GCMS-Pesticides	11	5	7	0	0
4,4'-DDE	GCMS-Pesticides	13	3	7	0	0
4,4'-DDT	GCMS-Pesticides	14	2	60	0	0
Acetamiprid	LCMS-Pesticides	16	1	6	0	0
Aminomethylphosphoric acid (AMPA)	LCMS-Glyphos	0	2	9	0	0
Ammonia	Ammonia-N (NH3)	3	6	9	0	0
Azoxystrobin	LCMS-Pesticides	14	3	5	0	0
Bentazon	GCMS-Herbicides	12	3	5	0	0
Carbendazim	LCMS-Pesticides	16	1	2	0	0
Chlorantraniliprole	LCMS-Pesticides	16	1	19	0	0

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Chlorpropham	GCMS-Pesticides	14	2	7	0	0
Chlorpyrifos	GCMS-Pesticides	15	1	13	0	0
Clopyralid	GCMS-Herbicides	13	2	28	0	0
Clothianidin	LCMS-Pesticides	16	1	6	0	0
Diazinon	GCMS-Pesticides	14	2	4	0	0
Dicamba	GCMS-Herbicides	10	5	5	0	0
Dichlobenil	GCMS-Pesticides	8	8	8	0	0
Dimethoate	GCMS-Pesticides	15	1	14	0	0
Dinotefuran	LCMS-Pesticides	15	2	7	0	0
Eptam	GCMS-Pesticides	12	4	16	0	0
Fipronil	GCMS-Pesticides	14	2	14	0	0
Fludioxonil	GCMS-Pesticides	11	5	4	0	0
Glyphosate	LCMS-Glyphos	0	2	1	0	0
MCPA	GCMS-Herbicides	12	3	2	0	0
MCPP	GCMS-Herbicides	14	1	8	0	0
Metalaxyl	GCMS-Pesticides	12	4	4	0	0
Methoxyfenozide	LCMS-Pesticides	16	1	21	0	0
N,N-Diethyl-m-toluamide	GCMS-Pesticides	13	3	2	0	0
Napropamide	GCMS-Pesticides	15	1	7	0	0
Nitrate-Nitrite as N	Nitrate+Nitrite-N	0	6	2	0	0
Ortho-Phosphate	Phosphate, Ortho- (OP)	0	8	1	0	0
Oxamyl	LCMS-Pesticides	16	1	1	0	0
Oxamyl oxime	LCMS-Pesticides	16	1	7	0	0
Picloram	GCMS-Herbicides	13	2	10	0	0
Propiconazole	LCMS-Pesticides	15	2	15	0	0
Pyridaben	GCMS-Pesticides	15	1	51	0	0
Suspended Sediment Concentration	SSC	0	15	6	0	0
Tebuthiuron	GCMS-Pesticides	11	5	5	0	0
Tetrahydrophthalimide	GCMS-Pesticides	15	1	3	0	0
Thiamethoxam	LCMS-Pesticides	12	5	13	0	0
Total Phosphorus	Phosphorus, Total	0	5	2	0	0

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Treflan (Trifluralin)	GCMS-Pesticides	15	1	7	0	0
Triclopyr	GCMS-Herbicides	14	1	42	0	0

Staff estimated the uncertainty of replicate variability by using 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 82% of analytes (60 analytes) had inconsistent identified pair percentages of equal to or less than 25%. This analysis of variability can be useful when there are many replicate pairs with identified detections.

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 199 consistently identified replicate pairs for pesticides, eight had RPDs that were equal to or greater than the 40% RPD criterion. For SCC analysis, of the 15 consistently identified pairs, one pair had an RPD greater than or equal to 20% (RPD criterion) with a mean RPD of 6%. For nutrients analysis, the mean RPD of the consistently identified replicate-paired analytes was 4%. Of the 25 consistently identified nutrient pairs, there were no pairs with 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, and SSC field replicates were of acceptable data quality.

The majority of the 38 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 *UU* 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 2023, there were 22 detections in the 73 field blank samples collected for nutrients, SSC, and pesticide analysis (Table 36b). 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 detections with concentrations that were lower than five times the field blank detection concentration were re-qualified to *U*. There were 46 sample detections qualified to *U* in 2023 due to field blank detections.

Table 36b – Analyte detections in field blanks

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	Reporting limit (ng/L)	MDL (ng/L)	Qualifier
04/11	Upper Bertrand Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	2.83	5	1.28	J
04/17	Lower Bertrand Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	2.54	4.95	1.27	J
05/16	Lower Big Ditch	GCMS-Pesticides	2,6-Dichlorobenzamide	2.59	4.95	1.27	J
09/12	Burnt Bridge Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	2.03	5.15	1.32	J
04/11	Upper Bertrand Creek	GCMS-Pesticides	Acetochlor	36.8	5	3.51	
05/16	Lower Big Ditch	GCMS-Pesticides	Acetochlor	64.4	4.95	3.47	
05/01	Marion Drain	Ammonia-N (NH3)	Ammonia	0.033	0.01	0.002	
06/21	Dry Creek	Ammonia-N (NH3)	Ammonia	0.025	0.01	0.002	
05/16	Lower Big Ditch	GCMS-Pesticides	Chlorpropham	1.13	4.95	0.971	J
05/30	Marion Drain	GCMS-Pesticides	Chlorpropham	1.95	5.05	0.99	J
03/27	Snipes Creek Wasteway	GCMS-Pesticides	DEET	95.6	4.95	1.32	
04/04	Stemilt Creek	GCMS-Pesticides	DEET	96.5	4.95	1.32	
05/02	Brender Creek	GCMS-Pesticides	DEET	31.7	5	1.33	
05/30	Marion Drain	GCMS-Pesticides	DEET	53.7	5.05	1.35	
09/12	Burnt Bridge Creek	GCMS-Pesticides	DEET	11.6	5.15	1.37	
05/16	Lower Big Ditch	GCMS-Pesticides	Dichlobenil	1.51	4.95	1.39	J
05/30	Marion Drain	GCMS-Pesticides	Dichlobenil	3.11	5.05	1.42	J
06/05	Dry Creek	LCMS-Glyphos	Glyphosate	5.06	6.57	3.72	J
06/12	Marion Drain	LCMS-Pesticides	Imazapic	13.6	100	5.19	J
06/12	Marion Drain	LCMS-Pesticides	Inpyrfluxam	36	50	9.32	J
06/21	Upper Bertrand Creek	LCMS-Pesticides	Inpyrfluxam	10.9	50	9.32	J
07/17	Kamiache Creek	Phosphate, Ortho-(OP)	Ortho Phosphate	0.0721	0.003	0.0014	J

Matrix Spike/Matrix Spike Duplicate Results

Summary MS/MSD results for each analyte are shown in Table 37b, 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 37b – 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	20	65	135	103.05	93 - 117	0	0	10	5.19	0.9 - 10	17
2,4-D	18	39.3	142	71.33	58 - 87	0	0	9	7.41	0.7 - 27	130
2,6-Dichlorobenzamide	20	60	140	128.95	100 - 153	0	7	10	3.39	0.9 - 8	239
2-Hydroxyatrazine	20	52	176	102.25	91 - 139	0	0	10	4.69	0.9 - 14	89
4,4'-DDD	20	60	140	121.00	110 - 130	0	0	10	4.70	1 - 15	80
4,4'-DDE	20	60	140	87.50	73 - 97	0	0	10	5.38	0.03 - 12	52
4,4'-DDT	20	44	140	79.45	38 - 103	1	0	10	12.70	3 - 34	31
4-Nitrophenol	18	57.5	163	86.44	38 - 106	1	0	9	18.22	2 - 67	10
Acephate	20	59	135	91.90	69 - 113	0	0	10	2.81	0.5 - 7	18
Acetamiprid	20	65	163	120.70	109 - 139	0	0	10	2.05	0.1 - 10	7
Acetochlor	20	60	140	128.75	115 - 146	0	4	10	2.54	0.3 - 6	
Acetochlor ESA	20	57	156	105.75	78 - 133	0	0	10	4.67	0.8 - 12	
Afidopyropen	20	60	135	110.75	35 - 206	2	2	10	6.20	0.08 - 32	
Aminocyclopyrachlor	20	10	250	172.65	74 - 354	0	2	10	2.82	0.2 - 5	2
Aminomethylphosphoric acid (AMPA)	6	50	150	97.17	83 - 108	0	0	3	7.37	0.1 - 20	56
Atrazine	20	60	140	105.35	95 - 118	0	0	10	2.47	0.2 - 5	120
Azoxystrobin	20	57	153	95.95	74 - 124	0	0	10	7.97	0.7 - 16	45
Bensulide	20	35	135	100.65	62 - 206	0	2	10	17.30	6 - 31	
Bentazon	18	47.7	148	84.50	59 - 96	0	0	9	2.72	0.7 - 7	70
Bifenazate	20	10	250	169.40	107 - 211	0	0	10	7.76	0.6 - 15	2
Bifenthrin	20	58	140	103.85	75 - 119	0	0	10	8.80	2 - 18	7
Boscalid	20	60	141	153.05	125 - 173	0	15	10	3.58	0.4 - 7	224

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)
Bromacil	20	60	159	149.85	134 - 165	0	3	10	2.78	0.04 - 5	130
Bromoxynil	18	49.8	125	79.39	67 - 94	0	0	9	4.46	0.4 - 11	21
Captan	20	12	140	66.50	22 - 112	0	0	10	17.40	2 - 47	
Carbaryl	20	65	135	104.30	95 - 112	0	0	10	4.91	0.09 - 13	3
Carbendazim	20	63	135	96.30	77 - 108	0	0	10	4.08	0.8 - 9	27
Chlorantraniliprole	20	44	161	103.45	88 - 139	0	0	10	8.33	0.3 - 23	26
Chlorothalonil	20	60	140	97.70	80 - 107	0	0	10	3.62	0.4 - 9	10
Chlorpropham	20	60	140	124.20	115 - 135	0	0	10	1.55	0.04 - 5	21
Chlorpyrifos	20	60	140	106.65	94 - 116	0	0	10	3.28	0.1 - 12	8
Chlorsulfuron	20	22	194	116.40	66 - 196	0	1	10	5.40	2 - 15	
cis-Permethrin	20	60	140	126.10	96 - 144	0	3	10	8.09	0.9 - 19	1
Clethodim sulfone	20	35	180	107.40	81 - 140	0	0	10	4.60	2 - 8	1
Clethodim sulfoxide	20	43	177	110.85	82 - 133	0	0	10	3.45	0.5 - 11	2
Clopyralid	18	11.6	125	29.89	19 - 42	0	0	9	24.22	Jul-50	21
Clothianidin	20	56	135	69.85	36 - 97	3	0	10	9.60	1 - 24	32
Cyantraniliprole	20	61	149	114.85	98 - 132	0	0	10	2.84	0.3 - 7	
Cyfluthrin-Total	20	60	146	142.05	114 - 179	0	7	10	6.86	0.6 - 15	
Cypermethrin-Total	20	60	153	160.00	126 - 194	0	15	10	7.41	0.3 - 18	
Cyprodinil	20	63	135	101.85	68 - 120	0	0	10	4.80	1 - 13	
Dacthal (DCPA)	18	52.1	143	87.22	71 - 103	0	0	9	4.45	0.08 - 10	
Deisopropyl atrazine	20	58	158	82.95	71 - 94	0	0	10	2.98	0.4 - 11	3
Deltamethrin	20	60	147	142.80	103 - 178	0	8	10	7.99	0.9 - 18	
Desethyl atrazine	20	51	157	75.35	62 - 86	0	0	10	2.50	0.1 - 7	10
Diazinon	20	60	140	112.25	103 - 122	0	0	10	1.98	0.003 - 6	63
Dicamba acid	18	41.6	125	73.33	63 - 85	0	0	9	7.78	2 - 19	83
Dichlobenil	20	60	140	94.15	69 - 103	0	0	10	7.05	0.5 - 24	126
Dichlorprop	18	47.4	134	80.83	68 - 89	0	0	9	4.93	0.4 - 13	
Dichlorvos (DDVP)	20	60	157	128.35	104 - 142	0	0	10	7.25	0.5 - 24	
Dicofol	20	60	250	184.95	142 - 237	0	0	10	5.31	0.4 - 13	1
Difenoconazole	20	31	146	98.85	55 - 169	0	2	10	9.00	2 - 22	2
Diflubenzuron	20	54	148	98.55	72 - 144	0	0	10	10.94	0.4 - 28	
Dimethenamid ESA	20	57	136	101.95	88 - 130	0	0	10	6.36	0.1 - 16	

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)
Dimethenamid OA	20	56	135	99.10	84 - 126	0	0	10	2.74	0.07 - 8	
Dimethoate	20	60	146	136.30	125 - 154	0	3	10	2.20	0.005 - 5	15
Dinotefuran	20	65	146	113.45	85 - 130	0	0	10	3.34	0.4 - 6	32
Dithiopyr	20	60	140	112.90	103 - 126	0	0	10	3.79	0.4 - 13	32
Diuron	20	65	135	107.35	99 - 117	0	0	10	3.04	0.02 - 11	66
Eptam	20	60	140	96.40	72 - 114	0	0	10	7.26	0.8 - 26	91
Ethalfuralin	20	60	140	107.60	92 - 123	0	0	10	2.70	0.05 - 7	1
Ethoprop	20	60	140	131.40	121 - 142	0	1	10	2.18	0.5 - 5	6
Etoxazole	20	60	140	129.65	121 - 139	0	0	10	4.91	0.08 - 12	10
Etridiazole	20	60	140	80.75	51 - 103	2	0	10	10.10	1 - 23	
Fenarimol	20	60	164	144.35	132 - 162	0	0	10	2.71	0.05 - 4	1
Fenbutatin oxide	20	22	163	98.10	58 - 148	0	0	10	12.60	2 - 39	1
Fenpropathrin	20	60	140	105.00	87 - 115	0	0	10	6.30	2 - 12	1
Fenvalerate	20	60	140	128.25	98 - 151	0	4	10	8.07	0.7 - 16	
Fipronil	20	60	152	146.50	132 - 159	0	5	10	3.41	0.09 - 8	30
Fipronil disulfinyl	20	60	140	130.60	121 - 141	0	1	10	2.76	0.07 - 8	6
Fipronil sulfide	20	60	140	130.70	123 - 139	0	0	10	3.02	0.3 - 10	46
Fipronil sulfone	20	60	144	140.80	130 - 150	0	7	10	3.41	0.1 - 12	37
Fludioxonil	20	60	146	137.75	123 - 153	0	4	10	3.37	0.8 - 7	124
Flumioxazin	20	60	140	154.45	102 - 183	0	16	10	3.75	0.02 - 10	6
Fluopicolide	20	50	154	105.40	91 - 133	0	0	10	9.50	5 - 18	
Flupyradifurone	20	48	215	135.60	82 - 183	0	0	10	3.34	0.4 - 12	39
Fluroxypyr 1-methylheptyl ester	20	60	156	139.60	122 - 157	0	1	10	4.81	0.09 - 16	1
gamma-Cyhalothrin	20	60	140	116.95	93 - 137	0	0	10	8.02	0.2 - 17	5
Glufosinate-ammonium	6	50	150	93.83	84 - 104	0	0	3	6.87	0.6 - 11	
Glyphosate	6	50	150	94.17	86 - 101	0	0	3	2.67	1 - 4	56
Hexazinone	20	60	141	130.10	118 - 141	0	0	10	3.57	0.7 - 8	75
Hexythiazox	20	44	145	92.50	50 - 127	0	0	10	9.70	1 - 23	
Imazapic	20	42	230	157.35	102 - 234	0	1	10	4.20	2 - 9	9
Imazapyr	20	10	250	139.35	94 - 207	0	0	10	3.34	0.1 - 9	95
Imidacloprid	20	65	135	105.95	98 - 114	0	0	10	5.01	0.4 - 14	31

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)
Indaziflam	20	54	146	102.25	82 - 118	0	0	10	2.98	0.3 - 9	9
Inpyrfluxam	20	50	151	97.00	74 - 133	0	0	10	9.60	2 - 23	5
Isoxaben	20	59	153	106.05	92 - 131	0	0	10	7.60	3 - 17	3
Linuron	20	63	140	101.45	67 - 140	0	0	10	12.56	0.6 - 40	
Malaoxon	20	65	148	109.10	98 - 119	0	0	10	3.14	0.1 - 9	5
Malathion	20	60	144	137.25	125 - 150	0	3	10	3.29	0.9 - 9	34
MCPA	18	37.2	146	77.78	69 - 89	0	0	9	6.09	0.8 - 18	22
Mecoprop (MCP)	18	52.1	139	85.94	72 - 95	0	0	9	5.89	2 - 10	17
Metalaxyl	20	60	140	128.75	116 - 141	0	1	10	3.49	0.9 - 10	74
Methamidophos	20	22	135	82.90	56 - 105	0	0	10	3.51	0.07 - 7	14
Methiocarb	20	52	156	105.40	92 - 122	0	0	10	8.70	1 - 18	
Methomyl	20	65	135	103.70	99 - 110	0	0	10	2.92	0.05 - 8	
Methomyl oxime	20	40	135	91.30	76 - 110	0	0	10	5.10	1 - 13	
Methoxyfenozide	20	51	150	109.10	93 - 131	0	0	10	8.60	3 - 14	10
Metolachlor	20	60	140	118.15	105 - 129	0	0	10	3.61	0.2 - 7	160
Metribuzin	20	60	140	103.80	77 - 121	0	0	10	4.68	0.8 - 9	74
Metsulfuron-methyl	20	10	217	123.60	69 - 228	0	1	10	3.14	0.4 - 6	
Myclobutanil	20	48	156	104.85	92 - 135	0	0	10	8.20	4 - 18	
N,N-Diethyl-m-toluamide (DEET)	20	60	140	112.25	102 - 130	0	0	10	2.14	0.4 - 5	47
Napropamide	20	60	140	132.05	121 - 148	0	4	10	2.75	0.09 - 7	19
Norflurazon	20	60	140	140.65	128 - 158	0	9	10	2.78	0.8 - 5	124
Oryzalin	20	45	180	94.90	64 - 117	0	0	10	14.50	2 - 27	
Oxadiazon	20	60	140	117.50	105 - 130	0	0	10	3.97	0.2 - 14	3
Oxamyl	20	65	135	104.50	97 - 116	0	0	10	3.36	0.6 - 9	37
Oxamyl oxime	20	65	166	112.75	75 - 132	0	0	10	3.37	0.8 - 12	17
Oxyfluorfen	20	60	159	127.85	115 - 137	0	0	10	3.97	0.04 - 14	
Paclobutrazol	20	65	137	116.25	96 - 219	0	2	10	4.23	0.3 - 11	
Pendimethalin	20	60	140	117.70	84 - 129	0	0	10	3.90	1 - 13	115
Pentachloronitrobenzene (PCNB)	20	60	140	93.90	83 - 104	0	0	10	2.88	0.02 - 7	
Pentachlorophenol	18	48.2	125	81.56	67 - 98	0	0	9	4.31	0.8 - 14	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)
Phosmet	20	60	141	119.40	100 - 139	0	0	10	3.10	0.3 - 7	3
Picloram	18	10	125	41.67	18 - 57	0	0	9	17.73	0.6 - 48	20
Piperonyl butoxide (PBO)	20	60	165	149.80	137 - 164	0	0	10	3.25	0.04 - 13	4
Prodiamine	20	60	148	111.85	99 - 126	0	0	10	5.00	1 - 18	1
Prometon	20	60	140	119.25	111 - 134	0	0	10	2.10	0.09 - 5	81
Prometryn	20	60	140	125.20	113 - 135	0	0	10	2.94	0.1 - 9	7
Propargite	20	38	145	125.90	111 - 143	0	0	10	5.69	0.9 - 15	
Propiconazole	20	44	143	105.35	86 - 144	0	1	10	6.56	0.6 - 15	54
Pyraclostrobin	20	51	146	92.80	48 - 131	1	0	10	8.80	1 - 20	1
Pyrethrins	20	10	250	81.95	24 - 144	0	0	10	19.67	0.7 - 38	
Pyridaben	20	60	140	139.05	123 - 155	0	10	10	5.35	0.6 - 13	3
Pyrimethanil	20	65	135	93.00	83 - 99	0	0	10	2.93	0.03 - 10	30
Pyriproxyfen (Nylar)	20	60	140	122.60	110 - 132	0	0	10	3.79	0.2 - 13	4
Pyroxasulfone	20	54	145	105.60	83 - 143	0	0	10	11.39	0.9 - 26	
Simazine	20	60	140	107.80	96 - 117	0	0	10	2.42	0.4 - 5	125
Simetryn	20	60	140	112.95	101 - 130	0	0	10	3.05	0.3 - 7	2
Spirotetramat	20	23	176	97.15	62 - 131	0	0	10	10.91	0.1 - 33	
Sulfentrazone	20	60	163	120.75	10 - 149	2	0	10	17.26	0.3 - 100	210
Sulfometuron-methyl	20	44	183	118.70	95 - 161	0	0	10	1.89	0.02 - 9	1
Sulfoxaflor	20	65	142	114.55	86 - 131	0	0	10	2.52	0.7 - 9	
tau-Fluvalinate	20	60	147	145.95	111 - 180	0	9	10	8.83	0.3 - 18	1
Tebuthiuron	20	60	156	138.50	118 - 164	0	4	10	5.42	0.2 - 14	99
Tefluthrin	20	60	140	91.70	75 - 102	0	0	10	7.38	0.8 - 14	
Terbacil	20	10	250	149.90	132 - 170	0	0	10	2.84	0.4 - 7	94
Tetrahydrophthalimide (THPI)	20	60	150	137.30	112 - 162	0	4	10	5.80	3 - 13	54
Tetramethrin	20	60	140	142.80	117 - 164	0	12	10	5.22	0.4 - 14	
Thiamethoxam	20	59	135	86.75	62 - 101	0	0	10	8.03	0.3 - 16	84
Thiram	20	10	194	109.95	69 - 178	0	0	10	4.38	0.8 - 8	
Tolfenpyrad	20	31	149	86.65	23 - 146	1	0	10	13.70	1 - 36	1
Tralomethrin	20	60	147	144.35	106 - 175	0	11	10	7.96	0.6 - 19	
trans-Permethrin	20	60	140	126.40	100 - 143	0	2	10	7.45	0.5 - 15	

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)
Triadimefon	20	60	140	126.15	114 - 143	0	2	10	3.70	1 - 7	7
Triallate	20	60	140	108.40	100 - 121	0	0	10	1.60	0.3 - 5	11
Triclopyr acid	18	57.4	145	89.89	74 - 106	0	0	9	4.63	0.8 - 15	45
Triclopyr butoxyethyl ester	20	60	140	121.85	100 - 139	0	0	10	2.64	0.07 - 9	2
Triclosan	20	60	168	165.50	149 - 187	0	6	10	3.72	0.2 - 9	2
Trifloxystrobin	20	51	140	86.45	40 - 126	2	0	10	13.60	2 - 39	3
Trifluralin	20	60	140	96.40	81 - 105	0	0	10	2.18	0.2 - 6	30

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

There was a total of 3,188 spiked results (1,594 MS/MSD pairs) from MS and MSD recoveries that were unqualified or *J* qualified. Overall, the mean recovery was 112% with a standard deviation of 28%. 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 (15 recoveries) fell below the control limits for MS/MSD samples,
- 93% of analyte recoveries (2,978 recoveries) were within the control limits for MS/MSD samples,
- 6% of analyte recoveries (195 recoveries) were above the control limits for MS/MSD samples.

RPDs calculated for 1,594 MS/MSD pairs were below the 40% RPD control limit over 99% of the time; only 8 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 5%. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 55% with a standard deviation of 19%.

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 38b lists the analyte detections that occurred in the method blanks (179 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 four sample detections qualified to *U* in 2023 due to method blank detections.

Table 38b – 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	6	0.98	0.8	1.37	5	1.28
4,4'-DDD	GCMS-Pesticides	2	1.10	0.879	1.32	5	0.66
4,4'-DDE	GCMS-Pesticides	3	1.12	0.521	1.66	5	1.37
4,4'-DDT	GCMS-Pesticides	5	1.51	0.824	2.05	5	0.79
cis-Permethrin	GCMS-Pesticides	1	3.01	3.01	3.01	5	2.19
Dichlobenil	GCMS-Pesticides	5	1.11	0.852	1.48	5	1.40
Ethoprop	GCMS-Pesticides	2	1.69	1.47	1.91	5	1.43
Fenarimol	GCMS-Pesticides	33	6.03	1.43	27.3	5	1.07
Fenbutatin oxide	LCMS-Pesticides	1	8.20	8.2	8.2	20	3.02
Fenvalerate	GCMS-Pesticides	1	1.21	1.21	1.21	5	0.86
Fipronil sulfide	GCMS-Pesticides	2	1.06	1.04	1.08	5	0.86
gamma-Cyhalothrin	GCMS-Pesticides	1	1.09	1.09	1.09	5	0.81
Hexazinone	GCMS-Pesticides	14	1.53	0.893	2.43	5	1.04
Metolachlor	GCMS-Pesticides	6	0.86	0.686	1.09	5	0.58
N,N-Diethyl-m-toluamide (DEET)	GCMS-Pesticides	38	2.52	1.2	6.9	5	1.33
Phosmet	GCMS-Pesticides	6	1.43	1.15	1.7	5	1.60
Prometryn	GCMS-Pesticides	1	2.67	2.67	2.67	10	1.31
Pyridaben	GCMS-Pesticides	8	1.22	0.873	1.47	5	1.09
Pyriproxyfen (Nylar)	GCMS-Pesticides	7	1.31	0.955	2.35	10	1.40
Simetryn	GCMS-Pesticides	1	3.14	3.14	3.14	25	2.17
Tefluthrin	GCMS-Pesticides	1	0.72	0.718	0.718	5	0.56
Thiram	LCMS-Pesticides	1	115.00	115	115	200	51.30
trans-Permethrin	GCMS-Pesticides	1	2.08	2.08	2.08	5	1.12
Triadimefon	GCMS-Pesticides	4	2.75	1.52	3.89	5	1.47
Triclosan	GCMS-Pesticides	26	13.45	2.08	32.9	10	1.73
Trifloxystrobin	LCMS-Pesticides	1	4.99	4.99	4.99	20	1.65

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 39b presents summary statistics for surrogate recoveries of only field samples and field replicates.

Table 39b – Pesticide surrogates summary

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
<u>Carbamate pesticides:</u>						
Carbaryl C13	LCMS-Pesticides	452	100	100	65	135
Carbendazim-D4	LCMS-Pesticides	452	98	98.9	65	135
<u>Acid-derivitizable herbicides:</u>						
2,4,6-Tribromophenol	GCMS-Herbicides	436	80	98.2	48.2	125
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	436	97	98.9	63.7	133
<u>Nitrogen containing pesticides:</u>						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	485	92	100	50	132
<u>Chlorinated pesticides:</u>						
4,4'-DDE-13C12	GCMS-Pesticides	485	92	99.8	65	125
Decachlorobiphenyl	GCMS-Pesticides	485	78	100	28	125
<u>Glyphosate related pesticides:</u>						
AMPA-C13N15	LCMS-Glyphos	118	87	99.2	20	200
Glufosinate-d3	LCMS-Glyphos	118	95	98.3	20	200
Glyphosate-C13N15	LCMS-Glyphos	118	85	98.3	20	200
<u>Neonicotinoid pesticides:</u>						
Clothianidin-D3	LCMS-Pesticides	452	78	91.6	58	135
Clothianidin-D3-Neg	LCMS-Pesticides	452	97	99.1	36	159
Difenoconazole-D4	LCMS-Pesticides	452	99	92.5	54	136
<u>Organophosphate pesticides:</u>						
Chlorpyrifos-D10	GCMS-Pesticides	485	109	100	68	134
Triphenyl Phosphate	GCMS-Pesticides	485	133	99.4	66	163
<u>Chlorine and nitrogen containing pesticides:</u>						
Atrazine-D5	GCMS-Pesticides	485	115	100	58	151
Trifluralin-D14	GCMS-Pesticides	485	97	99.8	54	137

In 2023, the overall mean recovery for surrogates was 96% and 75% of surrogate recoveries were within control limits.

Laboratory Control Samples

Table 40b 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 40b – 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	50	65	135	109	99 - 126	0	0	25	4.73	0.2 - 15
2,4-D	76	54	125	64	28 - 88	0	10	38	8.97	0.3 - 32
2,6-Dichlorobenzamide	76	54	147	127	109 - 148	1	0	38	3.81	0.1 - 13
2-Hydroxyatrazine	50	65	136	103	82 - 132	0	0	25	4.73	0.06 - 13
4,4'-DDD	76	69	151	121	103 - 132	0	0	38	3.25	0.4 - 12
4,4'-DDE	76	67	133	99	87 - 111	0	0	38	3.49	0.03 - 14
4,4'-DDT	76	72	152	118	96 - 135	0	0	38	3.44	0.03 - 13
4-Nitrophenol	76	51	160	94	57 - 136	0	0	38	15.65	0.8 - 57
Acephate	50	65	135	106	93 - 124	0	0	25	4.71	0.05 - 17
Acetamiprid	50	65	137	99	84 - 116	0	0	25	5.54	0.1 - 20
Acetochlor	76	64	152	125	107 - 145	0	0	38	2.84	0.07 - 14
Acetochlor ESA	50	59	143	102	79 - 124	0	0	25	4.98	0.3 - 15
Afidopropen	50	60	135	111	87 - 211	3	0	25	6.47	0.03 - 14
Aminocyclopyrachlor	50	65	137	102	68 - 137	0	0	25	6.80	0.4 - 42
Aminomethylphosphoric acid (AMPA)	34	22	193	100	88 - 112	0	0	17	4.83	0.3 - 11
Atrazine	76	64	148	104	88 - 126	0	0	38	2.89	0.03 - 13
Azoxystrobin	50	65	135	95	74 - 122	0	0	25	7.22	0.1 - 18
Bensulide	50	42	135	100	68 - 183	2	0	25	7.67	0.7 - 24
Bentazon	76	70	132	87	70 - 115	0	1	38	5.52	0.1 - 20
Bifenazate	76	10	250	113	41 - 205	0	0	38	8.27	0.1 - 34
Bifenthrin	76	57	132	112	89 - 132	0	0	38	5.30	0.06 - 17
Boscalid	76	59	162	144	121 - 166	1	0	38	3.29	0.2 - 15
Bromacil	76	72	174	132	115 - 158	0	0	38	4.08	0.1 - 13

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* (%)
Bromoxynil	76	60	125	78	66 - 100	0	0	38	4.45	0.04 - 21
Captan	62	10	125	76	7 - 139	9	2	31	21.24	0.5 - 150
Carbaryl	50	65	135	108	96 - 120	0	0	25	4.51	0.2 - 13
Carbendazim	50	65	135	99	83 - 118	0	0	25	4.79	0.1 - 13
Chlorantraniliprole	50	61	140	100	75 - 118	0	0	25	7.11	0.9 - 22
Chlorothalonil	76	63	145	100	84 - 112	0	0	38	3.24	0.2 - 14
Chlorpropham	76	64	159	118	96 - 136	0	0	38	3.60	0.3 - 17
Chlorpyrifos	76	61	141	106	95 - 117	0	0	38	3.15	0.07 - 14
Chlorsulfuron	50	35	143	96	70 - 114	0	0	25	5.94	0.4 - 13
cis-Permethrin	76	62	140	132	105 - 160	19	0	38	5.15	0.04 - 18
Clethodim sulfone	50	46	137	100	82 - 117	0	0	25	4.09	0.2 - 19
Clethodim sulfoxide	50	51	144	107	91 - 138	0	0	25	3.79	0.3 - 11
Clopyralid	76	13	125	37	21 - 59	0	0	38	16.42	1 - 46
Clothianidin	50	65	135	107	85 - 130	0	0	25	6.78	0.1 - 29
Cyantraniliprole	50	50	157	107	94 - 126	0	0	25	4.48	0.9 - 14
Cyfluthrin-Total	76	60	147	139	103 - 184	22	0	38	5.46	0.1 - 19
Cypermethrin-Total	76	58	151	146	103 - 178	27	0	38	6.32	0.2 - 26
Cyprodinil	50	65	135	102	79 - 120	0	0	25	4.83	0.1 - 10
Dacthal (DCPA)	76	69	125	89	69 - 115	0	0	38	4.39	0.1 - 19
Deisopropyl atrazine	50	65	142	104	87 - 128	0	0	25	4.44	0.2 - 13
Deltamethrin	76	60	144	131	103 - 164	8	0	38	6.23	0.09 - 22
Desethyl atrazine	50	65	142	107	88 - 123	0	0	25	4.57	0.04 - 13
Diazinon	76	60	151	110	93 - 128	0	0	38	3.80	0.02 - 16
Dicamba acid	76	56	125	73	59 - 95	0	0	38	5.87	0.4 - 22
Dichlobenil	76	61	139	98	67 - 115	0	0	38	5.51	0.07 - 36
Dichlorprop	76	58	125	75	53 - 101	0	1	38	6.32	0.3 - 21
Dichlorvos (DDVP)	76	57	156	111	79 - 135	0	0	38	5.06	0.07 - 37
Dicofol	76	13	250	228	104 - 667	18	0	38	8.20	0.09 - 37
Difenoconazole	50	56	135	98	74 - 151	2	0	25	7.50	0.7 - 17
Diflubenzuron	50	58	139	100	73 - 122	0	0	25	7.88	0.2 - 23
Dimethenamid ESA	50	48	147	98	79 - 127	0	0	25	7.05	0.1 - 19
Dimethenamid OA	50	59	138	102	83 - 131	0	0	25	4.87	0.1 - 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* (%)
Dimethoate	76	54	159	126	105 - 147	0	0	38	3.66	0.3 - 14
Dinotefuran	50	65	135	104	87 - 114	0	0	25	4.02	0.4 - 11
Dithiopyr	76	56	140	114	96 - 129	0	0	38	3.26	0.07 - 12
Diuron	52	65	135	108	94 - 122	0	0	26	4.32	0.07 - 18
Eptam	76	51	145	99	57 - 126	0	0	38	5.57	0.6 - 43
Ethalfuralin	76	58	142	107	81 - 128	0	0	38	4.65	0.3 - 25
Ethoprop	76	60	159	123	100 - 141	0	0	38	3.84	0.05 - 21
Etoxazole	76	58	143	128	104 - 148	6	0	38	3.75	0.01 - 13
Etridiazole	76	66	151	96	59 - 119	0	2	38	5.64	0.09 - 41
Fenarimol	76	54	184	123	89 - 149	0	0	38	5.13	0.4 - 16
Fenbutatin oxide	50	33	170	97	61 - 136	0	0	25	12.00	2 - 42
Fenpropathrin	76	61	135	112	96 - 128	0	0	38	4.80	0.3 - 18
Fenvalerate	76	56	131	122	95 - 145	17	0	38	5.85	0.04 - 20
Fipronil	76	62	158	131	114 - 151	0	0	38	3.62	0.07 - 14
Fipronil disulfenyl	76	59	150	123	108 - 142	0	0	38	3.36	0.005 - 15
Fipronil sulfide	76	58	149	122	105 - 139	0	0	38	3.10	0.1 - 13
Fipronil sulfone	76	60	160	131	116 - 154	0	0	38	3.11	0.02 - 14
Fludioxonil	76	66	172	126	110 - 144	0	0	38	2.97	0.2 - 13
Flumioxazin	67	10	125	99	0 - 164	22	5	33	12.99	0.7 - 91
Fluopicolide	50	65	137	104	78 - 123	0	0	25	8.33	0.2 - 20
Flupyradifurone	50	65	135	98	71 - 114	0	0	25	5.90	0.2 - 14
Fluroxypyr 1-methylheptyl ester	76	61	151	140	110 - 172	15	0	38	5.08	0.4 - 16
gamma-Cyhalothrin	76	55	133	111	85 - 133	0	0	38	5.88	0.3 - 18
Glufosinate-ammonium	34	62	153	97	81 - 108	0	0	17	4.41	0.9 - 10
Glyphosate	34	50	143	98	87 - 113	0	0	17	4.49	0.5 - 14
Hexazinone	76	65	163	125	113 - 144	0	0	38	2.75	0.2 - 9
Hexythiazox	50	60	135	100	80 - 124	0	0	25	7.52	1 - 18
Imazapic	50	65	135	95	70 - 125	0	0	25	4.63	0.03 - 10
Imazapyr	50	65	135	101	72 - 131	0	0	25	4.67	0.2 - 15
Imidacloprid	50	65	135	104	92 - 120	0	0	25	6.28	1 - 22
Indaziflam	50	65	136	104	82 - 122	0	0	25	4.78	0.09 - 13
Inpyrfluxam	50	62	142	99	70 - 138	0	0	25	9.06	0.6 - 24

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* (%)
Isoxaben	50	65	135	103	86 - 127	0	0	25	7.06	0.4 - 17
Linuron	50	65	135	100	81 - 121	0	0	25	10.48	0.2 - 26
Malaoxon	50	65	139	106	95 - 118	0	0	25	3.94	0.006 - 12
Malathion	76	60	155	126	102 - 144	0	0	38	3.37	0.1 - 13
MCPA	76	55	125	71	45 - 90	0	3	38	6.78	0.6 - 24
Mecoprop (MCP)	76	60	125	84	67 - 104	0	0	38	6.73	0.06 - 19
Metalaxyl	76	68	155	122	111 - 138	0	0	38	3.09	0.4 - 11
Methamidophos	50	65	135	107	90 - 128	0	0	25	4.72	0.2 - 20
Methiocarb	50	65	147	105	85 - 127	0	0	25	7.56	0.04 - 20
Methomyl	50	65	135	105	95 - 115	0	0	25	4.47	0.3 - 14
Methomyl oxime	50	65	135	101	83 - 124	0	0	25	6.20	0.3 - 22
Methoxyfenozide	50	65	138	105	82 - 132	0	0	25	7.84	0.5 - 19
Metolachlor	76	65	153	113	96 - 132	0	0	38	2.86	0.09 - 13
Metribuzin	76	60	139	93	72 - 121	0	0	38	3.47	0.06 - 14
Metsulfuron-methyl	50	30	147	98	76 - 161	1	0	25	5.73	0.1 - 46
Myclobutanil	50	65	135	102	77 - 126	0	0	25	8.14	0.07 - 17
N,N-Diethyl-m-toluamide (DEET)	76	63	155	112	90 - 133	0	0	38	3.80	0.007 - 22
Napropamide	76	56	162	123	106 - 143	0	0	38	2.92	0.08 - 13
Norflurazon	76	67	158	131	114 - 154	0	0	38	2.83	0.06 - 13
Oryzalin	50	36	181	94	62 - 121	0	0	25	10.22	0.5 - 22
Oxadiazon	76	60	147	116	99 - 132	0	0	38	2.67	0.2 - 13
Oxamyl	50	65	135	108	98 - 123	0	0	25	4.03	0.02 - 12
Oxamyl oxime	50	57	136	100	78 - 119	0	0	25	6.28	0.5 - 14
Oxyfluorfen	76	75	167	120	100 - 140	0	0	38	4.22	0.02 - 15
Paclobutrazol	50	65	135	112	88 - 225	4	0	25	5.14	0.009 - 21
Pendimethalin	76	69	149	118	99 - 134	0	0	38	3.22	0.02 - 14
Pentachloronitrobenzene (PCNB)	76	63	139	96	74 - 111	0	0	38	4.20	0.04 - 25
Pentachlorophenol	76	42	125	74	37 - 94	0	1	38	6.38	0.0009 - 27
Phosmet	76	10	132	90	2 - 142	6	4	38	12.96	0.4 - 70
Picloram	76	10	125	56	28 - 78	0	0	38	13.89	1 - 54

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
Piperonyl butoxide (PBO)	76	55	164	136	116 - 160	0	0	38	3.38	0.03 - 14
Prodiamine	76	61	150	109	86 - 124	0	0	38	4.12	0.08 - 17
Prometon	76	62	152	115	99 - 132	0	0	38	3.03	0.02 - 13
Prometryn	76	64	152	114	98 - 132	0	0	38	2.94	0.2 - 14
Propargite	76	38	145	123	104 - 141	0	0	38	4.32	0.1 - 15
Propiconazole	50	60	135	105	74 - 131	0	0	25	9.08	2 - 22
Pyraclostrobin	50	65	135	97	72 - 119	0	0	25	7.56	0.1 - 16
Pyrethrins	50	10	250	109	76 - 144	0	0	25	11.25	0.009 - 42
Pyridaben	76	61	145	137	115 - 164	14	0	38	4.74	0.2 - 17
Pyrimethanil	50	65	135	101	88 - 117	0	0	25	4.50	0.006 - 17
Pyriproxyfen (Nylar)	76	62	147	125	111 - 140	0	0	38	3.27	0.2 - 11
Pyrooxasulfone	50	62	135	103	76 - 140	1	0	25	8.84	1 - 27
Simazine	76	64	150	105	90 - 126	0	0	38	2.86	0.02 - 12
Simetryn	76	61	145	102	78 - 127	0	0	38	2.69	0.04 - 13
Spirotetramat	50	38	151	97	78 - 124	0	0	25	6.70	0.01 - 23
Sulfentrazone	76	10	137	63	0 - 140	1	16	37	26.04	0.7 - 133
Sulfometuron-methyl	50	53	143	99	75 - 118	0	0	25	4.53	0.5 - 14
Sulfoxaflor	50	65	135	100	76 - 121	0	0	25	4.24	0.09 - 12
tau-Fluvalinate	76	59	143	130	95 - 159	14	0	38	6.55	0.05 - 24
Tebuthiuron	76	38	185	117	73 - 162	0	0	38	5.97	0.09 - 22
Tefluthrin	76	56	125	96	76 - 115	0	0	38	6.39	0.2 - 23
Terbacil	76	71	175	133	108 - 159	0	0	38	4.14	0.4 - 13
Tetrahydrophthalimide (THPI)	76	43	125	110	86 - 135	8	0	38	5.24	0.05 - 20
Tetramethrin	76	20	128	105	15 - 150	18	3	38	9.19	0.5 - 44
Thiamethoxam	50	65	135	108	94 - 122	0	0	25	6.18	0.7 - 15
Thiram	50	25	196	113	82 - 190	0	0	25	5.81	0.5 - 21
Tolfenpyrad	50	57	135	103	76 - 149	1	0	25	7.52	0.08 - 24
Tralomethrin	76	61	143	131	101 - 165	11	0	38	5.78	0.03 - 22
trans-Permethrin	76	62	140	128	105 - 151	9	0	38	5.67	0.1 - 17
Triadimefon	76	65	158	117	101 - 145	0	0	38	2.73	0.08 - 13
Triallate	76	50	144	108	86 - 133	0	0	38	4.26	0.1 - 18
Triclopyr acid	76	69	125	85	60 - 109	0	4	38	6.01	0.1 - 18

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* (%)
Triclopyr butoxyethyl ester	76	57	155	123	92 - 142	0	0	38	3.20	0.07 - 12
Triclosan	76	44	178	130	98 - 160	0	0	38	6.33	0.4 - 17
Trifloxystrobin	50	65	135	101	78 - 124	0	0	25	7.03	0.1 - 17
Trifluralin	76	57	139	97	80 - 113	0	0	38	3.89	0.02 - 20

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

There was a total of 9,971 spiked results from LCS and LCSD recoveries that were unqualified or *J* qualified and 23 spiked results that were *U* qualified. Overall, the mean recovery was 109% with a standard deviation of 26%. 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 (52 recoveries) fell below the control limits for LCS/LCSD samples,
- 97% of analyte recoveries (9,659 recoveries) were within the control limits for LCS/LCSD samples,
- 3% of analyte recoveries (260 recoveries) were above the control limits for LCS/LCSD samples.

RPDs calculated for 4,986 LCS/LCSD pairs were below the 40% RPD control limit 99% of the time; only 36 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 5% with a standard deviation of 5%. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 61% with a standard deviation of 27%.

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

Additional Inorganic Chemical and Parameter Analysis

MEL uses split sample duplicates to evaluate the precision of nutrients and specific conductivity analyses per batch (Table 41b). Overall, laboratory duplicate results were of acceptable data quality.

Table 41b – Laboratory duplicate results

Analyte or parameter	Results (n)	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Ammonia	48	20	5	10
Nitrate-Nitrite as N	47	20	0	0
Ortho-Phosphate	62	20	0	0
Specific Conductivity	13	20	0	0
Total Phosphorus	27	20	0	0

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 (%)
<u>Manchester Environmental Laboratory:</u>					
Ammonia	43	80	120	98.4	81 - 112
Nitrate-Nitrite as N	46	80	120	100.7	94 - 108
Ortho-Phosphate	62	80	120	100.9	94 - 108
Total Phosphorus	27	80	120	98	90 - 102
Specific Conductivity	13	95	105	100.9	99 - 103
Suspended Sediment Concentration	26	90	110	99.3	97 - 101
<u>Onsite Environmental Laboratory:</u>					
Ammonia	5	85	114	4.70	4.49 - 5.01
Nitrate-Nitrite as N	2	90	120	2	1.94 - 2.08

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 2023). All field meters were post-checked, using known standards, at the end of the sampling week.

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

Streamflow measurements were taken with OTT MF Pro flow meters and top-setting wading rods for sites that did not already have established gaging stations managed by other agencies. Each flow meter was calibrated 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 the 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. The 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 for lower Big Ditch Creek and Indian Slough. Specific conductivity replicates were collected at every site once on average.

Table 43b – Quality control results for conventional water quality 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	3% RPD
Streamflow	10% RPD	4% RPD	8% RPD	6% RPD	25% RPD	5% RPD	15% RPD

Of the total 17 conductivity replicates taken, one specific conductivity replicate that was at Indian Slough was considered an outlier and excluded from this analysis (25% RPD). Indian Slough's specific conductivity can vary thousands of $\mu\text{S}/\text{cm}$ within a 2 ft. water depth since it is at a tide gate.

Out of the 58 streamflow replicate comparisons, 3 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 precipitation events or irrigation practices occurring during flow measurement.

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).

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

Parameter	Units	Accept	Qualify	Reject	Resolution
Water temperature	$^{\circ}\text{C}$	± 0.2	N/A	$> \pm 0.2$	0.1
pH	standard units	$\leq \pm 0.15$	$> \pm 0.15$ and $\leq \pm 0.20$	$> \pm 0.20$	0.01
Conductivity*	$\mu\text{S}/\text{cm}$	$\leq 5\%$ RPD	$> \pm 5\%$ and $\leq \pm 15\%$ RPD	$> \pm 15\%$ RPD	0.1
DO	mg/L	$\leq \pm 0.05$	$> \pm 0.05$ and $\leq \pm 0.10$	$> \pm 0.10$	0.01

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

- Central YSI meter DO post-check failed MQOs the week of March 20, and July 24.
 - The field DO readings were requalified and not used in the technical report analysis.
- Palouse YSI meter DO post-check failed MQOs the week of June 12.
 - The field DO readings were requalified and not used in the technical report analysis.
- West YSI meter temperature post-check failed MQOs the week of August 28.
 - The field DO readings were requalified and not used in the technical report analysis.
- West YSI meter DO post-check failed MQOs the week of September 25.
 - The field DO readings were requalified and not used in the technical report analysis.

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 7, 2023, the Central and Westside NRAS surface water monitoring teams and the Palouse Conservation District monitoring team conducted a field audit to compare 2023 sampling procedures. Each team proceeded to Naneum Creek (46.93806, -120.50618) outside the town of Ellensburg in Kittitas County, Washington to conduct the field audit. The Westside and Palouse teams calibrated their YSI ProDSS meters either the day of, or the day prior to the field audit. All three teams calibrated their YSI ProDSS for Dissolved Oxygen together at the same time on the day of the field audit, in the Central NRAS surface water monitoring teams' utility van at the field audit location. 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 50 minutes to complete. After flow was measured, values from each team's ProDSS meters were recorded. Results and RSDs are displayed in Table 45b.

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

Team	Temperature (°C)	pH	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Central	4.6	8.59	163.4	14.64	119.1	37.10
Palouse	4.6	8.53	164.3	14.41	117.2	37.57
Westside	4.6	8.72	164.5	14.33	116.5	37.42
All 3	±0.0° C	1% RSD	<1% RSD	±0.31 mg/L	1% RSD	<1% RSD
MQO	±0.2° C	10% RSD	10% RSD	±0.2 mg/L	10% RSD	10% RSD

Field meters met MQOs, except for Dissolved Oxygen concentration. Failing the dissolved oxygen MQO at the field audit indicates variability between the meters. The Westside YSI meter passed post-check MQO's found in Table 44b for all parameters except Dissolved Oxygen. The variability between the units is recognized. Data analysis utilizing the dissolved oxygen values is compared to criteria and not between meters. The post-check readings for the Central and Palouse teams YSI meters could not be located but are assumed to have been of passing quality because subsequent post checks of these meters passed post check MQO's.

Quality Assurance Summary References

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