Washington State Department of Agriculture

Ambient Monitoring for Pesticides in Washington State Surface Water

2022 Technical Report

May 2024

Washington State Department of Agriculture
Natural Resources and Agricultural Sciences

Derek I. Sandison, Director

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2022 Report Revisions (Made Dec. 2024)

- Page 41 – *Incorrect:* "From May 15 through September 15, the 7-DADMax temperature should remain below 13°C, while September 16 through the end of the sampling season should remain below 16°C (WAC 2023). The 7-DADMax temperature exceeded the standard on 119 days, primarily from May 20 through September 15. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit."
    - *Corrected:* "From September 15 through May 15, the 7-DADMax temperature should remain below 13ºC, while May 16 through September 14 should remain below 16 ºC (Ecology 2011; WAC 2024). The 7-DADMax temperature exceeded the standard on 98 days, occurring intermittently from June 24 through October 11. Pesticide exceedances coincided with 7-DADMax temperature exceedances at two site visits."
    - *Corrected References:*
        - [Ecology] Washington State Department of Ecology. 2011. Waters Requiring Supplemental Spawning and Incubation Protection for Salmonid Species.
        - [WAC] Washington State Legislature. 2024. Water Quality Standards for Surface Waters of the State of Washington.

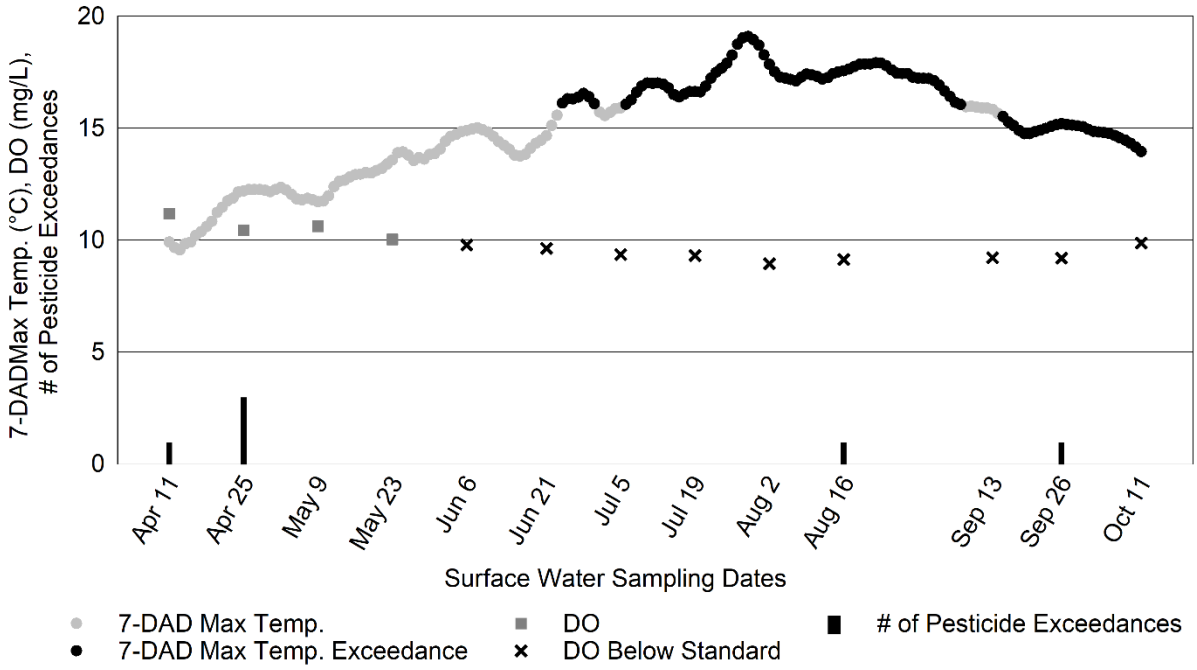

Figure 1 – Juanita Creek water quality measurements and exceedances of assessment criteria

- Page 45 – *Incorrect:* "The 7-DADMax Temperature exceeded the standard of 17.5°C on 82 days throughout the sampling season, from June 22 through September 11. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit."
    - *Corrected:* "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 13ºC, while temperatures should remain below 17.5ºC June 16 through February 14 (Ecology 2011; WAC 2024). The 7-DADMax temperature exceeded the standard on 109 days, occurring intermittently from May 2 through September 11. Pesticide exceedance coincided with 7-DADMax temperature exceedances at one site visit."
    - Corrected References:
        - [Ecology] Washington State Department of Ecology. 2011. Waters Requiring Supplemental Spawning and Incubation Protection for Salmonid Species.
        - [WAC] Washington State Legislature. 2024. Water Quality Standards for Surface Waters of the State of Washington.

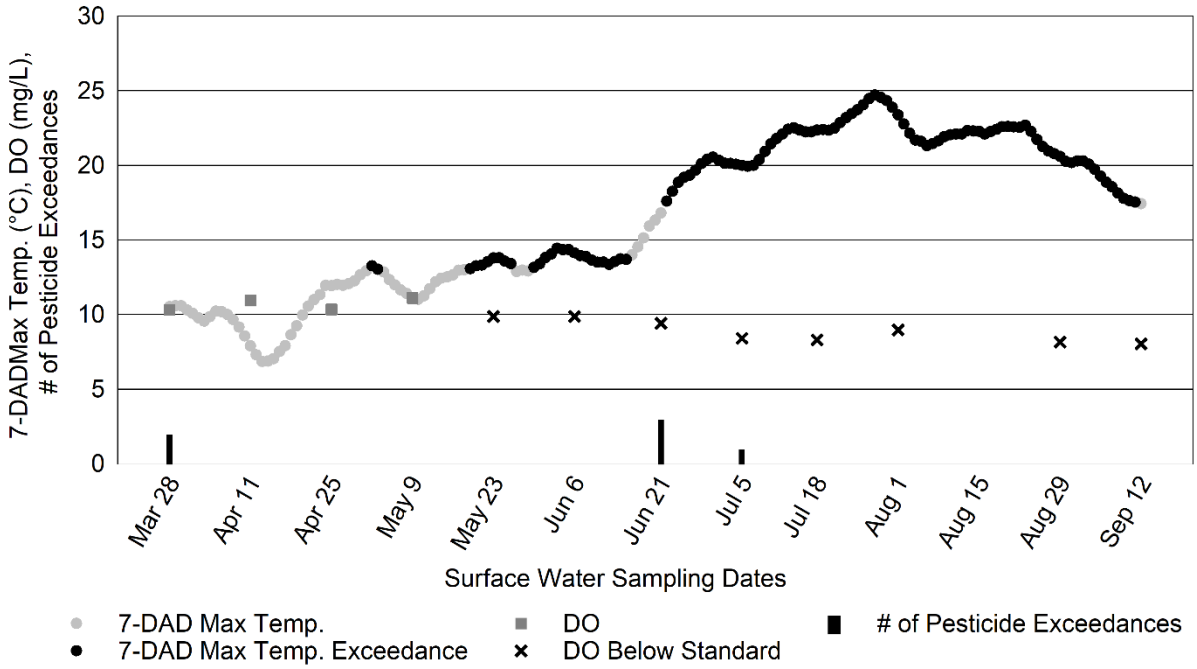

Figure 2 – Ahtanum Creek water quality measurements and exceedances of assessment criteria

- Page 78 – *Incorrect:* "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…"
    - *Corrected:* "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…"

- Page 82 – *Incorrect:* "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…"

    - *Corrected:* "Although Thorn Creek does not provide habitat for salmonids, the water from the creek eventually flows into the Columbia River which contains many salmonid species. The WAC categorizes Thorn Creek under the following guideline…"

- Page 88 – *Incorrect:* "Draft" Watermark
    - *Corrected:* No Watermark

➢ Page 119 – Corrected Values in *Table 34b – Variability of pesticide detections in field replicates and mean RPDs*

- The highlighted values below have been corrected.

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
4-Nitrophenol	GCMS-Herbicides	15	0		1	100
Acephate	LCMS-Pesticides	16	0		1	100
Chlorantraniliprole	LCMS-Pesticides	15	0		2	100
Dacthal (DCPA)	GCMS-Herbicides	15	0		1	100
Ethoprop	GCMS-Pesticides	16	0		1	100
Fenarimol	GCMS-Pesticides	16	0		1	100
Fenvalerate	GCMS-Pesticides	16	0		1	100
gamma-Cyhalothrin	GCMS-Pesticides	16	0		1	100
Indaziflam	LCMS-Pesticides	15	0		2	100
Linuron	LCMS-Pesticides	16	0		1	100
Methomyl oxime	LCMS-Pesticides	16	0		1	100
Methoxyfenozide	LCMS-Pesticides	16	0		1	100
Oxamyl oxime	LCMS-Pesticides	16	0		1	100
Paclobutrazol	LCMS-Pesticides	16	0		1	100
Picloram	GCMS-Herbicides	14	0		2	100
Pyridaben	GCMS-Pesticides	16	0		1	100
Pyriproxyfen (Nylar)	GCMS-Pesticides	16	0		1	100
tau-Fluvalinate	GCMS-Pesticides	16	0		1	100
Tefluthrin	GCMS-Pesticides	16	0		1	100
Triclosan	GCMS-Pesticides	16	0		1	100
Clopyralid	GCMS-Herbicides	13	1	27	2	67
Desethyl atrazine	LCMS-Pesticides	14	1	21	2	67
1-(3,4-Dichlorophenyl)-3-methylurea	LCMS-Pesticides	12	2	17	3	60
4,4'-DDE	GCMS-Pesticides	13	2	4	2	50
Deisopropyl atrazine	LCMS-Pesticides	15	1	22	1	50
Fipronil sulfone	GCMS-Pesticides	15	1	20	1	50
Sulfometuron-methyl	LCMS-Pesticides	15	1	1	1	50
Carbendazim	LCMS-Pesticides	10	4	6	3	43

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Propiconazole	LCMS-Pesticides	12	3	11	2	40
4,4'-DDD	GCMS-Pesticides	9	5	33	3	38
4,4'-DDT	GCMS-Pesticides	14	2	8	1	33
Ammonia	Ammonia-N (NH3)	2	4	19	2	33
Tetrahydrophthalimide	GCMS-Pesticides	11	4	16	2	33
Flupyradifurone	LCMS-Pesticides	13	3	3	1	25
Norflurazon	GCMS-Pesticides	13	3	10	1	25
Pendimethalin	GCMS-Pesticides	9	6	8	2	25
Sulfentrazone	GCMS-Pesticides	5	9	11	3	25
Thiamethoxam	LCMS-Pesticides	13	3	8	1	25
Imazapyr	LCMS-Pesticides	12	4	3	1	20
Tebuthiuron	GCMS-Pesticides	11	5	11	1	17
Atrazine	GCMS-Pesticides	10	6	7	1	14
Azoxystrobin	LCMS-Pesticides	9	7	9	1	13
Hexazinone	GCMS-Pesticides	8	8	6	1	11
Boscalid	GCMS-Pesticides	6	10	7	1	9
2,4-D	GCMS-Herbicides	4	11	24	1	8
2,6-Dichlorobenzamide	GCMS-Pesticides	5	12	5	0	0
2-Hydroxyatrazine	LCMS-Pesticides	11	6	10	0	0
Aminomethylphosphoric acid (AMPA)	LCMS-Glyphos	0	2	26	0	0
Bentazon	GCMS-Herbicides	13	3	6	0	0
Bromacil	GCMS-Pesticides	12	5	15	0	0
Bromoxynil	GCMS-Herbicides	14	2	14	0	0
Chlorpropham	GCMS-Pesticides	16	1	26	0	0
Clothianidin	LCMS-Pesticides	16	1	10	0	0
Cyantraniliprole	LCMS-Pesticides	16	1	14	0	0
Diazinon	GCMS-Pesticides	13	4	3	0	0
Dicamba acid	GCMS-Herbicides	6	10	11	0	0
Dichlobenil	GCMS-Pesticides	10	7	9	0	0
Dimethoate	GCMS-Pesticides	14	3	6	0	0
Dinotefuran	LCMS-Pesticides	14	3	6	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 (%)
Diuron	LCMS-Pesticides	11	6	14	0	0
Eptam	GCMS-Pesticides	14	3	7	0	0
Fipronil	GCMS-Pesticides	16	1	20	0	0
Fipronil sulfide	GCMS-Pesticides	14	3	5	0	0
Fludioxonil	GCMS-Pesticides	12	5	5	0	0
Fluopicolide	LCMS-Pesticides	16	1	38	0	0
Glyphosate	LCMS-Glyphos	0	2	19	0	0
Imidacloprid	LCMS-Pesticides	14	3	12	0	0
Malathion	GCMS-Pesticides	15	2	3	0	0
MCPA	GCMS-Herbicides	14	2	5	0	0
Mecoprop (MCPP)	GCMS-Herbicides	12	4	6	0	0
Metalaxyl	GCMS-Pesticides	15	2	18	0	0
Metolachlor	GCMS-Pesticides	10	7	4	0	0
Metribuzin	GCMS-Pesticides	11	6	9	0	0
N,N-Diethyl-m-toluamide	GCMS-Pesticides	13	4	7	0	0
Napropamide	GCMS-Pesticides	16	1	10	0	0
Nitrate-Nitrite as N	Nitrate+Nitrite-N	0	8	7	0	0
Ortho phosphate	Phosphate, Ortho- (OP)	0	8	4	0	0
Oxamyl	LCMS-Pesticides	16	1	4	0	0
Pentachlorophenol	GCMS-Herbicides	15	1	5	0	0
Prometon	GCMS-Pesticides	13	4	6	0	0
Pyraclostrobin	LCMS-Pesticides	16	1	7	0	0
Pyrimethanil	LCMS-Pesticides	14	3	5	0	0
Simazine	GCMS-Pesticides	12	5	10	0	0
Suspended sediment concentration	SSC	0	16	6	0	0
Terbacil	GCMS-Pesticides	12	5	11	0	0
Total phosphorus	Phosphorus, Total	0	7	1	0	0
Triclopyr acid	GCMS-Herbicides	12	4	5	0	0
Trifloxystrobin	LCMS-Pesticides	16	1	13	0	0

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Acknowledgments

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- 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.
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- Roza-Sunnyside Board of Joint Control: Forrest Chapin
- Chelan County Natural Resource Department: Mike Kaputa and Pete Cruickshank
- The many private landowners who allow us to access our monitoring sites through their property.

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Executive Summary

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

In 2022, WSDA's Natural Resources and Agricultural Sciences team (NRAS) collected surface water samples weekly or biweekly from March into November at 17 monitoring sites. Staff selected sites where pesticide contamination and poor water quality conditions were expected based on land use with high pesticide usage or historic pesticide detections. Sites were located in Benton, Chelan, Clark, King, Skagit, Whatcom, Whitman, and Yakima counties with watershed areas ranging from 2,000 acres to over 100,000 acres. Land use within each watershed varied from commercial, residential, and urban to agricultural uses like tree fruit, berry, wheat, corn, grass hay, and potato production. The Manchester Environmental Laboratory (MEL) in Port Orchard, Washington provided the sample analysis.

The United States Endangered Species Act lists several species of endangered salmonids found in Washington State's waterways including some in the waterways NRAS monitors (ESA 1973). Salmonids are valuable in the Pacific Northwest due to their cultural significance, contribution to the economy, and function in the ecosystem. All the watersheds sampled in 2022 either have historically supported salmonid populations, contain habitat, or flow into habitat conducive to salmonid use. To assess potential biological effects and to be protective of endangered and non-endangered species, NRAS compares detected pesticide concentrations from surface water samples to WSDA assessment criteria. WSDA assessment criteria are adapted from toxicity study criteria and state and national water quality standards. Exceedances of WSDA assessment criteria indicate pesticide concentrations approaching levels with possible adverse effects to aquatic life such as fish, invertebrates, and aquatic plants. NRAS maintains and updates a list of current-use pesticides that qualify as either statewide or watershed Pesticides of Concern (POC) by evaluating the most recent 3 years of pesticide detection data using a POC decision matrix. Statewide POCs were bifenthrin, chlorpyrifos, diuron, gamma-cyhalothrin, and imidacloprid. Additional pesticides identified as watershed POCs were carbaryl, clothianidin, deltamethrin, diazinon, fenvalerate, fipronil, indaziflam, linuron, malathion, metsulfuron-methyl, permethrin, pyriproxyfen, pyroxasulfone, and tolfenpyrad.

This report summarizes activities and data from the 17 separate sites selected for the 2022 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 291 surface water sampling events between March 21 and November 16.
- Out of 153 pesticide active ingredients and breakdown products tested for, there were 125 unique pesticides detected.
- There were 4,687 positively identified pesticide detections.
- Out of 291 sampling events, mixtures of two or more pesticides were detected at 287 of them.
- Sulfentrazone was the most frequently detected herbicide (165 times), boscalid was the most frequently detected fungicide (183 times), and thiamethoxam was the most frequently detected insecticide (79 times) of the pesticides WSDA tested for.
- 2,6-dichlorobenzamide, a breakdown product of the herbicide dichlobenil or fungicide fluopicolide, had the most total detections with 222. Detections of this analyte occurred at over 76% of sampling events.

- There were 317 unique pesticide detections with concentrations exceeding WSDA assessment criteria (7% of total detections), approaching levels that could adversely affect aquatic life.
    - Legacy pesticides and their breakdown products accounted for 164 of the exceedances (52% of total exceedances). The chemicals include:
        - 4,4'-DDD (85 exceedances),
        - 4,4'-DDE (46 exceedances),
        - 4,4'-DDT (33 exceedances).
    - Current-use pesticides accounted for 149 of the exceedances (47% of total exceedances). The chemicals include:
        - bifenthrin (7 exceedances),
        - chlorpyrifos (7 exceedances),
        - cis-permethrin (2 exceedances),
        - clothianidin (11 exceedances),
        - dimethoate (1 exceedance),
        - diuron (13 exceedances),
        - fenvalerate (1 exceedance),
        - fipronil (12 exceedances),
        - gamma-cyhalothrin (14 exceedances),
        - imidacloprid (49 exceedances),
        - linuron (3 exceedances),
        - malathion (12 exceedances),
        - metsulfuron-methyl (1 exceedance),
        - pyriproxyfen (4 exceedances),
        - tefluthrin (6 exceedances),
        - tolfenpyrad (4 exceedances),
        - trans-permethrin (2 exceedances).
    - One degradate of a pesticide accounted for four of the exceedances (1% of total exceedances).
        - malaoxon (4 detections).

Of the 317 detections that exceeded WSDA assessment criteria, many (77% or 244 detections) also exceeded state, national, or toxicity study criteria that WSDA assessment criteria was derived from. Current-use pesticides accounted for 40% (98 detections) of those exceedances of assessment criteria without the WSDA safety factor. All seven detections of bifenthrin exceeded the acute and chronic invertebrate toxicity study criterion; four of those exceeded the chronic fish toxicity study criterion. Gamma-Cyhalothrin, found at seven of the monitoring sites, exceeded the acute invertebrate toxicity study criterion 14 times out of a total of 14 detections with three of those detections also exceeding the chronic invertebrate toxicity study criterion. Another insecticide detected frequently, imidacloprid, exceeded the chronic invertebrate toxicity study criterion 41 times out of 49 detections and was found at 10 of the 17 monitoring sites. Three reasons those pesticides were detected so often exceeding toxicity study criteria was that they had very low laboratory method detection levels, low toxicity criteria, and common usage across the state. Other pesticide and pesticide-related chemicals detected less often that still exceeded state, national, or toxicity study criteria included chlorpyrifos, clothianidin, dimethoate, diuron, fenvalerate, fipronil, linuron, malathion, malaoxon, permethrin, and pyriproxyfen. Legacy insecticide DDT and its associated degradates accounted for the remaining 59% (144 detections) of the total detected exceedances of state or national standards.

NRAS collected samples for suspended sediment concentration analysis and measured dissolved oxygen, pH, conductivity, water temperature, and streamflow in the field at sampling events. We also collected continuous air and water temperature measurements during the entire monitoring season in situ. Dissolved oxygen, pH, and water temperature measurements were compared to Water Quality Standards for Surface Waters of the State of Washington (WAC 2022). At least one conventional water quality parameter did not meet state water quality standards on one or more occasions at 15 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 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 2017). Appendix B provides a summary of quality assurance and quality control sample results with a detailed analysis of how the field and laboratory methods performed over the season.

The NRAS ambient monitoring program is a tool for identifying state-specific pesticide issues. The program also forms the groundwork for additional studies focusing on particular scientific questions of interest regarding pesticide fate and transport. WSDA shares the data generated by this program with the agricultural community, regulatory and scientific community, and the public through WSDA's website, reports, watershed-specific fact sheets, and numerous public presentations.

Introduction

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

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

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

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

The technical report:

- Summarizes results, data quality, and monitoring activities conducted in 2022.
- 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 2022 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 2022, 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. For the 2022 monitoring season, the Touchet River site in Walla Walla County was discontinued due to few detections and no watershed POCs.

NRAS sent water samples to the Manchester Environmental Lab for analysis of pesticide and pesticide-related chemicals such as insecticides, herbicides, fungicides, degradates, an antimicrobial, a wood preservative, an insect repellent, and synergists. In 2022, NRAS tested for 153 chemicals, with 125 confirmed chemicals detected in surface water samples. Between the 2021 and 2022 monitoring seasons, 20 chemicals were taken off the testing list. The list of chemicals analyzed for every year may change because of new use restrictions, changes in pesticide registration, analytical cost, or lack of detections in surface water.

We compare the surface water data to internal assessment criteria that are derived by applying a safety factor to state and national water quality standards and toxicity study criteria to be protective of aquatic life. Persistent contamination of surface waters with pesticides or pesticide-related

chemicals can 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 simple practices that can protect surface water.

Study Area

Since the ambient surface water monitoring program began in 2003, sampling sites and subbasins have been both added and removed based on pesticide detection history, changing pesticide usage practices, site conditions, land use patterns, and the presence of federally-listed threatened or endangered species. Water Resource Inventory Areas (WRIA) are typically used to study and manage water resources within Washington. State agencies also use these subbasin boundaries for implementing surface water quality standards (WAC 2022). Figure 1 shows the boundaries of the 8 subbasins that NRAS sampled in 2022, identified by their WRIA codes and corresponding subbasin names.

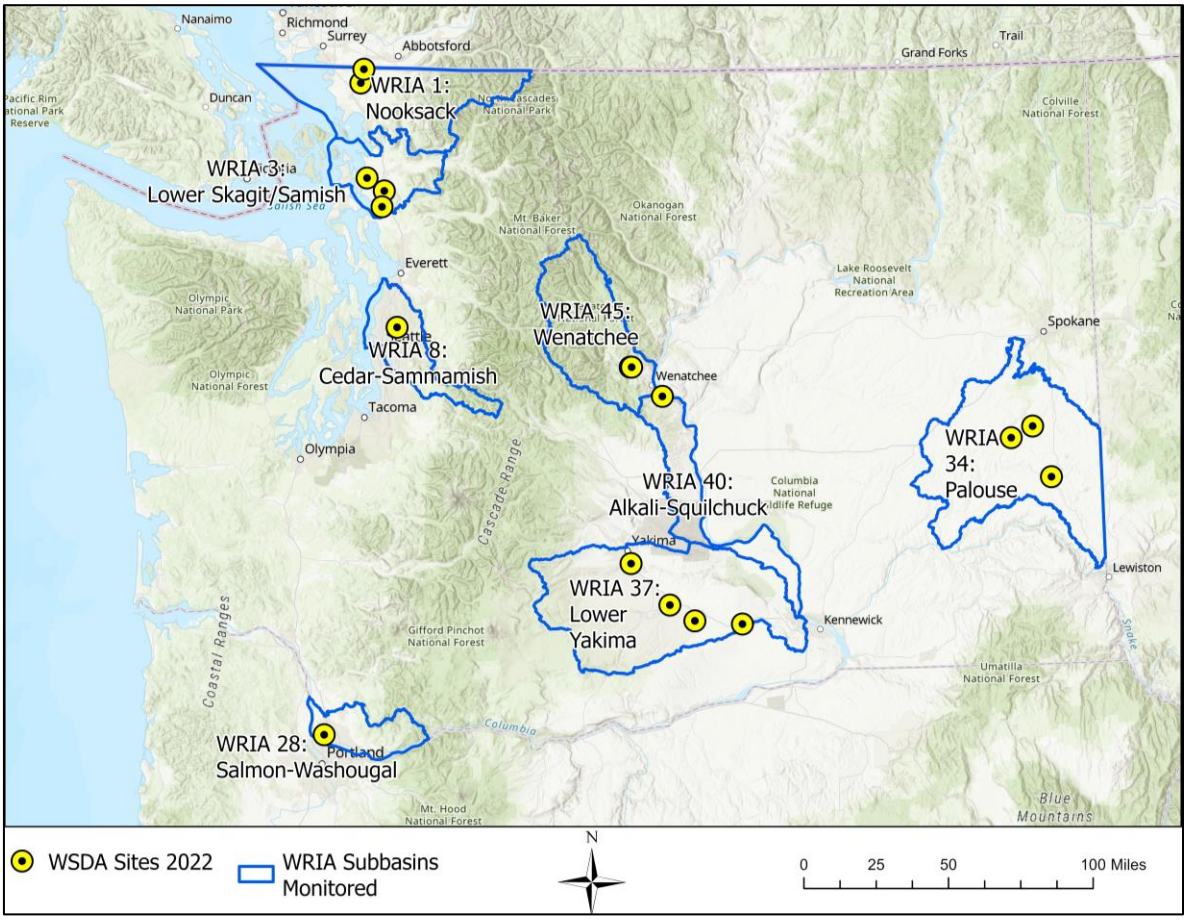


Figure 1 – Subbasins monitored in Washington State in 2022

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 8 monitoring sites. The nutrients sampled were total phosphorus, orthophosphate, ammonia as N, and nitrate-nitrite as N. Due to equipment malfunctions at MEL, some nutrient and conductivity samples were analyzed by OnSite Environmental Inc. in Redmond, King County Environmental Laboratory in Seattle, and ALS Lab Group in Kelso. 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 (Bischof et al. 2022).

Field Procedures

Surface water samples were collected using a 1-liter glass jar by hand grab or pole grab as described in the NRAS Standard Operating Procedure (SOP): Water Quality and Pesticides Monitoring (Bischof 2021a). Before delivery to MEL, staff labeled and preserved all samples according to the Quality Assurance Project Plan (Bischof et al. 2022). Field staff used YSI ProDSS field meters to record water temperature, pH, dissolved oxygen, and specific conductivity at each sampling event. Field meters were calibrated and post-checked at the beginning and end of every sampling week based on the manufacturers' specifications, using the NRAS SOP: YSI ProDSS (Bischof 2021b) and YSI ProDSS User Manual (YSI 2020). NRAS followed Ecology's SOP for Continuous Temperature Monitoring of Fresh Water Rivers and Streams for continuous, 30-minute-interval temperature data collection at 14 monitoring sites (Ward 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). 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 2022 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, three labs analyzed nutrient and specific conductivity 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	3535A	SW8270E	GC/MS/MS
GCMS-Herbicides (Derivitizable acid herbicides)	3535A	SW8270E	GC/MS
LCMS-Glyphos	3535A	SW8321B	LC/MS/MS
LCMS-Pesticides	n/a	SW8321B	LC/MS/MS
SSC	n/a	ASTM D3977B	Gravimetric
Specific Conductivity	n/a	APHA SM2510B	Electrode
Nitrate+Nitrite-N	n/a	APHA SM4500NO3I	Lachat
Nitrate+Nitrite-N [1]	n/a	US EPA 353.2	Lachat
Ammonia-N (NH3)	n/a	APHA SM4500NH3H	Lachat
Ammonia-N (NH3) [1]	n/a	APHA SM4500NH3D	Lachat
Phosphate, Ortho- (OP)	n/a	APHA SM4500PG	Lachat
Phosphate, Ortho- (OP) [2]	n/a	APHA SM4500PE	Lachat
Phosphorus, Total	n/a	APHA SM4500PH	Lachat
Phosphorus, Total [3]	n/a	APHA SM4500PF	Lachat

*Analytical methods refer to EPA SW 846, unless otherwise noted.
[1]Analytical method used by OnSite Environmental Lab
[2]Analytical method used by ALS Lab Group
[3]Analytical method used by King County 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 employs blanks, replicates, and surrogate recoveries. As a laboratory component of QA/QC, MEL analyzed surrogate recoveries, method blanks, laboratory control samples, and laboratory control sample duplicates. Field blanks, field replicates, matrix spikes, and matrix spike duplicates integrate field and laboratory components. In 2022, 11% of the samples collected in the field were QC samples. The full QA/QC analysis is contained in Appendix B: 2022 Quality Assurance Summary.

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

Field Replicates

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

Precision between identified replicate pairs was evaluated using relative percent difference (RPD). Only 9 of the 282 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.

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 three replicate streamflow measurements were taken at random by the Palouse sampling team. A conductivity sample was collected once at each monitoring site for comparison to a YSI ProDSS meter. In 2022, all but 11 streamflow or specific conductivity measurements and their paired replicate measurements/samples were below the measurement quality objective of 10% RPD.

Blanks

Field and method blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. There were nine detections in field blanks and 172 detections in method blanks. Detections in field blanks included analytes such as 2,6-dichlorobenzamide and DEET, while detections in method blanks included analytes such as fenarimol, DEET, and triclosan. The origin of these detections was unknown. There were 41 regular field sample detections corresponding to a field or method blank sample in the same batch that were qualified as non-detects due to the regular sample concentration being less than five times the blank concentration.

Surrogates, Matrix Spikes, and Laboratory Control Samples

MEL spikes surrogates into all samples to evaluate recoveries for structurally similar groups of organic compounds. The majority (>99%) of surrogate recoveries fell within the control limits established by MEL in 2022. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

Matrix spikes (MS) and matrix spike duplicates (MSD) provide an indication of bias due to interferences from components of the sample matrix. We can use the duplicate spikes to estimate analytical precision at the concentration of the spiked samples and ensure the analytical method is efficient. For most compounds, percent recovery and relative percent differences (RPDs) of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Analyte recoveries from MS and MSD samples fell between both the upper and lower control limits 96% of the time and the RPDs of the paired recoveries fell below the 40% RPD upper control limit 99% of the time. If a MS/MSD sample exceeded MEL QC criteria, sample results were not qualified unless other QC criteria for that analyte was exceeded in the laboratory batch.

Laboratory control samples (LCS) are deionized water spiked with analytes at known concentrations and subjected to analysis. LCS help to evaluate precision and bias of pesticide residue recovery for a specific analyte. For most compounds, percent recovery and RPDs of LCS and LCS duplicates (LCSD) showed acceptable performance and were within limits for the project. Analyte recoveries from LCS and LCSD samples fell between both the upper and lower control limits 98% 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 regulations (WAC 2023). We apply a 0.5x safety factor to all of these reference values before comparison to detected pesticide concentrations to ensure that the criteria are protective of aquatic life and to detect potential water quality issues early on.

Several factors limit our ability to make comparisons between detection data and criteria. Assessment criteria and water quality standards are developed by evaluating the effects of a single chemical on a specific species and do not take into account the effects of multiple chemicals or pesticide mixtures on an organism. Mixtures are frequently present and the effects of several pesticides in combination may be either more or less toxic than their individual effects. In addition, toxicity values such as those used for pesticide registration are determined from continuous exposure over time. NRAS collects weekly or biweekly discrete grab samples that cannot be used to determine the exposure duration that would be needed to determine whether the time threshold has been exceeded. However, this comparison is consistent with Ecology practices; for Clean Water Act section 303(d) listing purposes instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards and assessment criteria for acute and chronic criteria (Ecology 2020). Appendix A lists the WSDA assessment criteria for fish, invertebrates, and aquatic plants.

Pesticide Registration Toxicity Data

Toxicity data from studies generated following EPA-provided test guidelines are commonly used to conduct screening-level risk assessments of pesticides and pesticide degradates. EPA uses these values to develop aquatic life criteria (published as the Office of Pesticide Programs' Aquatic Life Benchmarks) for pesticide active ingredients by applying their own safety factors (EPA 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 LC_{50} (concentration causing death to 50% of the organisms, in the case of fish) or EC_{50} (concentration causing immobility or growth reduction to 50% of the organisms, in the case of invertebrates or plants) is calculated. The test duration is 96 hours for fish and aquatic plants and 48 hours for invertebrates.

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

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

National Recommended Water Quality Criteria

EPA's National Recommended Water Quality Criteria (NRWQC) include a list of approximately 150 pollutants with criteria to protect aquatic life and human health (EPA 2023b). 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 2023). Washington State water quality standards include numeric criteria for current-use and legacy pesticides. For the purposes of this report, these values are referred to as "state water quality standards".

Washington State adopted some NRWQC data into the WAC. These criteria are primarily intended to avoid direct lethality to fish and other aquatic life within the specified exposure periods. The chronic criteria for some of the chlorinated pesticides like DDT are to protect fish-eating wildlife from adverse effects due to bioaccumulation.

Acute and chronic numeric criteria for fish, invertebrates, and aquatic plants from the WAC with the WSDA 0.5x safety factor, presented in Appendix A: Assessment Criteria for Pesticides. The exposure periods assigned to the acute criteria are: (1) an instantaneous concentration not to be exceeded at any time, or (2) a 1-hour average concentration not to be exceeded more than once every 3 years on average. The exposure periods for the chronic criteria are either: (1) a 24-hour average not to be exceeded at any time, or (2) a 4-day average concentration not to be exceeded more than once every three years on average.

Relationship between WSDA Assessment Criteria and Sources

NRAS uses a combination of pesticide registration toxicity study data and national and state standards to derive WSDA assessment criteria.

Table 2 provides a summary of how we use different sources to develop WSDA assessment criteria referred to in this report.

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

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

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

Pesticide of Concern Decision Matrix

Annually, NRAS identifies Pesticides of Concern and Pesticides of Interest (POIs) using the most recent surface water data. Washington and the other EPA Region 10 states (Oregon, Idaho, and Alaska) adopted the same method to identify statewide and watershed-specific POCs in 2019. For current-use pesticides detected in 2022, 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 2022, five watershed POCs were found in 6 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 2023), 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 2022 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 (ºC), 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). Two NRAS monitoring sites in 2022 had an additional temperature standard within the reaches of creek that encompassed the sites. The Upper Bertrand site had a 7-DADMax temperature standard of less than 13°C between February 15 and June 15 and the Juanita site had a 7-DADMax standard of less than 13°C between September 15 and May 15.

Although the Water Quality Standards for Washington State lists dissolved oxygen criteria as the lowest 1-day minimum, dissolved oxygen measurements are considered point estimates (not continuous) taken at the time of sampling. The point measurements may or may not be the lowest dissolved oxygen concentration of that day at an individual monitoring site.

Numeric Water Quality Standards for Nutrients

EPA has recommended ambient water quality criteria for nutrients in surface waters. Table 5 shows the criteria nutrients were compared to. Nutrients such as nitrate-nitrite (NO_2 + NO_3) and total phosphorus (TP) detections were compared to EPA’s Ambient Water Quality Criteria Recommendations (EPA 2000a, EPA 2000b). The criteria are specific to nutrient ecoregions and sub-ecoregions across the U.S. for surface water from rivers and streams. The empirically derived criteria represent environmental conditions within waters that have been minimally impacted by human activities; specifically reference conditions based on the upper 25th percentiles of all nutrient data in a sub-ecoregion collected from 1990 through 1999.

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

EPA Ecoregion	Level 3, Nutrient Ecoregion ID	Monitoring sites	Criteria type	Criteria (mg/L)
II, Western Forested Mountains	2	Upper Big Ditch	$NO_2 + NO_3$	0.26
			TP	0.0195
III, Xeric West	10	Ahtanum Creek, Dry Creek, Kamiache Creek, Marion Drain, Snipes Creek, Sulphur Creek Wasteway, Thorn Creek	$NO_2 + NO_3$	0.072
			TP	0.030

The ammonia detections were compared to the Water Quality Standards for Surface Waters of The State of Washington (WAC 2023). 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 2022 except for Dry Creek, Kamiache Creek, and Thorn Creek were considered salmonid present waterway as per the State Water Quality Standards.

For salmonids present:

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

For salmonids absent:

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

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

Monitoring Site Results

In 2022, 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 the local and regional meteorology, pest pressure, sampling schedule, and other influences.

The summaries below describe monitoring site information and data in detail, including pesticide calendars, maps, agricultural land-use statistics, and water quality. Pesticide calendars provide a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria. For specific values and information on the assessment criteria development, please refer to Appendix A: Assessment Criteria for Pesticides.

In the calendars, the number below the months indicates the day of the month the sampling event occurred and each column below the sampling event date indicates the data associated with that event. The blank cells in the calendars often indicate no chemical detection but can also mean a chemical was detected below reportable sample quantitation limits. Concentrations are presented in µg/L, rounded to the thousandth place.

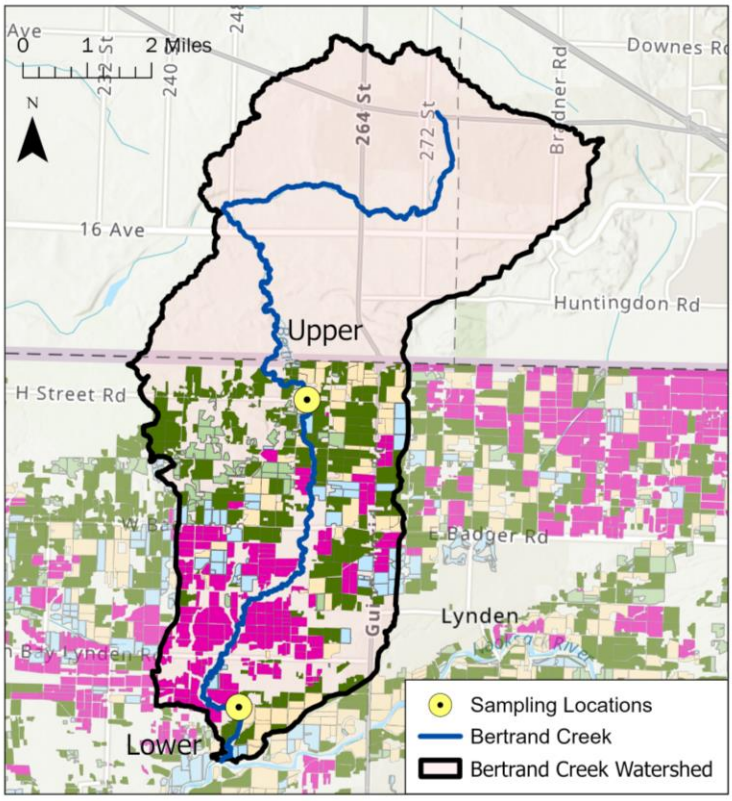
Detection of a pesticide concentration above the WSDA assessment criteria does not necessarily indicate an exceedance has occurred because the temporal component of the criteria must also be exceeded. For WSDA assessment criteria, measurements of instantaneous concentrations are assumed to represent 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



Bertrand Creek Crop Groups	Acres
Berry	2,278
Cereal Grain	1,232
Hay/Silage	3,038
Pasture	559
Other	823
Total U.S. Ag	7,930
Total U.S. Non-Ag	4,936
Watershed Total	26,893

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

Figure 3 – Upper Bertrand Creek site upstream view

In 2013, NRAS started sampling the Bertrand watershed in Whatcom County. Monitoring takes place at two locations along this stream to provide an opportunity to compare potential pesticide inputs from Canada to pesticide detections downstream in the United States. The headwaters of Bertrand Creek are located in Canada, and it flows approximately 11 miles before crossing the border. Currently, the Upper Bertrand Creek site is located approximately a quarter mile south of the Canadian border at the upstream side of H Street Road (latitude: 48.9935°, longitude: -122.5094°) (Figure 2, Figure 3). The Lower Bertrand Creek site is located about 7.8 miles downstream from the upper monitoring site and just upstream of the bridge crossing on Rathbone Road (latitude: 48.9241°, longitude: -122.5300°) (Figure 2, Figure 5). From the Lower Bertrand Creek site, the creek flows approximately one more mile south to where it enters the Nooksack River.

Bertrand Creek water drains into the Nooksack River subbasin, known for its endangered salmon runs. Precipitation events and irrigation influence streamflow in Bertrand Creek. Washington Department of Fish and Wildlife (WDFW) has documented the presence of coho, fall Chinook, fall chum, pink, and sockeye salmon, as well as bull, cutthroat, and winter steelhead trout within the reaches of creek that encompass both Bertrand sites (WDFW 2023). Staff have frequently observed

juvenile fish of unknown species and freshwater lamprey at the Upper Bertrand Creek monitoring site.

Figure 4 – Lower Bertrand Creek site upstream view

The Bertrand Creek watershed has flat, low-lying terrain. Within the U.S. side of the Bertrand watershed, the agricultural land use is predominately grass hay, caneberries, field corn, blueberries, 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 2022.

There were 452 total pesticide detections in Upper Bertrand Creek from five different use categories: 21 types of herbicides, 12 insecticides, 9 fungicides, 11 degradates, and 1 insect repellent.

- Of the total pesticide detections in Upper Bertrand Creek, 18 were above WSDA's assessment criteria (Table 6).
    - The single detection of fipronil exceeded the invertebrate NOAEC (0.011 µg/L).

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

- The single detection of bifenthrin exceeded the fish NOAEC (0.004 µg/L), invertebrate LC_{50} (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L). The detection also approached the Endangered Species Level of Concern (0.0075 µg/L).
- Of the three detections of chlorpyrifos, two approached the invertebrate NOAEC (0.005 µg/L).
- The single detection of diuron approached the invertebrate NOAEC (0.83 µg/L) and exceeded the plant EC_{50} (0.13 µg/L).
- All 13 detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).

The Upper Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2022 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

Month		Apr				May					Jun				Jul			Oct					Nov	
Day of the Month	Use*	5	12	19	26	3	10	16	24	31	7	13	22	27	6	12	19	3	10	17	24	31	7	15
1-(3,4-Dichlorophenyl)-3-methylurea	D																				0.121			
2,4-D	H	0.024		0.058	0.207			0.117		0.008	0.266	0.015				0.024					0.198	0.067	0.010	
2,6-Dichlorobenzamide	D	0.162	0.201	0.348	0.247	0.276	0.181	0.205	0.220	0.281	0.302	0.182	0.257	0.296	0.262	0.244	0.241	0.046	0.043	0.038	0.058	0.234	0.205	0.163
2-Hydroxyatrazine	D	0.010	0.009	0.010	0.010	0.010	0.010	0.011	0.011	0.010	0.008	0.008	0.009	0.011	0.010	0.008	0.007					0.034		0.016
4-Nitrophenol	D			0.031	0.097																0.084			
Acephate	I								0.007			0.055		0.027	0.013							0.042		
Acetamiprid	I																					0.011		
Atrazine	H	0.071	0.046	0.044	0.035	0.023	0.015	0.031		0.067		0.020	0.263	0.185	0.060	0.035	0.023	0.006	0.006	0.005	0.006			
Azoxystrobin	F				0.052	0.003	0.003	0.014	0.002	0.004	0.008	0.007												
Bentazon	H																				0.022	0.056		
Bifenthrin	I																						0.005	
Boscalid	F	0.103	0.065	0.080	0.138	0.139	0.085	0.148	0.087	0.101	0.312	0.174	0.175	0.122	0.084	0.078	0.077	0.023	0.019	0.018	0.028	0.153	0.180	0.077
Bromacil	H																				0.867			
Bromoxynil	H								0.035															
Carbendazim	F	0.005	0.004	0.005			0.004			0.013	0.004	0.008	0.007	0.004	0.003	0.003	0.002							
Chlorothalonil (Daconil)	F	0.005	0.003	0.002	0.004																			
Chlorpyrifos	I	0.003	0.002																				0.003	
Cyprodinil	F										0.008													
Deisopropyl atrazine	D								0.039		0.019													
Desethylatrazine	D									0.006				0.014	0.008	0.005								
Diazinon	I			0.002	0.017	0.003	0.004	0.005	0.003	0.002	0.005	0.002	0.004	0.004									0.006	
Dicamba	H	0.016		0.011	0.052		0.011	0.064		0.049	0.076	0.028										0.028	0.018	
Dichlobenil	H	0.045	0.183	0.314	0.214	0.245	0.115	0.648	0.219	0.337	0.351	0.134	0.107	0.116	0.054	0.037	0.032	0.003			0.003	0.021	0.020	0.011
Dimethoate	I							0.009			0.010	0.007										0.060	0.014	
Diuron	H																				0.539			
Ethoprop	I		0.004		0.029																			
Fipronil	I																				0.028			
Fipronil disulfinyl	D																				0.005			
Fipronil sulfide	D																				0.001			
Fipronil sulfone	D																				0.013			
Fludioxonil	F	0.004	0.004							0.004	0.017	0.009	0.005	0.004								0.005	0.004	
Flupyradifurone	I	0.018	0.009	0.016	0.411	0.061	0.091	0.415	0.258	0.231	0.191	0.128	0.252	0.175	0.066	0.055	0.033					0.195	0.143	0.044
Hexazinone	H											0.001	0.002	0.002	0.002	0.002								
Imidacloprid	I	0.031	0.028	0.045	0.034	0.049	0.033	0.025	0.020	0.016	0.019	0.023											0.048	0.013
MCPA	H	0.021	0.026		0.148			0.158			0.180											0.098	0.090	
MCPP	H	0.048		0.049	0.299	0.021	0.029	0.195		0.031	0.187	0.035										0.061	0.027	
Metalaxyl	F	0.016	0.020	0.025	0.016	0.080	0.022	0.016	0.021	0.034	0.020	0.018	0.047	0.024	0.021	0.015	0.013					0.045	0.027	0.018
Methamidophos	D											0.008		0.005										
Methomyl	I												0.005											
Metolachlor	H	0.039	0.017	0.023	0.142	0.026	0.037	0.151	0.017	0.017	0.038	0.019	0.011	0.008	0.005	0.005	0.004		0.002			0.019	0.022	0.006
Metribuzin	H	0.030	0.008	0.005	0.075	0.013	0.013	0.042	0.009	0.011	0.049	0.013	0.009	0.006	0.005							0.008	0.008	0.005
N,N-Diethyl-m-toluamide (DEET)	IR	X		0.008	0.013	X		X													0.017	0.038	0.015	0.006
Napropamide	H	0.018		0.009	0.218	0.015	0.013	0.057	0.007	0.005	0.070	0.011	0.007									0.022	0.012	0.005
Oxadiazon	H	0.005	0.004	0.003	0.003	0.003	0.003	0.002	0.002	0.002			0.002											
Propiconazole	F	0.138	0.029	0.108	0.145		0.026	0.121	0.012	0.039	0.031	0.021		0.014	0.008							0.105		
Pyrimethanil	F						0.005	0.458	0.018	0.020	0.083	0.013		0.003										
Simazine	H	0.057	0.024	0.038	0.100	0.036	0.020	0.102	0.857	0.084	0.151	0.072	0.064	0.041	0.025	0.020	0.017	0.010	0.010	0.010	0.011	0.736	0.098	0.044
Sulfentrazone	H	0.015		0.016	0.012	0.016	0.010	0.007	0.011	0.009	0.011	0.012	0.012	0.011	0.013	0.009	0.007				0.020	0.014	0.009	0.009
Sulfometuron-methyl	H																				0.055			
Tebuthiuron	H			0.004		0.004																		
Terbacil	H	0.024	0.027	0.048	0.024	0.036	0.024	0.012	0.028	0.019	0.016	0.018	0.028	0.030	0.027	0.017	0.014					0.022	0.015	0.018
Tetrahydrophthalimide	D			0.004	0.011	0.002	0.004	1.360	0.009	0.027	0.030	0.026	0.241	0.014							0.011	0.064	0.119	
Thiamethoxam	I			0.010	0.015	0.012																		
Triclopyr	H																				0.275			
Suspended sediment concentration		7	2	6	6	3	3	15	4	3	5	3	1	2	1	2	2	2	7	2	3	18	4	2
Streamflow (cubic ft/sec)		65.1	27.4	43.3	36.6	21.2	25.6	-	14.5	19.4	33.9	25.4	10.2	5.4	4.4	3.3	2.7	-	1.3	1.0	1.6	-	-	9.4
Precipitation (total in/week)†		0.85	0.78	0.60	0.58	0.43	1.26	1.20	0.19	1.14	1.61	1.24	0.34	0.17	0.14	0.13	0.05	0.03	0.04	0.02	0.48	4.14	3.56	0.01

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

Current-use exceedance 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 2022.

There were 571 total pesticide detections in Lower Bertrand Creek from six different use categories: 24 types of herbicides, 18 insecticides, 9 fungicides, 1 legacy, 8 degradates, and 1 insect repellent.

- Of the total pesticide detections in Lower Bertrand Creek, 31 were above WSDA's assessment criteria (Table 7).
    - The single detection of 4,4'-DDD, a legacy degradate, exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - The two detections of chlorpyrifos approached the invertebrate NOAEC (0.005 µg/L).
    - Of the 10 detections of malaoxon, four detections approached or exceeded the invertebrate LC_{50} (0.098 µg/L) and invertebrate NOAEC (0.06 µg/L).
        - The detection on April 5 also exceeded the Endangered Species Level of Concern (0.205 µg/L) and NRWQC chronic criteria (0.1 µg/L).
        - The detection on April 26 and June 22 also approached the NRWQC chronic criteria.

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

- The single detection of bifenthrin approached the fish NOAEC (0.004 µg/L). It also exceeded the invertebrate LC_{50} (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). The detection also approached the Endangered Species Level of Concern (0.00145 µg/L) and invertebrate NOAEC (0.00193 µg/L).
- Of the 13 detections of imidacloprid, 11 detections exceeded the invertebrate NOAEC, while the other two detections approached the criteria (0.01 µg/L).
- Of the 15 detections of malathion, six detections approached the invertebrate LC_{50}, and one detection (April 26) exceeded the criteria (0.098 µg/L).
    - The detections on April 5, April 19, May 3, and May 16 also approached the invertebrate NOAEC, and the detections on April 26 and May 10 exceeded the criteria (0.06 µg/L)
    - The detection on April 26 also approached the Endangered Species Level of Concern (0.205 µg/L) and exceeded the NRWQC chronic criteria (0.1 µg/L).
    - The detection on May 10 also approached the NRWQC chronic criteria.
- The single detections of cis-permethrin and trans-permethrin, both are isomers of permethrin, were combined for comparison to assessment criteria. The combined concentration exceeded the invertebrate LC_{50} (0.0066 µg/L) and invertebrate NOAEC (0.0042 µg/L).
- All the detections of diazinon in 2022 did not exceed any assessment criteria, but the insecticide was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Lower Bertrand Creek monitoring site pesticide calendars provide a chronological overview of the pesticides detected during the 2022 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

Month		Apr				May					Jun				Jul			Oct					Nov	
Day of the Month	Use*	5	12	19	26	3	10	16	24	31	7	13	22	27	6	12	19	3	10	17	24	31	7	15
2,4-D	H	0.024	0.021		0.031			0.038		0.059	0.919	0.016										0.100	0.012	
2,6-Dichlorobenzamide	D	0.157	0.153	0.175	0.177	0.189	0.142	0.216	0.161	0.192	0.313	0.154	0.163	0.168	0.153	0.152	0.143	0.118	0.109	0.106	0.112	0.191	0.169	0.139
2-Hydroxyatrazine	D	0.013	0.011	0.009	0.011	0.010	0.011	0.013	0.010	0.010	0.009	0.009	0.006	0.007	0.006	0.005	0.004					0.034	0.035	
4,4'-DDD	L																0.001							
Acephate	I											0.131										0.041		
Atrazine	H			0.021	0.030	0.014	0.010			0.051		0.012	0.013	0.072	0.020	0.011	0.015	0.005	0.005	0.006	0.006			0.010
Azoxystrobin	F							0.015		0.003	0.008	0.011												
Bentazon	H																						0.026	
Bifenthrin	I	0.004																						
Boscalid	F	0.090	0.051	0.038	0.067	0.076	0.057	0.118	0.071	0.079	0.219	0.162	0.119	0.076	0.045	0.043	0.045	0.023	0.018	0.019	0.022	0.136	0.164	0.063
Bromacil	H	0.008	0.015	0.011	0.008	0.012	0.011		0.013	0.011	0.008	0.011	0.014	0.017	0.016	0.021	0.022	0.026	0.020	0.022	0.026			0.013
Bromoxynil	H								0.063															
Carbendazim	F	0.015	0.011	0.009	0.006	0.027	0.040			0.019	0.005	0.006	0.005	0.003		0.002							0.008	
Chlorothalonil (Daconil)	F	0.004																						
Chlorpyrifos	I	0.003																					0.003	
cis-Permethrin	I							0.006																
Cyprodinil	F																0.004							
Deisopropyl atrazine	D	0.019							0.014	0.018							0.013							
Desethylatrazine	D	0.009								0.007					0.004									
Diazinon	I		0.005	0.006	0.010	0.006	0.021	0.014	0.027	0.007	0.006	0.003	0.001	0.001									0.005	
Dicamba	H	0.013	0.019		0.010		0.010	0.021		0.039	0.031	0.023						0.005				0.038	0.011	
Dichlobenil	H	0.043	0.036	0.064	0.068	0.102	0.069	0.466	0.136	0.118	0.332	0.113	0.044	0.042	0.017	0.013	0.009	0.003				0.014	0.014	0.006
Dimethoate	I							0.004			0.004	0.003											0.010	
Dinotefuran	I	0.036	0.041	0.023	0.014	0.062	0.078	0.038	0.216	0.157	0.066	0.047	0.026		0.011	0.008	0.004							
Diuron	H							0.008		0.004	0.005						0.020							
Ethoprop	I				0.004	0.002																		
Fludioxonil	F	0.004	0.004								0.009	0.007	0.004		0.005	0.004	0.006					0.005		
Flupyradifurone	I		0.007		0.153	0.033	0.053	0.321	0.100	0.117	0.162	0.100	0.143	0.058	0.022	0.013	0.006					0.133	0.117	0.025
gamma-Cyhalothrin	I														0.001									
Hexazinone	H	0.002		0.003	0.003	0.003	0.002	0.001	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.005	0.005	0.005	0.005			0.004
Imidacloprid	I	0.022	0.019	0.022	0.028	0.028	0.026	0.025		0.014	0.017	0.020				0.007	0.009						0.030	
Indaziflam	H							0.004																
Malaoxon	D	0.207	0.016	0.011	0.082	0.032	0.004	0.010					0.051	0.007										0.008
Malathion	I	0.034	0.019	0.050	0.162	0.047	0.062	0.042		0.025	0.015	0.012	0.024			0.009	0.013					0.022	0.010	
MCPA	H				0.046						0.356											0.107	0.031	
MCPP	H	0.046			0.045	0.016	0.025	0.060		0.034	0.094	0.033										0.072	0.021	
Metalaxyl	F	0.426	0.223	1.580	0.057	0.079	0.065	0.105	0.069	0.061	0.059	0.052	0.067	0.076	0.078	0.088	0.086	0.102	0.082	0.088	0.098	0.035	0.043	0.054
Methamidophos	D											0.013												
Methomyl	I												0.004	0.002										
Metolachlor	H	0.062	0.050	0.013	0.092	0.022	0.033	0.119	0.015	0.015	0.040	0.019	0.012	0.011	0.009	0.009	0.009	0.010	0.009	0.009	0.011	0.032	0.023	0.011
Metribuzin	H	0.022	0.007	0.004	0.011	0.008	0.008	0.036	0.007	0.009	0.040	0.010	0.007	0.005									0.007	
N,N-Diethyl-m-toluamide (DEET)	IR	X			0.005	X		X														0.040	0.014	
Napropamide	H	0.020	0.013	0.006	0.009	0.009	0.006	0.054			0.056	0.008										0.019	0.011	0.004
Norflurazon	H																0.002	0.004		0.003	0.003			
Oxadiazon	H						0.002																	
Oxamyl	I	0.058	0.072	0.060	0.042	0.061	0.056	0.016	0.067	0.050	0.035	0.043	0.065	0.084	0.091	0.118	0.111	0.181	0.131	0.131	0.130		0.019	0.070
Oxamyl oxime	D	0.058	0.077			0.076	0.059		0.081	0.075	0.054			0.081		0.082	0.109	0.128	0.110		0.081			
Phosmet (Imidan)	I							0.005																
Prometon	H																				0.005			
Propiconazole	F	0.113	0.021		0.018	0.015	0.014	0.049	0.007	0.038	0.018	0.013			0.006							0.018	0.028	
Pyrimethanil	F							0.169	0.015	0.023	0.071	0.015	0.011	0.006			0.005							
Simazine	H	0.401	0.226	0.051	0.067	0.033	0.028	0.087	0.335	0.067	0.097	0.045	0.044	0.020	0.011	0.017	0.041	0.009	0.010	0.010	0.009	0.432	0.152	0.031
Sulfentrazone	H	0.058	0.073	0.062	0.048	0.060	0.048	0.021	0.050	0.043	0.038	0.045	0.062	0.065	0.066	0.080	0.072	0.103	0.092	0.099	0.112	0.019	0.017	0.041
Sulfometuron-methyl	H			0.003																				
Sulfoxaflor	I	0.028																						
Tebuthiuron	H					0.005	0.005				0.005		0.005							0.006	0.006			
Terbacil	H	0.019	0.012	0.014	0.026	0.016	0.010	0.017	0.010	0.009	0.012	0.008	0.010	0.006	0.006							0.028	0.014	0.008
Tetrahydrophthalimide	D	0.004	0.079	0.023	0.015	0.005	0.011	1.060	0.013	0.027	0.088	0.068	0.384	0.010	0.006	0.013	0.028	0.041	0.041	0.040	0.050	0.053	0.118	0.027
Thiamethoxam	I	0.014	0.020	0.024	0.022	0.022	0.023	0.026	0.016	0.025	0.027	0.018	0.028	0.033	0.036	0.037	0.050	0.063	0.054	0.062	0.064			0.031
trans-Permethrin	I							0.006																
Treflan (Trifluralin)	H							0.002																
Suspended sediment concentration		12	4	6	7	5	6	25	4	6	9	5	3	2	2	2	2	1	1	1	1	53	7	1
Streamflow (cubic ft/sec)		134	65.4	68.0	75.8	48.6	55.4	201	36.1	44.3	93.9	97.4	32.0	23.1	17.1	12.7	12.1	5.1	7.1	7.6	10.4	239	149	17.2
Precipitation (total in/week)†		0.85	0.78	0.60	0.58	0.43	1.26	1.20	0.19	1.14	1.61	1.24	0.34	0.17	0.14	0.13	0.05	0.03	0.04	0.02	0.48	4.14	3.56	0.01

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

Current-use exceedance DDT/degradate exceedance Detection No criteria

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

† Washington State University AgWeatherNet station: Lynden.N, (latitude: 48.98°, longitude: -122.43°)[4]

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 28 pesticides were detected at the same time in Upper Bertrand Creek and up to 34 in Lower Bertrand Creek.
- There were 46 pesticides that were detected at least once in both the Upper and Lower Bertrand Creek sites throughout the sampling season. Conversely, eight pesticides were found only at the upper site and 15 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 23 site visits (17%). In Lower Bertrand Creek, pesticide exceedances coincided with water quality measurements that did not meet the state standards at eight of the 23 site visits (35%). Water quality at the Upper Bertrand Creek site in Figure 5 and Lower Bertrand Creek site in Figure 6 are shown below.

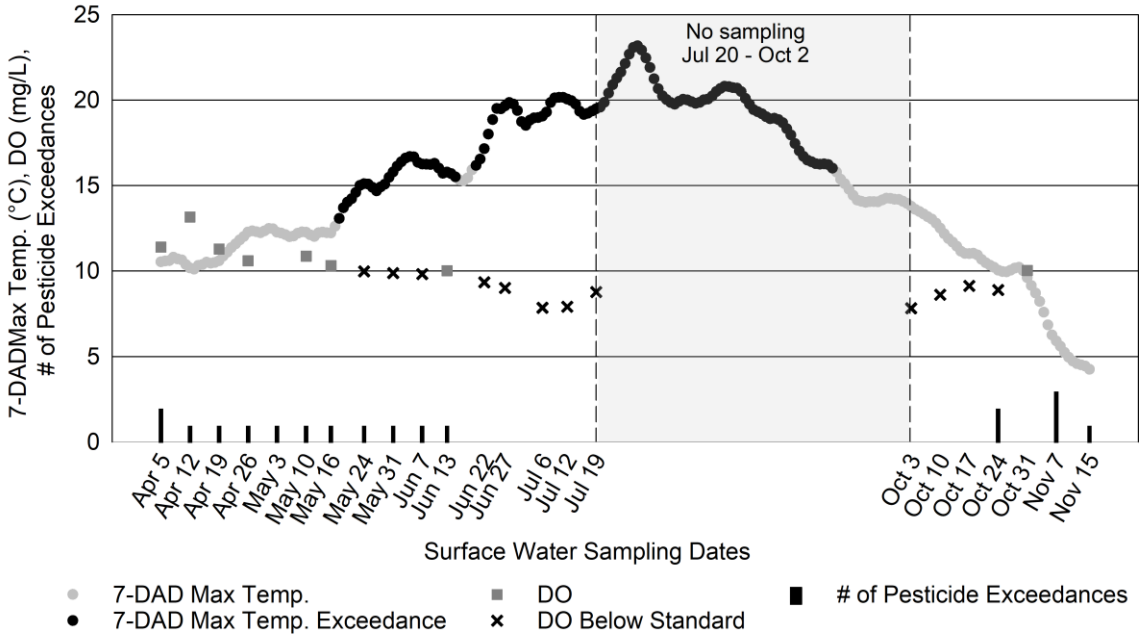


Figure 5 – Upper Bertrand Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state standard, ranging from 7.10 to 7.86 with an average of 7.48. DO measurements ranged from 7.82 mg/L to 13.16 mg/L with an average of 9.74 mg/L. More than half (60%) of the DO measurements did not meet the state standard, with 12 measurements falling below 10 mg/L. Four of the DO measurements that did not meet the state water quality standard coincided with one or two pesticide exceedances.

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

the end of the sampling season should remain below 16 ºC (WAC 2023). The 7-DADMax temperature exceeded the standard on 116 days, primarily from May 18 through September 14. Pesticide exceedances coincided with 7-DADMax temperature exceedances at four site visits.

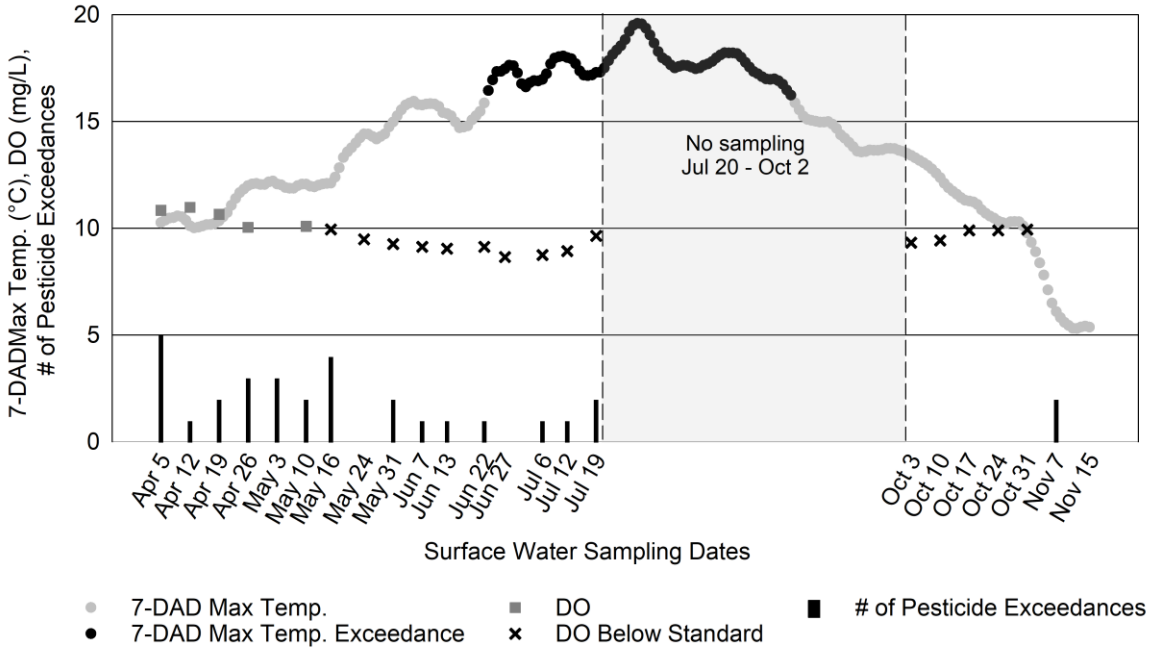
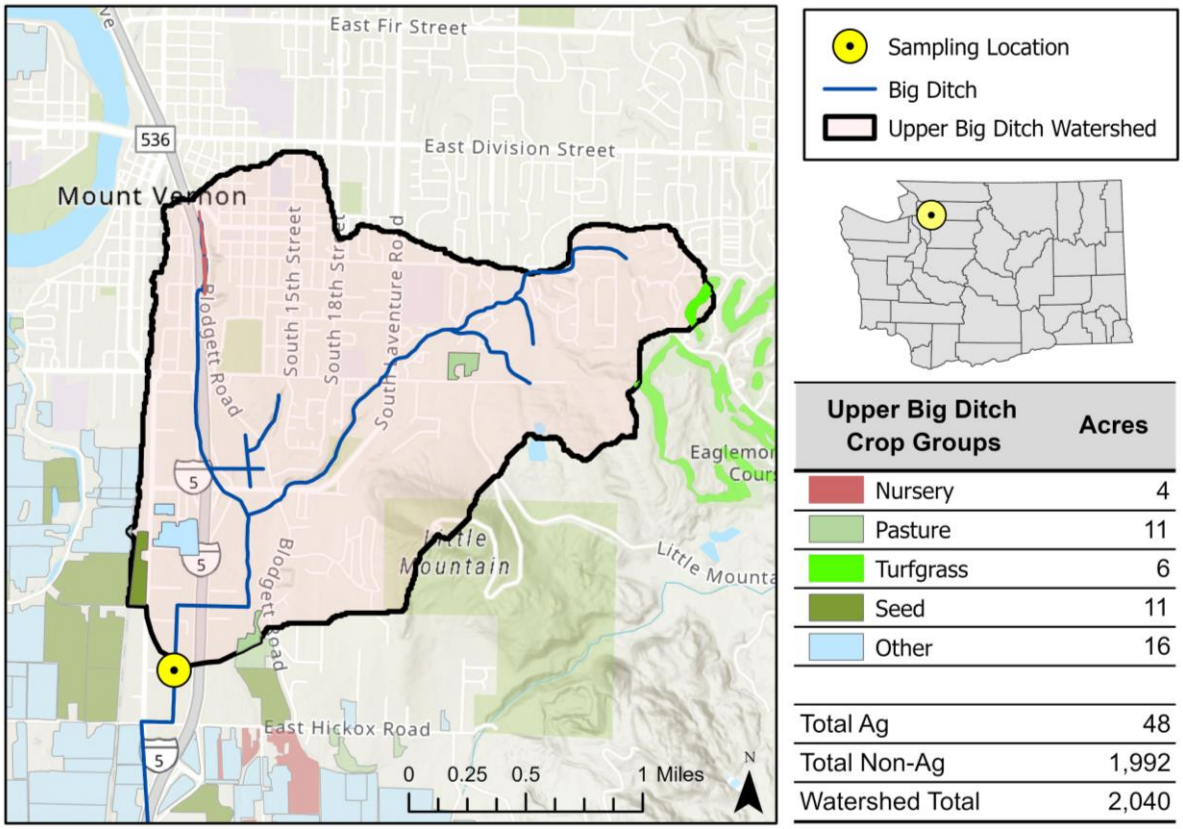


Figure 6 – Lower Bertrand Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.12 to 7.46 with an average of 7.35. DO measurements ranged from 8.65 mg/L to 10.98 mg/L with an average of 9.65 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. Eight of the DO measurements that did not meet the state water quality standard coincided with one, two, or four pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 74 days throughout the sampling season, from June 23 through September 4. Pesticide exceedances coincided with 7-DADMax temperature exceedances at three site visits.

Bertrand Creek has been designated as a freshwater body that provides a core summer habitat for salmonids by the WAC (WAC 2023). NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Upper Big Ditch



Upper Big Ditch Crop Groups	Acres
Nursery	4
Pasture	11
Turfgrass	6
Seed	11
Other	16
Total Ag	48
Total Non-Ag	1,992
Watershed Total	2,040

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

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

Figure 8 – Upper Big Ditch upstream view

Water from 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 and winter steelhead trout within the reach of ditch that encompasses the monitoring site (WDFW 2023). 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. Flows at the monitoring site were almost stagnant towards the end of the sampling season due to dense aquatic vegetation. The water sampling method was adapted to double- or single-point sampling where the highest velocity water was flowing in the ditch for the sampling season. Big Ditch stretches north approximately 3 miles from the monitoring site to its headwaters. Within the Upper Big Ditch

drainage area, the agricultural land use is predominantly commercial nursery and greenhouse. No other watersheds NRAS monitors have nursery or greenhouse crop groups as their main agricultural commodity. The 'Other' crop group category 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 2022.

- NRAS tested for 150 unique pesticides in Upper Big Ditch.
- There were 461 total pesticide detections from seven different use categories: 24 types of herbicides, 10 insecticides, 10 fungicides, 2 legacies, 9 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 24 sampling events.
- Up to 29 pesticides were detected at the same time.
- Of the total pesticide detections, five were above WSDA's assessment criteria (Table 8).
    - All the 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 Upper Big Ditch watershed POCs were bifenthrin, chlorpyrifos, and imidacloprid. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- The single detection of bifenthrin exceeded the fish NOAEC (0.004 µg/L), invertebrate LC_{50} (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L). It also approached the Endangered Species Level of Concern (0.0075 µg/L).
- There was no detection of chlorpyrifos or imidacloprid at the site, however, chlorpyrifos and imidacloprid were still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Upper Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 8). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

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

Month		Apr				May				Jun					Jul	Sep			Oct				Nov		
Day of the Month	Use*	5	12	19	26	3	10	17	24	1	7	14	22	28	6	13	20	27	4	11	18	25	1	8	16
2,4-D	H	0.034	0.143	0.149	0.036	0.265	0.017	0.097		0.011	0.134	0.827			0.042	0.011	0.009	0.007			0.019	0.321	0.111	0.028	
2,6-Dichlorobenzamide	D	0.290	0.259	0.229	0.216	0.259	0.211	0.196	0.164	0.150	0.236	0.242	0.182	0.134	0.148	0.097	0.091	0.107	0.078	0.080	0.081	0.171	0.280	0.302	0.154
2-Hydroxyatrazine	D	0.008			0.009	0.009	0.010	0.009		0.008	0.004		0.006	0.007	0.007	-	0.016	0.018	0.020	0.016		0.015			
4,4'-DDD	L			0.003			<0.001	0.001																	
4,4'-DDE	L			0.002																					
4-Nitrophenol	D	0.026				0.023							0.063									0.090	0.019		
Acephate	I								4.770	0.129	0.084					-									
Atrazine	H																						0.004	0.004	
Azoxystrobin	F		0.015	0.166	0.110	0.012	0.031	0.010	0.018	0.038	0.013	0.010	0.034	0.083	0.008	-									
Bifenthrin	I											0.005													
Boscalid	F	0.012	0.010	0.014	0.025	0.010	0.015	0.010	0.013	0.010	0.019	0.015	0.054	0.035	0.005	0.002		0.002	0.002	0.001	0.002	0.008	0.003	0.002	0.003
Bromacil	H																				0.005				
Carbendazim	F		0.003	0.005	0.004	0.012	0.013			0.015	0.003		0.013			-			0.005			0.011	0.007	0.006	
Chlorothalonil (Daconil)	F										0.003														
Cyantraniliprole	I			0.152	0.259	0.090	0.098	0.056	0.087	0.116	0.057			0.143		-									
Diazinon	I			0.003																					
Dicamba	H	0.012	0.005	0.005		0.013		0.063			0.012	0.027										0.017	0.015		
Dichlobenil	H	0.020	0.008	0.014	0.006	0.019	0.006	0.010	0.004	0.004	0.013	0.032	0.004	0.003	0.004							0.004	0.016	0.012	0.002
Dimethoate	I														0.005										
Dinotefuran	I	0.048	0.123	0.093	0.236	0.096	0.178	0.089	0.166	0.133	0.115	0.038	0.178	0.160	0.120	-	0.014	0.013	0.006			0.006		0.030	0.114
Dithiopyr	H	0.008	0.004	0.005	0.002	0.006	0.003	0.003			0.004	0.005											0.008	0.007	0.002
Diuron	H	0.007			0.004	0.005		0.007			0.007	0.011			0.006	-						0.025	0.020		
Eptam	H				0.003	0.002	0.002	0.001	0.002	0.003	0.002		0.003	0.002	0.001										
Etridiazole	F			0.001		<0.001							0.003												
Fipronil	I											0.002											0.002	0.002	
Fipronil disulfinyl	D																						0.002	0.002	
Fipronil sulfide	D																						0.002	0.002	
Fipronil sulfone	D																						0.003		
Fludioxonil	F	0.021	0.030	0.057	0.096	0.070	0.055	0.048	0.083	0.058	0.068	0.041	0.140	0.303	0.029	0.012	0.010	0.012	0.010	0.008	0.010	0.019	0.011	0.006	0.011
Fluopicolide	F			0.004			0.007	0.011	0.015							-									
Flupyradifurone	I	0.012	0.038	0.077	0.963	0.339	0.241	0.227	0.034	0.017	0.129	0.066	0.108	0.321	0.018	-									
Hexazinone	H																					0.004			
Imazapic	H										0.006	0.012				-								0.009	
Imazapyr	H	0.053	0.056	0.053	0.060	0.063	0.059	0.061	0.057	0.049	0.034	0.045	0.024	0.022	0.030	-		0.018	0.017			0.024	0.064	0.041	0.022
Indaziflam	H		0.005	0.005	0.005	0.005	0.005				0.003					-									
Isoxaben	H	0.010		0.003												-						0.010			
MCPA	H										0.177														
MCPP	H	0.019				0.037						0.382										0.045	0.032		
Metalaxyl	F			0.755	0.021		0.013		0.020	0.018			0.018	0.013											
Methamidophos	D								0.728	0.252	0.039					-									
Methiocarb	I								0.104	0.095			0.045	0.005		-									
Methomyl oxime	D						0.011									-									
Metolachlor	H		0.003	0.001	0.002	0.003	0.001	0.003	0.003	0.003	0.006	0.012	0.006	0.002	0.002								0.003	0.002	0.002
Metribuzin	H											0.005													
N,N-Diethyl-m-toluamide (DEET)	IR	X	0.038	0.022	0.024	X	0.010	X	0.014	0.011		0.011		0.020	0.052	0.010	0.007		0.006		0.005	0.075	0.040	0.024	0.008
Paclobutrazol	F						0.032									-									
Pentachlorophenol	WP	0.018										0.019											0.016		
Picloram	H	0.064	0.120	0.125	0.164	0.131	0.119	0.143	0.248	0.352	0.078	0.030	0.338	0.523	0.277	0.234	0.234	0.187	0.195	0.149	0.150				
Prometon	H	0.009	0.008	0.010	0.010	0.011	0.007	0.007	0.007	0.007	0.007	0.005	0.007	0.007	0.006	0.009	0.008	0.009	0.008	0.008	0.008	0.008	0.007	0.008	0.008
Propiconazole	F	0.017						0.006			0.006	0.017				-						0.040		0.025	
Simazine	H							0.004														0.012			
Sulfentrazone	H	0.007		0.005	X	0.009	0.003	0.005			0.012	0.012	0.004		0.005							0.049	0.013	0.010	X
Sulfometuron-methyl	H			0.003												-									
Tebuthiuron	H	0.012	0.015	0.017	0.022	0.021	0.017	0.014	0.025	0.025	0.017	0.009	0.028	0.043	0.035	0.038	0.042	0.042	0.038	0.034	0.036	0.017		0.010	0.029
Tetrahydrophthalimide	D											0.003										0.005			
Thiamethoxam	I				0.004											-									
Triclopyr	H	0.042	0.507	0.307	0.101	0.203	0.048	0.047			0.576	0.259			0.092							0.248	0.278	0.143	0.024
Suspended sediment concentration		12	8	6	9	7	7	8	7	8	11	20	6	6	3	8	3	4	4	3	11	5	11	5	3
Streamflow (cubic ft/sec)		7.6	4.8	3.8	2.3	2.7	3.1	-	2.0	1.2	3.9	8.3	1.8	1.3	1.7	0.5	0.3	0.4	0.5	0.1	0.1	1.0	4.3	-	1.7
Precipitation (total in/week)†		0.61	0.51	0.27	0.19	0.64	0.91	0.65	0.06	0.37	1.54	1.52	0.00	0.00	0.31	0.00	0.02	0.00	0.00	0.00	0.00	0.75	2.64	3.77	0.01

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

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet state standards at three of the 24 site visits (13%). Water quality at the Upper Big Ditch site is shown below (Figure 9).

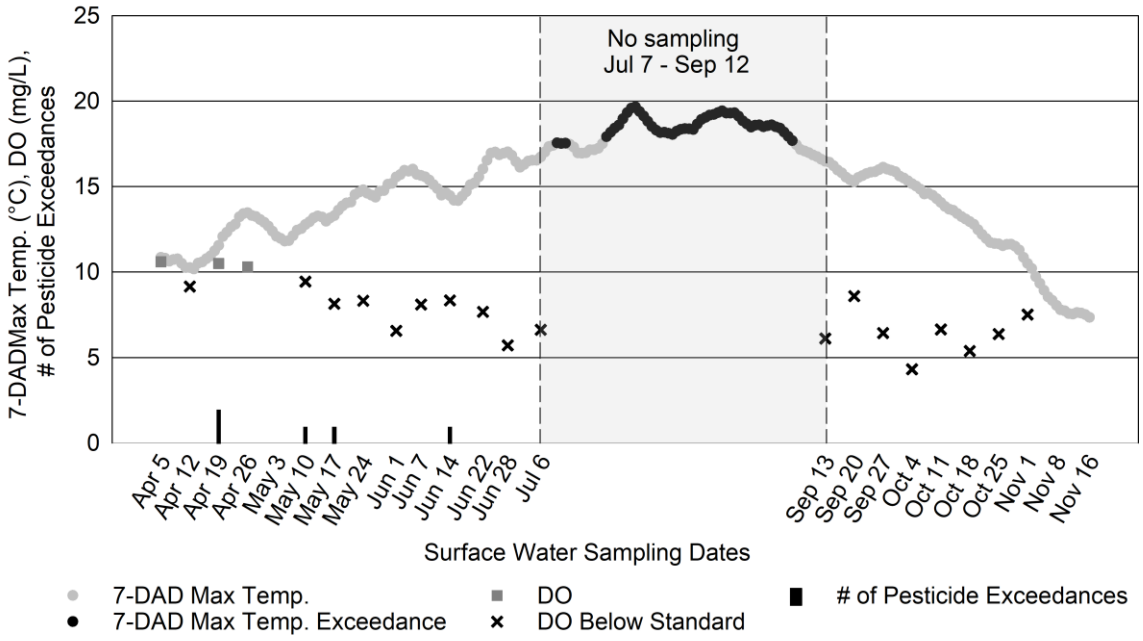
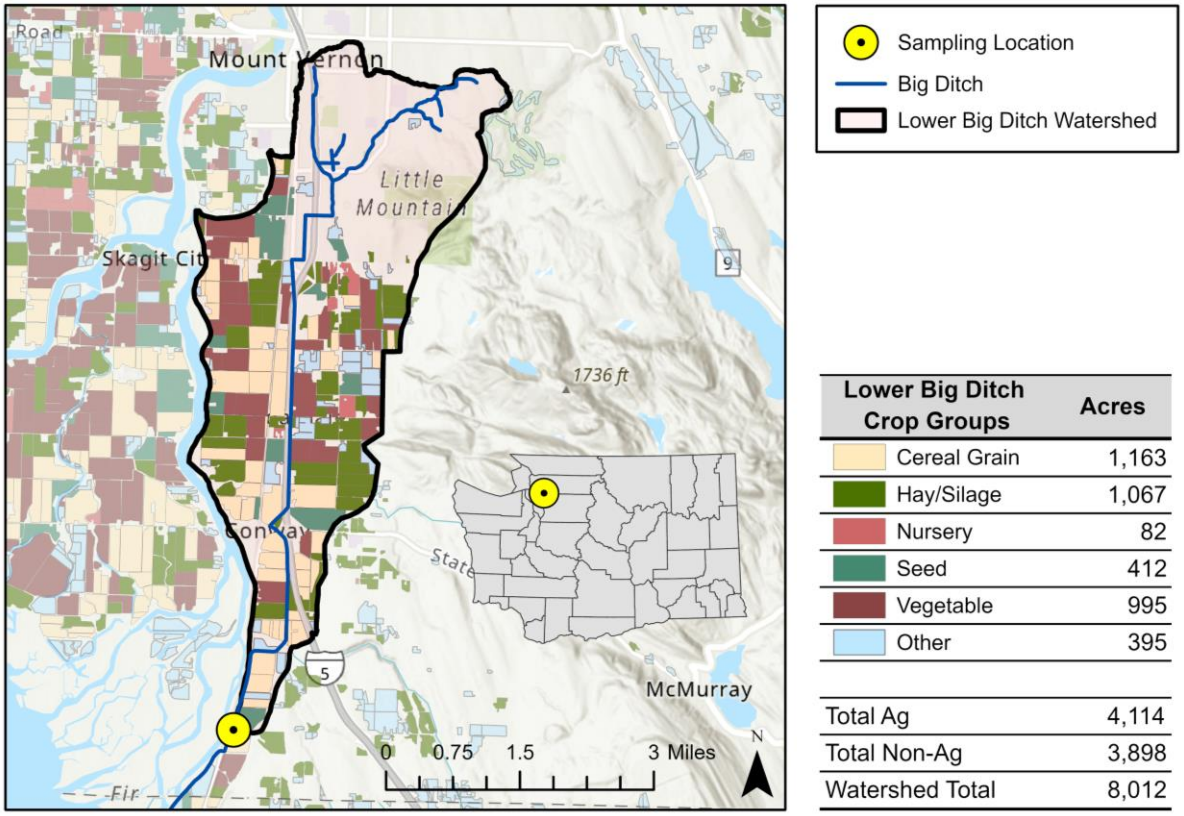


Figure 9 – Upper Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 6.96 to 7.22 with an average of 7.11. DO measurements ranged from 4.31 mg/L to 10.60 mg/L with an average of 7.66 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. Three of the DO measurements that did not meet the state water quality standard coincided with one pesticide exceedance. 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 49 days throughout the sampling season, occurring intermittently from July 10 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 2023). Flow in the ditch towards the end of summer was slowed substantially due to constriction from aquatic vegetation. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs.

Lower Big Ditch



Lower Big Ditch Crop Groups	Acres
Cereal Grain	1,163
Hay/Silage	1,067
Nursery	82
Seed	412
Vegetable	995
Other	395
Total Ag	4,114
Total Non-Ag	3,898
Watershed Total	8,012

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

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

We only sampled this site when the tide gate located downstream of the monitoring site was open and the water was flowing from Big Ditch into Puget Sound to avoid sample contamination with saltwater or pooling backwater. Staff occasionally observed small fish. WDFW has documented the presence of coho, fall Chinook, fall chum, kokanee, and pink salmon, as well as rainbow and winter steelhead trout within the reach of ditch that encompasses the monitoring site (WDFW 2023).

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 2022.

- NRAS tested for 150 unique pesticides in Lower Big Ditch.
- There were 418 total pesticide detections from six different use categories: 30 types of herbicides, 12 insecticides, 10 fungicides, 3 legacies, 9 degradates, and 1 insect repellent.
- Pesticides were detected at all 14 sampling events.
- Up to 41 pesticides were detected at the same time.
- Of the total pesticide detections, 26 were above WSDA's assessment criteria (Table 9).
    - All detections of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT, approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- The single detection of bifenthrin approached the fish NOAEC (0.004 µg/L) and exceeded the invertebrate LC_{50} (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- Of the 11 detections of fipronil, two approached the invertebrate NOAEC and seven exceeded the invertebrate NOAEC (0.011 µg/L).
    - The detections on May 31 and June 14 also approached invertebrate LC_{50} (0.22 µg/L).
- Both detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- All detections of diuron in 2022 did not exceed any assessment criteria, but the herbicide was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Lower Big Ditch monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 9). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 9 – Lower Big Ditch pesticide calendar, µg/L

Month		Apr				May					Jun			Sep	Oct
Day of the Month	Use*	4	11	18	25	2	9	17	23	31	6	14	21	27	10
1-(3,4-Dichlorophenyl)-3-methylurea	D		0.007	0.007			0.008						0.007		
2,4-D	H		0.179	0.006	0.016	0.040	0.020	0.098		0.042	0.588	0.041		0.458	0.017
2,6-Dichlorobenzamide	D	0.152	0.176	0.142	0.113	0.107	0.129	0.076	0.050	0.043	0.098	0.138	0.127	0.034	0.017
2-Hydroxyatrazine	D	0.039	0.040	0.036	0.034	0.036	0.048	0.032	0.030	0.018	0.011	0.045	0.055	0.046	0.036
4,4'-DDD	L	0.005	0.003	0.001		0.002	<0.001	<0.001	<0.001					0.002	0.002
4,4'-DDE	L	0.003	0.001			0.002								0.001	
4,4'-DDT	L	0.002													
4-Nitrophenol	D	0.022	0.044		0.083	0.183					0.043				
Acephate	I								0.057	0.024	0.016	0.023			
Acetamiprid	I										0.003				
Aminocyclopyrachlor	H									0.061					
Atrazine	H		0.005	0.003		0.003	0.002	0.020			0.012	0.004			
Azoxystrobin	F	0.033	0.054	0.019	0.072	0.037	0.048	0.079	0.033	0.210	0.080	0.097	0.067		
Bentazon	H	0.032	0.110	0.044		0.048	0.038	0.041					0.418	0.014	0.009
Bifenthrin	I										0.003				
Boscalid	F	0.005	0.008	0.004	0.010	0.007	0.010	0.009	0.003	0.003	0.074	0.012	0.007	0.003	0.002
Bromacil	H		0.005		0.015					0.011	0.009				
Carbendazim	F		0.010			0.005									
Chlorpropham	H	0.003	0.003	0.002		0.002					0.001				
Clopyralid	H										0.038				
Cyantraniliprole	I							0.080		0.029					
Diazinon	I			0.029			0.002								
Dicamba	H	0.007	0.009	0.006		0.011	0.016	0.040			0.142	0.032			
Dichlobenil	H	0.004	0.011	0.003	0.006	0.004	0.004	0.005		0.002	0.016	0.008	0.005		
Difenoconazole	F						0.006								
Dimethoate	I					0.088		0.008		0.017	0.006				
Dinotefuran	I	0.032	0.035	0.042	0.051	0.041	0.039	0.022	0.022	0.018	0.018	0.053	0.047		
Dithiopyr	H	0.002	0.003												
Diuron	H	0.015	0.015	0.013	0.013	0.014	0.017	0.015	0.010	0.007	0.016	0.021	0.015		
Eptam	H	0.010	0.008	0.008	0.005	0.013	0.006	0.014	0.005	0.006	0.002	0.005	0.007		
Fipronil	I	0.017	0.007	0.003		0.004	0.008	0.050	0.017	0.086	0.029	0.073	0.032		
Fipronil disulfinyl	D	0.004						0.006	0.003	0.015	0.007	0.009	0.008		
Fipronil sulfide	D	0.007	0.005	0.006	0.001	0.005	0.004	0.007	0.007	0.007	0.007	0.013	0.014	0.005	0.003
Fipronil sulfone	D	0.016	0.007	0.004		0.005	0.006	0.007	0.004	0.009	0.006	0.012	0.012	0.004	
Fludioxonil	F	0.072	0.061	0.089	0.005	0.102	0.102	0.044	0.045	0.033	0.057	0.071	0.060	0.034	0.020
Fluopicolide	F					0.007	0.008								
Flupyradifurone	I	0.018	0.026	0.013	0.024	0.331	0.101	0.077		0.010		0.137	0.021		
Hexazinone	H	0.002		0.002	0.016	0.002	0.002				0.001	0.002	0.002	0.004	
Imazapic	H										0.006	0.016			
Imazapyr	H	0.065	0.064	0.068	0.067	0.069	0.069	0.058		0.030	0.037	0.083	0.039	0.011	
Imidacloprid	I											0.170	0.019		
Indaziflam	H		0.030					0.004			0.009				
MCPA	H	0.028	0.044		0.221	0.299					0.260				
MCPP	H										0.029				
Metalaxyl	F	0.017	0.021	0.022			0.041	0.045	0.009	0.026		0.125	0.076		
Methamidophos	D									0.080	0.029	0.016			
Methiocarb	I									0.038					
Metolachlor	H	0.450	0.260	0.238	0.004	0.323	0.304	0.189	0.203	0.123	0.143	0.185	0.201	0.003	0.003
Metribuzin	H	0.011	0.010	0.004			0.007	0.005	0.005	0.014	0.010	0.047	0.018		
Metsulfuron-methyl	H										0.023				
N,N-Diethyl-m-toluamide (DEET)	IR	X	0.017	0.015		X	0.010	X				0.010			
Picloram	H	0.042	0.040	0.048	0.050	0.068		0.044		0.039		0.037			
Prometon	H	0.006	0.005	0.009		0.008	0.004	0.003	0.003	0.002	0.004	0.005	0.005	0.006	0.006
Propiconazole	F					0.024	0.008	0.012					0.018		
Pyraclostrobin	F										0.005				
Pyrimethanil	F											0.258	0.016		
Simazine	H	0.010	0.008	0.004			0.005	0.004			0.004		0.115		
Sulfentrazone	H	0.041	0.090	0.035	0.059	0.033	0.039	0.023	0.011	0.007	0.008	0.118	0.096		
Sulfometuron-methyl	H		0.107		0.017						0.021				
Tebuthiuron	H	0.021	0.019	0.023	0.062	0.027	0.015	0.009	0.013	0.010	0.009	0.016	0.026	0.015	0.009
Terbacil	H				0.019										
Tetrahydrophthalimide	D		0.008	0.028		0.013	0.004					0.790	0.013		
Thiamethoxam	I	0.002													
Treflan (Trifluralin)	H						0.008	0.002							
Triclopyr	H		0.411	0.048	0.021	0.021	0.048	0.071			0.770	0.111		0.194	
Suspended sediment concentration		20	13	14	23	14	20	29	17	11	18	12	12	20	25
Streamflow (cubic ft/sec)		-	-	7.1	20.1	8.2	40.5	-	10.7	18.8	-	-	6.0	2.1	1.2
Precipitation (total in/week)†		0.35	0.86	0.08	0.29	0.28	1.36	0.65	0.07	0.37	1.55	1.52	0.01	0.00	0.00

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

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

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

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 11 of the 14 site visits (79%). Water quality at the Lower Big Ditch site is shown below (Figure 12).

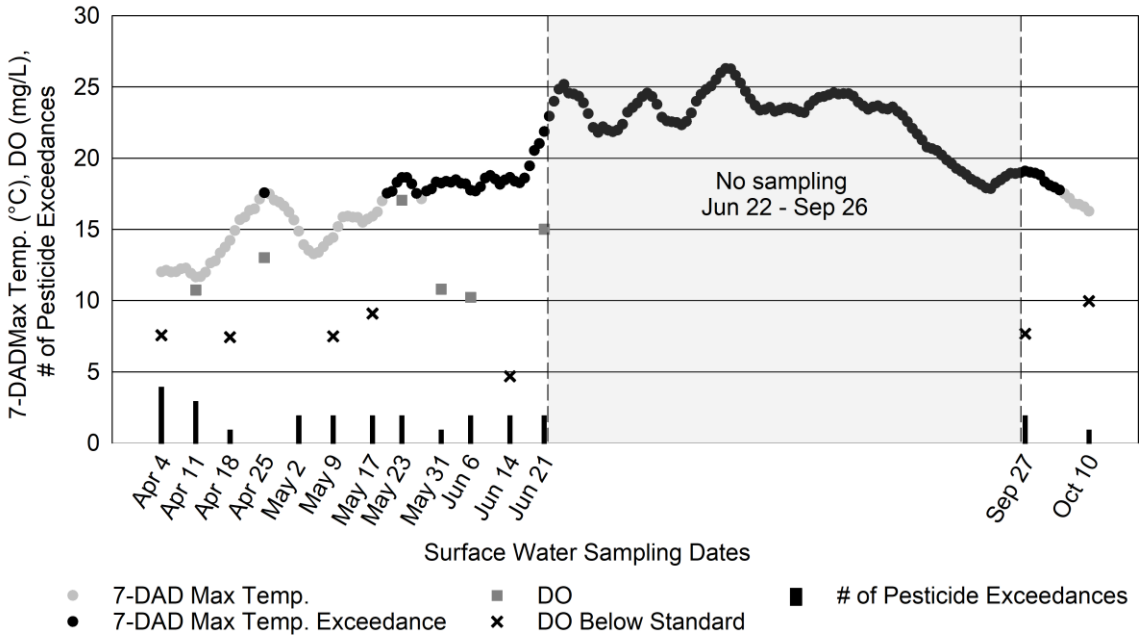
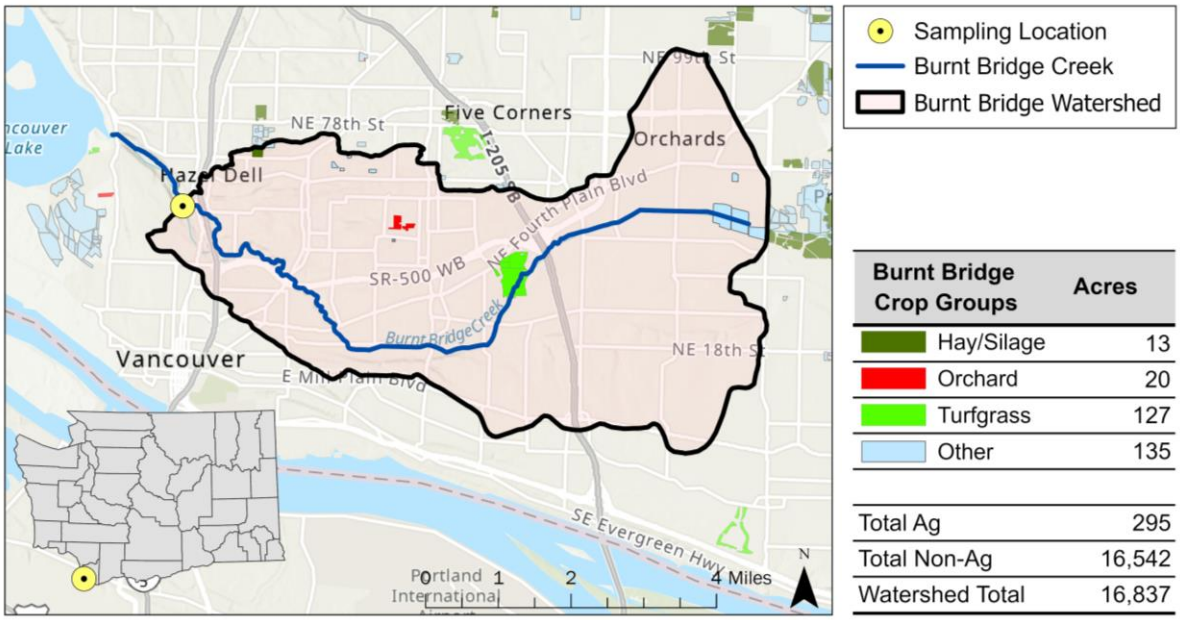


Figure 12 – Lower Big Ditch water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.09 to 8.22 with an average of 7.49. DO measurements ranged from 4.68 mg/L to 17.04 mg/L with an average of 10.05 mg/L. More than half (54%) of these measurements did not meet the state water quality standard, with seven measurements falling below 10 mg/L. DO variability potentially can be attributed to the effects of tidal fluctuations. The 7-DADMax temperature exceeded the standard of 17.5°C on 138 days throughout the sampling season, occurring intermittently from May 20 through October 4. Pesticide exceedances coincided with 7-DADMax temperature exceedances at six 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 2023). WSDA will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

Burnt Bridge Creek



Burnt Bridge Crop Groups	Acres
Hay/Silage	13
Orchard	20
Turfgrass	127
Other	135
Total Ag	295
Total Non-Ag	16,542
Watershed Total	16,837

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: 45.6614º, longitude: -122.6720º) (Figure 13, Figure 14). Roughly 10 miles of Burnt Bridge Creek flows through the center of Vancouver, Washington. The watershed is highly impacted by residential, commercial, and industrial development (Figure 13). The 'Other' crop group category includes mostly land used for conservation purposes. This site was one of two urban sites monitored in 2022.

Figure 14 – Burnt Bridge Creek upstream view

Burnt Bridge Creek flows into Vancouver Lake, which drains into the Columbia River. Precipitation events generally influence streamflow in this creek. In summer, inflow from groundwater, residential irrigation, and industrial discharge from a manufacturing facility near the headwaters maintain the creek's base flow. WDFW has documented the presence of coho and fall Chinook, as well as rainbow and winter steelhead trout within the Burnt Bridge watershed (WDFW 2023). Staff observed fish of unknown species at this site.

Below is a brief overview of the pesticide findings in Burnt Bridge Creek in 2022.

- NRAS tested for 150 unique pesticides in Burnt Bridge Creek.
- There were 150 total pesticide detections from six different use categories: 20 types of herbicides, 3 insecticides, 3 fungicides, 1 legacy, 4 degradates, and 1 insect repellent.
- Pesticides were detected at all 13 sampling events.
- Up to 18 pesticides were detected at the same time.
- Of the total pesticide detections, 11 were above WSDA's assessment criteria (Table 10).
    - Of all the detections of 4,4'DDD, a legacy degradate of DDT, half exceeded the NRWQC and WAC chronic criteria, while the other half approached the criteria (both 0.001 µg/L).

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

- Of the three diuron detections, one detection exceeded the plant EC_{50} (0.13 µg/L).
- There was no detection of imidacloprid at the site, however, imidacloprid was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Burnt Bridge Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 10). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 10 – Burnt Bridge Creek pesticide calendar, µg/L

Month		Apr		May		Jun			Jul		Aug		Sep		Oct
Day of the Month	Use*	6	20	4	18	1	15	29	11	25	9		6	21	5
1-(3,4-Dichlorophenyl)-3-methylurea	D			0.007											
2,4-D	H		0.014		0.012	0.018					0.012				
2,6-Dichlorobenzamide	D	0.226	0.196	0.214	0.191	0.187	0.182	0.225	0.199	0.051	0.198		0.198	0.215	0.183
2-Hydroxyatrazine	D					0.002									
4,4'-DDD	L	0.003	0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001					0.002
Atrazine	H	0.006	0.005	0.005	0.004	0.003	0.003	0.003	0.003	0.003	0.002		0.006	0.006	0.006
Bromacil	H												0.003	0.005	
Carbendazim	F	0.003	0.003	0.003		0.005	0.004	0.001	0.001						
Desethylatrazine	D	0.009						0.004	0.003		0.004				
Dichlobenil	H	0.009	0.034	0.009	0.008	0.004	0.007	0.004	0.003	0.002	0.002			0.009	0.004
Dithiopyr	H	0.003	0.004	0.003	0.003		0.002								
Diuron	H		0.004	0.202	0.021										
Ethoprop	I	0.003													
Fenbutatin oxide	I				0.005										
Fipronil	I				0.002		0.003								
Hexazinone	H													0.004	
Imazapic	H			0.008	0.006										
Imazapyr	H		0.046			0.020	0.015	0.010	0.013	0.014	0.010			0.021	0.011
Isoxaben	H					0.007									
Metolachlor	H		0.002	0.001	0.001	<0.001	<0.001								0.002
Metribuzin	H						0.005								
N,N-Diethyl-m-toluamide (DEET)	IR		0.008	X	X	1.370	0.008		0.016	0.010				0.009	0.020
Pendimethalin	H	0.004	0.005	0.004	0.010	0.005	0.006		0.002	0.002					0.004
Prometon	H						0.006								
Propiconazole	F	0.039	0.082	0.056	0.139	0.046	0.065	0.017	0.017		0.011				
Simazine	H	0.013	0.020	0.008	0.008	0.005	0.004								0.012
Sulfentrazone	H	X	X		X	0.004	0.006		0.004	0.004				0.014	
Tebuthiuron	H		0.005												
Terbacil	H	0.007		0.003											
Treflan (Trifluralin)	H				0.002		0.002								
Triadimefon	F												0.003		
Triclopyr	H	0.018	0.126	0.032	0.067		0.071	0.087							0.022
Suspended sediment concentration		6	9	10	9	10	12	10	10	19	6		4	4	37
Streamflow (cubic ft/sec)		13.5	22.7	17.4	20.3	13.8	22.8	11.2	9.5	7.4	5.7		5.0	4.3	6.7
Precipitation (total in/week)†		0.72	1.13	1.37	1.30	0.93	2.20	0.00	0.22	0.00	0.00		0.00	0.00	0.62

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: Vancouver RE, (latitude: 45.68°, longitude: -122.65°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at six of the 13 site visits (46%). Water quality at the Burnt Bridge Creek site is shown below (Figure 15).

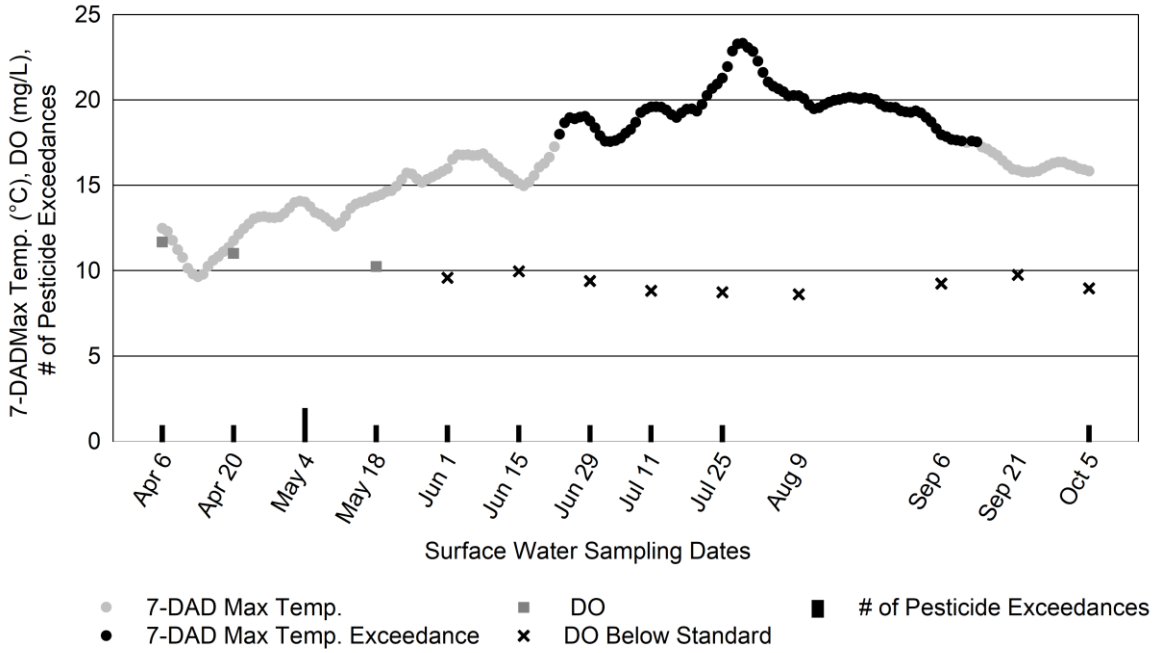


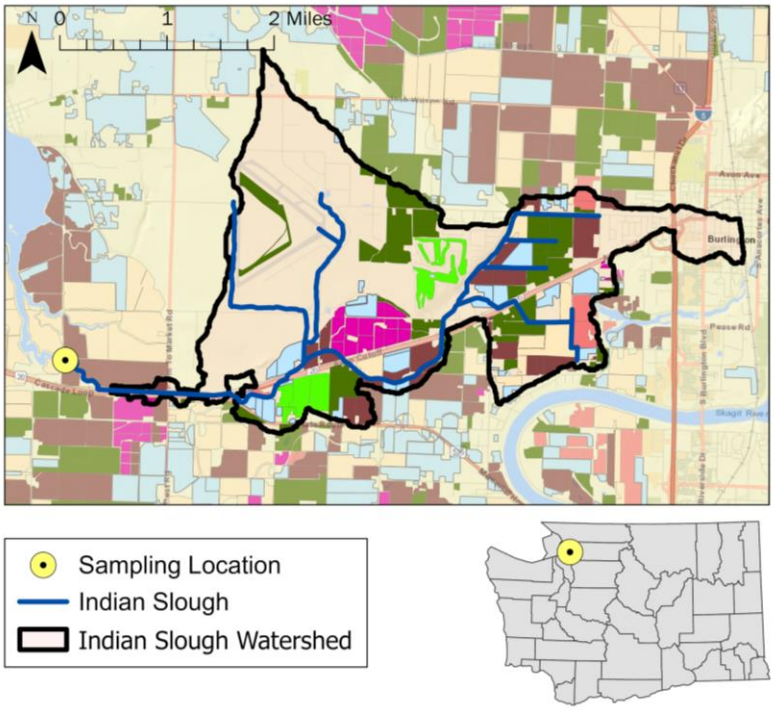
Figure 15 – Burnt Bridge Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.79 to 8.09 with an average of 8.00. DO measurements ranged from 8.61 mg/L to 11.68 mg/L with an average of 9.66 mg/L. Three-quarters (75%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L. Six 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 82 days throughout the sampling season, occurring intermittently from June 23 through September 13. 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 2023). 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.

Indian Slough



Indian Slough Crop Groups	Acres
Berry	154
Cereal Grain	182
Hay/Silage	625
Nursery	91
Turfgrass	175
Vegetable	389
Other	331
Total Ag	1,947
Total Non-Ag	3,078
Watershed Total	5,025

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

Figure 17 – Indian Slough upstream view

In 2006, NRAS started sampling the Indian Slough watershed, also referred to as Little Indian Slough, in Skagit County. The monitoring site is located just upstream from the tide gate at Bayview-Edison Road near Mt. Vernon (latitude: 48.4506º, longitude: -122.4650º) (Figure 16, Figure 17).

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 2023). Staff frequently observe juvenile fish of unknown species at the site. In the late fall of 2021, adult salmon of unknown species were observed by staff.

The Indian Slough watershed is a web of drainage ditches that pass through agricultural and industrial/residential areas. Indian Slough stretches approximately 6 miles from its sources to the monitoring site. Within the watershed, the agricultural land use is predominantly 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 2022.

- NRAS tested for 150 unique pesticides in Indian Slough.
- There were 378 total pesticide detections from six different use categories: 31 types of herbicides, 7 insecticides, 10 fungicides, 2 legacies, 8 degradates, and 1 insect repellent.
- Pesticides were detected at all 14 sampling events.
- Up to 39 pesticides were detected at the same time.
- Of the total pesticide detections, 12 were above WSDA's assessment criteria (Table 11).
    - All the 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 Indian Slough watershed POCs were diuron, fipronil, imidacloprid, indaziflam, and malathion. Below, each POC detected is compared to any corresponding state, national, or toxicity criteria that were exceeded.

- Of the 12 detections of diuron, one detection approached the plant EC_{50} (0.13 µg/L).
- Of the seven detections of fipronil, one detection approached the invertebrate NOAEC (0.011 µg/L).
- The single detection of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- The three detections of indaziflam did not exceed any assessment criteria in 2022, however, this herbicide was still considered a watershed POC because of detections that did exceed criteria in recent years.
- There was no detection of malathion at the site, however, malathion was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Indian Slough monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 11). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 11 – Indian Slough pesticide calendar, µg/L

Month		Apr				May					Jun				Jul
Day of the Month	Use*	4	11	18	25	2	9	17	23	31	6	14	21	28	5
1-(3,4-Dichlorophenyl)-3-methylurea	D										0.005	0.006			0.013
2,4-D	H					0.013	0.011	0.010			0.257	0.315			0.029
2,6-Dichlorobenzamide	D	0.152	0.149	0.119	0.121	0.123	0.156	0.156	0.107	0.101	0.231	0.150	0.120	0.106	0.116
2-Hydroxyatrazine	D	0.015	0.015	0.014	0.013	0.013	0.015	0.016	0.013	0.011	0.012	0.015	0.012	0.011	0.012
4,4'-DDD	L	0.003	0.003	<0.001	0.001		<0.001		<0.001				0.001		
4,4'-DDE	L	0.001	0.001												
4-Nitrophenol	D	0.026			0.072	0.096									
Atrazine	H	0.005		0.003	0.002	0.003	0.003				0.019				
Azoxystrobin	F	0.015	0.010	0.018		0.003		0.006		0.005	0.011	0.019	0.012	0.011	0.010
Bentazon	H	0.071	0.057	0.027	0.026	0.024	0.038	0.037	0.028	0.024			0.052	0.037	0.019
Boscalid	F	0.022	0.018	0.011	0.006	0.010	0.010	0.009	0.008	0.006	0.014	0.022	0.008	0.009	0.008
Bromacil	H	0.015	0.016	0.015		0.017	0.013	0.010	0.015	0.013	0.027	0.009	0.013	0.015	0.020
Bromoxynil	H				0.036										
Carbaryl	I						0.042								
Carbendazim	F					0.003					0.007				
Chlorothalonil (Daconil)	F	0.004													
Chlorpropham	H				0.002										
Clopyralid	H				0.032										
Cyprodinil	F										0.043				
Dacthal	H	0.017		0.013	0.062				0.061	0.047				0.067	
Desethylatrazine	D										0.006				
Diazinon	I		0.016	0.003	0.002		0.004	0.002			0.002				
Dicamba	H										0.034	0.010			
Dichlobenil	H	0.013	0.010	0.005	0.003	0.018	0.025	0.070	0.015	0.030	0.103	0.019	0.014	0.010	0.012
Dimethoate	I														0.014
Dithiopyr	H										0.002				
Diuron	H	0.007	0.006			0.004	0.008	0.008	0.005	0.004	0.009	0.007	0.057	0.028	0.085
Eptam	H	0.001	0.001	0.002	0.010	0.010	0.003	0.005	0.004	0.004	0.003	0.002	0.004	0.004	0.005
Fipronil	I	0.005	0.006				0.003	0.005			0.002	0.005	0.002		
Fipronil sulfide	D	0.002	0.002	0.001	0.005		<0.001	0.004	0.004	0.004	0.004	0.005	0.004	0.004	0.004
Fipronil sulfone	D	0.005	0.005		0.003		0.002	0.002				0.004			
Fludioxonil	F	0.012	0.009	0.019	0.081	0.014	0.015	0.017	0.005	0.013	0.053	0.011	0.027	0.010	0.011
Flumioxazin	H							0.025			0.019				
Hexazinone	H	0.018	0.017	0.015		0.015	0.012	0.009	0.013	0.011	0.010	0.011	0.011	0.013	0.012
Imazapic	H										0.006	0.010			
Imazapyr	H	0.114	0.177	0.094	0.085	0.110	0.238	3.610	0.219	1.850	6.480	2.910	0.461	0.132	1.980
Imidacloprid	I											0.020			
Indaziflam	H						0.011	0.013			0.011				
Isoxaben	H											0.007			
MCPA	H				0.094			0.428							0.012
Metalaxyl	F				0.024							0.025			
Methoxyfenozide	I	0.002	0.003							0.003					
Metolachlor	H		0.008	0.004	0.186	0.006	0.009	0.121	0.011	0.015	0.105	0.171	0.048	0.007	0.009
Metribuzin	H	0.008	0.008	0.004	0.003		0.004	0.005		0.007	0.031	0.042	0.013	0.005	
Myclobutanil	F							0.036							
N,N-Diethyl-m-toluamide (DEET)	IR				0.012						0.051	0.009			
Norflurazon	H							0.002			0.003	0.002			
Prometon	H	0.003		0.006	0.008		0.003	0.003			0.008	0.004			
Propiconazole	F	0.029	0.036		0.025	0.021	0.024	0.040		0.022	0.030				0.034
Pyrimethanil	F													0.003	
Simazine	H			0.005							0.006	0.012	0.004		
Sulfentrazone	H	0.093	0.079	0.055	0.031	0.054	0.049	0.039	0.049	0.032	0.052	0.050	0.040	0.045	0.044
Sulfometuron-methyl	H						0.043				0.050	0.012	0.005		0.006
Tebuthiuron	H	0.061	0.053	0.062	0.021	0.062	0.035	0.030	0.051	0.045	0.017	0.032	0.050	0.067	0.049
Terbacil	H	0.017	0.012	0.016		0.016		0.007	0.014	0.014			0.013	0.021	0.008
Tetrahydrophthalimide	D						0.002		0.003	0.010	1.230	0.022	0.006	0.051	0.016
Thiamethoxam	I	0.025	0.020	0.017	0.018	0.013		0.021	0.013	0.013	0.051	0.026		0.013	0.010
Treflan (Trifluralin)	H							0.002		0.003	0.003	0.003			
Triclopyr	H						0.041	0.090			0.284	0.299			0.040
Suspended sediment concentration		14	14	11	9	10	11	11	12	15	13	17	12	10	7
Streamflow (cubic ft/sec)		59.6	46.3	41.3	41.5	33.0	24.6	-	14.2	-	39.3	21.1	-	14.9	20.5
Precipitation (total in/week)†		0.35	0.86	0.08	0.29	0.28	1.36	0.65	0.07	0.37	1.55	1.52	0.01	0.00	0.34

The "-" signifies a sample or measurement that was not collected or could not be analyzed. The "X" signifies data rejected by failing quality assurance performance measures. 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: 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 nine of the 14 site visits (64%). Water quality at the Indian Slough site is shown below (Figure 18).

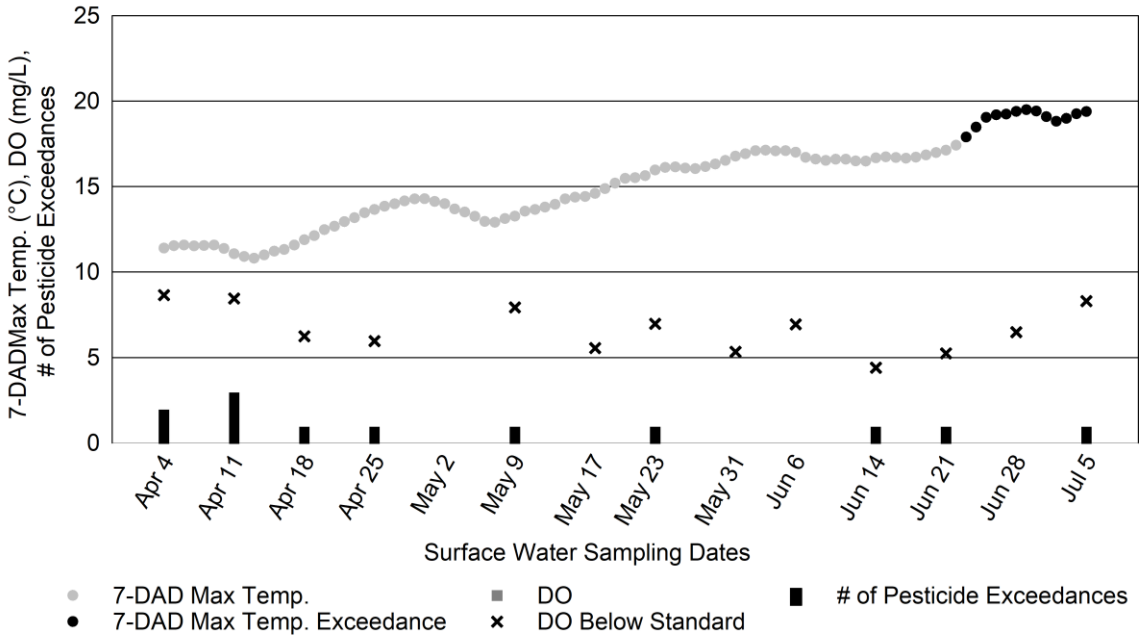


Figure 18 – Indian Slough water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 6.76 to 6.98 with an average of 6.87. All (13) of the DO measurements, ranging from 4.40 mg/L to 8.65 mg/L with an average of 6.65 mg/L, did not meet the state water quality standard of 10 mg/L. Nine of the DO measurements that did not meet the state water quality standard coincided with one, two, or three pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 13 days throughout the sampling season, from June 23 through July 5. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit.

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 2023). NRAS will continue to monitor this drainage because of its representative regional land use.

Juanita Creek

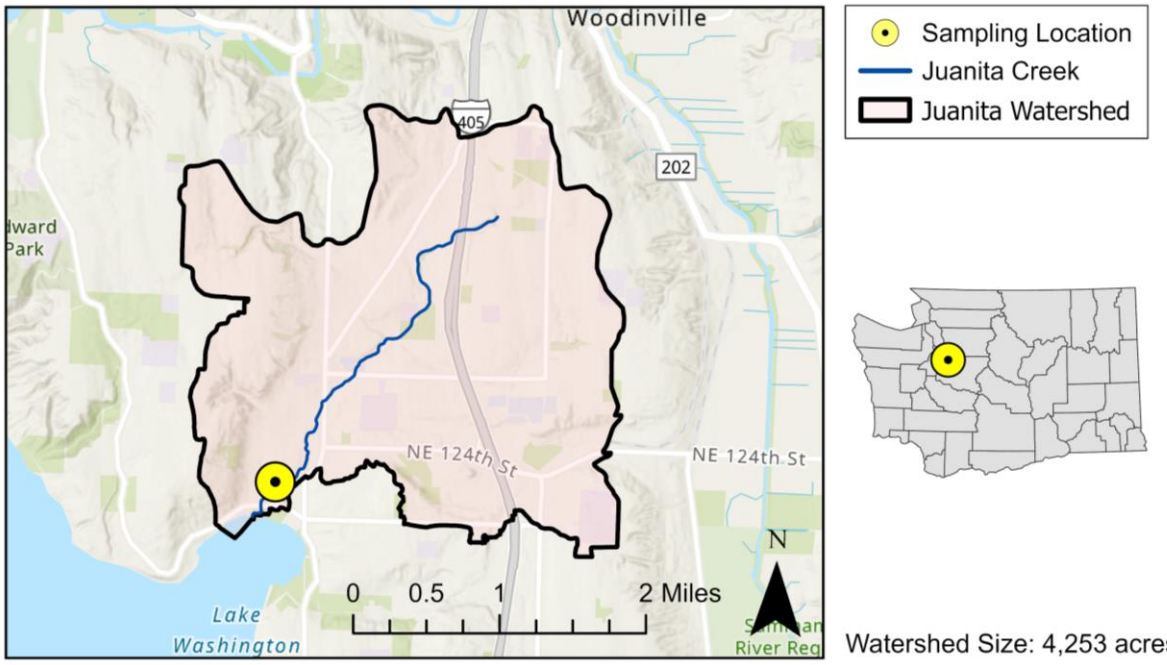


Figure 19 – Map of Juanita Creek and its drainage area with associated sampling location and crop groups identified

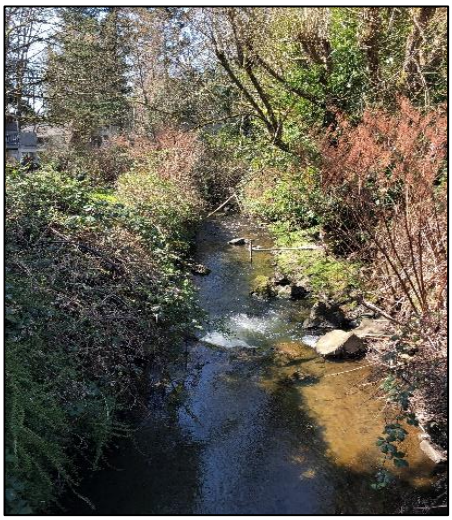


Figure 20 – Juanita Creek downstream view

In 2020, NRAS started monitoring the Juanita watershed in King County. Juanita Creek flows roughly 5 miles through Kirkland, Washington. The Juanita monitoring site is located just downstream of an open-bottom culvert where an ephemeral tributary also drains alongside NE 120th Street (latitude: 47.7077º, longitude: -122.2148º). Within the Juanita drainage area, the land use is predominantly residential (Figure 19, Figure 20). This site was one of two urban sites NRAS monitored in 2022.

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 and winter steelhead trout within the reach of creek that encompasses the monitoring site (WDFW 2023). 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 2022.

- NRAS tested for 150 unique pesticides in Juanita Creek.
- There were 138 total pesticide detections from seven different use categories: 17 types of herbicides, 5 insecticides, 3 fungicides, 3 legacies, 6 degradates, 1 insect repellent, and 1 synergist.

- Pesticides were detected at all 13 sampling events.
- Up to 24 pesticides were detected at the same time.
- Of the total pesticide detections, six were above WSDA's assessment criteria (Table 12).
    - The two detections of 4,4'-DDD, one detection of 4,4'-DDE, and one detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the nine detections of diuron, one detection exceeded plant EC_{50} (0.13 µg/L).
- Of the six detections of fipronil, one detection approached the invertebrate NOAEC (0.011 µg/L).
- There was no detection of deltamethrin at the site in 2022, however, deltamethrin was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Juanita Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 12). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 12 – Juanita Creek pesticide calendar, µg/L

Month		Apr		May		Jun		Jul		Aug		Sep		Oct
Day of the Month	Use*	11	25	9	23	6	21	5	19	2	16	13	26	11
1-(3,4-Dichlorophenyl)-3-methylurea	D							0.004			0.016			
2,4-D	H		0.076	0.046	0.011			0.015		0.007				
2,6-Dichlorobenzamide	D	0.285	0.259	0.282	0.280	0.255	0.297	0.276	0.282	0.299	0.274	0.281	0.279	0.225
2-Hydroxyatrazine	D	0.009	0.008		0.008	0.004	0.004	0.004	0.003	0.007	0.007	0.009	0.008	
4,4'-DDD	L		0.002										0.002	
4,4'-DDE	L		0.002											
4,4'-DDT	L		0.001											
4-Nitrophenol	D		0.171											
Acephate	I				0.020									
Atrazine	H		0.003									0.005	0.005	0.005
Bromacil	H									0.008				
Carbendazim	F	0.006	0.008			0.005		0.005	0.002		0.145	0.007	0.005	0.006
Chlorothalonil (Daconil)	F		0.033											
Dichlobenil	H	0.018	0.025	0.008	0.009	0.023	0.008	0.007	0.006	0.003	0.026			
Dimethoate	I							0.032						
Dinotefuran	I	0.006				0.004								
Dithiopyr	H	0.003	0.005	0.002										
Diuron	H	0.009	0.015	0.006	0.004	0.012	0.005	0.012			0.179	0.006		
Ethoprop	I		0.001											
Fipronil	I	0.011	0.005	0.003	0.002	0.004				0.002				
Fipronil sulfide	D	0.002	0.001		0.004	0.005	0.004	0.004	0.004	0.001	0.001	0.001	0.001	
Fipronil sulfone	D	0.005		0.003										
Imazapyr	H					0.021	0.009	0.007						
Isoxaben	H		0.004											
MCPP	H		0.023											
Metolachlor	H													0.002
N,N-Diethyl-m-toluamide (DEET)	IR	0.007	0.013						0.066					
Pendimethalin	H		0.002											
Piperonyl butoxide (PBO)	Sy		0.004											
Prometon	H	0.006	0.011	0.004	0.004	0.006	0.005	0.004	0.004	0.004	0.003	0.006	0.006	0.006
Simazine	H	0.005												
Sulfentrazone	H		X	0.010		0.007	0.004	0.006						
Tebuthiuron	H	0.008	0.007	0.005		0.008	0.004					0.005		
Treflan (Trifluralin)	H	0.003				0.003								
Triadimefon	F					0.005								
Triclopyr	H	0.016	0.020	0.014										
Suspended sediment concentration		2	4	3	2	8	4	2	3	4	3	1	2	1
Streamflow (cubic ft/sec)		10.5	6.8	6.1	4.2	10.5	4.2	3.4	2.5	2.4	2.4	2.1	1.9	1.8
Precipitation (total in/week)†		1.09	0.46	1.77	0.19	1.30	0.45	0.19	0.08	0.01	0.01	0.01	0.01	0.03

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 repellant, 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 two of the 13 site visits (15%). Water quality at the Juanita Creek site is shown below (Figure 21).

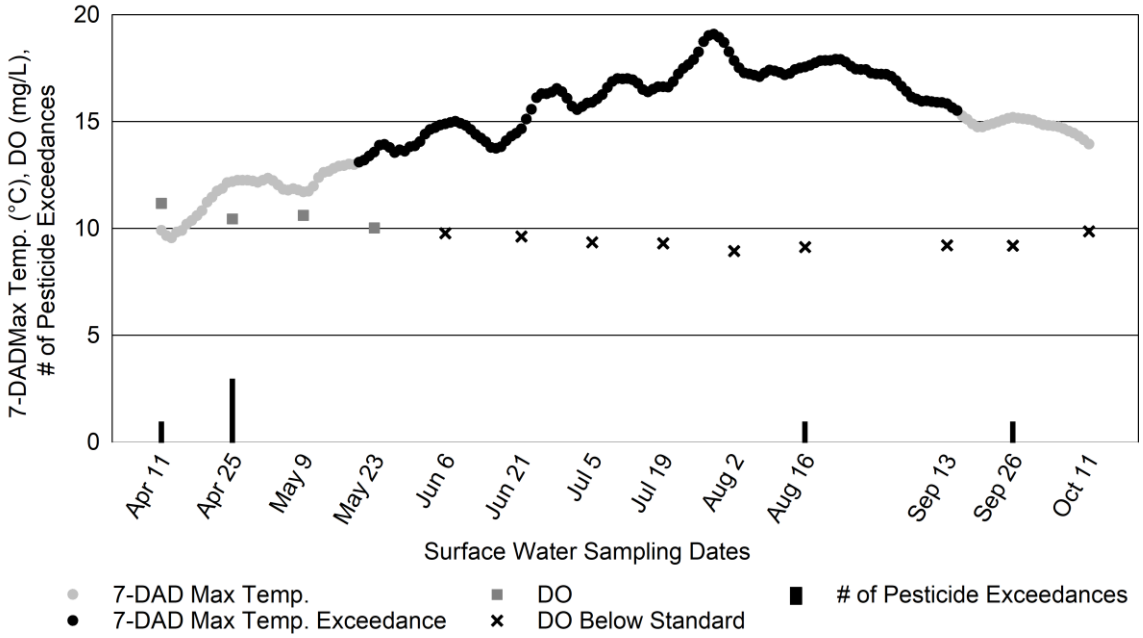


Figure 21 – Juanita Creek water quality measurements and exceedances of assessment criteria *

All pH measurements met the state water quality standard, ranging from 7.31 to 7.65 with an average of 7.56. DO measurements ranged from 8.94 mg/L to 11.17 mg/L with an average of 9.74 mg/L. Almost three-quarters (69%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L. Two of the DO measurements that did not meet the standard coincided with one pesticide exceedance.

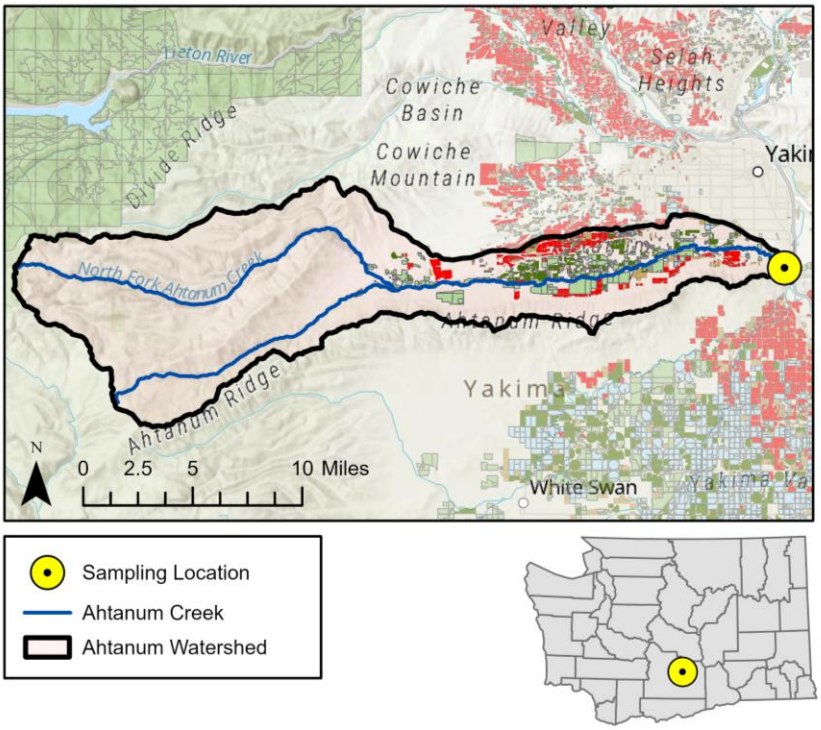
Juanita Creek has been identified by the Department of Ecology as a waterbody requiring special protection for salmonid spawning and incubation. Therefore, two different 7-DADMax temperature standards are applied during different periods of the sampling season. *From May 15 through September 15, the 7-DADMax temperature should remain below 13ºC, while September 16 through the end of the sampling season should remain below 16 ºC (WAC 2023). The 7-DADMax temperature exceeded the standard on 119 days, primarily from May 20 through September 15. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit.

Juanita Creek has been designated as a freshwater body that provides a core summer habitat for salmonids by the WAC (WAC 2023). NRAS will continue to monitor this drainage because of its representative regional urban land use and exceeding detections of pesticides.

* See revisions page Rev. 1 for revised figure 21 and revised text

Central Region

Ahtanum Creek



Ahtanum Creek Crop Groups	Acres
Hay/Silage	1,853
Orchard	2,852
Fallow	941
Pasture	4,923
Other	344
Total Ag	10,913
Total Non-Ag	98,327
Watershed Total	109,240

Figure 22 – 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 22, Figure 23). 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, and summer steelhead trout within the Ahtanum Creek watershed (WDFW 2023). Staff observed juvenile fish of unknown species at this site.

Figure 23 – Ahtanum Creek downstream view

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 22).

Below is a brief overview of pesticide findings in Ahtanum Creek in 2022.

- NRAS tested for 150 unique pesticides in Ahtanum Creek.
- There were 52 total pesticide detections from six different use categories: 9 types of herbicides, 6 insecticides, 3 fungicides, 2 legacies, 5 degradates, and 1 insect repellent.
- Pesticides were detected at all 13 sampling events.
- Up to 14 pesticides were detected at the same time.
- Of the total pesticide detections, six were above WSDA's assessment criteria (Table 13).
    - One detection of 4,4'-DDD exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L). Two other detections of 4,4'-DDD approached both criteria.
    - The single detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - The single detection of tefluthrin approached the Endangered Species Level of Concern (0.003 µg/L) and fish NOAEC (0.004 µg/L).

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

- The single detection of gamma-cyhalothrin exceeded the Endangered Species Level of Concern (0.00145 µg/L), exceeded the invertebrate LC_{50} (0.00008 µg/L), and approached the invertebrate NOAEC (0.00193 µg/L).
- There was no detection of chlorpyrifos at the site, however, chlorpyrifos was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Ahtanum Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 13). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 13 – Ahtanum Creek pesticide calendar, µg/L

Month		Mar	Apr		May		Jun		Jul		Aug			Sep
Day of the Month	Use*	28	11	25	9	23	6	21	5	18	1	15	29	12
2,4-D	H								0.006			0.007	0.010	
2,6-Dichlorobenzamide	D		0.001	0.002	0.002	0.002	X	0.003	0.003	0.003	0.004	0.003	0.004	0.003
4,4'-DDD	L	0.003						<0.001	<0.001					
4,4'-DDT	L							0.002						
4-Nitrophenol	D		0.029											
Boscalid	F						<0.001	0.002						
Bromacil	H		0.005											
Diazinon	I	0.011	0.004											
Dichlobenil	H	0.002								0.003				
Dimethoate	I				0.007									
Fipronil	I							0.003						
Fipronil disulfinyl	D							0.002						
Fipronil sulfide	D							0.005						
Fipronil sulfone	D							0.007						
Fludioxonil	F	0.003											0.004	
gamma-Cyhalothrin	I							0.001						
Hexazinone	H							0.002						
Metolachlor	H		0.003											
N,N-Diethyl-m-toluamide (DEET)	IR										0.013			
Norflurazon	H										0.002	0.002	0.004	0.003
Pendimethalin	H	0.003	0.003											
Prometon	H							0.003						0.005
Pyriproxyfen	I							0.002						
Sulfentrazone	H	X		X	0.005		0.005	0.007	0.005					
Tefluthrin	I	0.002												
Triadimefon	F							0.005						
Suspended sediment concentration		19	9	14	53	18	156	34	14	6	5	4	5	2
Streamflow (cubic ft/sec)		86.8	71.3	83.2	149	95.9	231	104	44.4	33.7	13.5	17.8	18.6	17.2
Precipitation (total in/week)†		0.00	0.03	0.32	0.47	0.01	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00

The "X" signifies data rejected by failing quality assurance performance measures. 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: Ahtanum, (latitude: 46.55°, longitude: -120.71°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at two of the 13 site visits (15%). Water quality at the Ahtanum Creek site is shown below (Figure 24).

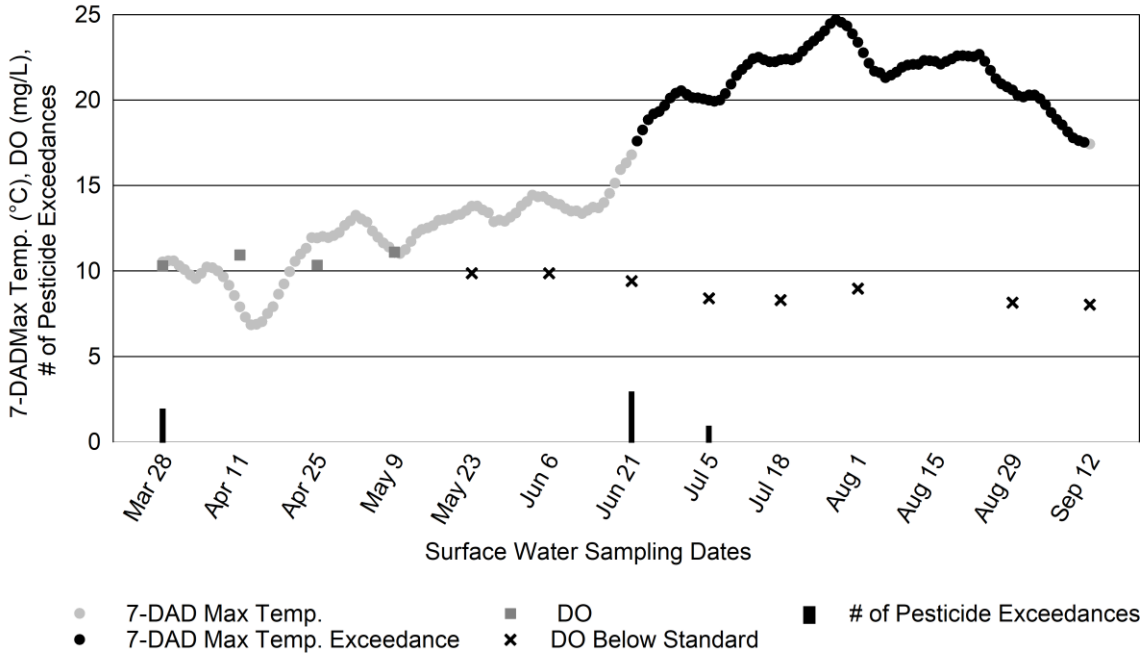


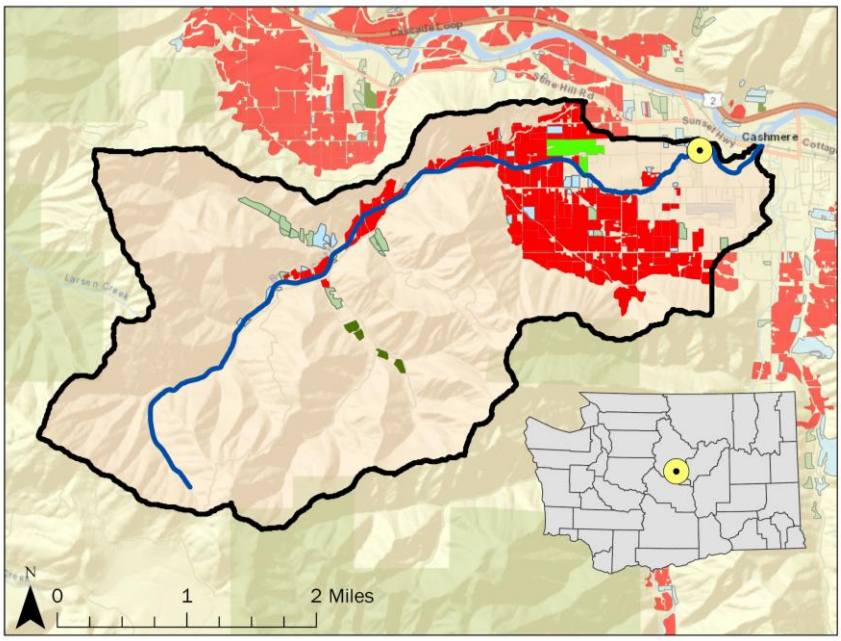
**Figure 24 – Ahtanum Creek water quality measurements and exceedances of assessment criteria*

All pH measurements met the state water quality standard, ranging from 7.03 to 7.88, with an average of 7.54. DO measurements ranged from 8.03 mg/L to 11.10 mg/L with an average of 9.47 mg/L. More than half (67%) of the DO measurements did not meet the state water quality standard, with eight measurements falling below 10 mg/L. Two of the DO measurements that did not meet the standard coincided with one or three pesticide exceedances. *The 7-DADMax temperature exceeded the standard of 17.5°C on 82 days throughout the sampling season, from June 22 through September 11. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit.

Ahtanum Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2023). NRAS will continue to monitor this drainage because of its representative regional land use.

* See revisions page Rev. 2 for revised figure 24 and revised text

Brender Creek



Brender Crop Groups	Acres
Hay/Silage	14
Pasture	60
Orchard	746
Turfgrass	35
Other	55
Total Ag	910
Total Non-Ag	5,954
Watershed Total	6,864

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

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

The Brender site is located in Cashmere, on the upstream side of the culvert at Evergreen Drive (latitude: 47.5211°, longitude: -120.4863°) (Figure 25, Figure 26). Brender Creek is approximately 6.8 miles long and drains into the Wenatchee River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the creek. WDFW has documented the presence of spring Chinook salmon, rainbow trout, and summer steelhead within the lower reaches of the creek (WDFW 2023).

Figure 26 – 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 25).

Below is a brief overview of the pesticide findings in Brender Creek in 2022.

- NRAS tested for 137 unique pesticides in Brender Creek.
- Pesticides were detected at all 23 sampling events.
- There were 232 total pesticide detections from seven different use categories: 9 types of herbicides, 15 insecticides, 3 fungicides, 3 legacies, 3 degradates, 1 insect repellent, and 1 synergist.

- Up to 20 pesticides were detected at the same time.
- Of the total pesticide detections, 83 were above WSDA's assessment criteria (Table 14).
    - DDT and its degradates account for 66 of these exceedances. The 23 detections of 4,4'-DDD, 23 detections of 4,4'-DDE, and 20 detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - Of two detections of pyriproxyfen, one exceeded the invertebrate NOAEC (0.015 µg/L).
    - The two detections of tefluthrin approached the Endangered Species Level of Concern (0.003 µg/L) and fish NOAEC (0.004 µg/L).

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

- The five detections of gamma-cyhalothrin approached or exceeded the Endangered Species Level of Concern (0.00145 µg/L) and exceeded the invertebrate LC_{50} (0.00008 µg/L).
    - The detection on March 29 and April 12 also exceeded the invertebrate NOAEC (0.00193 µg/L).
    - The detections on April 5 and June 28 approached the invertebrate NOAEC.
- The four detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the five detections of malathion, one detection exceeded the invertebrate LC_{50} (0.098 µg/L), invertebrate NOAEC (0.06 µg/L), and NRWQC chronic criteria (0.1 µg/L). It is also approached the Endangered Species Level of Concern (0.205 µg/L).
    - The detection on April 12 approached the invertebrate LC_{50} and invertebrate NOAEC criteria.
- The three detections of tolfenpyrad exceeded the Endangered Species Level of Concern (0.00815 µg/L).
    - The detections on May 10 and May 24 also approached the fish LC_{50} (0.163 µg/L).
- There was no detection of carbaryl at the site, however, carbaryl was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.
- The four detections of chlorpyrifos did not exceed any assessment criteria in 2022, however, this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years.

The Brender Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 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 uncommon historic detections.

Table 14 – Brender Creek pesticide calendar, µg/L

Month		Mar		Apr				May					Jun			Jul				Aug				
Day of the Month	Use*	22	29	5	12	19	26	3	10	17	24	31	7	14	28	6	12	19	26	2	9	16	23	30
2,6-Dichlorobenzamide	D	0.006	0.006	0.007	0.007	X	0.006	0.005	0.004	X	0.005	0.004	X	0.004	0.005	0.005	0.005	0.005	0.002	0.005	0.005	0.005	0.004	0.006
4,4'-DDD	L	0.004	0.004	0.004	0.004	0.002	0.002	0.003	0.003	0.002	0.003	0.002	0.003	0.003	0.004	0.004	0.004	0.004	0.006	0.006	0.006	0.004	0.006	0.006
4,4'-DDE	L	0.006	0.007	0.005	0.009	0.005	0.004	0.018	0.014	0.011	0.015	0.009	0.016	0.014	0.022	0.024	0.025	0.022	0.024	0.024	0.034	0.027	0.036	0.021
4,4'-DDT	L			0.002		0.002	0.002	0.007	0.005	0.003	0.005	0.003	0.005	0.005	0.006	0.009	0.007	0.005	0.053	0.022	0.010	0.026	0.016	0.014
Acetamiprid	I				0.028	0.003		0.010	0.020	0.004	0.005											0.003	0.002	0.003
Bifenazate	I																0.022							
Boscalid	F	0.002	0.002	0.002	0.003			0.001									<0.001						0.014	0.003
Bromacil	H				0.004		0.005				0.003	0.006			0.005		0.006	0.005	0.007	0.004			0.004	0.006
Carbendazim	F	0.003		0.003	0.005	0.003		0.003	0.003		0.002													
Chlorpyrifos	I				0.002	0.002	0.001	0.001																
Clothianidin	I			0.003			0.003																	
Diazinon	I		0.008	0.007	0.016	0.005	0.003	0.002																
Dichlobenil	H	0.002	0.002		0.002																			
Dimethoate	I														0.004						0.008			
gamma-Cyhalothrin	I		0.005	0.002	0.002										0.001	<0.001								
Hexazinone	H							0.011	0.011	0.005	0.003	0.002	0.002	0.002										
Imazapyr	H							0.044																
Imidacloprid	I																			0.015	0.010		0.161	0.100
Malaoxon	D				0.023																			
Malathion	I		0.183	0.011	0.041	0.004		0.010																
N,N-Diethyl-m-toluamide (DEET)	IR																		0.011					0.009
Norflurazon	H	0.011	0.011	0.013	0.013	0.010	0.010	0.004	0.004	0.004	0.004	0.005	0.003	0.005	0.007	0.006	0.009	0.004	0.006	0.004	0.005	0.004	0.005	0.009
Pendimethalin	H	0.003	0.003	0.003	0.004	0.003	0.041	0.015	0.015	0.014	0.009	0.005	0.009	0.007	0.005		0.003	0.003	0.005	0.003	0.004		0.002	0.002
Piperonyl butoxide (PBO)	Sy		0.006	0.004																				
Pyraclostrobin	F																						0.005	
Pyridaben	I			0.001																				
Pyriproxyfen	I		0.031		0.007																			
Simazine	H			0.006	0.006	0.004	0.005																	
Spirotetramat	I								0.090															
Sulfentrazone	H	X		X		0.006	X		X	X		0.004							0.003					0.011
Tefluthrin	I			0.003	0.003																			
Tetrahydrophthalimide	D									0.002														
Thiamethoxam	I																0.027		0.080					
Tolfenpyrad	I				0.039				0.047		0.050													
Triclopyr butoxyethyl ester	H				0.009																			
Suspended sediment concentration		5	6	4	6	4	3	22	14	12	22	10	23	18	27	29	31	46	94	30	39	38	73	22
Streamflow (cubic ft/sec)		1.2	1.0	1.0	0.9	1.0	0.8	5.4	7.1	7.1	5.9	2.2	9.1	4.6	3.4	4.5	2.7	2.6	1.4	2.4	1.7	3.1	2.1	1.5
Precipitation (total in/week)†		0.02	0.00	0.27	0.05	0.67	0.10	0.36	0.04	0.32	0.14	0.01	0.86	0.23	0.00	0.12	0.14	0.00	0.00	0.00	0.00	0.03	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.

Current-use exceedance DDT/degradate exceedance Detection

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

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at 10 of the 23 site visits (43%). Water quality at the Brender site is shown below (Figure 27).

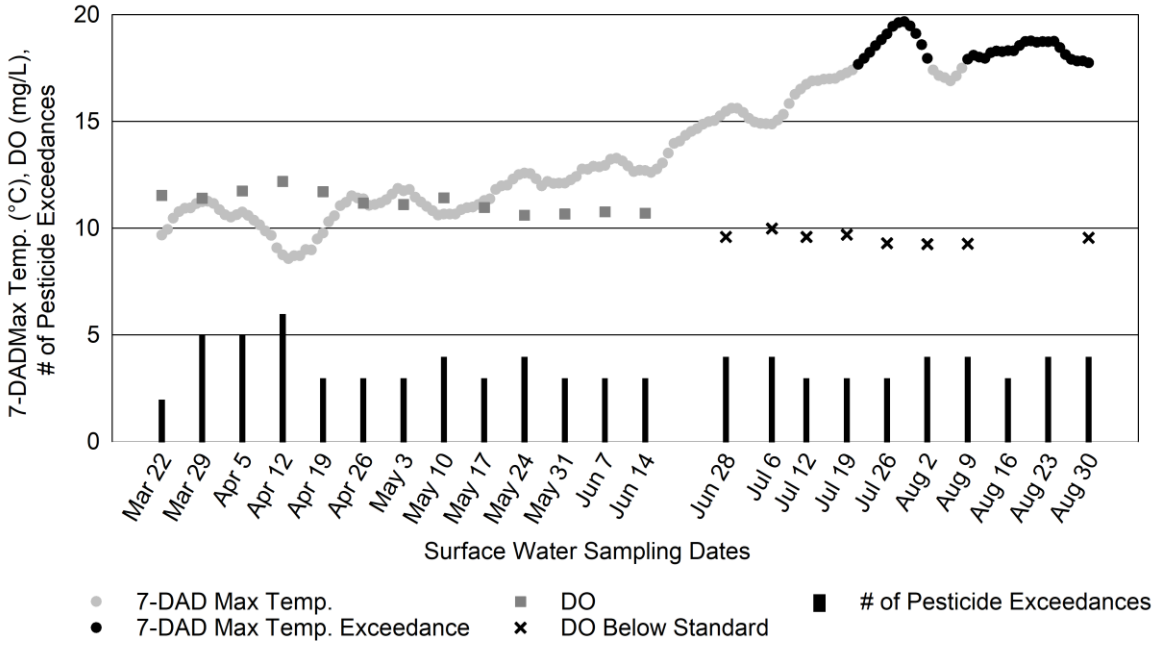
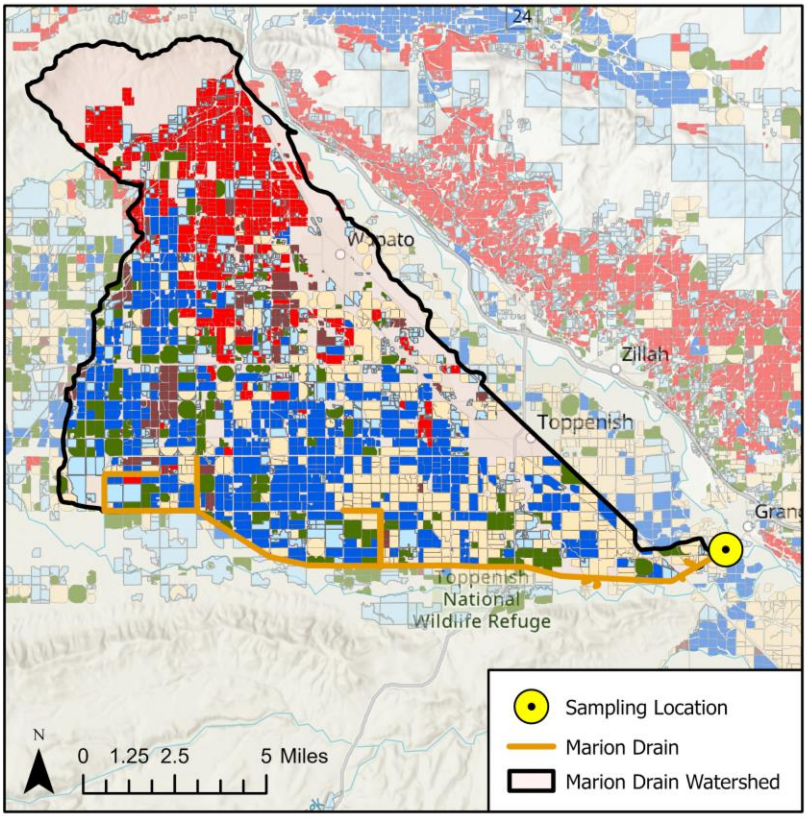


Figure 27 – Brender Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.89 to 8.16 with an average of 8.03. DO measurements ranged from 9.25 mg/L to 12.19 mg/L with an average of 10.58 mg/L. More than a third (41%) of the DO measurements did not meet the state water quality standard, with nine measurements falling below 10 mg/L. All eight of the DO measurements that did not meet the standard coincided with three or four pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 35 days throughout the sampling season, occurring intermittently from July 21 through August 30. Pesticide exceedances coincided with 7-DADMax temperature exceedances at six 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 2023). Staff observed juvenile fish of unknown species. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Marion Drain



Marion Drain Crop Groups	Acres
Cereal Grain	12,798
Hay/Silage	6,570
Herb	16,315
Orchard	9,531
Vegetable	2,659
Other	7,980
Total Ag	55,853
Total Non-Ag	26,562
Watershed Total	82,415

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

In 2003, NRAS started monitoring the Marion Drain watershed in Yakima County. The monitoring site is located near Granger, approximately 140 meters upstream from the bridge crossing at Indian Church Road (latitude: 46.3306º, longitude: -120.2000º) (Figure 28, Figure 29). WSDA selected this watershed to represent irrigated agricultural practices in Central Washington.

Figure 29 – Marion Drain upstream view

Marion Drain flows directly into the Yakima River. Melting snowpack, precipitation events, groundwater, and irrigation generally influence flows in the stream. There 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 and summer steelhead trout within the Marion Drain watershed (WDFW 2023).

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 28).

Below is a brief overview of the pesticide findings in Marion Drain in 2022.

- NRAS tested for 150 unique pesticides in Marion Drain.
- There were 469 total pesticide detections from six different use categories: 22 types of herbicides, 11 insecticides, 8 fungicides, 1 legacy, 4 degradates, and 1 insect repellent.
- Pesticides were detected at all 28 sampling events.
- Up to 24 pesticides were detected at the same time.
- Of the total pesticide detections, 14 were above WSDA's assessment criteria (Table 15).
    - The single detection of 4,4'-DDD exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- The single detection of bifenthrin exceeded the invertebrate LC_{50} (0.000493 µg/L) and invertebrate NOAEC (0.00005 µg/L).
- Of the 24 detections of clothianidin, six approached the invertebrate NOAEC and five exceeded the invertebrate NOAEC (0.05 µg/L).
- The single detection of gamma-cyhalothrin approached the Endangered Species Level of Concern (0.00145 µg/L) and the invertebrate NOAEC (0.00193 µg/L) and exceeded invertebrate LC_{50} (0.00008 µg/L).
- There was no detection of chlorpyrifos or imidacloprid at the site, however, they were still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Marion Drain monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 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

Month		Mar		Apr				May				Jun					Jul				Aug				Oct			Nov	
Day of the Month	Use*	21	28	4	11	18	25	2	9	16	23	1	6	13	21	27	5	11	18	25	1	8	15	22	17	24	31	7	16
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.009		0.009	0.015	0.012			0.004	0.005																
2,4-D	H							0.018	0.013	0.026		0.093	0.023	0.024			0.013	0.027	0.035	0.018	0.011	0.018	0.025	0.020		0.022			
2,6-Dichlorobenzamide	D				0.001	X		0.001	0.002	X	0.002		X	0.002	0.002		0.001	0.002	0.002		0.002	0.002	0.002	0.001	0.001				
2-Hydroxyatrazine	D							0.007								0.003	0.004	0.004		0.004	0.009	0.009	0.009	0.013					
4,4'-DDD	L	0.004																											
Atrazine	H	0.009	0.010	0.007	0.024	0.009	0.013	0.025	0.015	0.017	0.015	0.037	0.011	0.009	0.009	0.012	0.011	0.007	0.008	0.006	0.006	0.005	0.011	0.008	0.009	0.009	0.009	0.010	0.011
Azoxystrobin	F				0.002	0.004	0.005	0.017	0.011	0.011	0.014			0.010	0.009				0.010										
Bentazon	H		0.013												0.067	0.022				0.047	0.015	0.011	0.010						
Bifenthrin	I															0.002													
Boscalid	F	0.002	0.002	0.003	0.003	0.002	0.003	0.003	0.003	0.002	0.003	0.002	0.003	0.003	0.006	0.004	0.006	0.009	0.007	0.006	0.005	0.004	0.006	0.005	0.002	0.004	0.002	0.003	0.001
Bromacil	H	0.005		0.013	0.024	0.008	0.023	0.012	0.007	0.009	0.014	0.005	0.008	0.007	0.006	0.005	0.004	0.006	0.006	0.004	0.007				0.004	0.008			
Bromoxynil	H				0.027		0.020	0.031	0.022	0.020																			
Carbendazim	F					0.003		0.002																					
Chlorantraniliprole	I	0.021			0.012			0.013															0.015	0.020	0.026				
Clothianidin	I	0.032	0.038	0.017	0.014		0.014	0.014	0.011			0.013	0.014		0.014	0.013	0.022	0.026	0.015	0.025	0.032	0.025	0.027	0.021	0.066	0.053	0.098	0.079	0.099
Desethylatrazine	D	0.013	0.013				0.010					0.007				0.004								0.004					
Diazinon	I			0.003	0.003																								
Dicamba	H				0.007			0.005									0.010	0.012	0.011	0.010	0.010	0.009	0.010	0.007		0.005			
Dimethoate	I								0.007	0.017																			
Diuron	H	0.005		0.007	0.044	0.014	0.029	0.061	0.056	0.026	0.031	0.041	0.032	0.013	0.006		0.010	0.006		0.007		0.005		0.004					
Eptam	H										0.001		0.001	0.001	0.002														
Ethoprop	I				0.003																								
Fludioxonil	F			0.017	0.024	0.018	0.015	0.016	0.015	0.015	0.011	0.010	0.011	0.012	0.012	0.012	0.009	0.015	0.011	0.011	0.012	0.015	0.013	0.009	0.006	0.006			
gamma-Cyhalothrin	I															0.001													
Hexazinone	H								0.003	0.003	0.004	0.001		0.001				0.002					0.001			0.004	0.004	0.004	0.004
Imazapyr	H							0.040																					
Malathion	I																0.002												
MCPA	H								0.128																				
Metolachlor	H								0.002	0.008	0.003	0.001	0.001	0.001		0.026	0.017	0.004	0.007	0.004	0.002	0.003		0.004				0.002	
Metribuzin	H													0.011	0.008	0.006	0.006	0.007	0.005		0.004	0.004	0.004	0.005					
N,N-Diethyl-m-toluamide (DEET)	IR																0.014	0.020		0.009	0.010							0.003	
Norflurazon	H	0.004	0.004	0.003	0.002	0.002		0.002		0.002	0.003		0.002	0.001				0.002		0.001	0.002	0.002	0.002	0.002	0.005	0.006	0.006	0.006	0.005
Oxamyl	I											0.004	0.002									0.003	0.004						
Pendimethalin	H	0.007	0.006	0.010	0.014	0.005	0.004	0.015	0.013	0.016	0.014	0.021	0.015	0.011	0.007	0.003		0.005		0.002	0.002	0.003	0.002						0.002
Phosmet (Imidan)	I													0.003															
Prometon	H																								0.006	0.006	0.005	0.005	0.006
Prometryn	H																									0.007			0.003
Propiconazole	F							0.022	0.062	0.030	0.025	0.050				0.010													
Pyrimethanil	F			0.015		0.023	0.018	0.014	0.010				0.004			0.006	0.004	0.008		0.005	0.009	0.007	0.006	0.003					
Simazine	H	0.009	0.009	0.008	0.037	0.011	0.013	0.027	0.013	0.013	0.013	0.011	0.010	0.008	0.008	0.007	0.007	0.006	0.005	0.004	0.005		0.004	0.011	0.011	0.011	0.007	0.008	0.009
Sulfentrazone	H	X	X	X		X	X		0.014	0.010	0.010	0.015	0.011	0.013	0.008		0.005	0.006	0.005	0.006	0.008	0.006	0.007	0.020	0.022	0.024	0.012	X	X
Terbacil	H				0.012		0.003	0.059	0.189	0.239	0.077	0.120	0.058	0.123	0.155	0.078	0.032	0.117	0.120	0.133	0.152	0.087	0.081	0.038	0.018	0.013	0.006	0.005	0.003
Thiamethoxam	I	0.011		0.003	0.003		0.005	0.007	0.004		0.006		0.004	0.007	0.009	0.006	0.009	0.011	0.011	0.014	0.020	0.021	0.026	0.033	0.067	0.072	0.079	0.066	0.081
Treflan (Trifluralin)	H								0.002	0.003	0.003	0.003	0.005	0.003	0.003		0.002												
Triadimefon	F																									0.003			
Triclopyr	H							0.012		0.015														0.015					
Trifloxystrobin	F																						0.017						
Suspended sediment concentration		7	8	21	2	2	2	1	3	6	6	12	15	22	12	3	1	10	7	5	4	11	13	12	20	12	11	17	12
Streamflow (cubic ft/sec)		151	148	-	18.6	16.9	14.4	14.5	18.4	63.9	63.7	79.7	-	-	88.7	16.1	11.6	43.5	19.2	21.8	29.7	59.6	69.8	86.9	227	230	214	204	200
Precipitation (total in/week)†		0.00	0.00	0.00	0.00	0.80	0.22	0.02	0.29	0.21	0.28	0.02	0.30	0.41	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.27	0.01

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

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at eight of the 28 site visits (29%). Water quality at the Marion Drain site is shown below (Figure 30 and Figure 31).

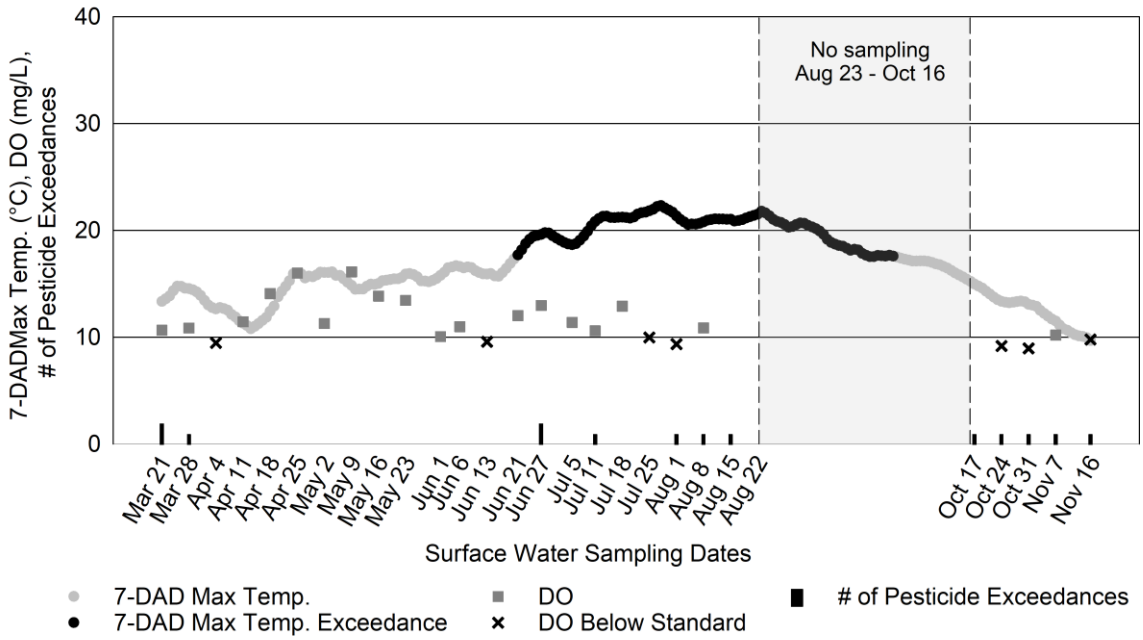


Figure 30 – Marion Drain water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

DO measurements ranged from 8.95 mg/L to 16.12 mg/L with an average of 11.44 mg/L. More than a quarter (28%) of the DO measurements did not meet the state water quality standard, with seven measurements falling below 10 mg/L. Four 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 98 days throughout the sampling season, from June 21 through September 26. Pesticide exceedances coincided with 7-DADMax temperature exceedances at five site visits.

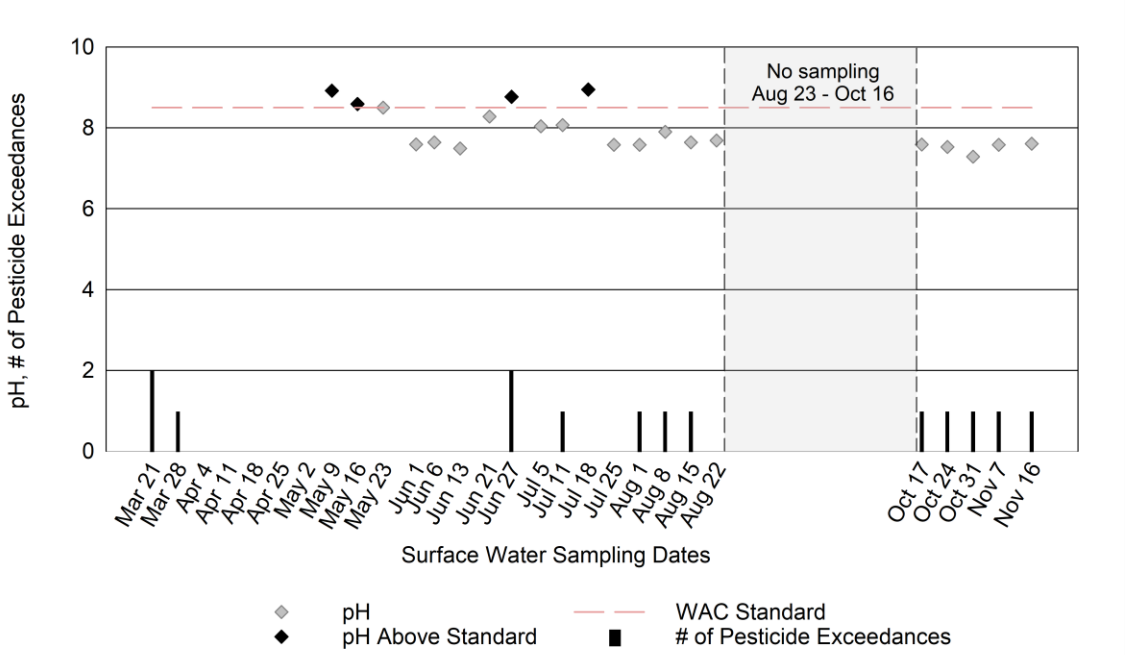
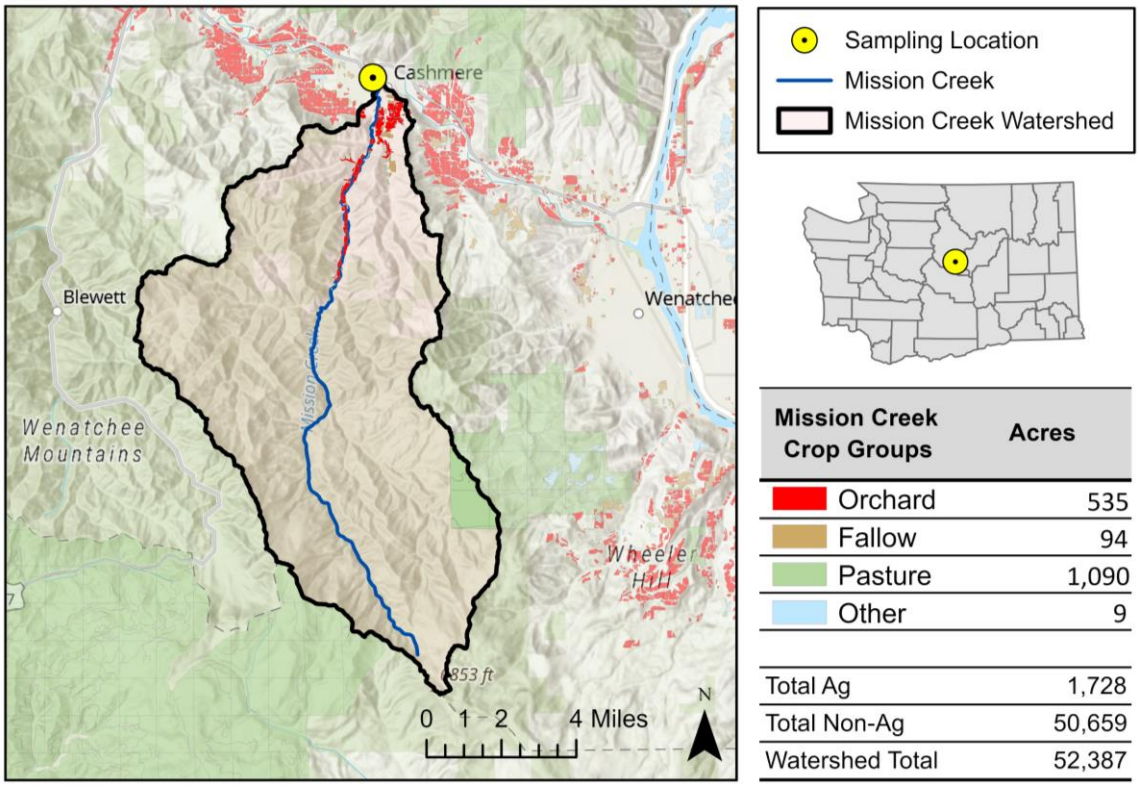


Figure 31 – Marion Drain pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.29 to 8.95 with an average of 7.94. Less than a quarter (19%) of these measurements exceeded the state water quality standard; four measurements were above 8.50. One of the pH exceedances coincided with two pesticide exceedances (Figure 31). Pesticide exceedances overlapped with both pH and 7-DADMax temperature exceedances on June 27.

Marion Drain has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2023). Staff at the site frequently observed juvenile fish of an unknown species. NRAS will continue to monitor this drainage because of its representative regional land use, historical sampling, and consistent, yearly detections of POCs.

Mission Creek



Mission Creek Crop Groups	Acres
Orchard	535
Fallow	94
Pasture	1,090
Other	9
Total Ag	1,728
Total Non-Ag	50,659
Watershed Total	52,387

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

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

Figure 33 – 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 2023). Staff at the site frequently observed juvenile fish of unknown species.

Below is a brief overview of the pesticide findings in Mission Creek in 2022.

- NRAS tested for 137 unique pesticides.
- There were 58 total pesticide detections from six different use categories: 3 types of herbicides, 10 insecticides, 2 fungicides, 3 legacies, 2 degradates, and 1 synergist.

- Pesticides were detected at all 12 sampling events.
- Up to 14 pesticides were detected at the same time.
- Of the total pesticide detections, 21 were above WSDA's assessment criteria (
- Table *16*).
    - DDT and its degradates account for 12 of these exceedances. The four detections of 4,4'-DDD, five detections of 4,4'-DDE, and three detections of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - The two detections of tefluthrin approached the Endangered Species Level of Concern (0.0015 µg/L) and fish NOAEC (0.004 µg/L).

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

- The two detections of gamma-cyhalothrin exceeded the Endangered Species Level of Concern (0.00145 µg/L) and invertebrate LC_{50} (0.00008 µg/L).
    - The detections also approached or exceeded the invertebrate NOAEC (0.00193 µg/L).
- The two detections of malathion exceeded the invertebrate NOAEC (0.06 µg/L).
    - The detection on March 29 also exceeded the invertebrate LC_{50} (0.098 µg/L) and NRWQC chronic criteria (0.1 µg/L). The detection also approached the Endangered Species Level of Concern (0.205 µg/L).
    - The detection on April 12 approached the invertebrate LC_{50} and NRWQC chronic criteria.
- Of the six detections of pyriproxyfen, two detections approached or exceeded the invertebrate NOAEC (0.015 µg/L).
- The single detection of tolfenpyrad exceeded the Endangered Species Level of Concern (0.00815 µg/L) and approached the fish LC_{50} (0.163 µg/L).
- The single detection of chlorpyrifos did not exceed any assessment criteria in 2022, however, this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years.

The Mission Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 16). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. In addition, there were 11 herbicides, 1 degradate, and a wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 16 – Mission Creek pesticide calendar, µg/ L

Month		Mar		Apr				May					Jun
Day of the Month	Use*	22	29	5	12	19	26	3	10	17	24	31	7
2,6-Dichlorobenzamide	D			0.002	0.002	X		0.001	0.002	X	0.002	0.002	X
4,4'-DDD	L		0.005		0.003		0.001	0.002					
4,4'-DDE	L		0.005		0.002		0.015	0.012					0.002
4,4'-DDT	L						0.006	0.006					0.001
Acetamiprid	I				0.003							0.028	
Boscalid	F							0.002					
Carbendazim	F										0.001		
Chlorpyrifos	I				0.002								
Diazinon	I				0.003								
gamma-Cyhalothrin	I		0.004		0.002								
Hexazinone	H	0.015	0.030	0.033	0.023	0.012	0.011	0.017	0.015	0.010	0.007	0.005	0.004
Hexythiazox	I											0.022	
Malaoxon	D				0.005								
Malathion	I		0.107		0.080								
Pendimethalin	H				0.004		0.003	0.002					0.007
Piperonyl butoxide (PBO)	Sy		0.032										
Pyridaben	I		0.001										
Pyriproxyfen	I		0.075	0.007	0.012			0.004			0.003		0.003
Tefluthrin	I		0.003		0.003								
Tolfenpyrad	I				0.052								
Treflan (Trifluralin)	H		0.003										
Suspended sediment concentration		11	60	18	10	12	205	410	82	63	49	35	196
Streamflow (cubic ft/sec)		33.0	62.1	40.0	33.4	38.4	91.7	110.0	68.8	62.5	53.1	46.0	50.4
Precipitation (total in/week)†		0.02	0.00	0.27	0.05	0.67	0.10	0.36	0.04	0.32	0.14	0.01	0.86

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; Sy: Synergist)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. There were no pesticide exceedances that coincided with water quality measurements that did not meet the state standards. Water quality at the Mission Creek site is shown below (Figure 34).

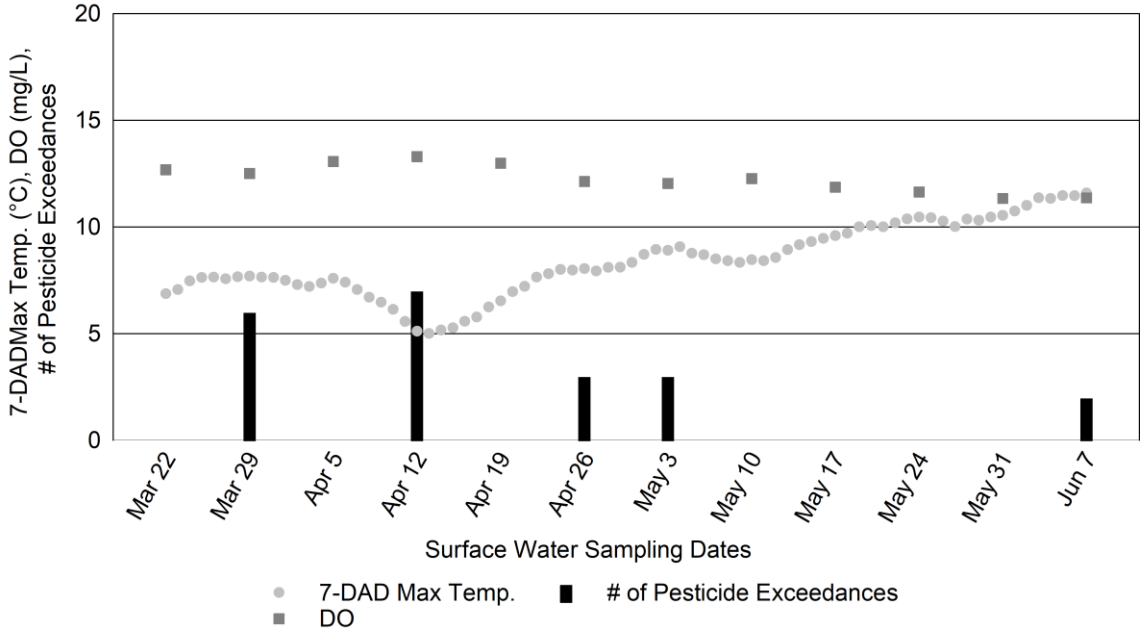
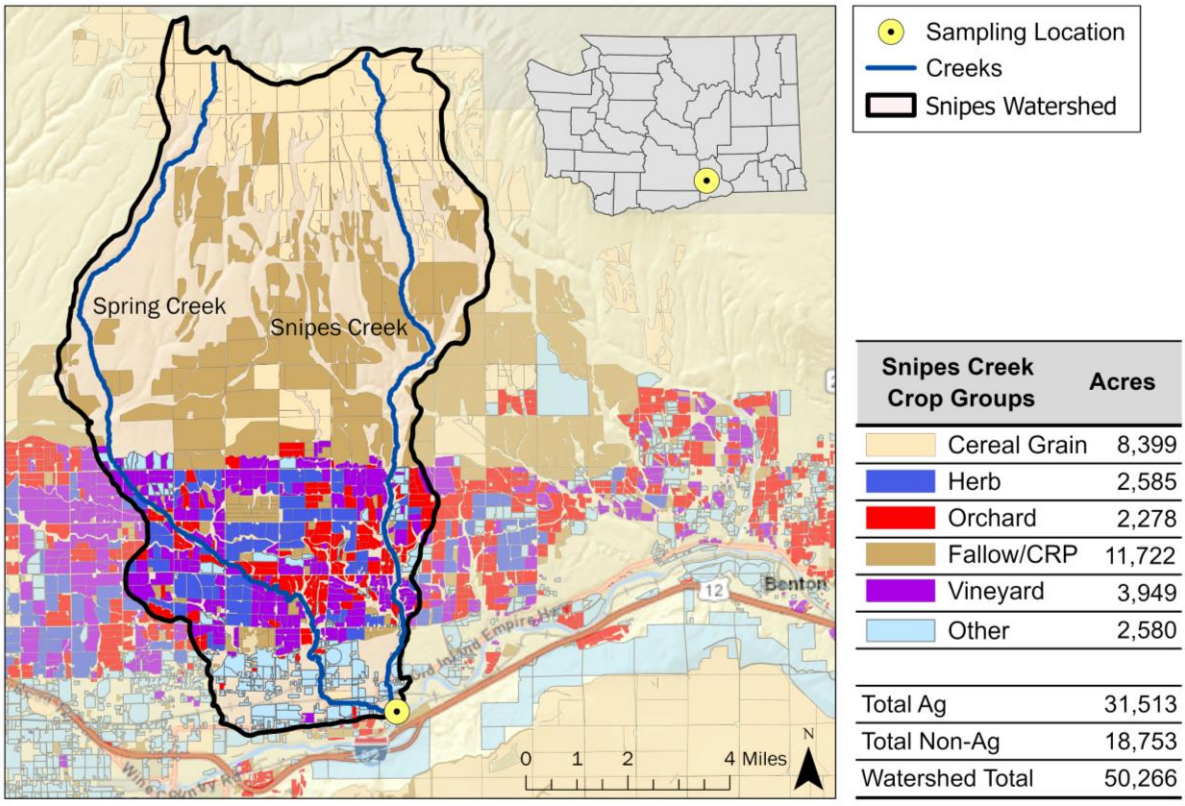


Figure 34 – Mission Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 8.18 to 8.28 with an average of 8.24. All DO measurements met the state water quality standard, ranging from 11.34 to 13.30 with an average of 12.27. 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 2023). Dense riparian vegetation for most of the creek's length helps prevent pesticide contamination from runoff and application drift. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as chlorpyrifos and malathion.

Snipes Creek



Snipes Creek Crop Groups	Acres
Cereal Grain	8,399
Herb	2,585
Orchard	2,278
Fallow/CRP	11,722
Vineyard	3,949
Other	2,580
Total Ag	31,513
Total Non-Ag	18,753
Watershed Total	50,266

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

In 2016, NRAS started monitoring the Snipes Creek watershed in Benton County. A monitoring site within the Snipes Creek watershed on Spring Creek was sampled from 2003 to 2015. NRAS moved the monitoring site downstream in order to incorporate a larger watershed capture area. Currently, the site is located near Prosser, approximately 20 meters downstream from the confluence of Spring Creek and Snipes Creek (latitude: 46.2332°, longitude: -119.6774°) (Figure 35, Figure 36).

Figure 36 – Snipes Creek upstream view with average streamflow

The Snipes watershed contains the almost 15-mile-long Snipes Creek and 19-mile-long Spring Creek that drain directly into the Yakima River. Melting snowpack, precipitation events, and irrigation generally influence streamflow in the 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 and summer steelhead trout within the reach of creek that encompasses the monitoring site (WDFW 2023). 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 juice grapes, and apples. The 'Other' crop group category consists of hay, blueberries, nurseries, and other assorted small acreage crops (Figure 35).

Below is a brief overview of pesticide findings in Snipes Creek in 2022.

- NRAS tested for 150 unique pesticides in Snipes Creek.
- There were 266 total pesticide detections from seven different use categories: 21 types of herbicides, 16 insecticides, 6 fungicides, 3 legacies, 7 degradates, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 17 sampling events.
- Up to 22 pesticides were detected at the same time.
- Of the total pesticide detections, 22 were above WSDA's assessment criteria (Table 17).
    - Three detections of 4,4'-DDD, four detections of 4,4'-DDE, and one detection of 4,4'-DDT exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - One detection of 4,4'-DDD approached the NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the four detections of chlorpyrifos, two detections exceeded invertebrate NOAEC (0.005 µg/L). The two detections also approached or exceeded invertebrate LC_{50} (0.0138 µg/L).
    - The detection on March 21 approached the NRWQC and WAC chronic criteria (both 0.041 µg/L).
- Of the 16 detections of diuron, five detections approached or exceeded the plant EC_{50} (0.13 µg/L).
    - The detections on April 4 and April 11 approached or exceeded the invertebrate NOAEC (0.83 µg/L).
- The single detection of fenvalerate exceeded invertebrate LC_{50} (0.000848 µg/L) and invertebrate NOAEC (0.0000309 µg/L).
- The two detections of gamma-cyhalothrin approached or exceeded the Endangered Species Level of Concern (0.00145 µg/L) and exceeded the invertebrate LC_{50} (0.00008 µg/L).
    - The detection on April 18 also approached invertebrate NOAEC (0.00193 µg/L).
- The single detection of imidacloprid approached the invertebrate NOAEC (0.01 µg/L).
- The single detections of cis-permethrin and trans-permethrin, both are isomers of permethrin, were combined for comparison to assessment criteria. The combined concentration approached the invertebrate LC_{50} (0.0066 µg/L) and exceeded the invertebrate NOAEC (0.0042 µg/L).

The Snipes Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 17). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

Table 17 – Snipes Creek pesticide calendar, µg/L

Month		Mar		Apr				May			Jun					Jul		Aug
Day of the Month	Use*	21	28	4	11	18	25	9	16	23	1	6	13	21	27	11	25	8
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.009		0.035	0.036	0.009	0.020		0.013	0.038	0.009	0.008	0.008	0.005				
2,4-D	H		0.014	0.028	0.075	0.011	0.019	0.052	0.016	0.008	0.005	0.045	0.030			0.024	0.018	0.020
2,6-Dichlorobenzamide	D	0.004	0.006	0.006	0.005	X	0.007	0.005	X	0.008	0.005	X	0.005	0.008	0.010	0.005	0.002	0.008
4,4'-DDD	L				0.003	0.001									<0.001	0.001		
4,4'-DDE	L				0.003	0.002						0.002				0.001		
4,4'-DDT	L					0.001												
4-Nitrophenol	D	0.026																
Acetamiprid	I	0.002					0.003											
Atrazine	H		0.004	0.006	0.005	0.003	0.003	0.003	0.004	0.005		0.004	0.005		0.003	0.003		
Boscalid	F	0.004	0.004	0.004	0.006	0.003	0.003	0.002	0.003	0.004	0.005	0.003	0.003	0.006	0.011	0.005	0.005	0.006
Bromacil	H	0.007	0.006	0.007	0.297		0.006	0.004	0.004			0.010	0.008	0.005	0.006			0.023
Bromoxynil	H				0.019													
Carbendazim	F	0.002		0.002														
Chlorantraniliprole	I													0.016				
Chlorpyrifos	I	0.035	0.009	0.002	0.002													
cis-Permethrin	I														0.003			
Clopyralid	H							0.019										
Desethylatrazine	D	0.007									0.006							
Diazinon	I	0.007	0.050	0.013	0.006	0.002			0.002	0.005								
Dicamba	H				0.007		0.006	0.020	0.006	0.004		0.009	0.020			0.011	0.006	0.009
Dichlobenil	H	0.003	0.003	0.001	0.001		0.002											
Diuron	H	0.087	0.084	1.020	0.774	0.020	0.052	0.040	0.041	0.108	0.018	0.032	0.040	0.011	0.012	0.005	0.005	
Eptam	H								0.001	0.002	0.002	0.002						
Fenvalerate	I					0.002												
Fipronil sulfide	D																	0.002
Fipronil sulfone	D																	0.006
Fludioxonil	F	0.020	0.016	0.014	0.011		0.013	0.009	0.008	0.006	0.005	0.007	0.004		0.009	0.015	0.009	0.011
Flumioxazin	H				0.035			X										
Flupyradifurone	I										0.155							
gamma-Cyhalothrin	I					0.002									<0.001			
Hexazinone	H							0.016	0.002	0.005	0.003		0.001	0.002	0.002			0.003
Hexythiazox	I															0.008		
Imidacloprid	I										0.005							
Indaziflam	H	0.004																
Malathion	I	0.015													0.006			
Methoxyfenozide	I										0.002			0.003				
Metolachlor	H				0.003				<0.001			0.003	0.001	0.001	0.009	0.003	0.002	0.001
Metribuzin	H							0.004										
N,N-Diethyl-m-toluamide (DEET)	IR												0.017				0.009	
Norflurazon	H	0.004	0.004	0.005	0.010	0.006	0.006	0.003	0.005	0.005	0.004	0.004	0.005	0.005	0.008	0.004	0.003	0.004
Pendimethalin	H	0.016	0.011	0.017	0.054	0.016	0.010	0.010	0.006	0.004	0.005	0.007	0.006	0.004	0.002	0.003	0.006	0.004
Piperonyl butoxide (PBO)	Sy			0.004														
Propiconazole	F						0.008											
Pyridaben	I					0.001												
Pyrimethanil	F	0.022	0.012	0.012	0.009		0.017		0.011	0.005					0.009	0.008	0.004	
Simazine	H			0.006	0.005					0.006								
Sulfentrazone	H	X	X	X		X	X	X		0.006	0.006	0.004	0.010	0.005			0.003	0.006
Tau-fluvalinate	I					0.002												
Tefluthrin	I					<0.001												
Terbacil	H			0.008	0.009				0.004								0.003	0.003
Tetrahydrophthalimide	D								0.004									
trans-Permethrin	I														0.005			
Treflan (Trifluralin)	H								0.002									
Triclopyr	H							0.039	0.014									
Trifloxystrobin	F													0.014		0.010		
Suspended sediment concentration		52	24	23	212	51	13	17	18	10	10	69	36	14	29	26	18	17
Streamflow (cubic ft/sec)		-	-	48.7	-	68.5	51.2	63.3	63.2	18.8	15.6	-	-	21.2	38.9	71.7	52.2	54.9
Precipitation (total in/week)†		0.25	0.09	0.09	0.01	0.71	0.50	0.62	0.30	0.07	0.28	0.27	0.93	0.05	0.00	0.05	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 | DDT/degradate exceedance | Detection | No criteria

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

† 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 five of the 17 site visits (29%). Water quality at the Snipes Creek site is shown below (Figure 37 and Figure 38).

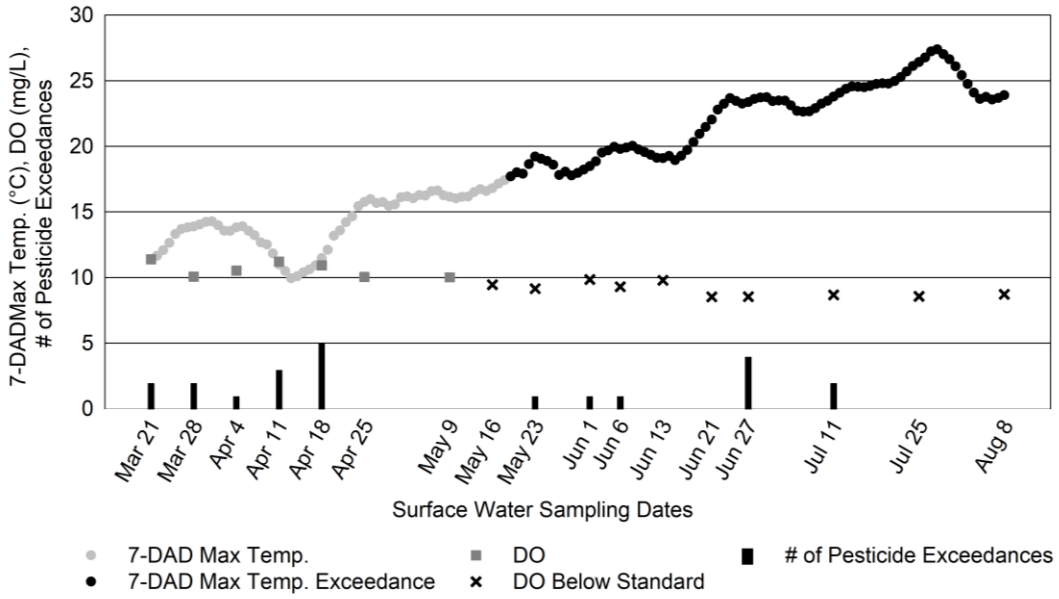


Figure 37 – Snipes Creek water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

DO measurements ranged from 8.52 mg/L to 11.38 mg/L with an average of 9.73 mg/L. More than half (56%) of the DO measurements did not meet the state water quality standard, with 10 measurements falling below 10 mg/L. The 7-DADMax temperature exceeded the standard of 17.5°C on 82 days throughout the sampling season, from May 19 through August 8. The DO measurements that did not meet the standard and 7-DADMax temperature exceedances at the same five site visits coincided with one, two, or four pesticide exceedances.

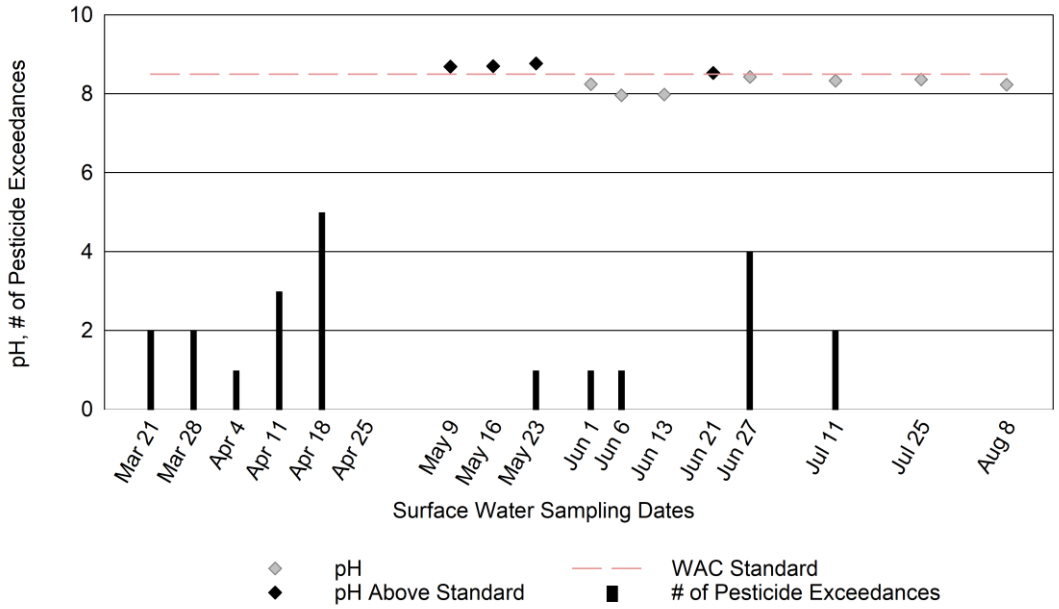
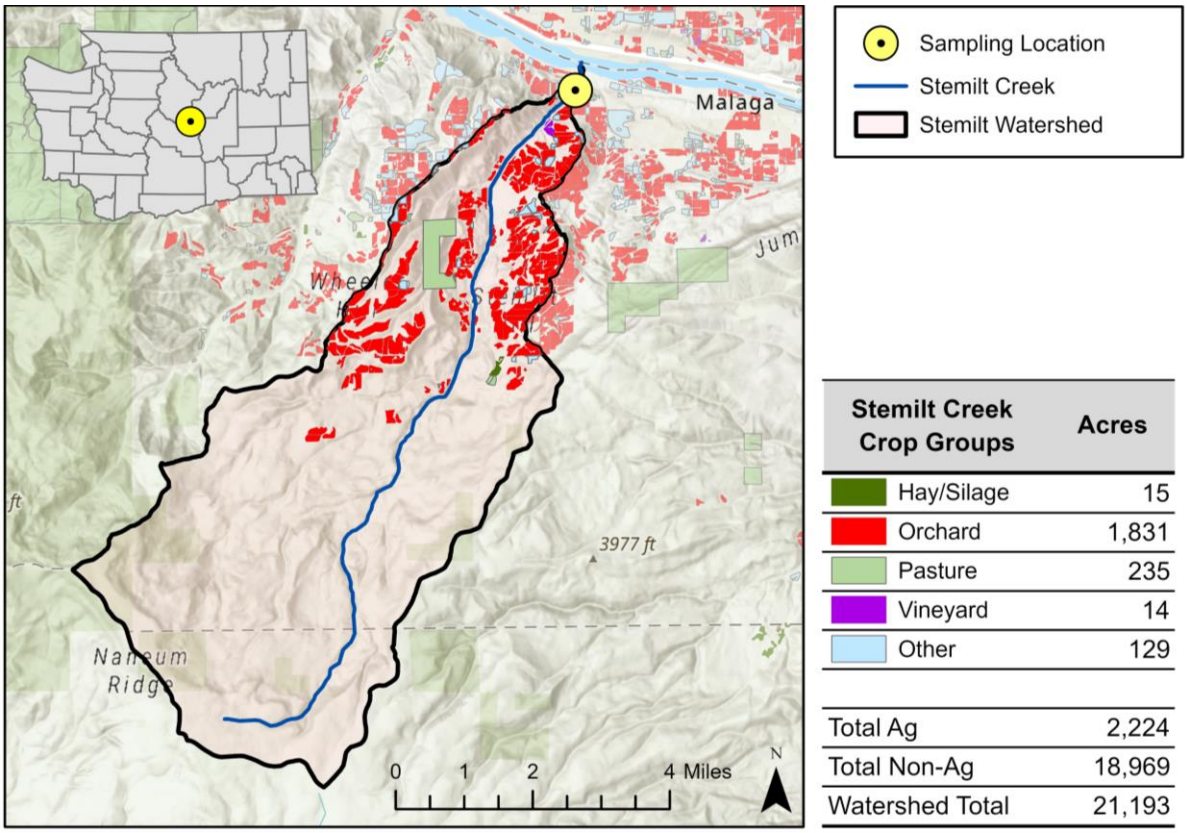


Figure 38 – Snipes Creek pH measurements and exceedances of assessment criteria

The pH measurements ranged from 7.96 to 8.77 with an average of 8.38. More than a third (36%) of these measurements exceeded the state water quality standard; four measurements were above 8.50. One of the pH exceedances coincided with one pesticide exceedance (Figure 38). Pesticide exceedance overlapped with pH, DO, and 7-DADMax temperature exceedances on May 23.

Snipes Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2023). Staff observed juvenile fish of an unknown species during the sampling season. A fish passage blockage restricts salmonids from migrating beyond Spring Creek's crossing with Hess Road. Snipes Creek is believed to be uninhibited from fish passage blockages. NRAS will continue to monitor this drainage because of its representative regional land use and consistent, yearly detections of POCs such as imidacloprid.

Stemilt Creek



Stemilt Creek Crop Groups	Acres
Hay/Silage	15
Orchard	1,831
Pasture	235
Vineyard	14
Other	129
Total Ag	2,224
Total Non-Ag	18,969
Watershed Total	21,193

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

In 2013, NRAS started monitoring the Stemilt Creek watershed in Chelan County. The site is located near Wenatchee, approximately 30 meters upstream of the bridge over the creek on Old West Malaga Road (latitude: 47.3748°, longitude: -120.2496°) (Figure 39, Figure 40). Stemilt Creek water drains directly into the Columbia River. Melting snowpack, precipitation events, and irrigation generally influenced streamflow in the creek. Within the reach of the creek that encompasses the monitoring site, WDFW has documented spring Chinook salmon, rainbow trout, and summer steelhead trout (WDFW 2023). 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 40 – 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 39).

Below is a brief overview of pesticide findings in Stemilt Creek in 2022.

- NRAS tested for 137 unique pesticides in Stemilt Creek.
- There were 58 total pesticide detections from five different use categories: 4 types of herbicides, 2 insecticides, 1 fungicide, 2 legacies, and 1 degradate.
- Pesticides were detected at all nine sampling events.
- Up to nine pesticides were detected at the same time.
- Of the total pesticide detections, 11 were above WSDA's assessment criteria (Table 18).
    - The seven detections of 4,4'-DDD and three detections of 4,4'-DDT approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- Of the four detections of malathion, one detection exceeded the invertebrate LC_{50} (0.098 µg/L), invertebrate NOAEC (0.06 µg/L), and NRWQC chronic criteria (0.1 µg/L). The detection also approached the Endangered Species Level of Concern (0.205 µg/L).
- There was no detection of chlorpyrifos at the site, however, chlorpyrifos was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.
- The nine detections of diazinon did not exceed any assessment criteria in 2022, however, this insecticide was still considered a watershed POC because of detections that did exceed criteria in recent years.

The Stemilt Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 18). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits. In addition, there were 11 herbicides, 1 degradate, and a wood preservative removed from testing at this site as a result of uncommon historic detections.

Table 18 – Stemilt Creek pesticide calendar, µg/L

Month		Mar	Apr				May			
Day of the Month	Use*	29	5	12	19	26	3	10	17	24
2,6-Dichlorobenzamide	D	0.026	0.031	0.025	0.045	0.035	0.023	0.015	0.022	0.009
4,4'-DDD	L	0.003	0.003	0.003		0.001	0.001		<0.001	<0.001
4,4'-DDT	L		0.001			0.002	0.001			
Boscalid	F	0.007	0.010	0.008	0.006	0.009	0.008	0.004	0.004	0.004
Diazinon	I	0.029	0.008	0.010	0.003	0.008	0.019	0.011	0.009	0.006
Dichlobenil	H		0.003			0.003				
Hexazinone	H					0.001		0.001	0.001	
Malathion	I	0.199	0.008	0.006	0.005					
Pendimethalin	H	0.003	0.003	0.003		0.003	0.005			
Sulfentrazone	H		0.026		0.031	0.018	0.022	0.008	0.006	0.008
Suspended sediment concentration		6	4	6	11	35	57	17	19	53
Streamflow (cubic ft/sec)		3.9	5.0	3.6	6.4	10.1	16.2	13.5	9.2	20.5
Precipitation (total in/week)†		0.00	0.02	0.04	0.73	0.19	0.67	0.08	0.10	0.42

Current-use exceedance DDT/degradate exceedance Detection

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, L: Legacy)
† Wash. State Univ. AgWeatherNet station: Stemilt (latitude: 47.33°, longitude: -120.26°)

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. 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 41).

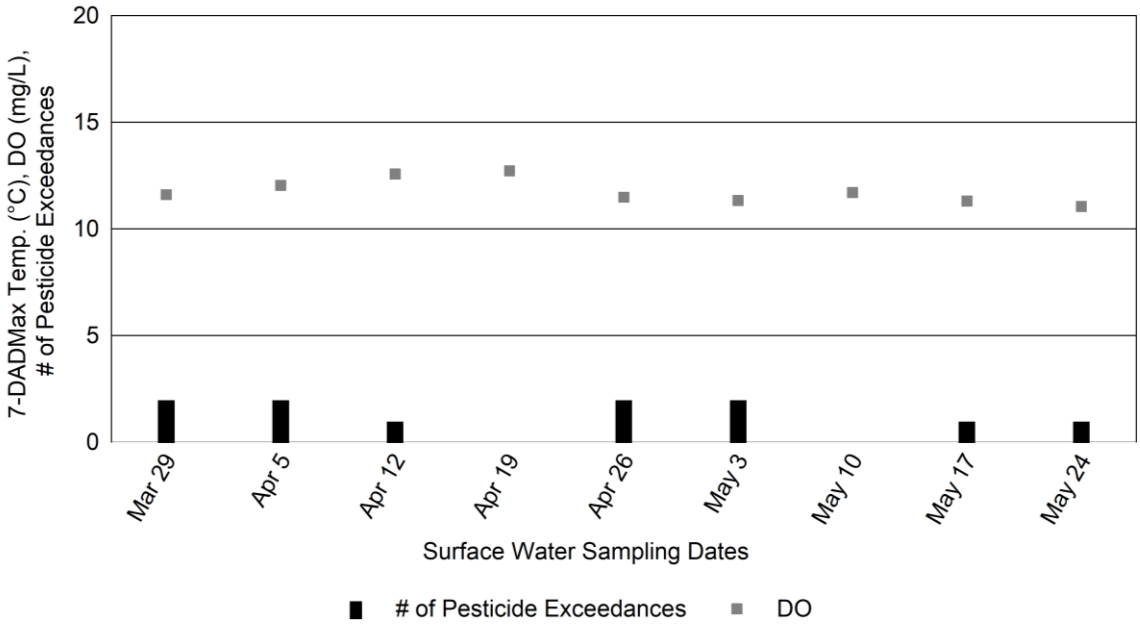


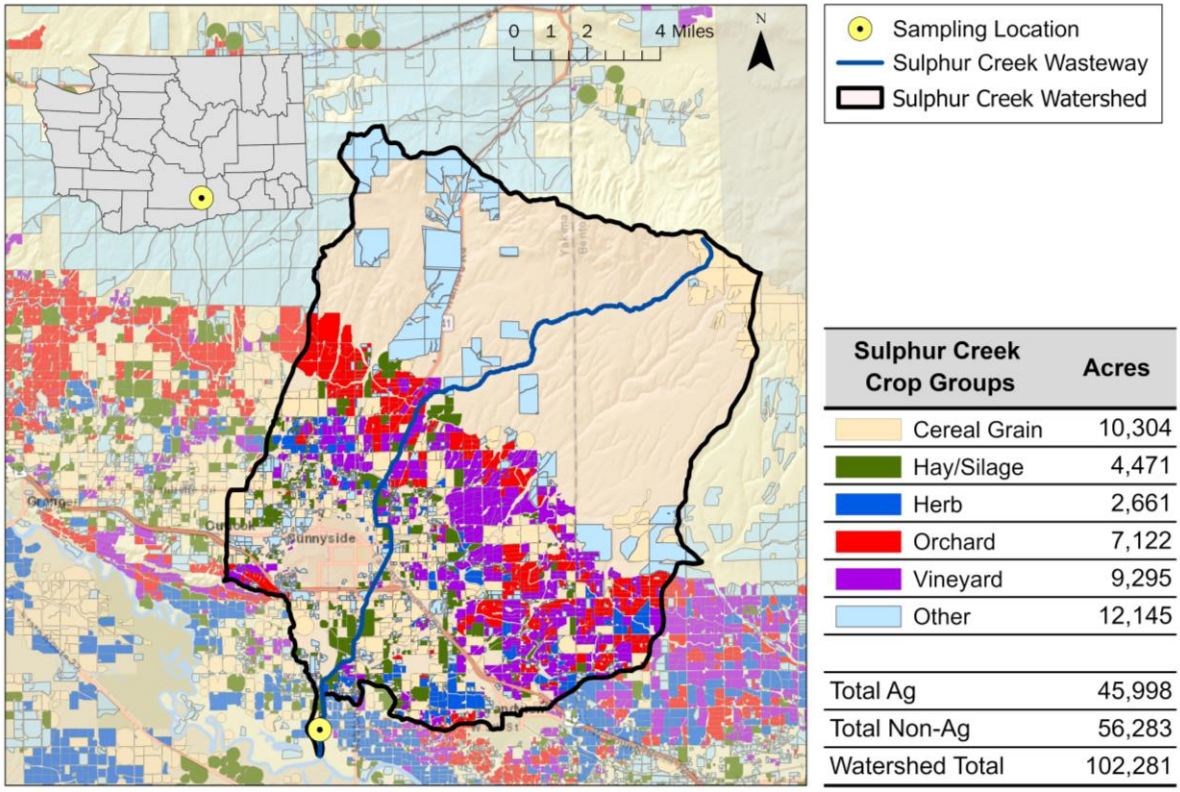
Figure 41 – Stemilt Creek water quality measurements (DO) and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 8.07 to 8.20 with an average of 8.15. All DO measurements met the state water quality standard, ranging from 11.05 mg/L to 12.72 mg/L with an average of 11.76 mg/L.

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

Stemilt Creek has been designated as a freshwater body that provides habitat for salmonid spawning, rearing, and migration by the WAC (WAC 2023). 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 malathion.

Sulphur Creek Wasteway



Sulphur Creek Crop Groups	Acres
Cereal Grain	10,304
Hay/Silage	4,471
Herb	2,661
Orchard	7,122
Vineyard	9,295
Other	12,145
Total Ag	45,998
Total Non-Ag	56,283
Watershed Total	102,281

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

In 2003, NRAS started monitoring the Sulphur Creek Wasteway watershed in Yakima County as one of the first monitoring locations in the program. The monitoring site is located near Sunnyside, just on the downstream side of the bridge crossing of Holaday Road, adjacent to the intersection of Midvale Road (latitude: 46.2510°, longitude: -120.0202°) (Figure 42, Figure 43).

Figure 43 – Sulphur Creek Wasteway downstream view

Sulphur Creek Wasteway water drains directly into the Yakima River approximately 0.8 miles downstream of the monitoring site. Precipitation events, irrigation, and groundwater generally influence streamflow in the wasteway. The majority of the water in the wasteway comes from the Yakima River through irrigation return flows from the Roza and Sunnyside canal systems. WDFW has documented coho, fall Chinook, and spring Chinook salmon, as well as rainbow 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 2023). 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 vegetables, grass, nurseries, and other assorted small acreage crops (Figure 42).

Below is a brief overview of pesticide findings in Sulphur Creek Wasteway in 2022.

- NRAS tested for 150 unique pesticides in Sulphur Creek Wasteway.
- There were 387 total pesticide detections from seven different use categories: 26 types of herbicides, 12 insecticides, 8 fungicides, 3 legacies, 9 degradates, 1 insect repellent, and 1 synergist.
- Pesticides were detected at all 18 sampling events.
- Up to 34 pesticides were detected at the same time.
- Of the total pesticide detections, 26 were above WSDA's assessment criteria (Table 19).
    - The eight detections of 4,4'-DDD, six detections of 4,4'-DDE, and two detections of 4,4'-DDT approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - The single detection of pyriproxyfen approached invertebrate NOAEC (0.0075 µg/L).
    - The single detection of tefluthrin approached the Endangered Species Level of Concern (0.003 µg/L) and fish NOAEC (0.004 µg/L).

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

- The single detection of bifenthrin exceeded the invertebrate LC_{50} (0.000493 µg/L), invertebrate NOAEC (0.00005 µg/L), and fish NOAEC (0.004 µg/L). The detection also approached the Endangered Species Level of Concern (0.0075 µg/L).
- Of the three detections of chlorpyrifos, one detection approached invertebrate LC_{50} (0.0138 µg/L) and invertebrate NOAEC (0.005 µg/L).
- Of the 15 detections of diuron, four detections approached or exceeded the plant EC_{50} (0.13 µg/L).
- The two detections of imidacloprid approached or exceeded the invertebrate NOAEC (0.01 µg/L).
- There was no detection of gamma-cyhalothrin at the site, however, gamma-cyhalothrin was still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Sulphur Creek Wasteway monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 monitoring season and a visual comparison to the WSDA assessment criteria (Table 19). The blank cells in the calendar indicate dates when no chemical was detected with confidence above reportable limits.

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

Month		Mar		Apr				May			Jun		Jul		Aug			Sep	
Day of the Month	Use*	21	28	4	11	18	25	2	9	23	6	21	5	18	1	15	29	12	26
1-(3,4-Dichlorophenyl)-3-methylurea	D	0.007		0.006	0.017	0.007	0.008	0.008	0.007	0.013	0.008			0.007					
2,4-D	H	0.015		0.010	0.090	0.006	0.025	0.189	0.011	0.015	0.072	0.133	0.089	0.047	0.033	0.042	0.108	0.053	0.025
2,6-Dichlorobenzamide	D	0.006	0.006	0.008	0.009	X	0.007	0.007	0.006	0.010	X	0.011	0.009	0.010	0.010	0.008	0.010	0.008	0.007
2-Hydroxyatrazine	D									0.002			0.002	0.003	0.008	0.008	0.009		
4,4'-DDD	L	0.003	0.003	0.003	0.003		0.003	<0.001										0.002	0.002
4,4'-DDE	L				0.002	0.002	0.003	0.002			0.002								0.002
4,4'-DDT	L						0.001				<0.001								
4-Nitrophenol	D	0.033			0.047														
Acetamiprid	I						0.002												
Acetochlor ESA	D											0.043					0.096		
Atrazine	H	0.005	0.005	0.006	0.009	0.004	0.004	0.005	0.003	0.022	0.005	0.006	0.022	0.007	0.005	0.004	0.008	0.007	0.007
Azoxystrobin	F												0.336						
Bentazon	H		0.014	0.009	0.013	0.009	0.013	0.013		0.011		0.045	0.021	0.026	0.059	0.031	0.039	0.023	0.018
Bifenthrin	I										0.004								
Boscalid	F	0.003	0.003	0.004	0.006	0.002	0.003	0.003	0.002	0.009	0.003	0.004	0.009	0.009	0.010	0.005	0.006	0.006	0.006
Bromacil	H	0.011	0.030	0.014	0.031	0.010	0.013	0.014	0.010	0.019	0.010	0.024	0.017	0.017	0.014	0.015	0.016	0.014	0.015
Bromoxynil	H			0.020	0.105		0.020	0.024											
Carbendazim	F	0.019	0.004		0.009	0.003	0.004	0.007	0.003	0.003		0.001					0.001		
Chlorantraniliprole	I													0.030					
Chlorpropham	H				0.002														
Chlorpyrifos	I		0.003	0.002	0.002														
Clopyralid	H																		0.047
Clothianidin	I													0.007		0.013	0.010		
Dacthal	H				0.007								0.011	0.010		0.009	0.007	0.007	
Desethylatrazine	D					0.008						0.007			0.007	0.007			
Diazinon	I	0.010	0.016	0.004	0.004	0.003	0.003			0.002								0.004	0.004
Dicamba	H				0.013		0.016	0.017	0.012		0.010		0.016	0.018	0.012	0.015	0.010	0.006	0.006
Dichlobenil	H	0.002	0.002																
Dimethoate	I						0.005		0.006										
Diuron	H	0.015	0.027	0.023	0.181	0.025	0.068	0.036	0.029	0.114	0.069	0.018		0.024	0.013	0.006	0.005		
Eptam	H									0.004	0.001	0.001							
Fludioxonil	F	0.013	0.016	0.010	0.014	0.008	0.010	0.010	0.005	0.007	0.006	0.006	0.010	0.010	0.012	0.009	0.008	0.009	0.010
Hexazinone	H	0.002		0.003	0.006	0.002	0.003	0.003	0.008	0.008	0.002	0.005	0.004	0.004	0.004	0.004	0.007	0.006	0.005
Imazapyr	H	0.043			0.048							0.010		0.008			0.010		
Imidacloprid	I			0.008	0.014														
Indaziflam	H			0.005	0.007														
Isoxaben	H				0.008														
Malathion	I	0.009											0.002						
Methamidophos	D												0.002						
Metolachlor	H				0.003			0.001		0.018	0.002	0.003	0.004	0.004	0.002		0.002	0.002	
Metribuzin	H		0.005		0.015					0.005		0.004	0.008	0.007	0.002				
N,N-Diethyl-m-toluamide (DEET)	IR				0.022								0.019	0.020	0.011		0.009		
Norflurazon	H	0.003		0.004	0.005	0.003	0.003	0.002	0.002	0.005	0.002	0.003	0.003	0.004	0.003	0.004	0.004	0.004	0.004
Oxamyl	I						0.014	0.007											
Oxamyl oxime	D							0.098											
Pendimethalin	H	0.020	0.015	0.034	0.050	0.025	0.020	0.032	0.009	0.023	0.019	0.007	0.004	0.004	0.005	0.003	0.002		0.002
Piperonyl butoxide (PBO)	Sy	0.004			0.004						0.003								
Prometon	H																	0.005	0.006
Propiconazole	F												0.157						
Pyraclostrobin	F												0.007						
Pyrimethanil	F	0.018		0.010	0.015	0.011	0.013	0.012	0.007		0.009	0.013					0.005	0.014	
Pyriproxyfen	I		0.008																
Simazine	H		0.007		0.007					0.004							0.009		
Sulfentrazone	H	X	X	X		0.008	X	0.011	X	0.016	0.008	0.015	0.010	0.013	0.012	0.009	0.027	0.028	0.028
Tefluthrin	I		0.003																
Terbacil	H	0.006	0.006	0.054	0.738	0.016	0.007	0.020	0.007	0.040	0.008	0.010	0.010	0.013	0.011	0.014	0.021	0.016	0.021
Tetrahydrophthalimide	D									0.002									
Treflan (Trifluralin)	H		0.003		0.003							0.002	0.003						
Triclopyr	H							0.034	0.042							0.011			
Trifloxystrobin	F											0.012							
Suspended sediment concentration		52	53	49	21	80	28	52	26	8	40	4	6	5	6	7	8	8	24
Streamflow (cubic ft/sec)		128	119	74	43	119	85	101	117	63	275	120	153	149	128	130	146	169	208
Precipitation (total in/week)†		0.02	0.08	0.01	0.00	1.01	0.33	0.11	0.40	0.01	0.29	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00

The "X" signifies data rejected by failing quality assurance performance measures. 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; Sy: Synergist)

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

When water quality parameters do not meet state water quality standards in concurrence with exceedances of pesticide assessment criteria, stress on aquatic life may be compounded. Pesticide exceedances coincided with water quality measurements that did not meet the state standards at four of the 18 site visits (22%). Water quality at the Sulphur Creek Wasteway site is shown below (Figure 44).

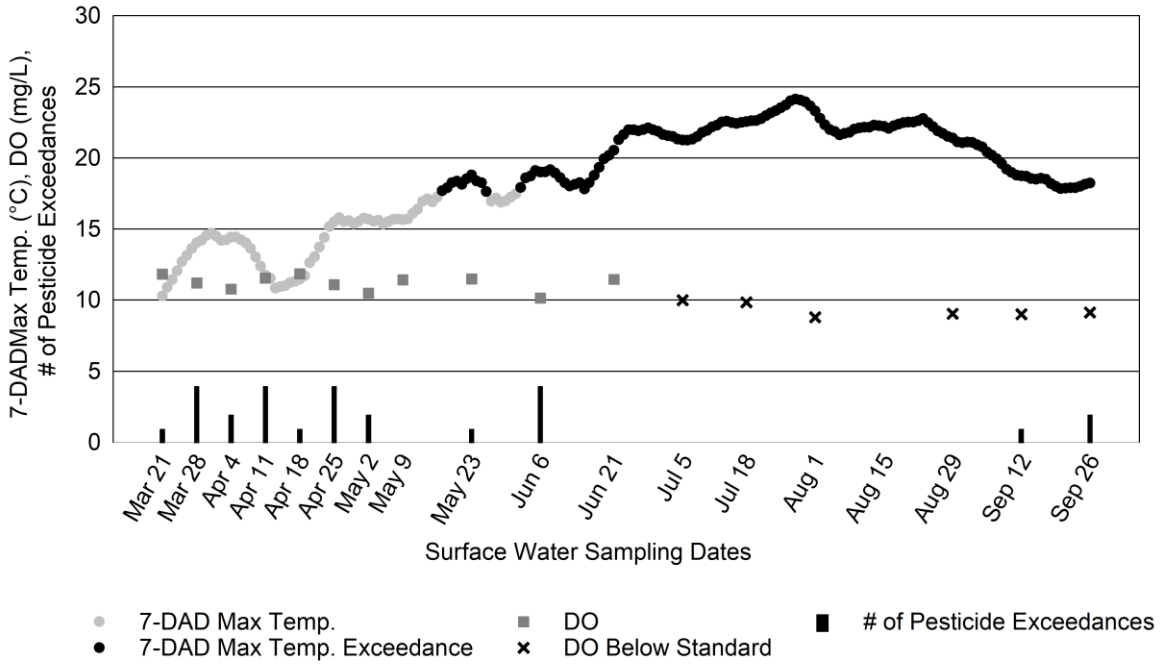


Figure 44 – Sulphur Creek Wasteway water quality measurements (7-DADMax Temp. and DO) and exceedances of assessment criteria

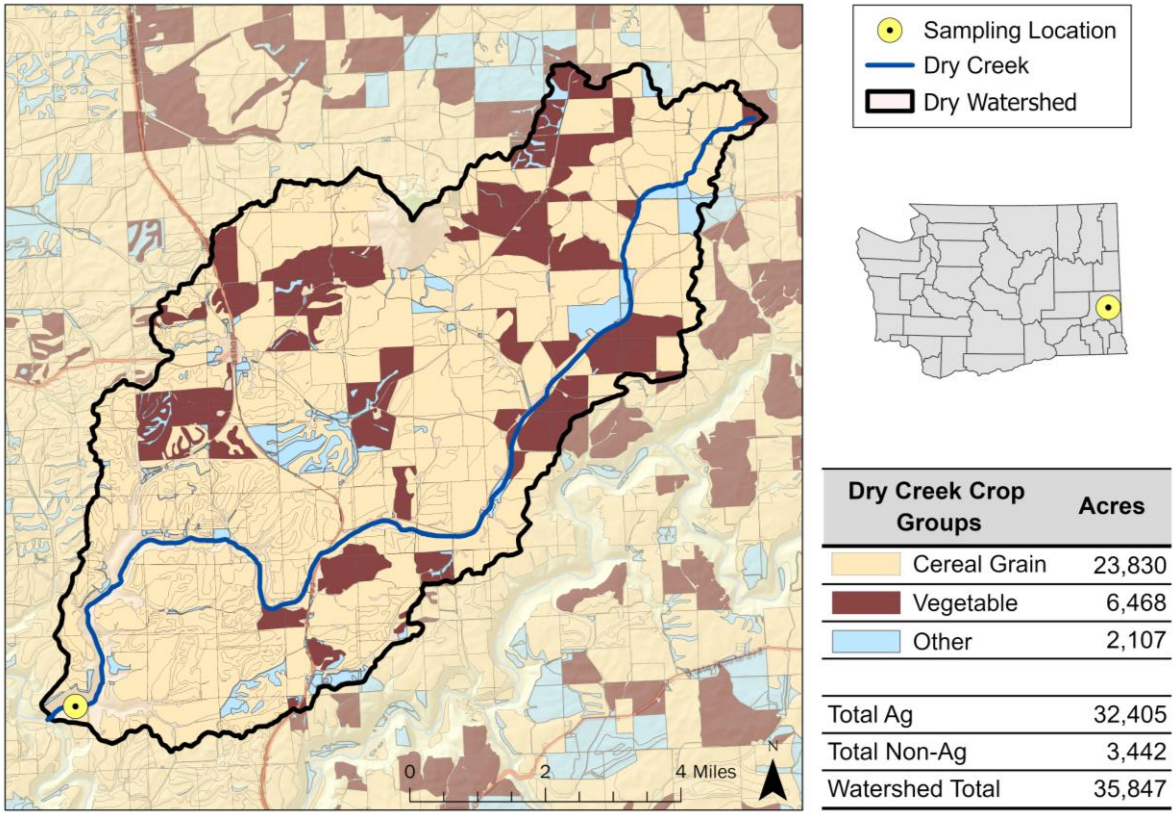
The pH measurements ranged from 7.70 to 8.80 with an average of 8.17. Almost a quarter (18%) of these measurements exceeded the state water quality standard; two measurements were above 8.50. One of the pH exceedances coincided with one pesticide exceedance. Pesticide exceedance overlapped with both pH and 7-DADMax temperature exceedances on May 23.

DO measurements ranged from 8.79 mg/L to 11.85 mg/L with an average of 10.53 mg/L. More than a third (35%) of the DO measurements did not meet the state water quality standard, with six measurements falling below 10 mg/L. Two 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 127 days throughout the sampling season, occurring intermittently from May 17 through September 26. Pesticide exceedances coincided with 7-DADMax temperature exceedances at four site visits.

Sulphur Creek Wasteway provides habitat for salmonid spawning, rearing, and migration (WAC 2023). 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



Dry Creek Crop Groups	Acres
Cereal Grain	23,830
Vegetable	6,468
Other	2,107
Total Ag	32,405
Total Non-Ag	3,442
Watershed Total	35,847

Figure 45 – 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 45, Figure 46).

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.

Figure 46 – Dry Creek upstream view

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 45).

NRAS tested for three additional analytes at this site in 2022 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were glyphosate, AMPA (a glyphosate breakdown product), and glufosinate-ammonium. Glyphosate is relied upon heavily in the cropping systems of the Palouse region. We do not test for it at each monitoring site due to the cost of lab analysis and the ubiquitous detections in Washington surface waters below WSDA assessment criteria. The results of the three chemicals were included in the Statewide Results section of this report which summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Dry Creek in 2022.

- NRAS tested for 153 unique pesticides in Dry Creek.
- There were 243 total pesticide detections from six different use categories: 24 types of herbicides, 5 insecticides, 5 fungicides, 3 legacies, 5 degradates, and 1 antimicrobial.
- Pesticides were detected at all 13 sampling events.
- Up to 32 pesticides were detected at the same time.
- Of the total pesticide detections, 13 were above WSDA’s assessment criteria (Table 20).
    - The single detections of 4,4’-DDD and 4,4’-DDT exceeded the NRWQC and WAC chronic criteria (both 0.001 µg/L).

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

- The single detection of bifenthrin approached the Endangered Species Level of Concern (0.0075 µg/L), exceeded the fish NOAEC (0.004 µg/L), invertebrate LC_{50} (0.000493 µg/L), and invertebrate NOAEC (0.00005 µg/L).
- The six detections of imidacloprid exceeded the invertebrate NOAEC (0.01 µg/L).
- Of the three detections of linuron, one detection approached invertebrate NOAEC and two detections exceeded invertebrate NOAEC (0.09 µg/L).
- The single detection of metsulfuron-methyl approached the plant EC_{50} (0.36 µg/L).
- There was no detection of chlorpyrifos or pyroxasulfone at the site, however, they were still classified as watershed POCs because of detections that did exceed criteria in recent years at the site.

The Dry Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 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

Month		Mar	Apr		May		Jun		Jul		Aug			Sep
Day of the Month	Use*	28	11	25	10	23	7	22	5	19	1	15	29	12
1-(3,4-Dichlorophenyl)-3-methylurea	D					0.004	0.014							
2,4-D	H					0.068	0.061	0.276	0.129	2.660	0.033		0.007	0.009
2,6-Dichlorobenzamide	D				0.002	0.002	X	0.002	0.002					
2-Hydroxyatrazine	D							0.002				0.008		
4,4'-DDD	L	0.003												
4,4'-DDT	L						0.001							
Aminomethylphosphoric acid (AMPA)	D	0.532	0.597	0.949	0.580	0.884	2.430	1.050	1.470	0.876	0.810	0.678	0.630	0.488
Atrazine	H						0.013		0.003					
Azoxystrobin	F				0.010	3.810	0.167	0.041	0.093	0.046	0.029	0.010	0.010	0.008
Bentazon	H	0.044	0.036	0.036	0.033	0.042		0.036	0.090	0.058	0.023			
Bifenthrin	I						0.005							
Bromacil	H		0.007				0.005							
Bromoxynil	H		0.059	0.023	0.114	0.153	0.657	0.046	0.022					
Carbendazim	F	0.003	0.003		0.007	0.006	0.012	0.004		0.002		0.004		
Clethodim sulfone	D							0.116						
Clopyralid	H	0.045	0.066	0.060	0.139	4.070	0.412		0.155	0.062	0.039			0.026
Clothianidin	I							0.006						
Dicamba	H	0.013	0.006			0.015	0.045	0.027	0.040	0.028	0.010	0.008		
Dimethoate	I								0.189	0.064				
Diuron	H					0.005	0.028							
Ethalfluralin (Sonalan)	H						0.003							
Fenarimol	L										0.007			
Glyphosate	H	0.262	0.718	1.700	0.490	0.533	2.010	0.508	0.986	0.185	0.158	0.132	0.123	0.080
Hexazinone	H						0.001							
Imidacloprid	I		0.011	0.014	0.032	0.016	0.071	0.022						
Indaziflam	H		0.010		0.009		0.007							
Linuron	H				0.201	0.075	0.198							
MCPA	H				0.157	14.800	0.300		0.057					
Metalaxyl	F	X	0.013	0.012	0.028		0.068	0.013	0.012					
Metolachlor	H		0.002	0.001	0.008	0.003	0.004	0.005	0.003	0.001	0.001		0.002	0.002
Metribuzin	H	0.026	0.017	0.017	0.370	0.225	1.540	0.160	0.301	0.018	0.009	0.005	0.007	0.007
Metsulfuron-methyl	H					0.182								
Pendimethalin	H	0.003	0.003	0.012	0.044	0.013	0.066	0.020	0.014	0.002	0.003			
Picloram	H	X	0.036	0.036					0.056		0.053	0.060	0.105	0.109
Prometon	H	0.005	0.009	0.007	0.004	0.004	0.005	0.003	0.005	0.004	0.004	0.003	0.007	0.007
Propiconazole	F	0.013	0.012	0.015	0.060	4.600	0.213	0.107	0.053	0.051	0.039		0.032	0.023
Pyraclostrobin	F				0.004	0.008	0.010	0.022	0.015					
Sulfentrazone	H		X	X	0.023	0.015	0.035	0.040	0.028	0.015	0.017	0.013	0.030	0.028
Sulfometuron-methyl	H				0.020	0.019	0.024							
Tebuthiuron	H	0.007	0.011	0.009	0.011	0.008	0.014		0.010		0.007		0.006	0.006
Thiamethoxam	I	0.018		0.008	0.022	0.011	0.077	0.021						
Triallate	H	0.006	0.006	0.005	0.025	0.024	0.117	0.022	0.021					
Triclosan	A										0.010			
Suspended sediment concentration		8	6	8	16	14	122	30	26	11	20	11	9	7
Streamflow (cubic ft/sec)		9.4	11.6	9.6	8.3	5.6	11.3	13.1	4.8	1.4	-	0.4	0.3	0.5
Precipitation (total in/week)†		0.10	0.45	0.24	0.97	0.27	1.37	0.70	0.56	0.00	0.00	0.41	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 | DDT/degradate exceedance | Detection | No criteria

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

† Washington State Univ. 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 13 site visits (8%). Water quality at the Dry Creek site is shown below (Figure 47).

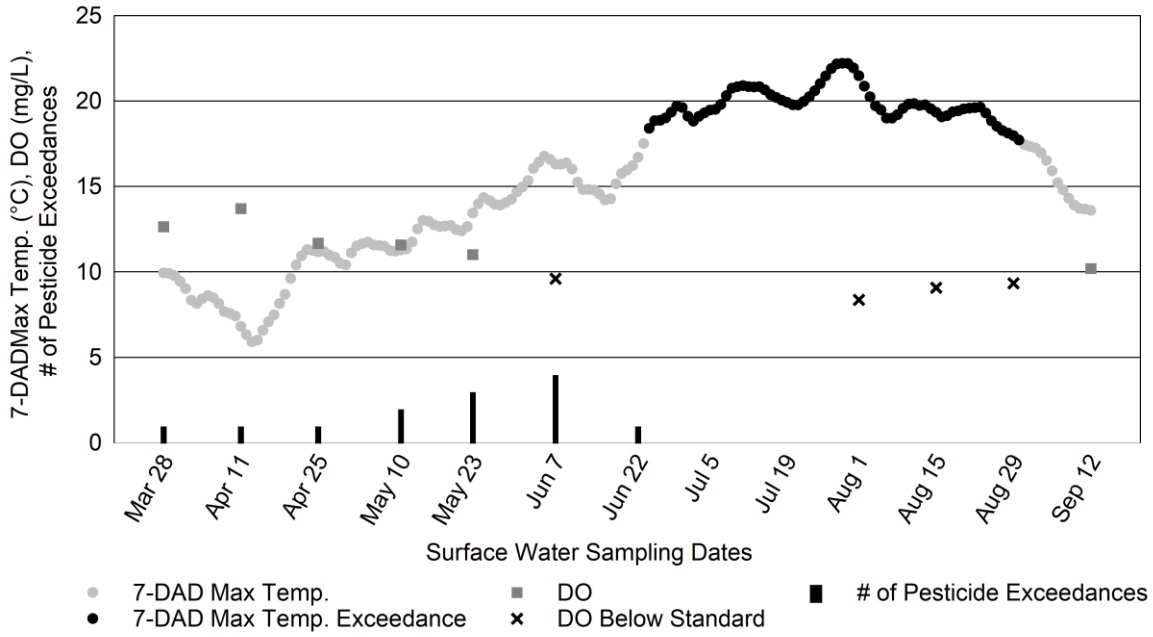


Figure 47 – Dry Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.97 to 8.40 with an average of 8.15. DO measurements ranged from 8.36 mg/L to 13.70 mg/L with an average of 10.72 mg/L. Almost half (40%) of the DO measurements did not meet the state water quality standard, with four measurements falling below 10 mg/L. One of the DO measurements that did not meet the standard coincided with four pesticide exceedances. The 7-DADMax temperature exceeded the standard of 17.5°C on 68 days throughout the sampling season, from June 24 through August 30.

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 2023). 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

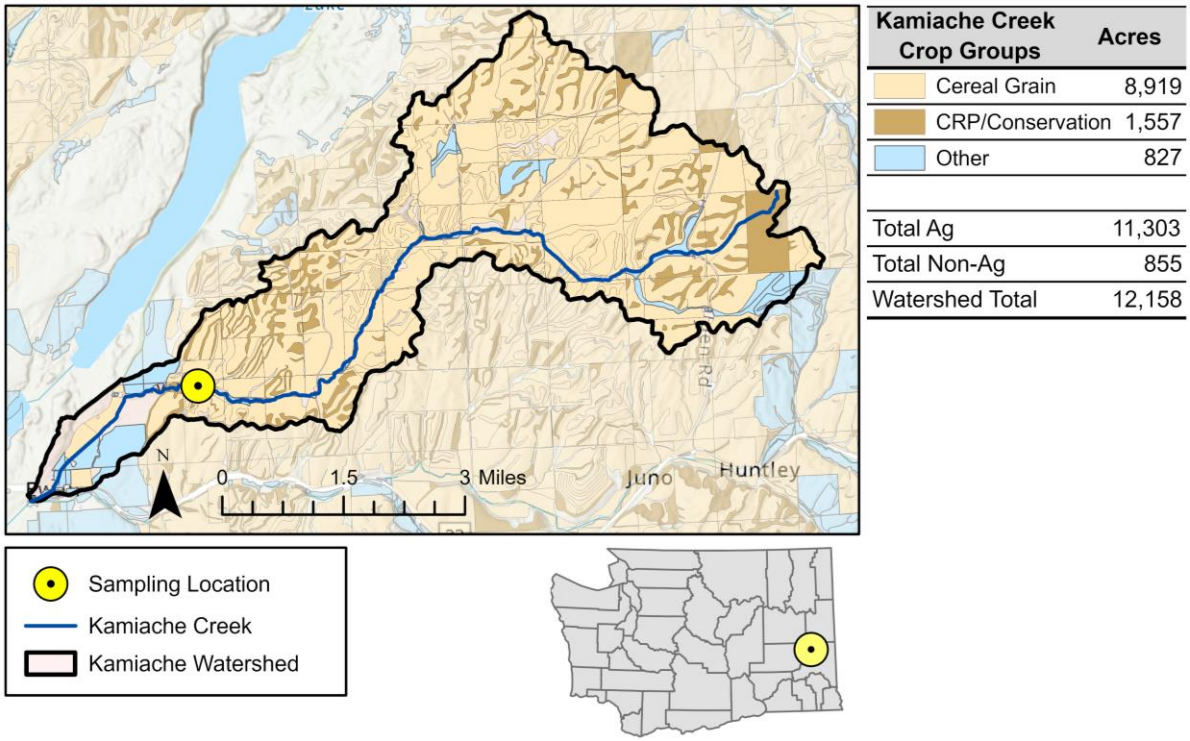


Figure 48 – Map of Kamiache Creek and its drainage area with associated sampling location and crop groups identified

Figure 49 – A colleague measuring streamflow in Kamiache Creek

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Kamiache Creek, in Whitman County, during the 2022 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 48, Figure 49).

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 48). There were efforts between 2016 and 2021 by a regional conservation partnership group to control sediment and nutrient loading into the creek. They used a voluntary incentive-based conservation program to convert or keep over 45,000

acres of farmland as conservation tilled in the area. Roughly 80% of the agricultural fields in this watershed were managed with mulch tilling instead of conventional tilling. Even after 2022, many farms were still managed with these conservation techniques.

NRAS tested for three additional analytes at this site in 2022 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were glyphosate, AMPA (a glyphosate breakdown product), and glufosinate-ammonium. Glyphosate is relied upon heavily in the cropping systems of the Palouse region. We do not test for it at each monitoring site due to the cost of lab analysis and the ubiquitous detections in Washington surface waters below WSDA assessment criteria. The results of the three chemicals were included in the Statewide Results section of this report which summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Kamiache Creek in 2022.

- NRAS tested for 153 unique pesticides in Kamiache Creek.
- There were 134 total pesticide detections from six different use categories: 14 types of herbicides, 4 insecticides, 8 fungicides, 5 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 17 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 21).

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

- The two detections of imidacloprid approached or 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 2022 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

Month		Mar	Apr		May		Jun		Jul		Aug			Sep		Oct		Nov
Day of the Month	Use*	28	11	27	9	23	6	21	5	18	1	15	29	12	26	10	24	7
2,4-D	H	0.008					0.029		0.195	0.015	0.022	0.095	0.056	0.012	0.019	0.007		0.188
2,6-Dichlorobenzamide	D				0.002													0.002
2-Hydroxyatrazine	D								0.002									
Aminomethylphosphoric acid (AMPA)	D	0.281	0.216	0.154	0.317	0.148	1.450	0.661	0.282	0.189	0.244	0.221	0.215	0.138	0.167	0.271	0.169	2.450
Azoxystrobin	F					0.011	0.009	0.040	1.230	0.016	0.014	0.017	0.016	0.007	0.006	0.012	0.012	0.014
Bentazon	H															0.012		
Boscalid	F																	<0.001
Bromacil	H															0.005		
Bromoxynil	H		0.019	0.022	0.051	0.049	0.290		0.015									0.012
Carbendazim	F								0.004									
Chlorsulfuron	H								0.129									
Clethodim sulfone	D						0.322	0.163										
Clethodim sulfoxide	D						3.620	0.143	0.814									
Clopyralid	H			0.094	0.111		0.500		0.031									0.101
Clothianidin	I								0.007									
Dicamba	H				0.006		0.034		0.017	0.007		0.125	0.117	0.011	0.017	0.006		0.422
Dimethoate	I								0.008									0.011
Glyphosate	H	0.405	0.231	0.152	0.321	0.096	1.900	0.520	0.236	0.138	0.360	0.258	0.299	0.228	0.176	0.117	0.263	2.840
Imidacloprid	I					0.006			0.030									
Inpyrfluxam	F													0.014				
Linuron	H								0.016									
MCPA	H			0.391	0.094		0.485											
Metalaxyl	F																	0.038
Metolachlor	H			0.001	<0.001		<0.001											
Metribuzin	H				0.002	0.005	0.108	0.013	0.005	0.004								0.649
Metsulfuron-methyl	H								0.028									
N,N-Diethyl-m-toluamide (DEET)	IR																	0.002
Pentachlorophenol	WP												0.112	0.065	0.043			0.043
Propiconazole	F			0.032		0.011	0.027	0.061	0.965	0.021								
Pyraclostrobin	F						0.036		0.067									
Sulfentrazone	H	X														0.018		X
Thiamethoxam	I						0.011		0.016									0.066
Triadimefon	F			0.002	0.003													
Suspended sediment concentration		8	2	3	3	5	5	5	4	35	11	11	5	12	6	9	2	2
Streamflow (cubic ft/sec)		1.9	2.3	1.6	1.6	1.1	1.9	-	0.7	0.4	0.2	0.2	0.1	0.4	0.2	0.6	0.3	0.5
Precipitation (total in/week)†		0.13	0.51	0.30	0.74	0.04	1.20	0.11	0.60	0.12	0.00	0.06	0.02	0.00	0.02	0.00	0.36	2.35

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 Detection No criteria

* (D: Degradate, F: Fungicide, H: Herbicide, I: Insecticide, IR: Insect repellent, 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 17 site visits (12%). Water quality at the Kamiache Creek site is shown below (Figure 50).

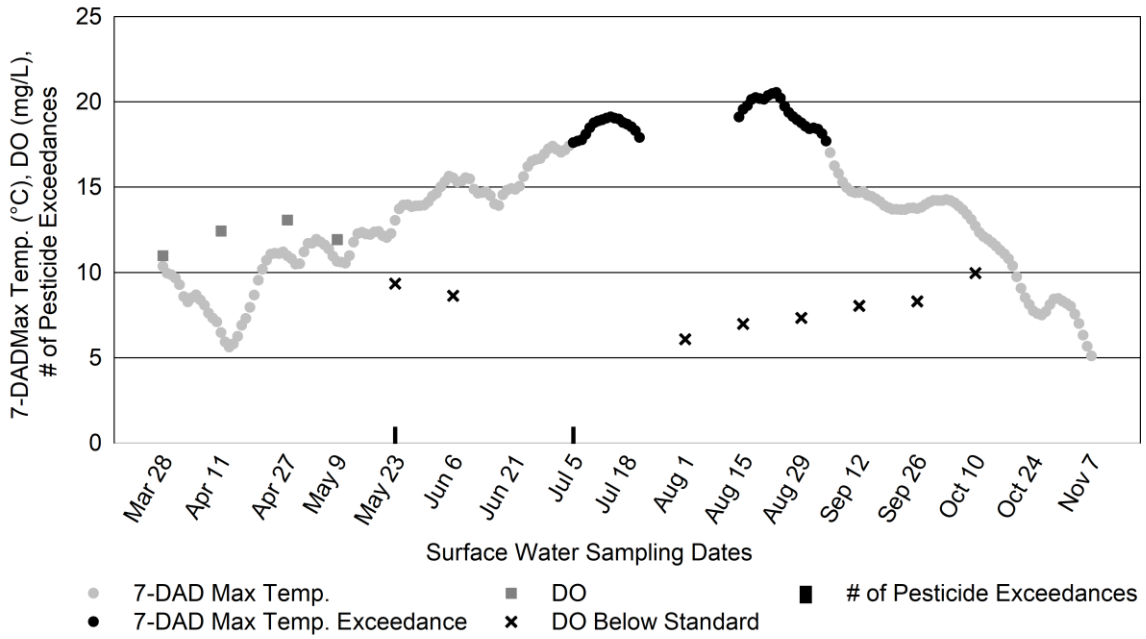


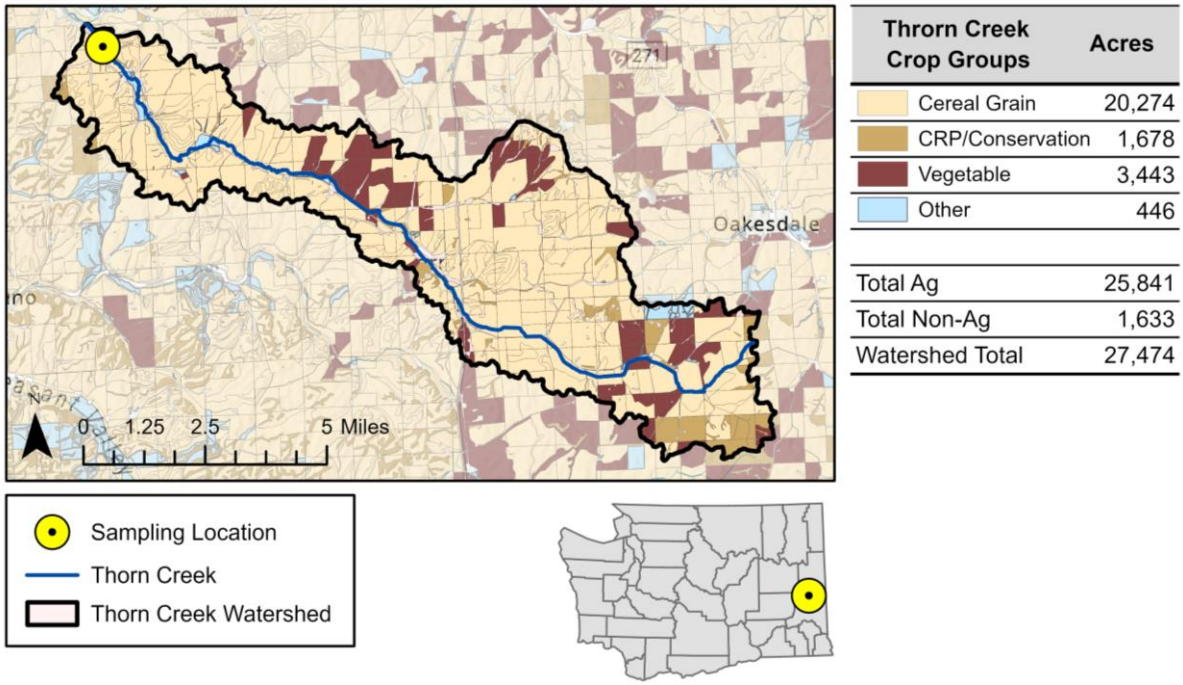
Figure 50 – Kamiache Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.78 to 8.41 with an average of 7.97. DO measurements ranged from 6.08 mg/L to 13.07 mg/L with an average of 9.42 mg/L. More than half (67%) of the DO measurements did not meet the state water quality standard, with eight measurements falling below 10 mg/L. One 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 39 days throughout the sampling season, from July 5 through July 21 and August 14 to September 4. Pesticide exceedances coincided with 7-DADMax temperature exceedances at one site visit.

*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 2023). Staff observed small, unknown fish during the sampling season. NRAS will continue to monitor this drainage because of its representative regional dryland agriculture land use.

* See revisions page Rev. 3 for revised text

Thorn Creek



Thrornn Creek Crop Groups	Acres
Cereal Grain	20,274
CRP/Conservation	1,678
Vegetable	3,443
Other	446
Total Ag	25,841
Total Non-Ag	1,633
Watershed Total	27,474

Figure 51 – Map of Thorn Creek and its drainage area with associated sampling location and crop groups identified

Continuing WSDA's expanded sampling across Eastern Washington, NRAS collaborated with the Palouse Conservation District to monitor Thorn Creek, in Whitman County, during the 2022 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 51, Figure 52).

Figure 52 - 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 51). Almost 80% of the agricultural fields in this watershed used conventional tillage practices.

NRAS tested for three additional analytes at this site in 2022 in conjunction with the regular surface water monitoring analytes. The additional three chemicals tested for were glyphosate, AMPA (a glyphosate breakdown product), and glufosinate-ammonium. Glyphosate is relied upon heavily in the

cropping systems of the Palouse region. We do not test for it at each monitoring site due to the cost of lab analysis and the ubiquitous detections in Washington surface waters below WSDA assessment criteria. The results of the three chemicals were included in the Statewide Results section of this report that summarizes all monitoring site results.

Below is a brief overview of the pesticide findings in Thorn Creek in 2022.

- NRAS tested for 153 unique pesticides in Thorn Creek.
- There were 220 total pesticide detections from seven different use categories: 23 types of herbicides, 6 insecticides, 6 fungicides, 1 legacy, 7 degradates, 1 insect repellent, and 1 wood preservative.
- Pesticides were detected at all 17 sampling events.
- Up to 23 pesticides were detected at the same time.
- Of the total pesticide detections, 10 were above WSDA's assessment criteria (Table 22).
    - The two detections of 4,4'-DDD approached or exceeded NRWQC and WAC chronic criteria (both 0.001 µg/L).
    - Of the two detections of dimethoate, one detection exceeded the invertebrate NOAEC (0.5 µg/L).

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

- The two detections of gamma-cyhalothrin approached the invertebrate NOAEC (0.00193 µg/L) and the Endangered Species Level of Concern (0.00145 µg/L) and exceeded the invertebrate LC_{50} (0.00008 µg/L).
- Of the five detections of imidacloprid, three detections approached the invertebrate NOAEC, and two detections exceeded the invertebrate NOAEC (0.01 µg/L).

The Thorn Creek monitoring site pesticide calendar provides a chronological overview of the pesticides detected during the 2022 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

Month		Mar	Apr		May		Jun		Jul		Aug			Sep		Oct		Nov
Day of the Month	Use*	28	11	25	9	23	6	21	5	19	1	15	29	12	26	10	24	7
1-(3,4-Dichlorophenyl)-3-methylurea	D				0.011				0.006									
2,4-D	H				0.017	0.011	0.027		-	0.030	0.144	0.022	0.043	0.010	0.008	0.014	0.234	0.064
2,6-Dichlorobenzamide	D				0.002		X											0.002
2-Hydroxyatrazine	D								0.003									
4,4'-DDD	L									<0.001			0.002					
Aminomethylphosphoric acid (AMPA)	D	0.383	0.398	0.371	1.030	5.770	1.480	0.754	0.690	0.609	0.416	0.423	0.373	0.234	0.219	0.139	0.238	0.774
Azoxystrobin	F				0.035	0.063	0.025	0.037	0.006	0.075	0.038	0.023	0.016	0.014	0.012	0.004	0.011	
Bentazon	H			0.010					-	0.009	0.010		0.014	0.012	0.011			
Boscalid	F												0.001					<0.001
Bromacil	H	0.013	0.008	0.008	0.008	0.007	0.005	0.007	0.007	0.008	0.005	0.005	0.006	0.004	0.005		0.005	0.006
Bromoxynil	H		0.038		0.099	0.057	0.148	0.038	-									0.029
Carbendazim	F		0.003			0.001												
Clethodim sulfoxide	D							0.164										
Clopyralid	H	0.034	0.037	0.044	0.411	0.051	0.709	0.127	-								0.021	0.058
Desethylatrazine	D								0.008									
Dicamba	H				0.024		0.041		-	0.184	0.010	0.021	0.008	0.010		0.013	0.119	0.086
Dimethoate	I								4.350	0.005								
Diuron	H				0.014				0.014									
Eptam	H				0.002		0.001											
Fipronil sulfone	D												0.003					
gamma-Cyhalothrin	I						0.001								0.001			
Glyphosate	H	0.553	0.302	0.220	0.852	13.70	1.710	0.566	0.339	0.273	0.189	0.151	0.158	0.163	0.135	0.168	0.307	1.480
Hexazinone	H			0.002	0.002		0.002	0.001										
Imazapyr	H								0.008									
Imidacloprid	I			0.007		0.007	0.015	0.012	0.007									
Indaziflam	H		0.009															
MCPA	H		0.087		0.244				-									0.016
Metalaxyl	F	X	0.011		0.010		0.019	0.005										0.025
Metolachlor	H				0.001	0.002	0.001	0.001										0.002
Metribuzin	H	0.005	0.004	0.004	0.291	0.012	1.140	0.076	0.018	0.009	0.003	0.002						0.007
N,N-Diethyl-m-toluamide (DEET)	IR											0.098	0.021	0.012				0.002
Oxamyl	I																0.003	
Pendimethalin	H																	0.002
Pentachlorophenol	WP								-							0.057	0.042	
Picloram	H	0.041	X						-	0.056		0.040						
Prometon	H		0.006	0.006				0.002	0.002									
Propiconazole	F	0.011	0.017	0.009	0.095	0.043	0.028	0.058		0.042	0.021	0.015	0.017					
Pyraclostrobin	F				0.003			0.007										
Sulfentrazone	H			X	0.028	0.008	0.031	0.018	0.012	0.010	0.008	0.007	0.021	0.018	0.021		0.021	0.017
Sulfometuron-methyl	H		0.053	0.003	0.003													
Sulfoxaflor	I								0.004									
Tebuthiuron	H	0.005	0.004		0.004													
Thiamethoxam	I	0.007	0.008	0.006			0.009	0.008										0.018
Treflan (Trifluralin)	H						0.002											
Triallate	H				0.001													
Suspended sediment concentration		7	3	4	9	4	31	28	8	6	62	9	3	25	5	3	7	8
Streamflow (cubic ft/sec)		5.1	5.0	5.4	6.3	3.3	7.5	7.4	3.1	1.2	0.7	0.4	0.3	0.2	0.3	0.3	0.6	2.5
Precipitation (total in/week)†		0.13	0.51	0.26	0.74	0.04	1.20	0.11	0.60	0.12	0.00	0.06	0.02	0.00	0.02	0.00	0.36	2.35

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/degradate exceedance | Detection | No criteria

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

† Washington State University AgWeatherNet station: 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 three of the 17 site visits (18%). Water quality at the Thorn Creek site is shown below (Figure 53).

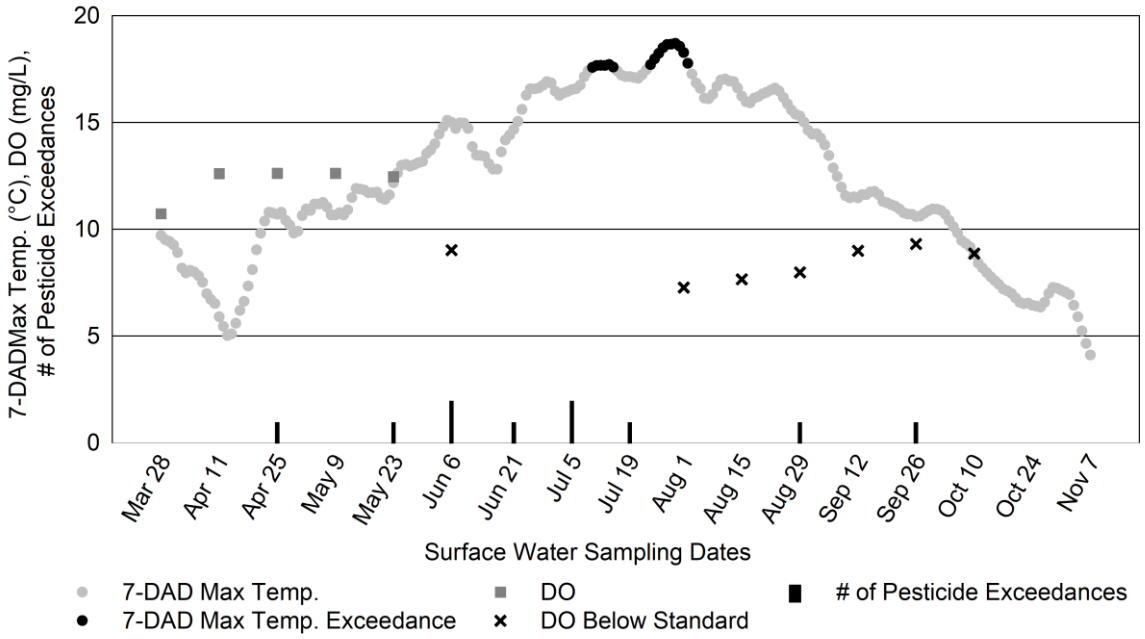


Figure 53 – Thorn Creek water quality measurements and exceedances of assessment criteria

All pH measurements met the state water quality standard, ranging from 7.25 to 8.32 with an average of 7.86. DO measurements ranged from 7.27 mg/L to 12.61 mg/L with an average of 10.01 mg/L. More than half (58%) of the DO measurements did not meet the state water quality standard, with seven measurements falling below 10 mg/L. Three 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 16 days throughout the sampling season, occurring intermittently from July 10 through August 2.

*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 2023). NRAS will continue to monitor this drainage because of its representative regional dryland agriculture land use.

* See revisions page Rev. 3 for revised text

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 (9 to 28 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 but should be used with caution.

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		1
Degradate	20	18	1	654
Fungicide	21	18		758
Herbicide	55	45	3	2,422
Insect repellent	1	1		63
Insecticide	48	36	14	607
Legacy pesticides	5	4	3	165
Synergist	1	1		8
Wood preservative	1	1		9
Total analytes	153	125	21	4,687

There were 125 different analytes detected in 2022 (Table 23). Across 17 monitoring sites, we identified 4,687 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 317 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 317 individual exceedances, 153 (48%) were currently registered pesticides or their associated degradates. The other 164 (52%) were detections of legacy pesticides or their degradates. Over half of the exceedances, 208 (66%), occurred at monitoring sites in Central Washington and the Palouse region including many of the statewide exceedances of DDT or its degradates (122). Imidacloprid, a neonicotinoid insecticide, accounted for 49 (15%) of the individual pesticide exceedances with 29 of the exceedances found at Western Washington monitoring sites; there was at least one exceedance detected at 10 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 2022. Appendix B: 2022 Quality Assurance Summary provides a list of all analytes tested.

Herbicide Detections

Herbicides were the most frequently detected group making up approximately 52% (2,422 detections) of the total pesticide detections. Of the 55 herbicides included in the laboratory analysis, 45 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 2022

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	249	165 (66%)		16		0.00269 - 0.118
Metolachlor	291	147 (51%)		14		0.000764 - 0.45
2,4-D	245	144 (59%)		14		0.0046 - 2.66
Atrazine	291	126 (43%)		11		0.00236 - 0.263
Bromacil	290	124 (43%)		15		0.00288 - 0.867
Dichlobenil	291	120 (41%)		12		0.00143 - 0.648
Hexazinone	291	113 (39%)		15		0.00118 - 0.0329
Pendimethalin	291	108 (37%)		11		0.00204 - 0.0659
Simazine	289	105 (36%)		11		0.00357 - 0.857
Metribuzin	288	104 (36%)		12		0.00188 - 1.54
Diuron	290	103 (36%)	13	12	6	0.00355 - 1.02
Dicamba acid	246	102 (41%)		11		0.0041 - 0.422
Terbacil	290	96 (33%)		8		0.00271 - 0.738
Norflurazon	291	89 (31%)		7		0.0013 - 0.0131
Prometon	291	85 (29%)		11		0.00222 - 0.0107
Tebuthiuron	291	79 (27%)		9		0.00398 - 0.0673
Imazapyr	288	66 (23%)		9		0.00732 - 6.48
Bentazon	246	62 (25%)		9		0.00858 - 0.418
Eptam	291	49 (17%)		7		0.00121 - 0.0138
Glyphosate	47	47 (100%)		3		0.0802 - 13.7
Triclopyr acid	246	47 (19%)		9		0.0115 - 0.77
Picloram	223	38 (17%)		4		0.0301 - 0.523
Bromoxynil	246	33 (13%)		9		0.0124 - 0.657
MCPA	245	31 (13%)		9		0.0122 - 14.8
Clopyralid	245	28 (11%)		7		0.0194 - 4.07
Mecoprop (MCPP)	246	28 (11%)		5		0.0163 - 0.382
Napropamide	291	26 (9%)		2		0.00394 - 0.218
Trifluralin	291	26 (9%)		10		0.00213 - 0.00822
Dithiopyr	291	23 (8%)		5		0.00182 - 0.00793
Indaziflam	290	20 (7%)		8		0.00315 - 0.0303
Sulfometuron-methyl	290	17 (6%)		7		0.00257 - 0.107
Dacthal (DCPA)	246	12 (5%)		2		0.00665 - 0.0665
Oxadiazon	291	11 (4%)		2		0.00151 - 0.00456
Imazapic	290	9 (3%)		4		0.00557 - 0.0161
Triallate	291	9 (3%)		2		0.00145 - 0.117
Chlorpropham	291	7 (2%)		3		0.00108 - 0.00278
Isoxaben	290	7 (2%)		5		0.00256 - 0.0103
Linuron	290	4 (1%)	3	2	1	0.0164 - 0.201

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)
Flumioxazin	264	3 (1%)		2		0.0193 - 0.0349
Metsulfuron-methyl	290	3 (1%)	1	3	1	0.0232 - 0.182
Prometryn	291	2 (1%)		1		0.00333 - 0.00712
Aminocyclopyrachlor	290	1 (<1%)		1		0.0614 - 0.0614
Chlorsulfuron	290	1 (<1%)		1		0.129 - 0.129
Ethalfluralin	291	1 (<1%)		1		0.00288 - 0.00288
Triclopyr butoxyethyl ester	291	1 (<1%)		1		0.00868 - 0.00868

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 165 and 147 detections, respectively. There were 20 unique herbicides found at more than 50% of monitoring sites throughout the sampling season.

Diuron, linuron, and metsulfuron-methyl were detected above the WSDA assessment criteria, accounting for roughly 5% of the total exceedances in 2022. 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 into the environment 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 12 monitoring sites),
  - → deisopropyl atrazine (detected at two monitoring sites),
  - → desethylatrazine (detected at eight monitoring sites),
- Dichlobenil → 2,6-dichlorobenzamide (detected at all 17 monitoring sites),
- Diuron → 1-(3,4-Dichlorophenyl)-3methylurea (detected at 10 monitoring sites),
- Glyphosate → aminomethylphosphoric acid (AMPA) (detected at three of three monitoring sites).

Fungicide Detections

Fungicides were the second most frequently detected group of pesticides making up 758 detections, or 16%, of the total number of detections. Out of 21 fungicides included in the laboratory analysis, 18 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 2022

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	291	183 (63%)		14		0.000537 - 0.312
Fludioxonil	291	128 (44%)		9		0.00341 - 0.303
Azoxystrobin	290	95 (33%)		10		0.00213 - 3.81
Propiconazole	290	91 (31%)		12		0.00576 - 4.6
Carbendazim	290	90 (31%)		15		0.00125 - 0.145
Metalaxyl	289	72 (25%)		8		0.0053 - 1.58
Pyrimethanil	290	53 (18%)		7		0.00266 - 0.458
Pyraclostrobin	290	12 (4%)		6		0.00257 - 0.0672
Chlorothalonil	291	8 (3%)		5		0.00165 - 0.0334
Fluopicolide	290	6 (2%)		2		0.00371 - 0.0145
Triadimefon	291	6 (2%)		5		0.00158 - 0.00519
Trifloxystrobin	290	4 (1%)		3		0.00988 - 0.0173
Cyprodinil	290	3 (1%)		3		0.00439 - 0.0435
Etridiazole	291	3 (1%)		1		0.000746 - 0.00275
Difenoconazole	290	1 (<1%)		1		0.00646 - 0.00646
Inpyrfluxam	290	1 (<1%)		1		0.0138 - 0.0138
Myclobutanil	290	1 (<1%)		1		0.0365 - 0.0365
Paclobutrazol	290	1 (<1%)		1		0.0323 - 0.0323

Boscalid, fludioxonil, and azoxystrobin were the most commonly detected fungicides with 183, 128, and 95 detections, respectively. Boscalid and fludioxonil have been among the most commonly detected fungicides each year since 2015. No fungicide detections exceeded WSDA assessment criteria in 2022.

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

- Azoxystrobin
- Boscalid
- Carbendazim
- Fludioxonil
- Propiconazole

Insecticide Detections

Current-use insecticides were the third most frequently detected group of pesticides representing approximately 13% (607 detections) of the total pesticide detections. Of the 48 current-use insecticides included in the laboratory analysis, 36 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 2022

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	290	79 (27%)		10		0.00249 - 0.0812
Diazinon	291	70 (24%)		12		0.00127 - 0.0504
Flupyradifurone	290	61 (21%)		5		0.00614 - 0.963
Dinotefuran	290	49 (17%)		4		0.00422 - 0.236
Imidacloprid	290	49 (17%)	49	10	10	0.00513 - 0.17

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)
Clothianidin	290	31 (11%)	11	5	1	0.00336 - 0.0992
Fipronil	291	31 (11%)	12	7	4	0.00182 - 0.0857
Malathion	291	31 (11%)	12	7	4	0.00175 - 0.199
Dimethoate	291	29 (10%)	1	13	1	0.0031 - 4.35
Oxamyl	290	29 (10%)		4		0.00189 - 0.181
Chlorpyrifos	291	17 (6%)	7	6	4	0.00127 - 0.0348
Acetamiprid	290	16 (6%)		6		0.00211 - 0.0284
Acephate	290	15 (5%)		5		0.00694 - 4.77
gamma-Cyhalothrin	291	14 (5%)	14	7	7	0.000838 - 0.00463
Cyantraniliprole	290	11 (4%)		2		0.0286 - 0.259
Pyriproxyfen	291	10 (3%)	4	4	3	0.00175 - 0.0754
Chlorantraniliprole	290	8 (3%)		3		0.0124 - 0.03
Bifenthrin	291	7 (2%)	7	7	7	0.0017 - 0.00522
Ethoprop	291	7 (2%)		5		0.00146 - 0.0294
Tefluthrin	291	7 (2%)	6	5	4	0.000578 - 0.00289
Methiocarb	290	5 (2%)		2		0.00485 - 0.104
Methoxyfenozide	290	5 (2%)		2		0.00235 - 0.00339
Tolfenpyrad	290	4 (1%)	4	2	2	0.0386 - 0.0519
Methomyl	290	3 (1%)		2		0.00165 - 0.00525
Pyridaben	291	3 (1%)		3		0.00117 - 0.00148
cis-Permethrin	291	2 (1%)	2	2	2	0.00274 - 0.00561
Hexythiazox	290	2 (1%)		2		0.00799 - 0.022
Phosmet	291	2 (1%)		2		0.0025 - 0.00455
Sulfoxaflor	290	2 (1%)		2		0.0038 - 0.0278
trans-Permethrin	291	2 (1%)	2	2	2	0.00486 - 0.00641
Bifenazate	291	1 (<1%)		1		0.0221 - 0.0221
Carbaryl	290	1 (<1%)		1		0.0419 - 0.0419
Fenvalerate	291	1 (<1%)	1	1	1	0.00176 - 0.00176
Fenbutatin oxide	290	1 (<1%)		1		0.00466 - 0.00466
Spirotetramat	290	1 (<1%)		1		0.0898 - 0.0898
tau-Fluvalinate	291	1 (<1%)		1		0.0016 - 0.0016

WSDA considers bolded analytes to be statewide POCs.

Thiamethoxam, diazinon, and flupyradifurone were the most commonly detected insecticides with 79, 70, and 61 detections, respectively. The neonicotinoids thiamethoxam and imidacloprid have been among the most commonly detected insecticides every year since 2015.

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

- Diazinon
- Dimethoate
- Imidacloprid
- Thiamethoxam

Detections of current-use insecticides accounted for almost 42% (132 detections) of all exceedances in 2022. All detections of bifenthrin, cis-permethrin, fenvalerate, gamma-cyhalothrin, imidacloprid, tolfenpyrad, and trans-permethrin were at concentrations above the WSDA assessment criteria. Of the 36 current-use insecticides that NRAS detected, 39% (14 insecticides) had a concentration detected that exceeded WSDA assessment criteria at least once.

The four statewide insecticide POCs identified in 2022 were bifenthrin, gamma-cyhalothrin, chlorpyrifos, and imidacloprid. This is the first 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. Similarly, this is the first year gamma-cyhalothrin has been identified as a statewide POC. It is used on crops like cereal grains, potatoes, pears, and some vegetables. 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 banned food and feed uses of the chemical. There were seven exceedances of chlorpyrifos found across two Central Washington sites and two Western Washington sites; many fewer exceedances in comparison to prior years (e.g. 81 in 2021). Imidacloprid, a neonicotinoid, has been a POC since 2017. This insecticide can be applied to over 250 commercial crop types and has residential uses; the exceedances and detections were found at all three monitoring regions as well. It is unknown by NRAS if the detections of imidacloprid that exceeded WSDA criteria were the result of applications to crops or residential uses.

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

- Acephate → methamidophos (detected at five monitoring sites),
- Fipronil → fipronil disulfinyl (detected at four monitoring sites),
  - → fipronil sulfide (detected at seven monitoring sites),
  - → fipronil sulfone (detected at eight monitoring sites),
- Malathion → malaoxon (detected at three monitoring sites),
- Oxamyl → oxamyl oxime (detected at two monitoring sites).

Degradate and Other Pesticide Detections

This group includes degradates of current-use pesticides as well as several other pesticide-related chemicals. Degradates represented 14% (654 detections) of total detections and pesticide-related chemicals represented less than 2% (81 detections) of total detections. Of the 20 degradates from current-use chemicals included in the laboratory analysis, 18 were detected in surface water samples. Each antimicrobial, insect repellent, synergist, and wood preservative tested for had at least one detection.

* See revision page Rev. 3 for watermark correction

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 2022

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	291	222 (76%)		17		0.00128 - 0.348
2-Hydroxyatrazine	290	110 (38%)		12		0.00158 - 0.0553
Tetrahydrophthalimide	288	56 (19%)		8		0.00156 - 1.36
AMPA	47	47 (100%)		3		0.138 - 5.77
Fipronil sulfide	291	43 (15%)		7		0.000959 - 0.0144
1-(3,4-Dichlorophenyl)-3-methylurea	290	42 (14%)		10		0.00372 - 0.121
Fipronil sulfone	291	25 (9%)		8		0.0022 - 0.0156
Desethylatrazine	290	25 (9%)		8		0.00285 - 0.0138
4-Nitrophenol	246	21 (9%)		8		0.0194 - 0.183
Oxamyl oxime	290	14 (5%)		2		0.0539 - 0.128
Malaoxon	290	12 (4%)	4	3	1	0.00398 - 0.207
Fipronil disulfinyl	291	11 (4%)		4		0.00173 - 0.0149
Methamidophos	290	10 (3%)		5		0.00213 - 0.728
Deisopropyl atrazine	290	6 (2%)		2		0.0126 - 0.039
Clethodim sulfoxide	290	4 (1%)		2		0.143 - 3.62
Clethodim sulfone	290	3 (1%)		2		0.116 - 0.322
Acetochlor ESA	290	2 (1%)		1		0.0429 - 0.0958
Methomyl oxime	290	1 (<1%)		1		0.0105 - 0.0105
Antimicrobial:						
Triclosan	291	1 (<1%)		1		0.0099 - 0.0099
Insect repellent:						
DEET	290	63 (22%)		14		0.00185 - 1.37
Synergist:						
Piperonyl butoxide	291	8 (3%)		5		0.00269 - 0.0316
Wood preservative:						
Pentachlorophenol	246	9 (4%)		3		0.0162 - 0.112

The most frequently detected degradate was 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil and fungicide fluopicolide) with 222 detections, followed by 2-hydroxyatrazine (a degradate of the herbicide atrazine) with 110 detections. The degradate 2,6-dichlorobenzamide was found ubiquitously throughout the season at all monitoring sites. The degradates detected that did not have a parent compound detected at any of the monitoring sites were acetochlor ESA, tetrahydrophthalimide, and 4-nitrophenol. Acetochlor ESA is the breakdown product of the herbicide acetochlor, tetrahydrophthalimide is the main breakdown product of the fungicide captan, and 4-nitrophenol is a breakdown product of several natural and synthetic products. Clethodim sulfone and clethodim sulfoxide are breakdown products of clethodim, an herbicide. In 2022, clethodim was not tested for due to analytical method compatibility issues.

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 63 times, was found at every monitoring site but three. The only federally registered uses of DEET are for application to horses, the human body, and clothing.

Legacy 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 3% (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 2022

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	291	85 (29%)	85	15	15	0.000676 - 0.0065
4,4'-DDE	291	46 (16%)	46	8	8	0.00137 - 0.0360
4,4'-DDT	291	33 (11%)	33	9	9	0.000794 - 0.0533
Fenarimol	291	1 (<1%)		1		0.00714 - 0.00714

One DDT degradate, 4,4'-DDD, was the most frequently detected legacy chemical with 85 detections, followed by another DDT degradate, 4,4'-DDE, with 46 detections. DDT or associated breakdown products were found at six of seven Western Washington sites, all seven 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'-DDE and 4,4'-DDD) accounted for 52% of the total exceedances detected in 2022. Of the 164 combined DDT exceedances, 66 (40%) were detected at the monitoring site on Brender Creek, where there was past use of the insecticide on orchards. Although every detection of 4,4'-DDT, 4,4'-DDE, and 4,4'-DDD exceeded the state water quality standards, these detections are not a result of current pesticide usage patterns.

Toxic Unit Analysis

A study by Broderius and Kahl (1985) found when a large number of chemicals are included in mixture experiments on organisms; an additive response is typically found (Lydy et al. 2004). One of the most common methods of assessing the additive effects of pesticide mixtures is by using toxic units (TUs). For this report, TUs were used to estimate the additive effects of pesticide mixtures, as described by Faust et al. in 1993 (in Lydy et al. 2004). To determine a TU for a sample, a criteria ratio is calculated for each pesticide detected in the sample by dividing the pesticide concentration by the corresponding pesticides LC_{50} or EC_{50} assessment criteria. Then, each of those ratios is summed to obtain an estimated TU for the whole sample. In this report, NRAS analyzed TU using the fish LC_{50}, invertebrate EC_{50}, and plant EC_{50} assessment criteria with WSDA's safety factor for a more conservative approach. If the TU ratio is above or equal to one, there is a higher possibility of lethal or sublethal effects on aquatic life. Of the 291 sampling events analyzed using TUs, there were 54 samples that had a TU above or equal to one. Of the 54 samples, four samples exceeded TUs

using fish criteria, 34 samples exceeded TUs using invertebrate criteria, and 16 samples exceeded TUs using plant criteria. The TU exceedances occurred at all monitoring sites. All 54 samples had exceeding TUs primarily due to an elevated concentration of one or two pesticides. The pesticides that contributed significantly to samples with TUs greater than or equal to one were gamma-cyhalothrin (TU ≥ 1 in 14 samples), diuron (TU ≥ 1 in 13 samples), and malathion (TU ≥ 1 in 12 samples). 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.

Nutrient Analysis

In 2022, we sampled nutrients at eight monitoring sites, two of which were sampled for the first time (Ahtanum Creek and Snipes Creek). Table 29 provides a summary of nutrient results at the eight sites. Collecting water samples for nutrient analysis (ammonia, nitrate+nitrite, orthophosphate, and total phosphorus) alongside samples for pesticide analysis provides an interpretive benefit for determining possible pathways of pesticide movement. For example, the concentration of nitrate in a particular sample may provide evidence as to the primary source of the water in a stream at a given point in time. Nitrate is a conservative constituent for which high concentrations typically occur in water that has percolated through agricultural soil and through subsurface drainage (Capel et al. 2018). If a high concentration for a particular pesticide occurs in the same sample that a relatively high nitrate concentration was found, it provides additional evidence that the pesticide may have entered the stream through a similar transport pathway or mechanism (Capel et al. 2018). Similarly, high pesticide concentrations occurring when SSC and/or total phosphorus concentrations are also high would suggest runoff/erosion is the primary transport pathway. The relationships described above are more evident with multiple years of data to assess, and since 2022 is the third 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 29 – Summary of 2022 nutrient sampling results

Nutrient	Monitoring site	Samples collected (n)	Detections (n) (% samples)	Detections exceeding criteria (n)	Median (mg/L)	Maximum (mg/L)
Ammonia as N	Ahtanum Creek	12	8 (67%)		0.014	0.024
	Upper Big Ditch	23	19 (83%)		0.137	0.304
	Dry Creek	12	10 (83%)		0.020	0.095
	Kamiache Creek	16	9 (56%)		0.017	0.076
	Marion Drain	28	12 (43%)		0.016	0.140
	Snipes Creek	17	10 (59%)		0.014	0.030
	Sulphur Creek	17	15 (88%)		0.014	0.111
	Thorn Creek	16	11 (69%)		0.029	0.137
Nitrate-nitrite as N	Ahtanum Creek	12	12 (100%)	12	0.151	0.433
	Upper Big Ditch	23	23 (100%)	23	0.453	2.60
	Dry Creek	12	12 (100%)	12	4.860	8.39
	Kamiache Creek	16	16 (100%)	16	5.590	6.80
	Marion Drain	28	28 (100%)	28	1.410	4.52
	Snipes Creek	17	17 (100%)	17	0.334	0.943
	Sulphur Creek	17	17 (100%)	17	4.230	7.73
	Thorn Creek	16	16 (100%)	16	6.240	7.10
Orthophosphate as P	Ahtanum Creek	12	12 (100%)	N/A	0.060	0.089
	Upper Big Ditch	24	21 (88%)	N/A	0.023	0.052
	Dry Creek	12	12 (100%)	N/A	0.132	0.208

Nutrient	Monitoring site	Samples collected (n)	Detections (n) (% samples)	Detections exceeding criteria (n)	Median (mg/L)	Maximum (mg/L)
	Kamiache Creek	16	16 (100%)	N/A	0.115	0.358
	Marion Drain	28	28 (100%)	N/A	0.082	0.268
	Snipes Creek	17	17 (100%)	N/A	0.023	0.042
	Sulphur Creek	17	17 (100%)	N/A	0.404	0.976
	Thorn Creek	16	16 (100%)	N/A	0.125	0.403
Total phosphorus as P	Ahtanum Creek	12	12 (100%)	12	0.082	0.238
	Upper Big Ditch	23	23 (100%)	23	0.103	0.134
	Dry Creek	12	12 (100%)	12	0.169	0.363
	Kamiache Creek	16	16 (100%)	16	0.132	0.372
	Marion Drain	28	28 (100%)	28	0.103	0.284
	Snipes Creek	17	17 (100%)	16	0.051	0.265
	Sulphur Creek	17	17 (100%)	17	0.447	0.711
	Thorn Creek	16	16 (100%)	16	0.150	0.414

All detections of nitrate-nitrite and total phosphorus except one total phosphorus detection in Snipes Creek 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 2024). 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 2022. Water samples were collected from the middle of March into November a total of 291 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, 125 unique pesticides were detected.
- NRAS detected pesticides in water samples a total of 4,687 times.
- Sulfentrazone and metolachlor were the most frequently detected herbicides (165 and 147 times, respectively).
- Thiamethoxam, diazinon, and flupyradifurone were the most frequently detected insecticides (79, 70, and 61 times, respectively).
- Boscalid, fludioxonil, and azoxystrobin were the most frequently detected fungicides (183, 128 and 95 times, respectively).
- Seven chemicals were detected at more than 50% of sampling events they were tested for. 2,6-dichlorobenzamide (a degradate) was detected at more than 76% 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 potential effects of pesticide exposure to aquatic life and endangered species, we compared detected pesticide concentrations to WSDA assessment criteria. There were 317 exceedances total with at least one exceedance at every monitoring site. Approximately 47% of the total exceedances (149 exceedances) were from 17 current-use pesticides. A summary of current-use pesticides with exceedances is below in Table 30. Every detection of seven pesticides exceeded WSDA assessment criteria; however, not every detection of the other ten pesticides did. Four detections of malaoxon, a breakdown product of malathion, exceeded criteria as well. Detections of legacy pesticides and associated degradates accounted for the remaining 52% (164 exceedances) of the total exceedances. DDT and/or one of its degradates tested for were detected at six Western Washington sites, ranging from one exceeding detection at the Lower Bertrand site to a maximum of 14 exceeding detections at the Lower Big Ditch site. In Central Washington and the Palouse region, DDT and/or one of its degradates were detected at nine sites; detections ranged from one exceedance at Marion Drain to a maximum of 66 exceedances at Brender Creek. Every detection of DDT exceeded WSDA assessment criteria.

Exceedances by current-use pesticide types are as follows.

- Out of 2,422 total herbicide detections, 17 detections exceeded criteria (<1%).
- Out of 758 total fungicide detections, no detection exceeded criteria (0%).
- Out of 607 total insecticide detections, 132 detections exceeded criteria (22%).

Table 30 – 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	103	13 (13%)	Herbicide
Imidacloprid	49	49 (100%)	Insecticide
Fipronil	31	12 (39%)	Insecticide
Malathion	31	12 (39%)	Insecticide
Clothianidin	31	11 (35%)	Insecticide
Dimethoate	29	1 (3%)	Insecticide
Chlorpyrifos	17	7 (41%)	Insecticide
gamma-Cyhalothrin	14	14 (100%)	Insecticide
Pyriproxyfen (Nylar)	10	4 (40%)	Insecticide
Bifenthrin	7	7 (100%)	Insecticide
Tefluthrin	7	6 (86%)	Insecticide
Tolfenpyrad	4	4 (100%)	Insecticide
Linuron	4	3 (75%)	Herbicide
Metsulfuron-methyl	3	1 (33%)	Herbicide
cis-Permethrin	2	2 (100%)	Insecticide
trans-Permethrin	2	2 (100%)	Insecticide
Fenvalerate	1	1 (100%)	Insecticide

In 2022, monitoring sites commonly contained mixtures of pesticides in samples. Approximately 99% of sampling events had two or more pesticide detections during the field season. The maximum number of detections (41) at a single sampling event occurred on June 6 at the Lower Big Ditch site. Although studies on the effects of pesticide mixtures are limited, there is evidence that indicates certain combinations of pesticides can have compounding adverse effects in aquatic systems (Broderius and Kahl, 1985). 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 15 of the 17 monitoring sites. Besides the sampling event on April 25 at Snipes Creek, 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 reduced the number of POCs identified. Identifying a smaller number of pesticides as statewide POCs allows for more consistent communication to pesticide applicators across the state. Maintaining watershed POC lists allows WSDA to communicate watershed-specific priorities based on results from each monitoring site. WSDA's statewide POCs were the 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.

Washington State had approximately 1,198 pesticide active ingredients (including pesticides, synergists, adjuvants, and additives) registered for use at the beginning of 2024 (WSPMRS 2024). Surface water samples in 2022 were tested for roughly 13% 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, and information from local and federal partners.

Generally speaking, pesticides are becoming more specific to the target organisms they are intended for. Insecticides usually have a low toxicity towards aquatic plants and vertebrates and a higher toxicity towards aquatic invertebrates. Meanwhile, herbicides and fungicides are often less toxic to fish and invertebrates but more toxic to aquatic plants. However, any pesticide at high enough concentrations in surface water can directly or indirectly affect ESA-listed salmonids. Invertebrates are the main food source of juvenile salmonids, and those invertebrates rely on aquatic plants to sustain their populations. If a pesticide is causing impairment to any organism, food webs and ecosystem functions can be potentially disrupted. Pesticide monitoring in Washington waterways is essential for understanding the fate and transport of pesticides that can cause water quality concerns. WSDA POCs should be given additional prioritization for management by WSDA and partners to ensure their concentrations are maintained or reduced below WSDA assessment criteria. WSDA will continue to 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 31a. The most recent versions of WAC 173-201A and EPA's NRWQC were included in the development of the assessment criteria. Pesticide detections at all monitoring sites were evaluated using freshwater assessment criteria.

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

- Fish:
  - ACR – Acute to chronic ratio
  - AS – Atlantic salmon
  - BS – Bluegill sunfish
  - BT – Brook trout
  - CC – Carp
  - CF – Catfish
  - CI – *Ctenopharyngodon idella* (grass carp)
  - FF – Flagfish
  - FM – Fathead minnow
  - JM – Japanese medaka
  - ND – Not described
  - OC – *Oncorhynchus clarkia* (cutthroat trout)
  - RT – Rainbow trout
- Invertebrate:
  - ACR – Acute to chronic ratio
  - CG – *Chloroperia grammatical* (stonefly)
  - CH – *Caenis horaria* (midge)
  - CL – *Cloeon dipterum* (midge)
  - CP – *Chironomus plumosus*
  - CR – *Chironomus riparius*
  - CT – *Chironomus tentans* (midge)
  - DD – *Ceriodaphnia dubia* (water flea)
  - DM – *Daphnia magna*
  - DP – Daphnia pulex
  - GF – *Gammarus fasciatus* (scud)
  - HA – *Hyalella azteca* (amphipod)
  - MATC – Maximum allowed toxic concentration
  - ND – Not described
  - PC – *Pteronarcys californica* (stonefly)
  - SV – *Simulium vittatum* (black fly)
- Aquatic plant:
  - AF – *Anabaena flos-aquae* (cyanobacteria)
  - AI – *Anabaena inaequalis* (blue-green cyanophyceae)
  - EN – *Elodea nuttali* (waterweed)
  - LG – *Lemna gibba*
  - LM – *Lemna minor*
  - ND – Not described
  - NP – *Navicula pelliculosa*
  - OL – *Oscillatoria lutea* (blue-green algae)
  - SC – *Pseudokirchneriella subcapitata*
  - SD – *Skeltonema costatum* (diatom)
  - SP – *Scenedesmus pannonicus*
  - SS – *Scendesmus subspicatus* (green algae)

In cases where different organisms were used for acute and chronic toxicity tests, the organism used for the acute test is noted first and the organism used for the chronic test is second. Table 31a contains only chemicals detected in 2022. Blank rows indicate detected chemicals with no WSDA assessment criteria. For a full list of all chemicals tested for, see Appendix B: 2022 Quality Assurance Summary.

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

Pesticide	Fish Endangered Species Acute	Fish Acute	Fish Chronic	Fish Spp.	Invertebrate Acute	Invertebrate Chronic	Invertebrate Spp.	Aquatic Plant Acute	Aquatic Plant Spp.	WAC Acute	WAC Chronic	NRWQC CMC	NRWQC 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				
Acetochlor ESA[8]	4500	45000		RT	31250		DM	4950	SC				
Aminocyclopyrachlor[9]	3000	30000	5500	BS/RT	9925	185	DM	3700	AF				
Aminomethylphosphoric acid (AMPA)[10]	12475	124750		RT	170750		DM						
Atrazine[11]	132.5	1325	2.5	RT/JM	180	30	DM/GF	0.5	OL				
Azoxystrobin[12]	11.75	117.5	73.5	RT/FM	65	22	DM	24.5	NP				
Bentazon[13]	4750	47500	4915	RT/FM	15575	50600	CR/DM	2250	SC				
Bifenazate[14]	14.5	145		BS	125	75	DM	445	SC				
Bifenthrin[15]	0.00375	0.0375	0.002	RT/ND	0.00012325	0.000025	HA	145	SC				
Boscalid[16]	67.5	675	58		1332.5	395		670					
Bromacil[17]	900	9000	1500	RT	30250	4100	DM	3.4	SC				
Bromoxynil[18]	52.5	525		RT	3977.5		DM						
Carbaryl[19]	5.5	55	3.4	AS/ACR	0.425	0.25	CG/ACR	170	SC			1.05	1.05
Carbendazim[20]	0.185	1.85	0.495	CF	27.5	1.55	DM	2290	SD				
Chlorantraniliprole[21]	345	3450	55	RT/RT	4.15	1.51	DM/DM	890	SC				
Chlorothalonil[22]	0.45	4.5	0.385	RT/FM	13.5	0.3	DM	6	NP				
Chlorpropham[23]	75.25	752.5		RT	927.5		DM						
Chlorpyrifos[24]	0.0425	0.425	0.1255	BS/FM	0.00345	0.0025	HA/DM	70		0.0415	0.0205	0.0415	0.0205

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Chlorsulfuron[25]	7500	75000	16000	RT	92500	10000	DM	0.175	LG				
cis-Permethrin[15]	0.01975	0.1975	0.026	BS/BS-ACR	0.00165	0.0021	HA	1.6	LG				
Clethodim sulfone													
Clethodim sulfoxide													
Clopyralid[26]	2575	25750	5000	RT/FM	58250	2350	DM	3450	SC				
Clothianidin[27]	2537.5	25375	4850	RT/FM	5.5	0.025	CR	32000					
Cyantraniliprole[28]	250	2500	5350	CF/RT	5.1	3.28	DM	5000	SD				
Cyprodinil[29]	54.5	545	115	BS/FM	8	4.1	DM	985	AF				
Dacthal (DCPA)[30]	165	1650		RT	4505		DM						
Deisopropyl atrazine[3]	425	4250			31500			1250					
Desethyl atrazine[3]								500					
Diazinon[31]	2.25	22.5	0.275	RT/BT	0.0525	0.085	DM	1850	SC			0.085	0.085
Dicamba acid[32]	700	7000	4950	RT/FM	25000	21000	DM	30.5	AF				
Dichlobenil[2]	123.25	1232.5	165	RT	1550	280	DM	15	LG				
Difenoconazole[33]	20.25	202.5	0.43	RT/FM	192.5	2.8	DM	49	NP				
Dimethoate[34]	155	1550	215	RT	10.75	0.25	PC	10000	AF				
Dinotefuran[35]	2477.5	24775	3180	CC/RT	242075	47650	DM	48800	SC				
Dithiopyr[36]	11.75	117.5	10	BS/FM	1300	40.5	DM	3.055	LG				
Diuron[37]	33	330	13.2	OC/FM	43.75	0.415	GF	0.065	LG				
Eptam[38]	350	3500	20	BS/FM-ACR	1625	400	DM	700	SC				
Ethalfluralin[39]	0.8	8	0.2	BS/RT	15	12	DM	3.65	LG				
Ethoprop[40]	7.5	75	12	RT/FM	11	0.4	DM	4200					
Etridiazole[41]	19.25	192.5	50.5	RT/FM	770	185	DM	36	SC				
Fenarimol[42]	22.5	225	90	RT	1700	56.5	DM	50	SC				
Fenbutatin oxide[43]	0.0425	0.425	0.155	RT	7.75	8	DM						
Fenvalerate[15]	0.00355	0.0355	0.0085	BS/FM	0.000212	0.00001545	HA	2.8	SC				
Fipronil[44]	2.075	20.75	3.3	BS/RT	0.055	0.0055	SV/ACR	38	SS				
Fipronil disulfinyl[44]	0.5	5	0.265	BS/ACR	88.75	20.5	DM/DD	38	SC				
Fipronil sulfide[44]	0.77	7.7	0.415	BS/BS-ACR	25	2.58	DM/ND	38	SS				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Fipronil sulfone[44]	0.625	6.25	0.335	BS/BS-ACR	7.25	0.11	DM/DM	38	SS				
Fludioxonil[45]	11.75	117.5	9	RT/FM	225	7	DM	140	SC				
Flumioxazin[46]	57.5	575	0.255	RT/FM	1375	14	DP/DM	0.245	LG				
Fluopicolide[47]	8.725	87.25	75.5	RT/FM	425	95	DM	1300	SC				
Flupyradifurone													
gamma-Cyhalothrin[15]	0.000725	0.00725		BS	0.00002	0.000965	HA	0.254	LG				
Glyphosate[10]	1075	10750	12850	BS/FM	13300	24950	CP/DM	5950	LG				
Hexazinone[48]	6850	68500	8500	RT/FM	37900	10000	DM	3.5	SC				
Hexythiazox[49]	3	30		RT		3.05	DM	60	LG				
Imazapic[50]	2500	25000	48000	RT/FM	25000	48000	DM	3.11	LM				
Imazapyr[51]	2500	25000	21550	RT/FM	25000	48550	DM	12	LM				
Imidacloprid[52]	5725	57250	4500	RT	0.1925	0.005	CL/CH						
Indaziflam[53]								0.0305	LG				
Inpyrfluxam[54]	0.775	7.75	2.45	RT/RT-ACR	275	70	DM	365	LG				
Isoxaben[55]	25	250	200	RT	325	345	DM	5	LG				
Linuron[56]	75	750	2.79	RT	30	0.045	DM	1.25	EN				
Malaoxon[57]	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020					0.05
Malathion[57]	0.1025	1.025	4.3	RT/FF	0.0245	0.03	DM	1020					0.05
MCPA[58]								85	SC				
Mecoprop (MCPP)[59]	2325	23250		RT	22750	25400	DM	7	SC				
Metalaxyl[60]	3250	32500	4550	RT/FM	7000	600	DM	42500	LG				
Methamidophos[61]	625	6250	86.8	RT	6.5	2.25	DM	25000	SD				
Methiocarb[62]	4.5	45	25	BS	1.375								
Methomyl[63]	12.5	125	28.5	CF/FM	2.2	0.3	DM/MATC						
Methomyl oxime													
Methoxyfenozide[64]	105	1050	265	RT/FM	14.25	1.55	CR	1700	SC				
Metolachlor[65]	80	800	15	BS/FM	5875	1600	DM	4	SC				
Metribuzin[66]	1050	10500	1500	RT	1050	645	DM	4.05					
Metsulfuron-methyl[67]	3750	37500	2250	BS	37500		DM	0.18	LG				

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Myclobutanil[68]	60	600	110	BS/BS-ACR	2750	1950	DM	61	SD				
N,N-Diethyl-m-toluamide (DEET)[69]	1875	18750		RT	18750		DM						
Napropamide[70]	300	3000	550	BS/RT	6175	550	DM	175	LM				
Norflurazon[71]	202.5	2025	385	RT	3750	500	DM	3.015	NP				
Oxadiazon[72]	30	300	0.44	RT	600	15	DM	2.6	SC				
Oxamyl[73]	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Oxamyl oxime[73]	105	1050	250	RT/FM	45	13.5	ACR	60	SC				
Paclobutrazol[74]	397.5	3975	24.5	CI/RT	60	4.5	DM	4	LG				
Pendimethalin[75]	3.45	34.5	3.15	RT/FM	70	7.25	DM	2.6	SC				
Pentachlorophenol[76]	0.375	3.75	5.5	RT	23	2.05	DM	25	SC			9.5	7.5
Phosmet[77]	1.75	17.5	0.5	RT/FM	2.16	0.375	DM	70	NP				
Picloram[78]	137.5	1375	275	RT	8600	5900	DM	17450	SC				
Piperonyl butoxide (PBO)[79]	72.5	725	3.9	RT/FM	10.55	15	HA/DM	605	SC				
Prometon[80]	490	4900	3265	RT/RT-ACR	6425	1725	DM	49	SC				
Prometryn[81]	72.75	727.5	310	RT/FM	2425	500	DM	0.52	NP				
Propiconazole[82]	21.25	212.5	7.5	RT/FM-ACR	1200	90	DM	10.5	ND				
Pyraclostrobin[83]	0.155	1.55	1.175	RT	3.925	2	DM	0.75	NP				
Pyridaben[84]	0.018	0.18	0.0435	RT	0.1325	0.022	DM	8.1	LG				
Pyrimethanil[85]	252.5	2525	10	RT	750	500	DM	900	ND				
Pyriproxyfen (Nylar)[86]	8.25	82.5	2.15	RT	100	0.0075	DM	0.09	LG				
Simazine[87]	160	1600	30	FM	250	20	DM/ACR	3	SC				
Spirotetramat[88]	35.25	352.5	267	RT/FM	165	50	CT	180	NP				
Sulfentrazone[89]	2345	23450	1475	BS/RT	15100	100	DM	14.4	SC				
Sulfometuron-methyl[90]	3700	37000		RT	37500	48500	DM	0.225	LG				
Sulfoxaflor[91]	9075	90750	330	BS/FM	100000	25250	DM	40600	NP				
tau-Fluvalinate[92]	0.00875	0.0875	0.032	CC/FM	0.235	0.05	DM						
Tebuthiuron[93]	2650	26500	4650	FM	74250	10900	DM	25	SC				
Tefluthrin[94]	0.0015	0.015	0.002	RT/FM	0.0175	0.004	DM						

Pesticide	Fish				Invertebrate			Aquatic Plant		WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Acute	Chronic	Spp.	Acute	Spp.	Acute	Chronic	CMC	CCC
Terbacil [95]	1155	11550	600	RT	16250	25	DM	5.5	NP				
Tetrahydrophthalimide (THPI)[96]	3000	30000		RT	28250		DM	90500	SC				
Thiamethoxam[97]	2850	28500	10000	BS/RT	8.75	0.37	CR	45100	LM				
Tolfenpyrad[98]	0.004075	0.04075	0.094	RT/FM	0.25	0.122	DM	5	SC				
trans-Permethrin[15]	0.01975	0.1975	0.026	BS/BS-ACR	0.00165	0.0021	HA	1.6	LG				
Triadimefon[99]	102.5	1025	20.5	RT	400	26	DM	550	LG				
Triallate[100]	30	300	19	RT	22.75	7	DM	10.5	SC				
Triclopyr acid[101]	2925	29250	37200	RT/FM	33250	28850	DM	2100	AF				
Triclopyr butoxyethyl ester[101]	9	90	13	BS/RT	87.5	85	DM	50	NP				
Triclosan[102]	7.2	72		FM	97.5		DM	0.35	SS				
Trifloxystrobin[103]	0.3575	3.575	2.15	RT	6.325	1.38	DM	18.55	SC				
Trifluralin[104]	0.4625	4.625	0.95		62.75	1.2		10.95					

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Appendix B: 2022 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 2022, QA/QC samples were 11% of all the samples collected in the field. There were 225 QC samples in total: 100 field replicates, 72 field blanks, 34 MS/MSD samples, and 19 conductivity check samples. The lab contributed the remaining LCS/LCSD and method blank samples.

Data Qualification

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

The Manchester Environmental Laboratory (MEL) qualify all sample results based on the analysis of LCS/LCSDs, MS/MSDs, surrogates, and method blanks. LCS/LCSD were generated by adding analytes at known concentrations to purified water free of all organics. An LCS/LCSD pair was extracted and analyzed with every batch of field samples and other QC samples. They were used to evaluate method performance for a specific analyte and to check for bias and precision of the lab's extraction and analytical processes. Detections from a batch may be qualified based on high/low recovery and/or high RPD between the paired LCS and LCSD. Similarly, samples collected in the field that had analytes added at known concentrations and analyzed are MS/MSD samples. The analysis of this type of QC sample can assess the potential for matrix interactions or interaction between analytes within field samples that can affect analytical results. Staff collected an MS/MSD sample once during the season at each site for at least one pesticide analytical method. In 2022, all pesticide and nutrient analytes tested for during the season were used to spike MS/MSDs and LCS/LCSDs, although the lab rotated between two spike mixtures for the GCMS-Pesticides analytical method to avoid coelution of analytes. Surrogates are analytes not normally found in environmental samples that were spiked into all field and QC samples to evaluate recoveries for groups of organic compounds. Results of surrogates can evaluate extraction efficiency and matrix interference within the sample.

WSDA staff qualify the remainder of the field sample data based on field replicates, field blanks, and MS/MSD results. Field replicates were used to evaluate variability in analytical results. No field sample results were qualified solely due to field replicate results in 2022. 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 2022) and standard deviation are presented in Table 32b.

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

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Method: LCMS-Pesticides; Reporting Limit: LLOQ				
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	2.01E+01	2.28E+00
Acetamiprid	135410-20-7	Insecticide	2.00E+01	0.00E+00
Acetochlor ESA	187022-11-3	Degradate	1.06E+02	2.43E+01
Afidopyropen	915972-17-7	Insecticide	2.00E+02	0.00E+00
Aminocyclopyrachlor	858956-08-8	Herbicide	1.21E+02	7.58E+01
Azoxystrobin	131860-33-8	Fungicide	2.01E+01	2.32E+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	1.01E+01	5.43E-01
Chlorantraniliprole	500008-45-7	Insecticide	5.00E+01	0.00E+00
Chlorsulfuron	64902-72-3	Herbicide	1.00E+02	0.00E+00
Clethodim sulfone	111031-17-5	Degradate	1.00E+02	0.00E+00
Clethodim sulfoxide	111031-14-2	Degradate	1.00E+02	0.00E+00
Clothianidin	210880-92-5	Insecticide	1.00E+02	0.00E+00
Cyantraniliprole	736994-63-1	Insecticide	1.00E+02	0.00E+00
Cyprodinil	121552-61-2	Fungicide	1.00E+01	0.00E+00
Deisopropyl atrazine	1007-28-9	Degradate	1.06E+01	2.45E+00
Desethyl atrazine	6190-65-4	Degradate	1.00E+01	0.00E+00
Difenoconazole	119446-68-3	Fungicide	2.34E+01	1.32E+01
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	1.00E+02	0.00E+00
Dinotefuran	165252-70-0	Insecticide	2.00E+01	0.00E+00
Diuron	330-54-1	Herbicide	1.00E+01	0.00E+00
Fenbutatin oxide	13356-08-6	Insecticide	4.58E+01	3.83E+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	1.04E+02	5.34E+01
Imidacloprid	138261-41-3	Insecticide	2.00E+01	0.00E+00
Indaziflam	950782-86-2	Herbicide	1.00E+01	0.00E+00
Inpyrfluxam	1352994-67-2	Fungicide	5.00E+01	0.00E+00
Isoxaben	82558-50-7	Herbicide	1.00E+01	0.00E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
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	2.25E+01	1.41E+01
Methiocarb	2032-65-7	Insecticide	2.00E+01	0.00E+00
Methomyl	16752-77-5	Insecticide	1.20E+01	5.40E+00
Methomyl oxime	13749-94-5	Degradate	1.00E+02	0.00E+00
Methoxyfenozide	161050-58-4	Insecticide	1.00E+01	0.00E+00
Metsulfuron-methyl	74223-64-6	Herbicide	5.00E+01	0.00E+00
Myclobutanil	88671-89-0	Fungicide	2.00E+01	0.00E+00
Oryzalin	19044-88-3	Herbicide	2.13E+02	6.15E+01
Oxamyl	23135-22-0	Insecticide	1.00E+01	0.00E+00
Oxamyl oxime	30558-43-1	Degradate	1.00E+02	0.00E+00
Paclobutrazol	76738-62-0	Fungicide	1.01E+01	9.68E-01
Propiconazole	60207-90-1	Fungicide	5.03E+01	5.74E+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	5.66E+02	3.08E+02
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	3.38E+02	4.42E+02
Tolfenpyrad	129558-76-5	Insecticide	5.00E+01	0.00E+00
Trifloxystrobin	141517-21-7	Fungicide	2.01E+01	3.08E-01
Method: LCMS-Glyphos; Reporting Limit: LLOQ				
AMPA	1066-51-9	Degradate	1.76E+01	4.56E+00
Glufosinate-ammonium	77182-82-2	Herbicide	6.51E+00	1.14E-01
Glyphosate	1071-83-6	Herbicide	6.54E+00	6.60E-02
Method: GCMS-Herbicides; Reporting Limit: LLOQ				
2,4-D	94-75-7	Herbicide	6.29E+01	3.55E+01
4-Nitrophenol	100-02-7	Degradate	6.06E+01	1.68E+00
Bentazon	25057-89-0	Herbicide	6.06E+01	1.69E+00
Bromoxynil	1689-84-5	Herbicide	6.06E+01	1.68E+00
Clopyralid	1702-17-6	Herbicide	6.06E+01	1.69E+00
Dacthal (DCPA)	1861-32-1	Herbicide	6.06E+01	1.69E+00
Dicamba acid	1918-00-9	Herbicide	6.06E+01	1.68E+00
Dichlorprop	120-36-5	Herbicide	6.06E+01	1.68E+00
MCPA	94-74-6	Herbicide	6.06E+01	1.73E+00
Mecoprop (MCPP)	93-65-2	Herbicide	6.06E+01	1.70E+00
Pentachlorophenol	87-86-5	Wood Preservative	6.06E+01	1.68E+00
Picloram	1918-02-1	Herbicide	3.03E+02	8.57E+00
Triclopyr acid	55335-06-3	Herbicide	6.07E+01	1.75E+00

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
Method: GCMS-Pesticides; Reporting Limit: LLOQ				
2,6-Dichlorobenzamide	2008-58-4	Degradate	6.64E+00	3.99E+00
4,4'-DDD	72-54-8	Degradate	5.04E+00	1.07E-01
4,4'-DDE	72-55-9	Degradate	5.05E+00	1.09E-01
4,4'-DDT	50-29-3	Insecticide	5.21E+00	6.72E-01
Acetochlor	34256-82-1	Herbicide	5.04E+00	1.06E-01
Atrazine	1912-24-9	Herbicide	5.05E+00	1.16E-01
Bifenazate	149877-41-8	Insecticide	5.81E+00	1.82E+00
Bifenthrin	82657-04-3	Insecticide	5.04E+00	1.07E-01
Boscalid	188425-85-6	Fungicide	5.06E+00	1.21E-01
Bromacil	314-40-9	Herbicide	5.05E+00	1.13E-01
Captan	133-06-2	Fungicide	5.05E+00	1.12E-01
Chlorothalonil	1897-45-6	Fungicide	5.04E+00	1.07E-01
Chlorpropham	101-21-3	Herbicide	5.04E+00	1.06E-01
Chlorpyrifos	2921-88-2	Insecticide	5.04E+00	1.07E-01
cis-Permethrin	54774-45-7	Insecticide	5.04E+00	1.06E-01
Cyfluthrin-Total	68359-37-5	Insecticide	5.04E+00	1.06E-01
Cypermethrin-Total	52315-07-8	Insecticide	5.04E+00	1.06E-01
Deltamethrin	52918-63-5	Insecticide	5.04E+00	1.06E-01
Diazinon	333-41-5	Insecticide	5.05E+00	1.10E-01
Dichlobenil	1194-65-6	Herbicide	5.05E+00	1.15E-01
Dichlorvos (DDVP)	62-73-7	Insecticide	5.04E+00	1.06E-01
Dicofol	115-32-2	Insecticide	2.52E+01	5.23E-01
Dimethoate	60-51-5	Insecticide	5.04E+00	1.02E-01
Dithiopyr	97886-45-8	Herbicide	5.04E+00	1.07E-01
Eptam	759-94-4	Herbicide	5.08E+00	2.90E-01
Ethalfluralin	55283-68-6	Herbicide	5.04E+00	1.06E-01
Ethoprop	13194-48-4	Insecticide	5.59E+00	2.16E+00
Etoxazole	153233-91-1	Insecticide	1.51E+01	3.16E-01
Etridiazole	2593-15-9	Fungicide	5.04E+00	1.06E-01
Fenarimol	60168-88-9	Fungicide	1.35E+01	8.12E+00
Fenpropathrin	39515-41-8	Insecticide	5.04E+00	1.06E-01
Fenvalerate	51630-58-1	Insecticide	5.04E+00	1.06E-01
Fipronil	120068-37-3	Insecticide	5.04E+00	1.08E-01
Fipronil disulfinyl	205650-65-3	Degradate	5.04E+00	1.07E-01
Fipronil sulfide	120067-83-6	Degradate	5.04E+00	1.07E-01
Fipronil sulfone	120068-36-2	Degradate	1.01E+01	2.09E-01
Fludioxonil	131341-86-1	Fungicide	5.05E+00	1.23E-01
Flumioxazin	103361-09-7	Herbicide	2.52E+01	5.38E-01
Fluroxypyr 1-methylheptyl ester	81406-37-3	Herbicide	2.52E+01	5.23E-01
gamma-Cyhalothrin	76703-62-3	Insecticide	5.04E+00	1.06E-01
Hexazinone	51235-04-2	Herbicide	5.10E+00	1.91E-01
Malathion	121-75-5	Insecticide	5.05E+00	1.09E-01
Metalaxyl	57837-19-1	Fungicide	1.11E+01	4.75E+00
Metolachlor	51218-45-2	Herbicide	6.03E+00	2.70E+00
Metribuzin	21087-64-9	Herbicide	5.04E+00	9.39E-02

Analyte	CAS number	Pesticide type	Mean LLOQ or MRL	Standard deviation
N,N-Diethyl-m-toluamide	134-62-3	Insect Repellent	1.71E+01	2.07E+01
Napropamide	15299-99-7	Herbicide	5.05E+00	1.09E-01
Norflurazon	27314-13-2	Herbicide	5.05E+00	1.09E-01
Oxadiazon	19666-30-9	Herbicide	5.04E+00	1.06E-01
Oxyfluorfen	42874-03-3	Herbicide	5.04E+01	1.06E+00
Pendimethalin	40487-42-1	Herbicide	5.04E+00	1.07E-01
Pentachloronitrobenzene (PCNB)	82-68-8	Fungicide	5.04E+00	1.06E-01
Phosmet	732-11-6	Insecticide	5.04E+00	1.06E-01
Piperonyl butoxide (PBO)	51-03-6	Synergist	5.05E+00	1.06E-01
Prodiamine	29091-21-2	Herbicide	2.52E+01	5.23E-01
Prometon	1610-18-0	Herbicide	5.05E+00	1.11E-01
Prometryn	7287-19-6	Herbicide	1.01E+01	2.08E-01
Propargite	2312-35-8	Insecticide	1.01E+01	2.08E-01
Pyridaben	96489-71-3	Insecticide	5.04E+00	1.06E-01
Pyriproxyfen (Nylar)	95737-68-1	Insecticide	1.01E+01	2.09E-01
Simazine	122-34-9	Herbicide	1.01E+01	2.23E-01
Simetryn	1014-70-6	Herbicide	2.52E+01	5.23E-01
Sulfentrazone	122836-35-5	Herbicide	8.41E+00	7.05E+00
tau-Fluvalinate	102851-06-9	Insecticide	5.04E+00	1.06E-01
Tebuthiuron	34014-18-1	Herbicide	1.01E+01	2.15E-01
Tefluthrin	79538-32-2	Insecticide	5.04E+00	1.06E-01
Terbacil	5902-51-2	Herbicide	5.05E+00	1.18E-01
Tetrahydrophthalimide (THPI)	27813-21-4	Degradate	5.05E+00	1.11E-01
Tetramethrin	7696-12-0	Insecticide	5.04E+00	1.06E-01
Tralomethrin	66841-25-6	Insecticide	5.04E+00	1.06E-01
trans-Permethrin	61949-77-7	Insecticide	5.04E+00	1.06E-01
Triadimefon	43121-43-3	Fungicide	5.05E+00	1.06E-01
Triallate	2303-17-5	Herbicide	5.04E+00	1.01E-01
Triclopyr butoxyethyl ester	64700-56-7	Herbicide	1.01E+01	2.08E-01
Triclosan	3380-34-5	Antimicrobial	3.04E+01	1.97E+01
Trifluralin	1582-09-8	Herbicide	1.01E+01	2.08E-01
Various Methods; Reporting Limit: MRL				
Specific conductivity			1.50E+01	
Suspended sediment concentration			9.95E-01	2.13E-02
Ammonia	7664-41-7	Nutrient	3.93E-02	5.98E-02
Nitrate-Nitrite as N		Nutrient	4.10E-02	3.57E-02
Ortho phosphate		Nutrient	1.42E-02	2.05E-02
Total phosphorus		Nutrient	1.00E-02	1.46E-06

Data qualifiers describe the level of confidence associated with the data points. Laboratory data was qualified according to the National Functional Guidelines for Organic Data Review (EPA 2017), Manchester Environmental Lab's data qualification criteria and professional judgement. The Manchester Environmental Lab provides a list of data qualifiers and their definitions in Table 33b that are used for sample analysis of pesticides, SSC, nutrients, and specific conductivity (MEL 2016).

Table 33b – Data qualification definitions

Qualifier	Definition
	The analyte was positively identified and was detected at the reported concentration.
E	Reported result is an estimate because it exceeds the calibration range.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
N	The analysis indicates the presence of an analyte for which there is presumptive evidence to make a “tentative identification”.
NJ	The analysis indicates the presence of an analyte that has been “tentatively identified,” and the associated numerical value represents its approximate concentration.
NAF	Not analyzed for.
NC	Not calculated.
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
U	The analyte was not detected at or above the reported sample quantitation limit.
UJ	The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

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

Analytical Quality Assurance and Quality Control Sample Summaries

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

Field Replicate Results

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

During 2022, 5% of pesticide, nutrient, and SSC samples were field replicates, which were evaluated using RPD control limits and detection rate variability. There were 239 consistently identified pairs for pesticide analysis, 27 consistently identified pairs for nutrient analysis, and 16 consistently identified pairs for SSC analysis. Consistently identified pairs are those where the analytes were identified in both the original sample and field replicate with unqualified, *J,* and *E* results. Conversely, inconsistently identified replicate pairs are those where the analyte was detected in only one of the two samples collected. Only 61 inconsistently identified pairs for pesticide analysis, 2 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 34b presents the variability of detections in field replicates with at least one detection in a replicate pair. RPDs were only calculated for consistently identified replicate pairs. Variability of detection and RPDs could not be calculated for the 70 analytes without replicate detections and, therefore, are not found in Table 34b.

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

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
4-Nitrophenol	GCMS-Herbicides	31	0		1	100
Acephate	LCMS-Pesticides	33	0		1	100
Chlorantraniliprole	LCMS-Pesticides	32	0		2	100
Dacthal (DCPA)	GCMS-Herbicides	31	0		1	100
Ethoprop	GCMS-Pesticides	33	0		1	100
Fenarimol	GCMS-Pesticides	33	0		1	100
Fenvalerate	GCMS-Pesticides	33	0		1	100
gamma-Cyhalothrin	GCMS-Pesticides	33	0		1	100
Indaziflam	LCMS-Pesticides	32	0		2	100

* See revisions page Rev. 4 for revised table 34b

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Linuron	LCMS-Pesticides	33	0		1	100
Methomyl oxime	LCMS-Pesticides	33	0		1	100
Methoxyfenozide	LCMS-Pesticides	33	0		1	100
Oxamyl oxime	LCMS-Pesticides	33	0		1	100
Paclobutrazol	LCMS-Pesticides	33	0		1	100
Picloram	GCMS-Herbicides	30	0		2	100
Pyridaben	GCMS-Pesticides	33	0		1	100
Pyriproxyfen (Nylar)	GCMS-Pesticides	33	0		1	100
tau-Fluvalinate	GCMS-Pesticides	33	0		1	100
Tefluthrin	GCMS-Pesticides	33	0		1	100
Triclosan	GCMS-Pesticides	33	0		1	100
Clopyralid	GCMS-Herbicides	29	1	27	2	67
Desethyl atrazine	LCMS-Pesticides	31	1	21	2	67
1-(3,4-Dichlorophenyl)-3-methylurea	LCMS-Pesticides	29	2	17	3	60
4,4'-DDE	GCMS-Pesticides	30	2	4	2	50
Deisopropyl atrazine	LCMS-Pesticides	32	1	22	1	50
Fipronil sulfone	GCMS-Pesticides	32	1	20	1	50
Sulfometuron-methyl	LCMS-Pesticides	32	1	1	1	50
Carbendazim	LCMS-Pesticides	27	4	6	3	43
Propiconazole	LCMS-Pesticides	29	3	11	2	40
4,4'-DDD	GCMS-Pesticides	26	5	33	3	38
4,4'-DDT	GCMS-Pesticides	31	2	8	1	33
Ammonia	Ammonia-N (NH3)	10	4	19	2	33
Tetrahydrophthalimide	GCMS-Pesticides	28	4	16	2	33
Flupyradifurone	LCMS-Pesticides	30	3	3	1	25
Norflurazon	GCMS-Pesticides	30	3	10	1	25
Pendimethalin	GCMS-Pesticides	26	6	8	2	25
Sulfentrazone	GCMS-Pesticides	22	9	11	3	25
Thiamethoxam	LCMS-Pesticides	30	3	8	1	25
Imazapyr	LCMS-Pesticides	29	4	3	1	20
Tebuthiuron	GCMS-Pesticides	28	5	11	1	17

Analyte	Analytical method	Consistent non-detect pairs (n)	Consistent identified pairs (n)	Mean RPD (%) consistent identified pairs	Inconsistent identified pairs (n)	Inconsistent identified pairs (%)
Atrazine	GCMS-Pesticides	27	6	7	1	14
Azoxystrobin	LCMS-Pesticides	26	7	9	1	13
Hexazinone	GCMS-Pesticides	25	8	6	1	11
Boscalid	GCMS-Pesticides	23	10	7	1	9
2,4-D	GCMS-Herbicides	20	11	24	1	8
2,6-Dichlorobenzamide	GCMS-Pesticides	22	12	5	0	0
2-Hydroxyatrazine	LCMS-Pesticides	28	6	10	0	0
Aminomethylphosphoric acid (AMPA)	LCMS-Glyphos	2	2	26	0	0
Bentazon	GCMS-Herbicides	29	3	6	0	0
Bromacil	GCMS-Pesticides	29	5	15	0	0
Bromoxynil	GCMS-Herbicides	30	2	14	0	0
Chlorpropham	GCMS-Pesticides	33	1	26	0	0
Clothianidin	LCMS-Pesticides	33	1	10	0	0
Cyantraniliprole	LCMS-Pesticides	33	1	14	0	0
Diazinon	GCMS-Pesticides	30	4	3	0	0
Dicamba acid	GCMS-Herbicides	22	10	11	0	0
Dichlobenil	GCMS-Pesticides	27	7	9	0	0
Dimethoate	GCMS-Pesticides	31	3	6	0	0
Dinotefuran	LCMS-Pesticides	31	3	6	0	0
Diuron	LCMS-Pesticides	28	6	14	0	0
Eptam	GCMS-Pesticides	31	3	7	0	0
Fipronil	GCMS-Pesticides	33	1	20	0	0
Fipronil sulfide	GCMS-Pesticides	31	3	5	0	0
Fludioxonil	GCMS-Pesticides	29	5	5	0	0
Fluopicolide	LCMS-Pesticides	33	1	38	0	0
Glyphosate	LCMS-Glyphos	2	2	19	0	0
Imidacloprid	LCMS-Pesticides	31	3	12	0	0
Malathion	GCMS-Pesticides	32	2	3	0	0
MCPA	GCMS-Herbicides	30	2	5	0	0
Mecoprop (MCPP)	GCMS-Herbicides	28	4	6	0	0
Metalaxyl	GCMS-Pesticides	32	2	18	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 (%)
Metolachlor	GCMS-Pesticides	27	7	4	0	0
Metribuzin	GCMS-Pesticides	28	6	9	0	0
N,N-Diethyl-m-toluamide	GCMS-Pesticides	30	4	7	0	0
Napropamide	GCMS-Pesticides	33	1	10	0	0
Nitrate-Nitrite as N	Nitrate+Nitrite-N	8	8	7	0	0
Ortho phosphate	Phosphate, Ortho- (OP)	8	8	4	0	0
Oxamyl	LCMS-Pesticides	33	1	4	0	0
Pentachlorophenol	GCMS-Herbicides	31	1	5	0	0
Prometon	GCMS-Pesticides	30	4	6	0	0
Pyraclostrobin	LCMS-Pesticides	33	1	7	0	0
Pyrimethanil	LCMS-Pesticides	31	3	5	0	0
Simazine	GCMS-Pesticides	29	5	10	0	0
Suspended sediment concentration	SSC	16	16	6	0	0
Terbacil	GCMS-Pesticides	29	5	11	0	0
Total phosphorus	Phosphorus, Total	7	7	1	0	0
Triclopyr acid	GCMS-Herbicides	28	4	5	0	0
Trifloxystrobin	LCMS-Pesticides	33	1	13	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 63% of analytes (55 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 10%. Of the 239 consistently identified replicate pairs for pesticides, six had RPDs that were equal to or greater than the 40% RPD criterion. For SCC analysis, of the 16 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 6%. Of the 27 consistently identified nutrient pairs, two had an RPD that was equal to or greater than the 20% RPD criterion. Results for field sample and replicate detections were not qualified as a result of the replicate analysis because RPD has limited effectiveness in assessing variability at low levels (Mathieu 2006). When concentrations are low, the RPD may be large even though the actual difference between the pairs is low. The remaining data for pesticide, nutrient, and SSC field replicates were of acceptable data quality.

The majority of the 63 inconsistently identified pairs were detections at concentrations between the LLOQ and the method detection limit (MDL) (below which the laboratory is unable to distinguish between instrument response due to the presence of analytes or background noise). Most of these replicate pairs consisted of a *J* qualified detection and a *U* or *UJ* qualified detection. There were no sample detections qualified due solely to inconsistent field replicate results.

Field Blank Results

Field blank detections indicate the potential for sample contamination in the field and laboratory or the potential for false detections due to analytical error. In 2022, there were nine detections in the 72 field blank samples collected for nutrients, SSC, and pesticide analysis (Table 35b). If a detection occurred in a field blank, all sample detections of the same analyte in the analytical batch were reviewed for qualification. Sample detection concentrations that were greater than five times the field blank detection concentration were not qualified. Sample detections with concentrations that were lower than five times the field blank detection concentration were re-qualified to *U*. There were 40 sample detections qualified to *U* in 2022 due to field blank detections.

Table 35b – Analyte detections in field blanks

Sampling date	Monitoring site	Analytical method	Analyte	Result (ng/L)	Reporting limit (ng/L)	MDL (ng/L)	Qualifier
4/19	Lower Bertrand Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	3.15	5	1.28	J
5/17	Lower Big Ditch	GCMS-Pesticides	2,6-Dichlorobenzamide	3.36	5	1.28	J
6/6	Indian Slough	GCMS-Pesticides	2,6-Dichlorobenzamide	3.45	5	1.28	J
9/21	Burnt Bridge Creek	GCMS-Pesticides	2,6-Dichlorobenzamide	2.75	5.1	1.31	J
10/24	Thorn Creek	Ammonia-N (NH3)	Ammonia	0.05	0.05	-	
4/5	Stemilt Creek	GCMS-Pesticides	DEET	10.8	5	1.33	
5/3	Brender Creek	GCMS-Pesticides	DEET	18.3	5	1.33	
5/17	Lower Big Ditch	GCMS-Pesticides	DEET	4.08	5	1.33	J
3/28	Snipes Creek	GCMS-Pesticides	Metalaxyl	6.66	10	4.77	J

Matrix Spike/Matrix Spike Duplicate Results

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

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

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
1-(3,4-Dichlorophenyl)-3-methylurea	20	65	135	109	99 - 123	0	0	10	4.64	0.2 - 17	47
2,4-D	18	34	125	92	71 - 139	0	1	9	7.56	2 - 15	159
2,6-Dichlorobenzamide	24	60	140	124	96 - 144	0	3	12	5.48	0.8 - 20	241
2-Hydroxyatrazine	20	52	176	109	92 - 131	0	0	10	3.95	0.5 - 15	117
4,4'-DDD	24	60	140	117	101 - 140	0	0	12	4.38	0.1 - 15	90
4,4'-DDE	24	60	140	91	75 - 118	0	0	12	6.97	0.6 - 15	48
4,4'-DDT	24	44	140	93	65 - 127	0	0	12	7.30	0.6 - 15	35
4-Nitrophenol	18	19	186	112	74 - 152	0	0	9	7.21	0.1 - 21	21
Acephate	20	59	135	97	78 - 110	0	0	10	6.30	2 - 16	17
Acetamiprid	20	65	163	132	111 - 156	0	0	10	5.50	0.3 - 15	16
Acetochlor	24	60	140	128	116 - 140	0	0	12	4.33	1 - 18	
Acetochlor ESA	20	57	156	117	90 - 158	0	1	10	5.76	0.01 - 11	2
Afidopyropen	20	60	135	112	92 - 139	0	2	10	6.40	1 - 20	
Aminocyclopyrachlor	20	10	250	118	77 - 176	0	0	10	6.04	0.5 - 16	1
AMPA	6	50	150	104	93 - 117	0	0	3	8.67	1 - 16	49
Atrazine	24	60	140	114	100 - 129	0	0	12	5.42	1 - 20	135
Azoxystrobin	20	57	153	103	87 - 140	0	0	10	9.00	1 - 23	104
Bensulide	20	35	135	114	76 - 183	0	4	10	13.90	2 - 29	
Bentazon	18	36	145	99	71 - 145	0	0	9	6.83	0.5 - 20	65
Bifenazate	24	10	250	211	127 - 400	0	2	12	8.40	0.8 - 25	1
Bifenthrin	24	58	140	108	94 - 122	0	0	12	8.00	2 - 21	7
Boscalid	24	60	141	143	100 - 163	0	14	12	3.95	0.2 - 21	196
Bromacil	24	60	159	149	133 - 166	0	4	12	4.42	0.09 - 19	130
Bromoxynil	18	51	125	87	68 - 116	0	0	9	6.78	3 - 16	35
Captan	24	12	140	85	43 - 129	0	0	12	10.07	0.9 - 28	
Carbaryl	20	65	135	103	76 - 120	0	0	10	8.44	0.4 - 26	1
Carbendazim	20	63	135	110	98 - 129	0	0	10	5.30	0.2 - 14	94
Chlorantraniliprole	20	44	161	105	82 - 134	0	0	10	8.63	0.3 - 31	8
Chlorothalonil	24	60	140	100	87 - 108	0	0	12	4.17	1 - 19	8

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)
Chlorpropham	24	60	140	129	117 - 140	0	0	12	4.11	0.1 - 21	8
Chlorpyrifos	24	60	140	114	99 - 134	0	0	12	4.75	1 - 16	17
Chlorsulfuron	20	22	194	138	87 - 225	0	2	10	7.13	0.3 - 16	1
cis-Permethrin	24	60	140	121	106 - 136	0	0	12	6.93	0.1 - 23	2
Clethodim sulfone	20	35	180	122	83 - 146	0	0	10	6.04	0.5 - 19	3
Clethodim sulfoxide	20	43	177	115	93 - 142	0	0	10	7.60	1 - 19	4
Clopyralid	18	22	125	59	34 - 80	0	0	9	15.98	0.8 - 40	29
Clothianidin	20	56	135	81	60 - 112	0	0	10	5.50	1 - 13	32
Cyantraniliprole	20	61	149	110	86 - 132	0	0	10	7.70	2 - 18	12
Cyfluthrin-Total	24	60	146	133	119 - 148	0	1	12	6.92	0.06 - 22	
Cypermethrin-Total	24	60	153	147	119 - 164	0	8	12	8.45	0.4 - 25	
Cyprodinil	20	63	135	108	87 - 123	0	0	10	8.20	2 - 20	3
Dacthal (DCPA)	18	52	128	97	82 - 136	0	1	9	6.78	1 - 17	12
Deisopropyl Atrazine	20	58	158	106	72 - 144	0	0	10	4.98	0.8 - 15	7
Deltamethrin	24	60	147	134	109 - 149	0	1	12	6.72	0.2 - 23	
Desethyl atrazine	20	51	157	111	72 - 139	0	0	10	4.53	0.3 - 13	26
Diazinon	24	60	140	114	101 - 126	0	0	12	5.23	0.8 - 21	74
Dicamba acid	18	48	125	80	55 - 114	0	0	9	8.33	1 - 21	114
Dichlobenil	24	60	140	99	61 - 132	0	0	12	8.79	0.5 - 23	127
Dichlorprop	18	54	125	92	77 - 134	0	1	9	5.94	0.1 - 16	
Dichlorvos (DDVP)	24	60	157	127	113 - 144	0	0	12	5.60	0.5 - 18	
Dicofol	24	60	250	222	139 - 278	0	4	12	7.54	0.5 - 21	
Difenoconazole	20	31	146	99	68 - 122	0	0	10	9.30	2 - 20	1
Diflubenzuron	20	54	148	112	86 - 167	0	1	10	17.10	4 - 52	
Dimethenamid ESA	20	57	136	108	89 - 128	0	0	10	8.62	0.2 - 21	
Dimethenamid OA	20	56	135	105	85 - 133	0	0	10	6.93	0.3 - 23	
Dimethoate	22	60	146	126	106 - 139	0	0	11	3.29	0.2 - 11	32
Dinotefuran	20	65	146	112	82 - 121	0	0	10	5.72	0.2 - 10	52
Dithiopyr	24	60	140	121	106 - 142	0	1	12	5.06	0.7 - 19	23
Diuron	20	65	135	115	104 - 131	0	0	10	7.99	0.9 - 19	112
Eptam	24	60	140	103	89 - 118	0	0	12	6.92	2 - 20	54

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)
Ethalfluralin	24	60	140	111	98 - 123	0	0	12	5.58	0.3 - 23	1
Ethoprop	24	60	140	129	119 - 141	0	1	12	4.82	0.9 - 23	7
Etoxazole	24	60	140	121	106 - 142	0	1	12	6.21	0.04 - 21	
Etridiazole	24	60	140	96	81 - 113	0	0	12	6.50	1 - 19	3
Fenarimol	24	60	164	146	130 - 163	0	0	12	3.49	0.1 - 21	1
Fenbutatin oxide	20	22	163	82	32 - 124	0	0	10	9.70	1 - 37	1
Fenpropathrin	24	60	140	108	94 - 124	0	0	12	7.58	2 - 25	
Fenvalerate	24	60	140	123	106 - 136	0	0	12	6.50	1 - 22	1
Fipronil	24	60	152	145	131 - 161	0	6	12	4.14	0.07 - 18	32
Fipronil disulfinyl	24	60	140	131	122 - 144	0	2	12	4.29	0.7 - 21	11
Fipronil sulfide	24	60	140	124	111 - 138	0	0	12	4.18	0.1 - 16	46
Fipronil sulfone	24	60	144	138	128 - 153	0	6	12	4.46	0.6 - 18	26
Fludioxonil	24	60	146	132	124 - 148	0	1	12	3.28	0.07 - 17	136
Flumioxazin	24	60	140	140	109 - 164	0	13	12	5.74	0.9 - 24	3
Fluopicolide	20	50	154	108	88 - 136	0	0	10	11.20	2 - 38	7
Flupyradifurone	20	48	215	156	121 - 227	0	2	10	7.00	0.02 - 17	64
Fluroxypyr 1-methylheptyl ester	24	60	156	131	112 - 154	0	0	12	5.52	0.5 - 13	
gamma-Cyhalothrin	24	60	140	122	109 - 138	0	0	12	7.06	0.7 - 21	14
Glufosinate-ammonium	6	50	150	106	95 - 121	0	0	3	5.97	0.9 - 16	
Glyphosate	6	50	150	96	81 - 104	0	0	3	11.43	0.3 - 21	49
Hexazinone	24	60	141	129	109 - 145	0	2	12	4.48	0.03 - 24	124
Hexythiazox	20	44	145	102	78 - 127	0	0	10	11.90	2 - 33	2
Imazapic	20	42	230	146	108 - 197	0	0	10	6.39	0.3 - 17	9
Imazapyr	20	10	250	124	101 - 171	0	0	10	5.40	1 - 13	74
Imidacloprid	20	65	135	103	94 - 113	0	0	10	4.09	0.4 - 12	52
Indaziflam	20	54	146	111	97 - 123	0	0	10	5.06	0.7 - 13	20
Inpyrfluxam	20	50	151	108	91 - 139	0	0	10	9.13	0.3 - 24	1
Isoxaben	20	59	153	108	94 - 146	0	0	10	8.70	1 - 21	8
Linuron	20	63	140	99	84 - 127	0	0	10	11.30	1 - 26	4
Malaoxon	20	65	148	112	84 - 134	0	0	10	5.61	0.5 - 17	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)
Malathion	24	60	144	137	125 - 149	0	6	12	4.14	0.2 - 17	33
MCPA	18	43	125	92	74 - 145	0	1	9	6.89	1 - 15	33
Mecoprop (MCPP)	18	52	125	96	84 - 140	0	1	9	6.34	0.4 - 20	32
Metalaxyl	24	60	140	120	109 - 134	0	0	12	3.71	0.2 - 17	75
Methamidophos	20	22	135	74	56 - 95	0	0	10	4.90	0.007 - 14	10
Methiocarb	20	52	156	102	71 - 134	0	0	10	11.27	0.7 - 41	5
Methomyl	20	65	135	109	96 - 123	0	0	10	4.16	0.7 - 12	3
Methomyl oxime	20	40	135	75	59 - 86	0	0	10	5.60	0.3 - 12	1
Methoxyfenozide	20	51	150	109	76 - 146	0	0	10	11.18	0.1 - 42	5
Metolachlor	24	60	140	122	93 - 139	0	0	12	4.40	0.8 - 18	156
Metribuzin	24	60	140	104	89 - 124	0	0	12	2.94	0.03 - 7	110
Metsulfuron-methyl	20	10	217	152	86 - 238	0	2	10	7.50	1 - 17	3
Myclobutanil	20	48	156	101	86 - 127	0	0	10	10.90	2 - 22	1
N,N-Diethyl-m-toluamide	24	60	140	120	111 - 132	0	0	12	4.67	2 - 21	70
Napropamide	24	60	140	130	111 - 146	0	3	12	3.07	0.05 - 15	27
Norflurazon	24	60	140	137	128 - 154	0	8	12	3.14	0.5 - 16	93
Oryzalin	20	45	180	93	73 - 158	0	0	10	12.10	1 - 31	
Oxadiazon	24	60	140	116	106 - 133	0	0	12	4.26	0.6 - 16	11
Oxamyl	20	65	135	101	64 - 115	1	0	10	4.35	0.5 - 12	30
Oxamyl oxime	20	65	166	113	94 - 128	0	0	10	7.30	2 - 17	14
Oxyfluorfen	24	60	159	122	106 - 137	0	0	12	5.15	0.8 - 16	
Paclobutrazol	20	65	137	115	86 - 165	0	2	10	7.80	1 - 21	1
Pendimethalin	24	60	140	122	109 - 136	0	0	12	4.42	1 - 14	117
Pentachloronitrobenzene (PCNB)	24	60	140	100	87 - 115	0	0	12	5.80	0.6 - 19	
Pentachlorophenol	18	47	125	85	72 - 115	0	0	9	7.00	2 - 16	10
Phosmet	24	60	141	116	97 - 129	0	0	12	4.78	0.1 - 25	2
Picloram	18	10	125	40	4 - 84	2	0	9	33.78	2 - 80	39
Piperonyl butoxide (PBO)	24	60	165	138	128 - 151	0	0	12	3.41	0.2 - 16	8
Prodiamine	24	60	148	112	100 - 129	0	0	12	5.80	0.7 - 18	1
Prometon	24	60	140	120	106 - 134	0	0	12	4.22	0.4 - 18	89

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)
Prometryn	24	60	140	130	121 - 143	0	2	12	4.18	0.6 - 17	2
Propargite	24	38	145	120	107 - 137	0	0	12	5.00	1 - 13	
Propiconazole	20	44	143	102	88 - 135	0	0	10	10.01	0.06 - 26	95
Pyraclostrobin	20	51	146	103	88 - 141	0	0	10	10.57	0.7 - 24	13
Pyrethrins	20	10	250	101	62 - 169	0	0	10	11.20	4 - 22	
Pyridaben	24	60	140	132	119 - 146	0	4	12	6.42	1 - 23	3
Pyrimethanil	20	65	135	101	81 - 119	0	0	10	5.92	0.5 - 16	59
Pyriproxyfen	24	60	140	124	106 - 142	0	1	12	4.88	0.1 - 21	10
Pyroxasulfone	20	54	145	110	83 - 151	0	1	10	12.40	4 - 21	
Simazine	24	60	140	114	91 - 132	0	0	12	4.72	0.7 - 21	111
Simetryn	24	60	140	113	101 - 129	0	0	12	4.65	0.3 - 16	
Spirotetramat	20	23	176	110	77 - 158	0	0	10	11.43	0.2 - 31	1
Sulfentrazone	24	60	163	115	5 - 165	5	1	12	22.00	0.3 - 178	176
Sulfometuron-methyl	20	44	183	130	103 - 159	0	0	10	7.30	3 - 17	18
Sulfoxaflor	20	65	142	117	107 - 132	0	0	10	6.23	0.3 - 15	2
tau-Fluvalinate	24	60	147	139	117 - 155	0	5	12	7.45	0.4 - 23	1
Tebuthiuron	24	60	156	134	109 - 157	0	1	12	6.17	1 - 19	84
Tefluthrin	24	60	140	98	85 - 118	0	0	12	7.42	2 - 19	7
Terbacil	24	10	250	148	128 - 162	0	0	12	4.79	0.2 - 19	104
Tetrahydrophthalimide	22	60	150	126	102 - 144	0	0	11	5.59	0.7 - 20	60
Tetramethrin	24	60	140	132	109 - 153	0	6	12	5.10	0.2 - 21	
Thiamethoxam	20	59	135	92	66 - 122	0	0	10	5.31	0.4 - 20	82
Thiram	18	10	194	46	3 - 112	4	0	9	11.14	0.3 - 64	
Tolfenpyrad	20	31	149	96	78 - 127	0	0	10	10.37	0.05 - 30	4
Tralomethrin	24	60	147	134	109 - 149	0	1	12	6.72	0.2 - 23	
trans-Permethrin	24	60	140	122	104 - 136	0	0	12	6.92	1 - 21	2
Triadimefon	24	60	140	126	114 - 137	0	0	12	3.29	0.1 - 15	7
Triallate	24	60	140	111	95 - 125	0	0	12	5.25	2 - 15	9
Triclopyr acid	18	43	141	102	86 - 144	0	1	9	7.67	1 - 17	52
Triclopyr butoxyethyl ester	24	60	140	120	105 - 139	0	0	12	3.68	0.2 - 15	1

Analyte	MS/MSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	MS/MSD recoveries below control limits	MS/MSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)	Total detections (n)
Triclosan	24	60	168	153	138 - 176	0	2	12	3.82	0.9 - 17	1
Trifloxystrobin	20	51	140	99	71 - 130	0	0	10	12.08	0.8 - 40	5
Trifluralin	24	60	140	101	92 - 113	0	0	12	4.43	0.2 - 24	26

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

There was a total of 3,290 spiked results (1,645 MS/MSD pairs) from MS and MSD recoveries that were unqualified or *J* qualified. Overall, the mean recovery was 116% with a standard deviation of 27%. 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 (12 recoveries) fell below the control limits for MS/MSD samples,
- 96% of analyte recoveries (3,145 recoveries) were within the control limits for MS/MSD samples,
- 4% of analyte recoveries (133 recoveries) were above the control limits for MS/MSD samples.

RPDs calculated for 1,645 MS/MSD pairs were below the 40% RPD control limit 99% of the time; only 10 pairs had RPDs above the control limit. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 6% with a standard deviation of 6%. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 65% with a standard deviation of 40%.

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 37b lists the analyte detections that occurred in the method blanks (172 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 was one sample detection qualified to *U* in 2022 due to method blank detections.

Table 37b – Analyte detections in method blanks

Analyte	Analytical method	Blank detections (n)	Mean Result (ng/L)	Min. Result (ng/L)	Max. Result (ng/L)	Mean LLOQ (ng/L)	Mean MDL (ng/L)
2,6-Dichlorobenzamide	GCMS-Pesticides	2	0.7	0.618	0.737	5	1.3
4,4'-DDE	GCMS-Pesticides	2	0.9	0.867	0.875	5	1.4
4,4'-DDT	GCMS-Pesticides	8	1.1	0.554	1.75	5	0.8
Aminocyclopyrachlor	LCMS-Pesticides	1	88.0	88.0	88.0	100	17.3
Carbendazim	LCMS-Pesticides	1	2.5	2.46	2.46	10	1.2
Dichlobenil	GCMS-Pesticides	16	0.5	0.164	0.773	5	1.4
Difenoconazole	LCMS-Pesticides	1	17.6	17.6	17.6	20	4.9
Eptam	GCMS-Pesticides	1	1.4	1.4	1.4	5	1.1
Ethoprop	GCMS-Pesticides	3	2.8	2.62	2.97	5	1.4
Fenarimol	GCMS-Pesticides	35	3.1	0.753	8.63	5	1.1
Fenbutatin oxide	LCMS-Pesticides	14	14.0	6.08	37.2	22	3.0
Hexazinone	GCMS-Pesticides	2	1.1	1.07	1.17	5	1.0
Methamidophos	LCMS-Pesticides	1	20.0	20.0	20.0	20	1.4
Methomyl	LCMS-Pesticides	4	4.4	1.68	5.37	10	0.7
Methomyl oxime	LCMS-Pesticides	1	10.2	10.2	10.2	100	8.7
Metolachlor	GCMS-Pesticides	6	2.2	0.47	2.8	5	0.6
N,N-Diethyl-m-toluamide	GCMS-Pesticides	34	2.0	0.517	10.1	5	1.3
Pyraclostrobin	LCMS-Pesticides	1	3.8	3.83	3.83	50	2.1
Sulfentrazone	GCMS-Pesticides	2	5.5	5.23	5.82	5	2.4
Tetrahydrophthalimide	GCMS-Pesticides	1	0.9	0.921	0.921	5	1.2
Thiram	LCMS-Pesticides	2	444.5	434.0	455.0	500	51.3
Triclosan	GCMS-Pesticides	31	7.5	1.99	19.5	10	1.7
Trifloxystrobin	LCMS-Pesticides	3	3.8	2.98	4.3	20	1.6

Surrogates

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

Table 38b – Pesticide surrogates summary

Analytes by structurally related group	Analytical method	Results (n)	Mean recovery (%)	Results within control limits (%)	Lower Control Limit (%)	Upper Control Limit (%)
Carbamate pesticides:						
Carbaryl C13	LCMS-Pesticides	432	101	100	65	135
Carbendazim-D4	LCMS-Pesticides	432	94	99.8	65	135
Acid-derivitizable herbicides:						
2,4,6-Tribromophenol	GCMS-Herbicides	400	88	98	63	125
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	400	98	96.8	61	125
Nitrogen containing pesticides:						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	471	89	99.8	50	132
Chlorinated pesticides:						
4,4'-DDE-13C12	GCMS-Pesticides	471	89	99.6	65	125
Decachlorobiphenyl	GCMS-Pesticides	471	80	100	28	125
Glyphosate related pesticides:						
AMPA-C13N15	LCMS-Glyphos	110	101	99.1	20	200
Glufosinate-d3	LCMS-Glyphos	109	100	99.1	20	200
Glyphosate-C13N15	LCMS-Glyphos	110	96	99.1	20	200
Neonicotinoid pesticides:						
Clothianidin-D3	LCMS-Pesticides	432	88	94.7	58	135
Clothianidin-D3-Neg	LCMS-Pesticides	432	88	100	36	159
Difenoconazole-D4	LCMS-Pesticides	432	93	95.1	54	136
Organophosphate pesticides:						
Chlorpyrifos-d10	GCMS-Pesticides	471	110	99.8	68	134
Triphenyl phosphate	GCMS-Pesticides	471	129	98.5	66	163
Chlorine and nitrogen containing pesticides:						
Atrazine-D5	GCMS-Pesticides	471	113	100	58	151
Trifluralin-D14	GCMS-Pesticides	471	96	100	54	137

In 2022, the overall mean recovery for surrogates was 97% and 99% of surrogate recoveries were within control limits.

Laboratory Control Samples

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

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

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
1-(3,4-Dichlorophenyl)-3-methylurea	56	65	135	105	84 - 128	0	0	28	8	0.5 - 22
2,4-D	71	50	125	84	62 - 123	0	0	35	6	0.1 - 26
2,6-Dichlorobenzamide	74	54	147	117	21 - 146	1	0	37	7	0.1 - 141
2-Hydroxyatrazine	56	65	136	101	84 - 141	0	1	28	9	2 - 22
4,4'-DDD	74	69	151	114	97 - 131	0	0	37	3	0.2 - 19
4,4'-DDE	74	67	133	97	84 - 112	0	0	37	3	0.2 - 10
4,4'-DDT	74	72	152	109	89 - 125	0	0	37	3	0.04 - 9
4-Nitrophenol	71	31	188	105	69 - 147	0	0	35	10	0.8 - 47
Acephate	56	65	135	103	64 - 118	1	0	28	9	0.08 - 47
Acetamiprid	56	65	137	108	88 - 143	0	1	28	9	0.3 - 24
Acetochlor	74	64	152	122	102 - 137	0	0	37	3	0.007 - 8
Acetochlor ESA	56	59	143	104	81 - 138	0	0	28	8	0.3 - 23
Afidopyropen	56	60	135	98	78 - 122	0	0	28	10	0.07 - 32
Aminocyclopyrachlor	56	65	137	99	63 - 167	1	2	28	9	0.3 - 40
AMPA	34	22	193	103	82 - 126	0	0	17	7	0.9 - 22
Atrazine	74	64	148	105	83 - 120	0	0	37	3	0.02 - 14
Azoxystrobin	56	65	135	105	72 - 140	0	1	28	9	0.7 - 28
Bensulide	56	42	135	102	75 - 150	0	1	28	12	0.3 - 30
Bentazon	71	72	138	101	88 - 134	0	0	35	5	0.02 - 26
Bifenazate	74	10	250	107	36 - 200	0	0	37	8	0.004 - 24
Bifenthrin	74	57	132	101	76 - 119	0	0	37	6	0.09 - 18
Boscalid	74	59	162	132	99 - 151	0	0	37	3	0.03 - 10

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* (%)
Bromacil	74	72	174	132	113 - 151	0	0	37	3	0.02 - 10
Bromoxynil	71	68	125	83	69 - 107	0	0	35	5	0.1 - 24
Captan	68	10	125	76	2 - 131	7	4	34	25	2 - 173
Carbaryl	56	65	135	104	86 - 124	0	0	28	9	0.4 - 25
Carbendazim	56	65	135	107	92 - 132	0	0	28	7	0.2 - 20
Chlorantraniliprole	56	61	140	105	70 - 141	0	1	28	11	0.4 - 30
Chlorothalonil	74	63	145	95	76 - 113	0	0	37	3	0.2 - 9
Chlorpropham	74	64	159	118	93 - 137	0	0	37	4	0.09 - 10
Chlorpyrifos	74	61	141	111	93 - 129	0	0	37	3	0.05 - 7
Chlorsulfuron	56	35	143	93	64 - 150	0	1	28	10	0.03 - 29
cis-Permethrin	74	62	140	117	90 - 140	0	0	37	5	0.2 - 17
Clethodim sulfone	56	46	137	92	64 - 143	0	1	28	9	0.09 - 26
Clethodim sulfoxide	56	51	144	93	65 - 139	0	0	28	9	0.5 - 22
Clopyralid	71	13	125	55	22 - 93	0	0	35	13	0.2 - 66
Clothianidin	56	65	135	103	63 - 151	1	3	28	11	0.2 - 47
Cyantraniliprole	56	50	157	104	83 - 141	0	0	28	10	0.7 - 31
Cyfluthrin-Total	74	60	147	118	85 - 138	0	0	37	5	0.3 - 14
Cypermethrin-Total	74	58	151	129	93 - 160	0	3	37	6	0.2 - 15
Cyprodinil	56	65	135	102	75 - 122	0	0	28	8	0.3 - 18
Dacthal (DCPA)	71	71	132	94	81 - 125	0	0	35	5	0.6 - 27
Deisopropyl atrazine	56	65	142	103	83 - 148	0	2	28	8	0.1 - 23
Deltamethrin	74	60	144	115	89 - 138	0	0	37	7	0.3 - 21
Desethyl atrazine	56	65	142	107	88 - 165	0	2	28	7	0.1 - 21
Diazinon	74	60	151	105	81 - 122	0	0	37	3	0.1 - 10
Dicamba acid	71	48	125	78	68 - 105	0	0	35	6	0.09 - 27
Dichlobenil	74	61	139	94	55 - 116	1	0	37	7	0.2 - 33
Dichlorprop	71	57	125	86	74 - 121	0	0	35	5	0.09 - 26
Dichlorvos (DDVP)	74	57	156	113	74 - 143	0	0	37	6	0.2 - 34
Dicofol	74	13	250	289	120 - 728	0	30	37	11	0.2 - 41
Difenoconazole	56	56	135	105	77 - 147	0	2	28	10	0.06 - 29
Diflubenzuron	56	58	139	102	73 - 145	0	1	28	13	0.7 - 38

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* (%)
Dimethenamid ESA	56	48	147	99	77 - 176	0	2	28	11	0.1 - 26
Dimethenamid OA	56	59	138	100	78 - 194	0	2	28	8	1 - 22
Dimethoate	74	54	159	115	84 - 139	0	0	37	4	0.1 - 23
Dinotefuran	56	65	135	101	84 - 121	0	0	28	8	0.03 - 19
Dithiopyr	74	56	140	117	97 - 136	0	0	37	3	0.3 - 10
Diuron	56	65	135	108	82 - 129	0	0	28	9	0.3 - 27
Eptam	74	51	145	97	54 - 118	0	0	37	7	0.3 - 38
Ethalfluralin	74	58	142	103	82 - 118	0	0	37	4	0.05 - 14
Ethoprop	74	60	159	119	90 - 137	0	0	37	4	0.05 - 14
Etoxazole	74	58	143	115	89 - 136	0	0	37	3	0.01 - 14
Etridiazole	74	66	151	95	54 - 120	1	0	37	7	0.3 - 36
Fenarimol	74	54	184	125	94 - 149	0	0	37	4	0.06 - 11
Fenbutatin oxide	56	33	170	95	28 - 204	1	7	28	15	2 - 47
Fenpropathrin	74	61	135	106	84 - 122	0	0	37	4	0.02 - 13
Fenvalerate	74	56	131	110	79 - 129	0	0	37	6	0.5 - 17
Fipronil	74	62	158	128	107 - 148	0	0	37	4	0.1 - 10
Fipronil disulfinyl	74	59	150	123	106 - 136	0	0	37	3	0.06 - 10
Fipronil sulfide	74	58	149	120	104 - 138	0	0	37	3	0.08 - 9
Fipronil sulfone	74	60	160	127	109 - 150	0	0	37	3	0.003 - 11
Fludioxonil	74	66	172	122	96 - 139	0	0	37	3	0.1 - 10
Flumioxazin	71	10	125	96	9 - 152	1	19	35	19	0.4 - 127
Fluopicolide	56	65	137	108	82 - 141	0	2	28	10	0.07 - 24
Flupyradifurone	56	65	135	106	86 - 134	0	0	28	8	0.4 - 23
Fluroxypyr 1-methylheptyl ester	74	61	151	125	100 - 141	0	0	37	5	0.06 - 15
gamma-Cyhalothrin	74	55	133	109	83 - 130	0	0	37	6	0.7 - 17
Glufosinate-ammonium	34	62	153	106	90 - 117	0	0	17	4	0.6 - 15
Glyphosate	34	50	143	103	91 - 115	0	0	17	4	0.03 - 18
Hexazinone	74	65	163	117	85 - 138	0	0	37	3	0.2 - 9
Hexythiazox	56	60	135	104	75 - 138	0	2	28	10	0.7 - 25
Imazapic	56	65	135	103	81 - 165	0	3	28	9	0.2 - 30

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* (%)
Imazapyr	56	65	135	99	81 - 144	0	1	28	8	0.2 - 19
Imidacloprid	56	65	135	103	72 - 127	0	0	28	9	0.2 - 19
Indaziflam	56	65	136	102	86 - 132	0	0	28	9	0.2 - 27
Inpyrfluxam	56	62	142	107	87 - 144	0	1	28	10	1 - 27
Isoxaben	56	65	135	107	82 - 134	0	0	28	9	0.1 - 44
Linuron	56	65	135	101	76 - 132	0	0	28	12	1 - 33
Malaoxon	56	65	139	104	83 - 127	0	0	28	8	0.4 - 22
Malathion	74	60	155	124	100 - 140	0	0	37	3	0.1 - 12
MCPA	71	53	125	83	68 - 120	0	0	35	5	0.2 - 25
Mecoprop (MCPP)	71	59	125	92	73 - 140	0	1	35	5	0.07 - 25
Metalaxyl	74	68	155	115	100 - 130	0	0	37	3	0.1 - 10
Methamidophos	56	65	135	102	53 - 137	1	1	28	9	0.3 - 60
Methiocarb	56	65	147	104	79 - 130	0	0	28	12	0.3 - 28
Methomyl	56	65	135	102	87 - 123	0	0	28	7	0.3 - 21
Methomyl oxime	56	65	135	95	61 - 114	1	0	28	9	0.2 - 40
Methoxyfenozide	56	65	138	109	86 - 143	0	1	28	10	0.1 - 34
Metolachlor	74	65	153	114	92 - 132	0	0	37	3	0.1 - 6
Metribuzin	74	60	139	95	74 - 139	0	0	37	5	0.1 - 34
Metsulfuron-methyl	56	30	147	95	61 - 142	0	0	28	10	0.4 - 21
Myclobutanil	56	65	135	103	77 - 140	0	1	28	12	0.3 - 26
N,N-Diethyl-m-toluamide	74	63	155	114	88 - 130	0	0	37	4	0.02 - 14
Napropamide	74	56	162	121	99 - 138	0	0	37	3	0.3 - 9
Norflurazon	74	67	158	126	109 - 144	0	0	37	3	0.1 - 9
Oryzalin	56	36	181	95	64 - 140	0	0	28	11	1 - 31
Oxadiazon	74	60	147	112	93 - 126	0	0	37	2	0.01 - 8
Oxamyl	56	65	135	102	83 - 123	0	0	28	7	2 - 22
Oxamyl oxime	56	57	136	98	78 - 123	0	0	28	9	0.1 - 24
Oxyfluorfen	74	75	167	114	94 - 139	0	0	37	4	0.7 - 12
Paclobutrazol	56	65	135	99	77 - 152	0	2	28	10	1 - 25
Pendimethalin	74	69	149	118	98 - 130	0	0	37	3	0.1 - 10
Pentachloronitrobenzene	74	63	139	96	70 - 115	0	0	37	5	0.2 - 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* (%)
Pentachlorophenol	71	52	125	73	48 - 103	2	0	35	6	0.09 - 26
Phosmet	74	10	132	92	22 - 128	0	0	37	10	0.04 - 72
Picloram	71	10	125	23	9 - 117	4	0	35	30	1 - 137
Piperonyl butoxide (PBO)	74	55	164	126	104 - 141	0	0	37	3	0.04 - 11
Prodiamine	74	61	150	109	92 - 126	0	0	37	4	0.1 - 12
Prometon	74	62	152	112	87 - 134	0	0	37	3	0.03 - 14
Prometryn	74	64	152	116	90 - 136	0	0	37	3	0.06 - 9
Propargite	74	38	145	115	93 - 136	0	0	37	4	0.8 - 13
Propiconazole	56	60	135	104	76 - 132	0	0	28	12	0.7 - 34
Pyraclostrobin	56	65	135	104	82 - 137	0	1	28	9	0.1 - 24
Pyrethrins	56	10	250	103	56 - 149	0	0	28	14	0.2 - 55
Pyridaben	74	61	145	125	92 - 144	0	0	37	4	0.06 - 14
Pyrimethanil	56	65	135	104	83 - 129	0	0	28	9	0.7 - 21
Pyriproxyfen	74	62	147	122	88 - 138	0	0	37	3	0.07 - 10
Pyroxasulfone	56	62	135	96	63 - 131	0	0	28	17	1 - 47
Simazine	74	64	150	105	79 - 123	0	0	37	3	0.02 - 16
Simetryn	74	61	145	102	80 - 122	0	0	37	3	0.03 - 10
Spirotetramat	56	38	151	100	66 - 145	0	0	28	10	0.3 - 35
Sulfentrazone	71	10	137	62	1 - 128	16	0	35	31	0.3 - 131
Sulfometuron-methyl	56	53	143	102	75 - 145	0	1	28	8	0.02 - 18
Sulfoxaflor	56	65	135	99	74 - 131	0	0	28	9	1 - 23
tau-Fluvalinate	74	59	143	114	78 - 138	0	0	37	7	0.5 - 21
Tebuthiuron	74	38	185	119	86 - 148	0	0	37	5	0.002 - 12
Tefluthrin	74	56	125	90	67 - 112	0	0	37	5	0.001 - 18
Terbacil	74	71	175	125	95 - 157	0	0	37	4	0.05 - 10
Tetrahydrophthalimide	74	43	125	100	10 - 136	1	7	37	9	0.2 - 161
Tetramethrin	74	20	128	101	30 - 129	0	2	37	9	0.1 - 59
Thiamethoxam	56	65	135	108	55 - 157	1	4	28	14	0.9 - 50
Thiram	56	25	196	96	49 - 132	0	0	28	15	3 - 51
Tolfenpyrad	56	57	135	107	63 - 163	0	11	28	13	0.3 - 46
Tralomethrin	74	61	143	115	89 - 138	0	0	37	7	0.3 - 21

Analyte	LCS/LCSD recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)	LCS/LCSD recoveries below control limits	LCS/LCSD recoveries above control limits	RPD (n)	Mean RPD (%)	Range of RPDs* (%)
trans-Permethrin	74	62	140	116	90 - 136	0	0	37	5	0.1 - 17
Triadimefon	74	65	158	116	93 - 132	0	0	37	3	0.1 - 8
Triallate	74	50	144	102	70 - 118	0	0	37	3	0.1 - 13
Triclopyr acid	71	67	133	95	77 - 123	0	0	35	5	0.2 - 28
Triclopyr butoxyethyl ester	74	57	155	116	95 - 132	0	0	37	3	0.09 - 9
Triclosan	74	44	178	125	100 - 149	0	0	37	6	0.07 - 16
Trifloxystrobin	56	65	135	107	78 - 152	0	5	28	12	0.03 - 30
Trifluralin	74	57	139	98	76 - 113	0	0	37	4	0.2 - 13

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

There was a total of 10,053 spiked results from LCS and LCSD recoveries that were unqualified or *J* qualified and 12 spiked results that were *U* qualified. Overall, the mean recovery was 107% with a standard deviation of 29%. 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 (41 recoveries) fell below the control limits for LCS/LCSD samples,
- 98% of analyte recoveries (9,880 recoveries) were within the control limits for LCS/LCSD samples,
- 1% of analyte recoveries (132 recoveries) were above the control limits for LCS/LCSD samples.

RPDs calculated for 5,027 LCS/LCSD pairs were below the 40% RPD control limit 99% of the time; only 51 pairs had RPDs above the control limit. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 6% with a standard deviation of 6%. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 74% with a standard deviation of 37%.

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 40b). Overall, laboratory duplicate results were of acceptable data quality.

Table 40b – Laboratory duplicate results

Analyte or parameter	Results (n)	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Ammonia	23	20	0	0
Nitrate-Nitrite as N	23	20	0	0
ortho-Phosphate	49	20	1	2
Specific conductivity	5	20	0	0
Total phosphorus	24	20	0	0

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

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

Analyte or parameter	LCS recoveries (n)	Lower control limit (%)	Upper control limit (%)	Mean recovery (%)	Range of recoveries (%)
Ammonia	23	80	120	103.8	98 - 112
Nitrate-Nitrite as N	22	80	120	98.4	97 - 101
ortho-Phosphate	49	80	120	97	91 - 102
Specific conductivity	4	95	105	101.2	101 - 102
Suspended sediment concentration	33	90	110	99.2	98 - 106
Total phosphorus	24	80	120	100.4	96 - 106

Field Data Quality Control Measures

A YSI ProDSS field meter was used at every sampling event. The field meters were calibrated the evening before, or the morning of the first field day of the week according to NRAS SOP: YSI ProDSS (Bischof 2021). All field meters were post-checked, using known standards, at the end of the sampling week.

To check specific conductivity meter results, surface water grab samples were obtained and sent to MEL for specific conductivity analysis. Approximately 6% of the conductivity meter readings were compared with MEL conductivity results.

Streamflow measurements were taken with OTT MF Pro flow meters and top-setting wading rods for sites that did not already have established gaging stations managed by other agencies. Each flow meter was calibrated on the morning of the first day of the week as described in the OTT MF Pro Basic User Manual (OTT 2018). A streamflow replicate measurement was taken once a week at a randomly selected site for each flow meter used in 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 42b. 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 42b – Quality control results for conventional water qualiter parameter replicates

Replicate parameter	MQO	Western Washington		Central Washington		Palouse	
		Mean	Maximum	Mean	Maximum	Mean	Maximum
Specific conductivity (field meter vs. laboratory)	10% RPD	4% RPD	8% RPD	3% RPD	5% RPD	4% RPD	10% RPD
Streamflow	10% RPD	5% RPD	22% RPD	6% RPD	18% RPD	2% RPD	6% RPD

Of the total 19 conductivity replicates taken, one specific conductivity replicate that was at Indian Slough was considered an outlier and excluded from this analysis (26% RPD). Indian Slough's specific conductivity can vary thousands of µS/cm within a 2 ft. water depth since it is at a tide gate.

Out of the 57 streamflow replicate comparisons, 10 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 43b describes measurement quality objectives for field meter post-checks as described in the 2023 WSDA QAPP (Nickleson et al. 2023). The 2023 MQOs were used because they were updated from the 2021 WSDA QAPP.

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

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

*Criteria expressed as a percentage of readings; for example, buffer or post-calibration value = 1,000 µS/cm and post-check YSI = 987.2 µS/cm; {|1,000 - 987.2| / [(1,000 + 987.2)/2]} * 100 = 1.29% variation, which would fall into the acceptable data criteria of equal to or less than 5%.

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

- Central YSI meter pH post-check failed MQOs the week of April 18.
  - The 4.0, 7.0, and 10.0 pH post-check units were outside of the acceptable range. All field pH values were requalified.
- Central YSI meter DO post-check failed MQOs the week of August 15, August 22, and October 17.
  - The field DO readings were requalified and not used in the technical report analysis.

- Palouse YSI meter temperature post-check failed MQOs the week of October 10.
    - The field temperature readings were requalified and not used in the technical report analysis
- Palouse YSI meter pH post-check failed MQOs the week of July 5.
    - The 4.0 pH calibration millivolts were outside of the acceptable range. There were no field pH values that were less than pH 4, so none were requalified.
- Palouse YSI meter DO post-check failed MQOs the week of July 5, July 18, and November 7.
    - 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 May 2, November 7, and November 15.
    - 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 1, 2022, the Central and Westside NRAS surface water monitoring teams and the Palouse Conservation District monitoring team conducted a field audit to compare 2022 sampling procedures. Each team calibrated their YSI ProDSS the day prior, or the day of the field audit. Each team then proceeded to the South Fork of Cowiche Creek (46.658955, -120.760830) near the town of Cowiche in Yakima County, Washington to conduct the field audit. All ProDSS meters were placed in the same location in the stream upon site arrival to allow ample time to equilibrate to stream conditions while each team measured streamflow. Using the same transect, each team consecutively measured streamflow using their own OTT MF Pro flow meter. Each team's flow measurement required approximately 40 minutes to complete. After flow was measured, values from each team's ProDSS meters were recorded. Results and RSDs are displayed in Table 44b.

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

Team	Temperature (°C)	pH	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Central	2.5	7.32	76.0	12.69	99.2	54.34
Palouse	2.5	6.79	77.9	12.82	100.3	49.00
Westside	2.5	7.50	76.4	12.77	99.7	56.67
All 3	±0.0° C	5% RSD	1% RSD	±0.13 mg/L	1% RSD	7% RSD
MQO	±0.2° C	10% RSD	10% RSD	±0.2 mg/L	10% RSD	10% RSD

Field meters met MQOs. All team's YSI meters post-check passed MQOs found in Table 43b.

Quality Assurance Summary References

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