Ambient Monitoring for Pesticides in Washington State Surface Water

April 2019

2016 Technical Report

Washington State Department of Agriculture
Natural Resources Assessment Section

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Executive Summary

The Washington State Department of Agriculture (WSDA) has been generating surface water monitoring data for pesticides since 2003 in an ongoing effort to assess the frequency and degree to which pesticides are found 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 2016, WSDA's Natural Resources Assessment Section (NRAS) collected surface water samples weekly or biweekly from March through November at 13 monitoring sites. These sites were located in Yakima, Chelan, Benton, Skagit, Whatcom, and Pierce counties with watershed areas ranging from 4,000 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, hay, and potato production. Sample analysis for pesticides was conducted at the Manchester Environmental Laboratory (MEL) in Port Orchard, Washington.

The United States Endangered Species Act lists many 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 contribution to the economy, cultural significance, and function in the ecosystem. All of the watersheds sampled in 2016 have historically supported salmonid populations or contain habitat conducive to salmonid use. In order to assess potential biological effects and be adequately protective of endangered and non-endangered species, detected pesticide concentrations from surface water samples are compared to WSDA assessment criteria derived by applying a 0.5x safety factor to state and federal water quality standards and criteria. Exceedances of assessment criteria indicate pesticide concentrations approaching levels with possible adverse effects to aquatic life such as fish, invertebrates, and aquatic plants. A current-use pesticide that has exceeded assessment criteria within recent years somewhere in the state is classified as a WSDA Pesticide of Concern (POC). WSDA's POC list of 16 chemicals in 2016 included pesticides such as bifenthrin, chlorpyrifos, diazinon, diuron, malathion, methiocarb, pyridaben, and simazine.

At many monitoring sites pesticide concentrations detected were above both WSDA's assessment criteria and the original state and federal criteria. At Upper Big Ditch in Skagit County, 3 unique insecticides on the POC list were detected with concentrations above federal fish or invertebrate chronic criteria. Malathion and/or chlorpyrifos were detected above state or federal water quality criteria at all 6 monitoring sites in eastern Washington. These 2 organophosphate insecticides have low criteria values due to their high toxicity to aquatic life. DDT, a legacy pesticide, was detected at concentrations above state water quality standards at 6 monitoring sites in both eastern and western Washington. The highest concentrations of DDT and its degradates were found in Brender and Mission Creeks draining into the Wenatchee River.

This report summarizes activities and data from the 13 separate sites selected for the 2016 ambient surface water monitoring season. Below is a brief overview of the findings.

- There were 282 surface water sampling events between March 14th and November 7th.
- Out of 154 pesticide active ingredients and breakdown products tested for, 76 unique pesticides were detected.
- There were 1,752 positively identified pesticide detections.
- At 223 of the 282 sampling events, mixtures of 2 or more pesticides were detected.
- A breakdown product of the herbicide dichlobenil (2,6-dichlorobenzamide) was the most frequently detected chemical (137 times). It was detected in over 50% of the sampling events it was tested for.
- 2,4-D was the most frequently detected herbicide (101 times), thiamethoxam and imidacloprid were the most frequently detected insecticides (78 and 74 times, respectively), and boscalid was the most frequently detected fungicide (111 times).
- There were 108 unique pesticide detections above WSDA assessment criteria, which means they are near levels that could adversely affect aquatic life (6.2% of total detections).
    - The legacy insecticide DDT and its breakdown products accounted for 71 of these detections (65.7% of total exceedances).
    - Current-use pesticides found at concentrations above assessment criteria were bifenthrin (1 detection), chlorpyrifos (19 detections), diazinon (1 detection), malathion (4 detections), methiocarb (1 detection), pyridaben (1 detection), pyriproxyfen (1 detection), and simazine (9 detection).
    - Clarks Creek was the only monitoring site where no detected pesticide concentrations were above WSDA assessment criteria.

Samples for total suspended solids as well as field measurements for pH, dissolved oxygen, conductivity, and streamflow were also collected at sampling events. Continuous temperature measurements were collected in situ during the entire monitoring season. Dissolved oxygen, pH, and temperature measurements were compared to Water Quality Standards for Surface Waters of the State of Washington (WAC, 2016). At least 1 conventional water quality parameter exceeded state water quality standards at each monitoring site. When these exceedances coincide with exceedances of WSDA pesticide assessment criteria, there could be additive compounding stress on aquatic life.

Maintaining the highest level of data quality is an essential component of the monitoring program. WSDA staff closely adhere to detailed field procedures while MEL staff reliably produce high quality testing results to achieve the highest quality assurance standards recommended by the Environmental Protection Agency (EPA) (EPA, 2008). Attachment 2 (Appendix C: 2016 Quality Assurance Summary) provides a summary of quality assurance and quality control sample results with a detailed analysis of how the field and laboratory methods performed over the season.

The NRAS ambient monitoring program is a tool for identifying state-specific pesticide issues that can be addressed according to WSDA's EPA-approved Pesticide Management

Strategy (Cook and Cowles, 2009). Maintaining an adaptive monitoring approach helps identify pesticide use patterns that can lead to water contamination. The statewide ambient surface water monitoring program also forms the groundwork for additional studies focusing on particular scientific questions of interest regarding pesticide fate and transport. The data generated by this program is shared with the agricultural community, regulatory community, and the public through WSDA’s website, reports, watershed-specific fact sheets, and numerous public presentations.

Introduction

The Washington State Department of Agriculture (WSDA) has authority as a state lead agency to regulate the sale and use of pesticides in Washington State under federal regulation according to the amended Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, 1947), and state regulation according to Washington Pesticide Control Act (WPCA, 1971) and Washington Pesticide Application Act (WPAA, 1967).

Since 2003, WSDA has received funding from the Washington State Legislature and the US EPA to administer a comprehensive program to assess the frequency and biological significance of pesticides detected in Washington State surface waters. To make that assessment WSDA's Natural Resources Assessment Section (NRAS) collects 3 kinds of information;

- pesticide use data: quantities and types of pesticides used on different crops,
- agricultural land use data: crop types grown and their locations in the state, and
- ambient monitoring data: pesticide concentrations in surface water.

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

The technical report is intended to:

- summarize results, data quality, and monitoring activities conducted in 2016,
- provide data for the pesticides that are listed for agency Endangered Species Act consultations,
- determine if any pesticides in surface waters may be present at concentrations that could adversely affect aquatic life,
- provide a basis for potential modifications to the program in upcoming years, and
- provide data to support implementation decisions under the agency's Pesticide Management Strategy (Cook and Cowles, 2009).

WSDA conducted ambient surface water monitoring for pesticides in 2016 from March through November throughout the state. During the first year of monitoring (2003) WSDA sampled at 9 monitoring sites in agricultural and urban areas. The program has since expanded to 13 monitoring sites in 2016, which included 1 of the 9 original monitoring sites. WSDA has monitored surface water in 16 unique watersheds since the start of the program. Site changes from 2015 to 2016 include 1 new site in western Washington, 1 movement of a site downstream in eastern Washington, and the removal of 3 sites (2 western Washington, 1 eastern Washington).

Water samples were sent to the Manchester Environmental Lab (MEL) for analysis of pesticide and pesticide-related chemicals such as insecticides, herbicides, fungicides, degradates, wood preservatives, an insect repellent, and synergists. In 2016, 154 chemicals were tested, with 76 confirmed chemicals detected in surface water samples. Between the 2015 and 2016 monitoring seasons, 11 new chemicals were added to the chemical testing list and 71 were removed. The chemicals tested for every year change because of new use restrictions, changes in pesticide registration, or lack of detections in surface water.

WSDA compares the surface water data to internal assessment criteria that are derived by applying a safety factor to state and federal water quality standards and criteria in order to be adequately protective of aquatic life. WSDA identifies a current-use pesticide as a Pesticide of Concern (POC) when it has been found somewhere in the state above WSDA assessment criteria in recent years. When persistent contamination of waters with POCs and other chemicals is documented, WSDA can implement its EPA-approved Pesticide Management Strategy (Cook and Cowles, 2009). WSDA's Pesticide Management Strategy specifies adaptive management techniques including voluntary BMPs, voluntary use prohibition, technical assistance, stakeholder outreach, and monitoring to investigate and eliminate surface or ground water contamination with pesticides.

WSDA's ambient surface water monitoring program provides a non-regulatory framework for addressing off-target pesticide movement into streams and rivers. The ambient monitoring program data can be used 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, watershed-specific fact sheets are published yearly to share data and improve awareness of simple BMPs 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 use practices, site conditions, land use patterns, and the presence of federally-listed threatened or endangered species. Hydrologic units and their associated hydrologic unit codes (HUC) are used to describe each monitoring location position within the regional hydrologic system. Figure 1 shows the boundaries of the 7 subbasins that were monitored in 2016 which are identified by their eight-digit HUC codes and corresponding subbasin names.

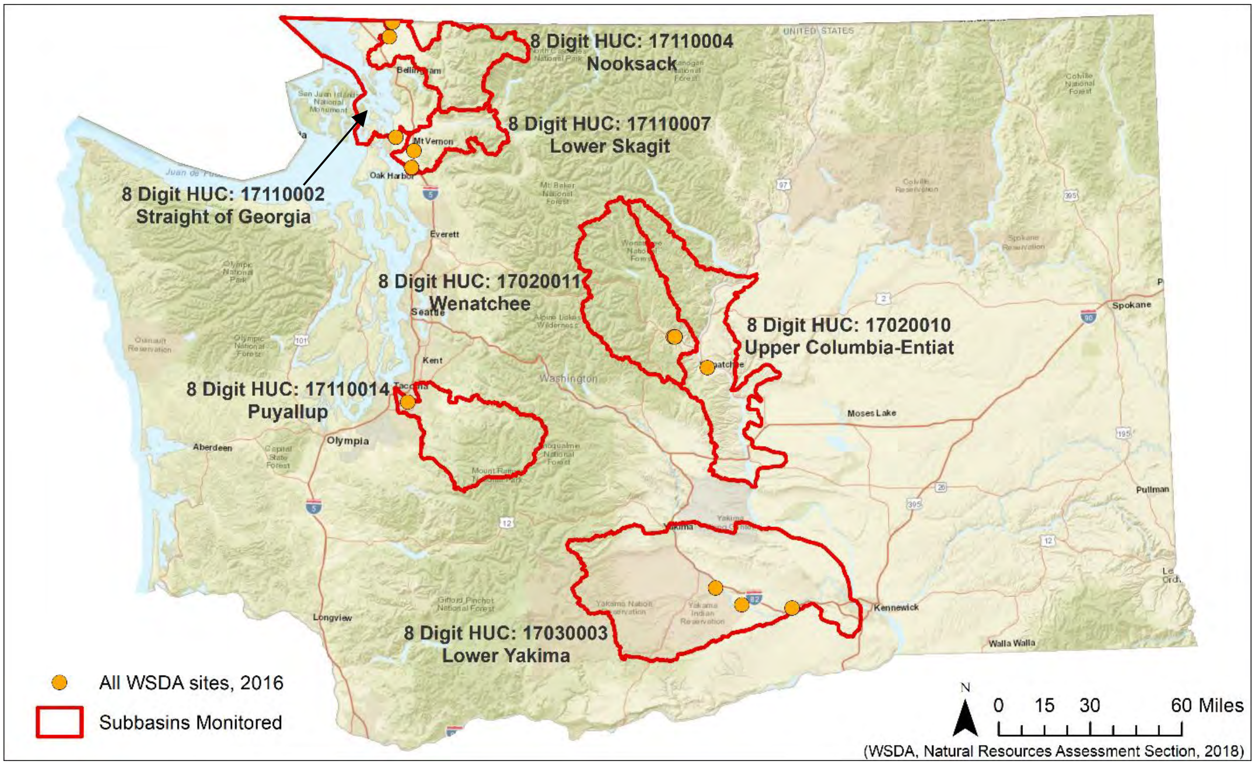

Figure 1 – Subbasins monitored in Washington State in 2016

All 7 subbasins exist within the greater Pacific Northwest Region (HUC 17). Of these, 1 subbasin represents mixed urban and residential landscapes and was selected due to land-use characteristics, history of pesticide detections, and the habitat provided for endangered species including pacific salmonids. The other 6 subbasins represent a variety of agricultural landscapes. These subbasins were chosen because they produce different varieties of agricultural commodities in close proximity to waterbodies, they have a wide range in terms of the percentage of the total areas in agricultural production, and they provide habitat for endangered pacific salmonids.

Subbasins Monitored in 2016

In 2016, WSDA monitored 13 sites located at private and public access points. Details including maps, site geographic coordinates, and agricultural land use statistics are included in Appendix A: Monitoring Site Data. Brief descriptions of the subbasins and monitoring locations are provided below.

Nooksack Subbasin

The Nooksack River flows from the Cascade Mountain Range to Bellingham Bay. Bertrand Creek is located in the Nooksack subbasin (HUC 17110004) in Whatcom County. Approximately half of the Bertrand watershed lies south of the US/Canadian border and at least 62% of the land in the subbasin is in agricultural production. Grass hay, caneberries, field corn, and blueberries make up a majority of the crops grown in the subbasin. Roughly, 28% of the agricultural acreage on the US side is currently producing blueberries, raspberries, blackberries, and strawberries[1].

There are 2 monitoring sites in the Nooksack subbasin. The Lower Bertrand Creek site (LBC), (Figure 6), was selected to represent berry farming in western Washington and is located near the bottom of the watershed approximately 1 mile upstream of where the tributary enters the Nooksack River. The Upper Bertrand Creek site (UBC), (Figure 6), is located just south of the US/Canada border in order to distinguish between potential water quality issues originating from Canada and those originating in the US. Both sites have been monitored since 2013.

Strait of Georgia & Lower Skagit Subbasins

Within the greater Puget Sound subregion (HUC 1711) lies the Strait of Georgia subbasin (HUC 17110002) and the Lower Skagit subbasin (HUC 17110007). Both subbasins include sections of the Skagit Valley which has a wide variety of landscapes and land use practices including extensive agricultural areas. The agricultural areas of the Skagit Valley consist largely of diked flood plains, which are characterized by a complex system of rotational agriculture that includes several vegetable crops grown for seed and flower bulbs. The agricultural production of the valley is dominated by potatoes, field corn, grass hay, and wheat.

In the Strait of Georgia subbasin, the Indian Slough site (IS), (Figure 11), is located on the upstream side of the tide gate at Bayview-Edison Road. In the Lower Skagit subbasin, the Lower Big Ditch site (LBD), (Figure 8), is located on the upstream side of the bridge at Milltown Road. The Indian Slough and Lower Big Ditch monitoring sites are tidally influenced by Puget Sound. These 2 sites were selected to represent irrigated agricultural land-use practices in western Washington and have been monitored since 2006. Also within the Lower Skagit subbasin, the Upper Big Ditch site (UBD), (Figure 7), is located on the upstream side of the bridge at Eleanor Lane in Mount Vernon, Washington. Upper Big Ditch

[1] WSDA NRAS agricultural land use mapping program, 2016 data.

was selected to represent urban/commercial land use and has been monitored since 2007. The Upper and Lower Big Ditch sites are both on Big Ditch waterway but have very different land use patterns.

Puyallup Subbasin

The Puyallup subbasin (HUC 17110014) is also within the Puget Sound subregion. This subbasin is characterized by a mixed landscape of mountainous terrain and residential and urban land uses.

Only 1 monitoring site was sampled in the Puyallup subbasin in 2016. The Clarks Creek site (CC), (Figure 10), is located just downstream of the bridge crossing at Tacoma Road East. Clarks Creek was selected to represent urban and residential practices in western Washington. Less than 1% of the Clarks Creek watershed that contains the Clarks Creek sampling site is in agricultural use. This was the first and last year this program will monitor Clarks Creek.

Lower Yakima Subbasin

The Lower Yakima subbasin (HUC 17030003) of the Yakima subregion (HUC 1703) is characterized by an extensive irrigated agricultural system with over 100 different commodities grown, making it one of the most agriculturally diverse subbasins in the Pacific Northwest. Of the commodities grown in the Lower Yakima subbasin, the 4 dominant crops in terms of land cover are corn, grapes, hops, and apples.

There are 3 monitoring sites within the Lower Yakima subbasin and Yakima County. The Marion Drain monitoring site (MA), (Figure 12), is located approximately 15 meters upstream of the bridge at Indian Church Road. The Sulphur Creek Wasteway site (SU), (Figure 16), is located on the downstream side of the bridge at Holaday Road. Marion Drain and Sulphur Creek have been sampled since 2003. The Snipes Creek site (SN), (Figure 14), is located approximately 20 meters downstream of the Spring Creek and Snipes Creek confluence. This is the first year Snipes Creek has been sampled. It replaced the Spring Creek site that was monitored from 2003 to 2015; this site allows WSDA to collect water from a larger agricultural drainage. All 3 sites in the Lower Yakima subbasin were selected to represent irrigated agricultural practices in eastern Washington.

Wenatchee Subbasin

The Wenatchee subbasin (HUC 1702001) is located within the Upper Columbia subregion (HUC 1702) and is characterized by mountainous terrain. Tree fruit, rangeland, and forestry are the dominant agricultural land uses in this subregion and this subbasin.

In 2016, WSDA monitored 3 sites in the Wenatchee subbasin. Of these, 2 were regular program sites (Mission Creek and Upper Brender Creek) with the full analyte list and weekly sampling schedule. The third, Lower Brender Creek, was sampled with a shortened analyte list and modified sampling schedule. The Mission Creek site (MI), (Figure 13), is located approximately 10 meters downstream from the bridge crossing on Sunset Highway. This was the first year WSDA has sampled this specific location even though WSDA has sampled Mission Creek since 2003. By moving the sampling location further downstream, a larger drainage was captured. The Upper Brender Creek site (UBR), (Figure 9), is located on the upstream side of the culvert at Evergreen Drive. These 2 sites, which are located in Chelan County, were selected to be representative of agricultural practices used in tree fruit cultivation in central Washington.

DDT has been detected consistently in Brender Creek since 2007, when WSDA began monitoring there. In response to continued detections of DDT and DDT breakdown products in Brender Creek, and in cooperation with the Cascadia Conservation District, a second sampling location was established on the creek in 2016. The new Lower Brender Creek site (LBR), (Figure 9), is located on the downstream side of the Sunset Highway bridge crossing of Brender Creek. In 2015, the Cascadia Conservation District implemented a restoration project to improve the conditions of the Brender Creek wetland located between the 2 sites (UBR is above the wetland and LBR is below the wetland). The purpose of collecting water samples at the lower and upper sites was to evaluate the effectiveness of this newly restored wetland at reducing suspended sediment and total DDT (DDT and DDT breakdown products) in the water. Samples from the Lower Brender site were only tested for DDT, its breakdown products, and the legacy organophosphates insecticides aldrin and dieldrin. In addition, this site was sampled biweekly rather than weekly.

Upper Columbia-Entiat Subbasin

The Upper Columbia-Entiat subbasin (HUC 17020010) is also located within the Upper Columbia subregion (HUC 1702) which is characterized by mountainous terrain. Tree fruit, rangeland, and forestry are the dominant agricultural land uses in this subregion and this subbasin.

A single monitoring site was sampled in the Upper Columbia-Entiat subbasin in 2016. The Stemilt Creek site (SC), (Figure 15), is located upstream of where Stemilt Creek flows into the Columbia River and is approximately 7 meters upstream of the Old West Malaga Road bridge. The Stemilt Creek site was selected to be representative of agricultural practices used in tree fruit cultivation in central Washington and has been sampled since 2013.

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. Surface water samples were collected and tested for 152 pesticide active ingredients and pesticide breakdown products at 12 monitoring sites across the state. A 13th monitoring site, Lower Brender Creek, was sampled for 8 legacy pesticides including dieldrin and aldrin that were only tested for at this site. Statewide result summaries included in this report contain Lower Brender Creek sample results unless noted otherwise. The sampling schedule was determined individually for each site by focusing sampling efforts during the duration of peak pesticide application as well as around the weeks with pesticide detections in previous years.

Conventional water quality parameters such as total suspended solids, pH, conductivity, continuous temperature data (collected at 30-minute intervals), dissolved oxygen, and streamflow were monitored at all sampling events to assess overall stream health in relation to Washington State water quality standards.

Detailed information on study design and methods are described in the Quality Assurance Project Plan (Johnson and Cowles, 2003), and subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009; Anderson, 2011; Anderson, 2012; Sargeant, 2013).

Field Procedures

Surface water samples were collected using a 1-liter glass jar by hand grab or pole grab as described in the Washington State Department of Ecology's (Ecology) *Standard Operating Procedure for Sampling of Pesticides in Surface Waters* (Anderson and Sargeant, 2011). After collection, all samples were labeled and preserved according to the Quality Assurance Project Plan (Johnson and Cowles, 2003) before being delivered to MEL.

At each sampling event, water temperature, pH, dissolved oxygen, and specific conductivity parameters were recorded using Hach Hydrolab MS5 or YSI ProDSS field meters. Field meters were calibrated and post-checked at the beginning and end of every sampling week based on the manufacturers' specifications, using Ecology's *Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes* (Swanson, 2010) or *YSI ProDSS User Manual* (YSI, 2014). Dissolved oxygen field measurements were compared to grab samples analyzed by Winkler Titration following Ecology standard operating procedure (SOP) EAP023 (Ward, 2016). Continuous, 30-minute interval temperature data was collected at every monitoring site except Mission Creek using Ecology SOP *Standard Operating Procedure for Continuous Temperature Monitoring of Fresh Water Rivers and Streams* (Ward, 2015). Mission Creek temperature data was obtained from an Ecology gauging station present at that monitoring site. The 2016 field data quality results are summarized in Attachment 2 (Appendix C of this report).

Streamflow data in cubic feet per second was measured for all monitoring sites excluding Clarks Creek, Upper Bertrand Creek, Lower Bertrand Creek, and Stemilt Creek using an OTT MF pro flow meter and top-setting wading rod, as described in Ecology SOP EAP056 (Shedd, 2014). Streamflow data for the other 4 sites was obtained from gauging stations managed by other agencies. Details of those gauging stations are listed below.

- Clarks Creek - USGS gauging station located at Tacoma Road East near Puyallup (Station ID: 12102075)
- Upper Bertrand Creek - USGS gauging station located upstream at the Canadian border (Station ID: 12212390)
- Lower Bertrand Creek - Ecology gauging station located at Rathbone Road (Station ID: 01N060)
- Sulphur Creek Wasteway - US Bureau of Reclamation gauging station at Holaday Road near Sunnyside (Station ID: SUCW).

The gauging stations provided 15-minute streamflow measurements throughout the sampling season. The recorded streamflow closest to the actual sampling start time was used in lieu of field measurements.

Laboratory Analyses

The surface water grab samples were analyzed by MEL for pesticides, TSS, and conductivity. Table 1 provides a summary of the extraction and analytical methods used by MEL. The GC-ECD-Pesticides analytical method was only used to test 8 analytes at the Lower Brender Creek monitoring site.

Table 1 – Summary of laboratory methods

Analytical method	Extraction method reference[1]	Analytical method reference[1]	Instrument
GCMS-Pesticides	3535A	8270D	GC/MS
GCMS-Herbicides (Derivitizable acid herbicides)	3535A	8270D	GC/MS
LCMS-Pesticides	n/a	8321B	LC/MS/MS
GC-ECD-Pesticides	3535A	8081B	GC/ECD
TSS	n/a	SM 2540D	Gravimetric
Conductivity	n/a	SM 2510	Electrode

[1] analytical methods refer to EPA SW 846, unless otherwise noted.
LC/MS/MS: high performance liquid chromatography/triple quadrupole mass spectrometry
GC/MS: gas chromatography/mass spectrometry
GC/ECD: gas chromatography/electron capture detector

Data Quality, Quality Assurance, and Quality Control Measures

The quality assurance and quality control protocol for this program employs blanks, replicates, and surrogate recoveries. Laboratory surrogate recoveries, laboratory blanks, laboratory control samples, and laboratory control sample duplicates are analyzed as the laboratory component of QA/QC. Field blanks, field replicates, matrix spikes, and matrix spike duplicates integrate field and laboratory components. In 2016, 12% of the samples collected in the field were QA/QC samples. The full QA/QC analysis is contained in Attachment 2 (Appendix C: 2016 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. All qualifiers are described in Attachment 2 (Appendix C: 2016 Quality Assurance Summary).

Field Replicates

Field replicate samples were obtained to determine total sampling and analytical method variance. Consistently and inconsistently paired replicate values were averaged for comparisons to pesticide assessment criteria and water quality standards.

Precision between replicate pairs was calculated using relative percent difference (RPD). The RPD is calculated by dividing the absolute value of the difference between the replicates by their mean and then multiplying by 100 for a percent value. Only 1 of the 82 consistently identified field replicate pairs for TSS and pesticide analysis exceeded the 40% RPD criterion. The results were not requalified for this 1 pair because RPD has limited effectiveness in assessing variability at low levels (Mathieu, 2006). Out of 15 inconsistently identified field replicate pairs for pesticide and TSS, 13 exceeded the 40% RPD criterion. In most cases the detections were at or below the reporting limit but above the detection limit.

All pesticide and TSS data for replicates are of acceptable data quality. There were no sample detections requalified due to consistently or inconsistently paired field replicate results.

Blanks

Field and laboratory blanks indicate the potential for sample contamination or the potential for false detections due to analytical error. In 2016, there were no detections in field blank samples for TSS and pesticide analysis. It is unlikely that samples are becoming contaminated during field operations. There were 11 analyte detections that occurred in laboratory blanks; however, of the 11 detections, 4 were less than 5 times the detection limit and were below the reporting limit. If lab blank detections occur outside MEL QC criteria, the analyte’s method reporting limit (MRL) may be increased, and detections may be qualified as estimates.

Surrogates, Matrix Spikes, and Laboratory Control Samples

Surrogates are spiked into all samples to evaluate recoveries for a group of organic compounds. A surrogate is not normally found in environmental samples but is similar to the target analyte it is being tested for. The majority (99%) of surrogate recoveries fell within the control limits established by MEL in 2016. 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. The duplicate spike can be used to estimate analytical precision at the concentration of the spiked samples and ensure the analytical method is efficient. For most compounds, percent recovery and relative percent differences (RPDs) of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Analyte recoveries from MS and MSD samples fell between both the upper and lower control limits 92% 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 requalified 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. They are used 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 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 93% of the time and the RPDs of the paired recoveries fell below the 40% RPD upper control limit 96% of the time. Sample results were qualified as estimates if the LCS/LCSD recoveries did not meet MEL QC criteria.

Assessment Criteria

The potential effects of pesticide exposure to aquatic life and endangered species were evaluated by comparing pesticide concentrations detected in surface water to reference values with known effects. The reference values WSDA uses as 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, 2016), and Washington State regulations (WAC, 2016). WSDA applies a 0.5x safety factor to all of these reference values before comparison to detected pesticide concentrations to ensure that the criteria are adequately protective of aquatic life and that potential water quality issues are detected early on.

WSDA’s ability to make these comparisons is limited by several factors. 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 detected and the effects of several pesticides in combination may be either more or less toxic than the effects of those pesticides individually. In addition, toxicity values such as those used for pesticide registration are determined from continuous exposure over time. WSDA sampling consists of a one-time grab sample, and it is not possible to determine if the time threshold has been exceeded based solely on an individual sample because the sampling frequency is often once a week or less. However, this comparison is consistent with Ecology practices, when for Clean Water Act section 303(d) listing purposes, measurements of instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards and assessment criteria for acute and chronic criteria (Ecology, 2018). WSDA assessment criteria for fish, invertebrates, and aquatic plants are shown in Attachment 1 (Appendix B: Assessment Criteria for Pesticides).

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.

Acute toxicity is calculated by a standardized testing method. A sensitive (representative) species at a susceptible life stage is exposed to a pesticide under a range of concentrations. 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. A pesticide's No Observable Adverse Effects Concentration (NOAEC) is often used to derive chronic toxicity study values. This concentration signifies the highest concentration in the toxicity test not showing a statistically significant difference from the control. The chronic toxicity test is longer than the 96-hour acute test (21 days for fish, 14 days for invertebrates, 5 to 60 days for plants) to simulate the type of exposure that would result from a persistent chemical or the effect of repeated applications.

To provide an additional level of protection for endangered species an increased safety factor is used. Rainbow trout is commonly used as a surrogate species to assess the potential risk of a pesticide to salmonids. As a result, the criterion for endangered species (in this case, typically salmonids) is $1/20^{th}$ of the most sensitive LC_{50} for fish.

National Recommended Water Quality Criteria

EPA's National Recommended Water Quality Criteria (NRWQC) (EPA, 2016) includes a list of approximately 150 pollutants that was created to protect aquatic life and human health. These criteria are published pursuant to Section 304(a) of the Clean Water Act (CWA, 1972) by the Office of Water and provide guidance for states and tribes to use in adopting water quality standards. The pesticide criteria established under the Clean Water Act are derived from acute and chronic toxicity criteria from the pesticide registration toxicity studies.

NRWQC that were updated before 2016 were used in the development of WSDA assessment criteria, which are presented in Attachment 1 (Appendix B: Assessment Criteria for Pesticides).

Washington State Water Quality Standards for Pesticides

Washington State maintains its own list of priority pollutants under the authority of Washington Administrative Code (WAC) 173-201A: Water Quality Standards for Surface Waters of The State of Washington (WAC, 2016). Washington State water quality standards include numeric criteria for current-use and legacy pesticides. For the purposes of this report, these values will be referred to as "state water quality standards".

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

The exposure periods assigned to the acute criteria are: (1) an instantaneous concentration not to be exceeded at any time, or (2) a 1-hour average concentration not to be exceeded more than once every 3 years on average. The exposure periods for the chronic criteria are either: (1) a 24-hour average not to be exceeded at any time, or (2) a 4-day average concentration not to be exceeded more than once every 3 years on average.

Acute and chronic numeric criteria for fish, invertebrates, and aquatic plants from the WAC with the WSDA 0.5x safety factor are presented in Attachment 1 (Appendix B: Assessment Criteria for Pesticides).

Relationship between WSDA Assessment Criteria and Sources

A combination of pesticide registration toxicity data and federal and state criteria are used to derive WSDA assessment criteria. Table 2 provides a summary of how these different sources are used in the WSDA assessment criteria referred to throughout this report.

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

Risk presumptions	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

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, 2016), waterbodies are required to meet numeric water quality standards based on the beneficial uses of the waterbody. Conventional parameters including temperature, dissolved oxygen, and pH were measured and compared to the numeric criteria of the Washington State water quality standards according to the aquatic life uses.

WSDA ambient monitoring sites contain 2 different aquatic life uses. Clarks Creek in western Washington is classified as freshwater core summer salmonid habitat. In this category, the 7-DADMax temperature should be below 16.0 ^{0}C, dissolved oxygen (lowest 1-day minimum) below 9.5 mg/L, and the pH between 6.5 and 8.5. The other 12 sites monitored this year are classified as freshwater salmonid spawning, rearing, and migration habitat. This category's 7-DADMax temperature should be below 17.5 ^{0}C, dissolved oxygen (lowest 1-day minimum) below 8.0 mg/L, and pH between 6.5 and 8.5.

Results Summary

Data presented in this section of the report only include results where pesticides were positively identified using the following data qualifiers: unqualified detected concentration, approximate concentration ("J"), or estimated concentration outside of a calibration range ("E"). Non-detect values qualified "U", "UJ", "N", or "NJ" may be referred to but are not specifically addressed in the results summary. Please refer to Attachment 2 (Appendix C: 2016 Quality Assurance Summary) for further information on performance measures.

Pesticide Detection Summary

There were 76 different pesticide and pesticide-related analytes detected in 2016. Across 13 monitoring sites, 1,752 detections containing pesticides were confirmed. The detection frequency is calculated by taking the number of times a chemical is detected divided by the total number of times the chemical could have been detected, and then multiplied by 100. This number can be useful in analyzing pesticide chemical occurrences to each other. The statewide summary of detections can be found in Table 3. Table 4 further summarizes the detections in 2016 by general use category.

Table 3 – Statewide summary of pesticides with 1 or more detections in 2016

Pesticides detected in 2016	Detections	Max concentration (µg/L)*	Average concentration (µg/L)*	Std. dev. (µg/L)*	Detection frequency (%)
Fungicides:					
Boscalid	111	0.63	0.11	0.10	41.4
Azoxystrobin	60	1.43	0.11	0.24	22.5
Fludioxonil	59	0.62	0.12	0.12	21.9
Metalaxyl	35	0.99	0.12	0.16	13.1
Propiconazole	31	0.40	0.08	0.08	11.6
Myclobutanil	24	0.06	0.01	0.01	9.0
Difenoconazole	23	0.19	0.04	0.05	8.6
Pyraclostrobin	11	0.06	0.02	0.02	4.1
Cyprodinil	8	0.03	0.01	0.01	3.0
Fenarimol	6	0.08	0.06	0.02	2.2
Etridiazole	4	0.11	0.07	0.04	1.5
Trifloxystrobin	2	0.03	0.03	0.01	0.8
Triadimefon	1	0.21	0.21	n/a	0.4
Synergists:					
Piperonyl Butoxide	5	0.70	0.19	0.28	1.9
Wood Preservatives:					
Pentachlorophenol	25	0.12	0.03	0.02	9.3

Pesticides detected in 2016	Detections	Max concentration (µg/L)*	Average concentration (µg/L)*	Std. dev. (µg/L)*	Detection frequency (%)
Herbicides:					
2,4-D	101	1.59	0.14	0.20	37.7
Diuron	85	0.52	0.03	0.06	31.8
Dichlobenil	65	0.16	0.02	0.02	24.3
Triclopyr	54	0.53	0.11	0.10	20.2
Dicamba	47	0.34	0.06	0.06	17.5
Metolachlor	36	0.27	0.07	0.06	13.4
Isoxaben	32	0.82	0.07	0.18	12.0
MCPA	30	0.83	0.15	0.19	11.2
MCPP	30	0.53	0.08	0.11	11.2
Terbacil	30	0.70	0.16	0.14	11.2
Imazapyr	29	0.06	0.02	0.01	10.9
Bentazon	24	0.15	0.09	0.03	9.0
Simazine	19	0.80	0.31	0.23	7.1
Sulfentrazone	18	0.21	0.08	0.04	6.7
Tebuthiuron	18	0.18	0.09	0.03	6.7
Bromacil	17	0.05	0.04	0.01	6.3
Monuron	16	0.01	0.01	0.00	6.0
Dacthal	12	0.06	0.03	0.01	4.5
Atrazine	8	0.18	0.07	0.05	3.0
Pendimethalin	7	0.23	0.09	0.06	2.6
Treflan (Trifluralin)	6	0.04	0.03	0.01	2.2
Chlorpropham	4	0.91	0.30	0.35	1.5
Oxadiazon	4	0.06	0.04	0.02	1.5
Chlorsulfuron	3	0.06	0.04	0.01	1.1
Sulfometuron methyl	3	0.02	0.02	0.00	1.1
Bromoxynil	2	0.04	0.04	0.01	0.8
Clopyralid	2	0.07	0.07	0.01	0.8
Metsulfuron-methyl	2	0.06	0.05	0.02	0.8
Diphenamid	1	0.02	0.02	n/a	0.4
Metribuzin	1	0.30	0.30	n/a	0.4
Picloram	1	0.17	0.17	n/a	0.4
Degradates:					
2,6-Dichlorobenzamide	137	0.36	0.08	0.06	50.9
Oxamyl Oxime	45	0.58	0.13	0.12	16.9
4,4'-DDE	44	0.05	0.02	0.01	15.7
4,4'-DDD	9	0.03	0.02	0.01	3.2
4-Nitrophenol	4	0.10	0.07	0.02	1.5
Desisopropyl Atrazine	3	0.05	0.02	0.02	1.1
Malaoxon	3	0.00	0.00	0.00	1.1
Tetrahydrophthalimide	3	0.13	0.09	0.03	1.1
Desethylatrazine	2	0.01	0.01	0.00	0.8

Pesticides detected in 2016	Detections	Max concentration (µg/L)*	Average concentration (µg/L)*	Std. dev. (µg/L)*	Detection frequency (%)
Insecticide:					
Thiamethoxam	78	0.41	0.05	0.07	29.2
Imidacloprid	74	0.13	0.03	0.03	27.7
Chlorantraniliprole	59	0.25	0.02	0.05	22.1
Oxamyl	43	0.50	0.08	0.09	16.1
Dinotefuran	42	0.79	0.15	0.17	15.7
Chlorpyrifos	19	1.26	0.13	0.27	7.1
4,4'-DDT	18	0.04	0.03	0.01	6.4
Diazinon	10	0.10	0.05	0.02	3.7
Clothianidin	7	0.03	0.02	0.01	2.6
Carbaryl	5	0.09	0.04	0.03	1.9
Malathion	4	0.23	0.14	0.06	1.5
Ethoprop	2	0.04	0.04	0.00	0.8
Baygon	1	0.01	0.01	n/a	0.4
Bifenthrin	1	0.03	0.03	n/a	0.4
Imidan	1	0.03	0.03	n/a	0.4
Methiocarb	1	0.12	0.12	n/a	0.4
Methoxyfenozide	1	0.01	0.01	n/a	0.4
Pyridaben	1	0.45	0.45	n/a	0.4
Pyriproxyfen	1	0.32	0.32	n/a	0.4
Tetrachlorvinphos (Gardona)	1	0.10	0.10	n/a	0.4

* Values have been rounded to 2 decimal places

Table 4 – Statewide pesticide detections summarized by general use category

Pesticide general use category	Number of analytes detected	Number of individual detections	Percentage of total detections
Synergist	1	5	0.3%
Insect repellent	1	21	1.2%
Wood preservative	1	25	1.4%
Degradate	9	250	14.3%
Insecticide	20	369	21.1%
Fungicide	13	375	21.4%
Herbicide	31	707	40.3%
Total analytes	76	1752	100.0%

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 factors. Summary statistics for pesticide detections by monitoring site are presented in Table 5. This table shows the lowest number of detections from a single sampling event at each site to the highest number and includes the mean number of analytes detected, 25th percentile, and 75th percentile.

Table 5 – Summary of pesticide detections by monitoring sites in 2016

Monitoring sites	Total detections	Min	25th percentile	Mean	75th percentile	Max	Std. dev.
Upper Big Ditch	295	8	11	12.3	14	21	3.2
Lower Bertrand Creek	290	6	10	12.1	12.75	24	4.2
Upper Bertrand Creek	250	3	6.5	10.4	13.75	22	5.1
Lower Big Ditch	239	2	5	10.0	14	20	5.0
Indian Slough	188	2	4.25	9.0	11	20	5.2
Marion Drain	143	3	4	5.7	7.5	11	2.4
Sulphur Creek Wasteway	100	3	3	4.5	5	8	1.4
Upper Brender Creek	89	1	3	4.1	5	7	1.5
Snipes Creek	66	1	2	3.3	4.75	6	1.7
Stemilt Creek	32	0	1	1.8	3	5	1.4
Clarks Creek	31	1	1	1.3	1	3	0.7
Mission Creek	20	0	0	0.9	2	2	0.9
Lower Brender Creek*	9	0	0.75	0.8	1	1	0.5

*Lower Brender Creek samples were analyzed for a subset of 8 analytes.

Table 6 shows a breakout of the new analytes for 2016 and their detection frequencies during the 2016 monitoring season. This is a subset of information found in Table 3 but includes the new analytes that were not detected as well.

Table 6 – Analytes added to the program in 2016

Analytes added to the program in 2016	Number of detections in 2016	Detection frequency (%)
2,6-Dichlorobenzamide	137	50.7
Chlorantraniliprole	59	22.5
Triazine DIA degradate	3	1.1
Triazine DEA degradate	2	0.8
Pyriproxyfen	1	0.4
Chlorethoxyfos	0	0.0
Dithiopyr	0	0.0
Prallethrin	0	0.0
Prodiamine	0	0.0
Pyrethrins	0	0.0
Spirotetramat	0	0.0
Tefluthrin	0	0.0

Herbicide Detections

Herbicides were the most frequently detected use group making up approximately 40% (707 detections) of the total pesticide detections. Of the 31 herbicides detected, 2,4-D, diuron, and dichlobenil were the most frequently detected with 101, 85, and 65 detections, respectively. These were also the most commonly detected herbicides in 2015. Of the 57 herbicides included in the laboratory analysis, 31 (54%) were detected in surface water. Simazine was the only herbicide that exceeded WSDA assessment criteria in 2016.

Fungicide Detections

Fungicides were the second most frequently detected group of pesticides making up 375 detections, or 21% of the total number of detections. For comparison, in 2015 the fungicides were also the second most frequently detected group of pesticides making up 25% of the total number of detections. Out of 19 fungicides included in the laboratory analysis, 13 (68%) were detected in surface water at the monitoring sites. Of those, boscalid, azoxystrobin, and fludioxonil were the most commonly detected fungicides with 111, 60, and 59 detections respectively. Detections of fungicides occur primarily at western Washington sampling sites (approximately 89%). The slight decrease of fungicide detections may be due to unseasonably dry conditions that occurred during spring 2016 in western Washington. Less rainfall reduced the likelihood of pesticides entering the streams via runoff and reduced pest pressure. There were no detections of fungicides above the assessment criteria in 2016.

Insecticide Detections

Insecticides were the third most frequently detected group of pesticides representing approximately 21% of the total detections. Of the 55 insecticides included in the laboratory analysis, 20 (36%) were detected in surface water. Thiamethoxam, imidacloprid, and chlorantraniliprole were the most commonly detected insecticides with 78, 74, and 59 detections respectively. Of the 19 current-use insecticides that were detected in 2016, bifenthrin, chlorpyrifos, diazinon, malathion, methiocarb, pyriproxyfen, and pyridaben all exceeded the assessment criteria at least once. Detections of the legacy pesticide 4,4'-DDT exceeded the assessment criteria at multiple monitoring sites as well.

Degradate Detections

There were 250 detections of pesticide degradates in 2016 accounting for approximately 14% of the total detections. Of the 18 pesticide degradates included in the laboratory analysis, 9 (50%) were detected. The most frequently detected of those were 2,6-dichlorobenzamide (degradate of the herbicide dichlobenil) with 137 detections, followed by oxamyl oxime (degradate of carbamate insecticide oxamyl) with 45 positive detections and 4,4'-DDE (degradate of 4,4'-DDT) with 44 detections. The degradate 2,6-dichlorobenzamide, a new analyte for 2016, was found ubiquitously throughout the season at the western Washington sites and June through July at the eastern Washington sites. The only pesticide degradates to exceed the criteria were 4,4’-DDE and 4,4'-DDD which are the primary breakdown products of the highly persistent legacy pesticide 4,4'-DDT.

Other Pesticide Detections

Other pesticide detections included the wood preservative pentachlorophenol which was detected 25 times, the insect repellent N,N-Diethyl-m-toluamide (commonly referred to as

DEET) which was detected 21 times, and the pesticide synergist piperonyl butoxide (PBO) which was detected 5 times.

Pesticide Exceedances Summary

There were 108 instances where pesticide analytes were detected at concentrations that exceeded the assessment criteria listed in Attachment 1 (Appendix B: Assessment Criteria for Pesticides). The 11 different pesticide analytes that exceeded the assessment criteria on 1 or more occasions are listed in Table 7. Individual pesticide exceedances are also discussed in more detail in the Pesticide Calendars section in this report.

Table 7 – Summary of pesticide exceedances of WSDA's assessment criteria

Pesticide	Pesticide category	Detections	Detections above the assessment criteria	Monitoring locations where exceedances occurred
4,4'-DDD	Organochlorine Degradate	9	9	Upper Brender Creek
4,4'-DDE	Organochlorine Degradate	44	44	Lower Big Ditch, Upper Brender Creek, Lower Brender Creek, Indian Slough, Mission Creek, Sulphur Creek
4,4'-DDT	Organochlorine Degradate	18	18	Upper Brender Creek, Mission Creek
Bifenthrin	Pyrethroid Insecticide	1	1	Upper Big Ditch
Chlorpyrifos	Organophosphate Insecticide	19	19	Upper Brender Creek, Indian Slough, Marion Drain, Mission Creek, Stemilt Creek, Snipes Creek, Sulphur Creek
Diazinon	Organophosphate Insecticide	10	1	Indian Slough
Malathion	Organophosphate Insecticide	4	4	Lower Bertrand Creek, Marion Drain, Mission Creek, Stemilt Creek, Snipes Creek
Methiocarb	Carbamate Insecticide	1	1	Upper Big Ditch
Pyridaben	Insecticide	1	1	Upper Big Ditch
Pyriproxyfen	Insecticide	1	1	Upper Brender Creek
Simazine	Herbicide	19	9	Lower Bertrand Creek, Upper Bertrand Creek, Indian Slough

Criteria Exceedances of Legacy Insecticides and Pesticide Degradates

Products containing DDT were banned for use by the US EPA 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 66% of the total exceedances detected in 2016. Of the 71 combined exceedances, 57 (80%) were detected at the monitoring sites on Brender Creek. Although the detections of 4,4’-DDT, 4,4'-DDE, and 4,4'-DDD exceeded the state water quality criteria, these detections are not a result of current pesticide use patterns.

Criteria Exceedances of Current-use Insecticides

Detections of current-use insecticides accounted for 26% of all exceedances. The current-use insecticides that were detected at concentrations above the assessment criteria were chlorpyrifos, malathion, and diazinon (organophosphates); bifenthrin (pyrethroid); pyridaben; pyriproxyfen; and methiocarb (carbamate).

Criteria Exceedances of Herbicides

Although there were 707 total detections of herbicides, only 1 herbicide, simazine, was detected above the assessment criteria accounting for less than 8% of the total exceedances in 2016. Simazine was the 13th most commonly detected herbicide in 2016 with 19 detections.

Criteria Exceedances of Fungicides

Of the 13 fungicides detected in 2016 (with 375 total detections), none exceeded the assessment criteria. In comparison, there were a total of 5 exceedances of fungicides in 2015. The decrease in exceedances is consistent with the decrease in overall fungicide detections from 2015 to 2016; it may be due in part to the variation in seasonal rainfall and temperature between 2015 and 2016.

Exceedances by Location

All pesticide detections were at concentrations below available pesticide assessment criteria and standards at Clarks Creek. There were a total of 108 detections that exceeded the assessment criteria at the other 12 monitoring sites. Of those 108, 37 (34%) were currently registered pesticides and the other 71 (66%) were detections of DDT or its degradates. Most of the exceedances, 90 (83%), occurred at monitoring sites in eastern Washington including almost all of the statewide exceedances of DDT or its degradates (69). Only 2 of the 18 total exceedances that occurred at monitoring sites in western Washington were from DDT or its degradates (Table 8).

Table 8 – Monitoring sites where pesticide exceedances occurred

Monitoring sites	Exceedances for all analytes	Percentage of total in 2016	Exceedances of currently registered pesticides	Exceedances of DDT, DDD, and DDE	Percentage of exceedances due to DDT, DDD, and DDE
Lower Bertrand Creek	4	4%	4	0	0%
Upper Bertrand Creek	5	5%	5	0	0%
Lower Big Ditch	1	1%	0	1	100%
Upper Big Ditch	3	3%	3	0	0%
Upper Brender Creek	54	50%	6	48	91%
Lower Brender Creek*	9	8%	0	9	100%
Indian Slough	5	5%	4	1	20%
Marion Drain	2	2%	2	0	0%
Mission Creek	10	9%	2	8	80%
Stemilt Creek	2	2%	2	0	0%
Snipes Creek	6	6%	6	0	0%
Sulphur Creek	7	7%	3	4	57%
Clarks Creek	0	0%	0	0	0%
Statewide-Total	108	100%	37	71	66%

*Lower Brender Creek samples were only analyzed for 8 analytes.

Pesticide Mixtures Analysis

For the purposes of this report, the term ‘pesticide mixtures’ will refer to environmental mixtures in surface water containing 2 or more pesticides. This is different from ‘pesticide tank mixtures’ that refers to a combination of 1 or more agricultural or non-agricultural chemicals intentionally mixed before pesticide application.

During 2016, pesticide mixtures were found at most of the 270 sampling events (excluding sampling events at Lower Brender Creek). The Lower Brender Creek site was excluded from the pesticide mixtures analysis because it was analyzed for a limited subset of analytes each sampling event. As for the other 12 monitoring sites, at least 1 pesticide mixture was detected at each one in 2016. Pesticide mixtures were detected every week of the 25 week monitoring season at Upper and Lower Bertrand Creek in the Nooksack subbasin, Upper and Lower Big Ditch in the Lower Skagit-Samish subbasin, and Marion Drain in the Lower Yakima subbasin. Not all sites were sampled for 25 weeks during the season; some sites were selectively sampled during times of likely pesticide application to distribute funds for additional sampling elsewhere. Indian Slough in the Skagit-Samish subbasin and Sulphur Creek Wasteway in the Lower Yakima subbasin were sampled for 21 and 22 weeks respectively, and each one of the samples contained a pesticide mixture.

There were 223 (83%) sampling events where 2 or more pesticides were detected, 34 (13%) sampling events where only 1 pesticide was detected, and 13 (5%) sampling events where no pesticides were detected. Every sampling event at western Washington sites (UBC, LBC, UBD, LBD, and IS) contained 2 or more pesticide detections with the exception of Clarks Creek. Marion Drain and Sulphur Creek Wasteway sites in eastern Washington also contained 2 or more pesticide detections at every sampling event. The other 4 eastern Washington monitoring sites (UBR, SC, SN, and MI) showed more variation among the sampling event mixtures (Figure 2).

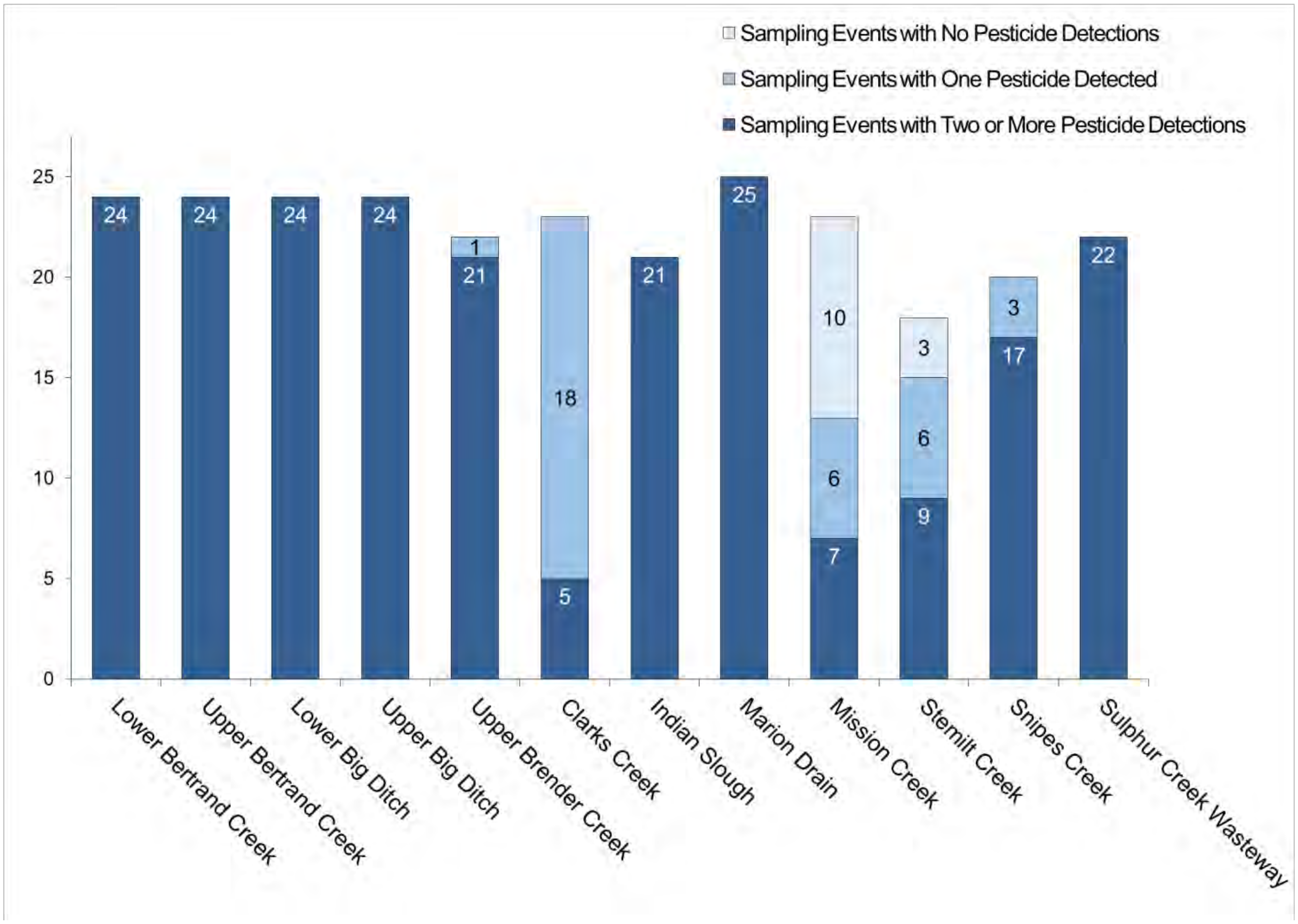

Figure 2 – Number of sampling events where mixtures were detected (Lower Brender Creek was not included in this chart)

The average number of pesticide detections per sampling event for all sampling events was 6.3 (Figure 3). The greatest number of pesticides detected during a single sampling event over the whole season was 24 at Lower Bertrand Creek on April 26th. Figure 3 shows that the average number of detections per site ranged from 12.3 detections (Upper Big Ditch) to 0.9 detections per sampling event (Mission Creek).

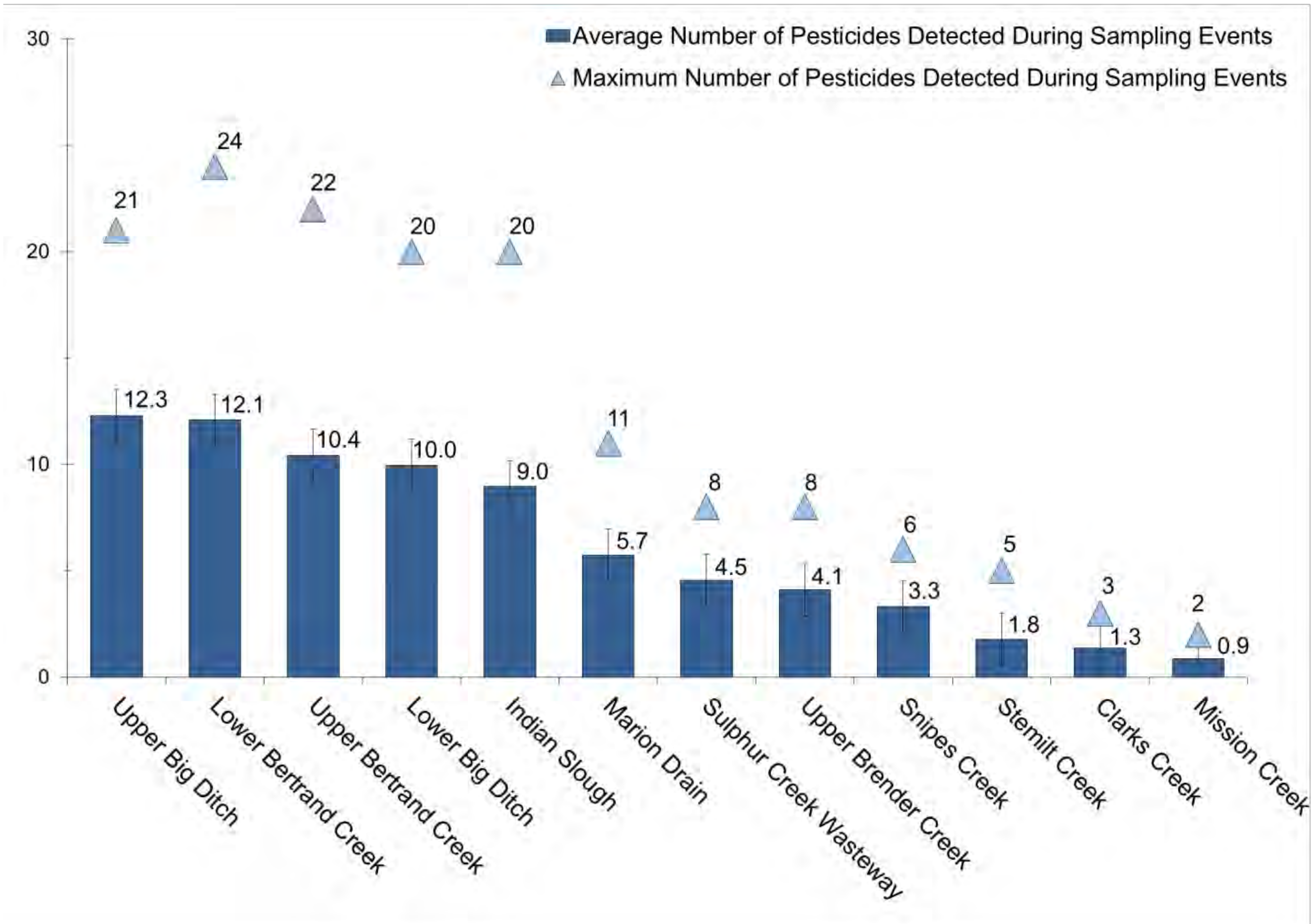

Figure 3 – Average and maximum number of pesticides detected at sampling events, with standard deviation (Lower Brender Creek was not included in this chart)

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 calculate TU, each pesticide concentration detected in the sample is divided by the corresponding pesticides LC50 or EC50 assessment criteria with WSDA's safety factor and then each of those ratios is summed. If the ratio is above or equal to 1, there is a higher possibility of lethal or sublethal effects on aquatic life. Of the 270 samples analyed using TUs, there were 25 samples that had a TU above or equal to 1. Of those, 24 samples had exceeding TUs primarily due to an elevated concentration of a single pesticide. The pesticides that contributed significantly to exceedances of TU values were bifenthrin, chlorpyrifos, diazinon, methiocarb, malathion, pyriproxyfen, and pyridaben. All of these chemicals were found in concentrations above WSDA assessment criteria at least once throughout the sampling season, often coinciding with the samples where TU was exceeded. The TU exceedances occurred at Lower Bertrand Creek, Upper Big Ditch, Upper

Brender Creek, Indian Slough, Marion Drain, Mission Creek, Stemilt Creek, Snipes Creek, and Sulphur Creek Wasteway.

Monitoring Site Summaries

Lower Bertrand Creek

- 24 sampling events
- 39 unique analytes identified
- 290 total pesticide detections
- 4 detections exceeding assessment criteria

On June 14th, 1 detection of malathion (0.155 µg/L) was greater than the NRWQC chronic criteria (0.1 µg/L) at Lower Bertrand Creek (Table 10). There were 3 detections of simazine, 2 in April (0.800, 0.367 µg/L), and another in July (0.342 µg/L) that were greater than WSDA's aquatic plant assessment criterion (50% of the most sensitive EC_{50} for aquatic plants).

Upper Bertrand Creek

- 24 sampling events
- 35 unique analytes identified
- 250 total pesticide detections
- 5 detections exceeding assessment criteria

All 5 detections above the criterion were for the herbicide, simazine, at Upper Bertrand Creek (Table 11). The concentrations of these 5 detections ranged from 0.318 and 0.779 µg/L. There were 3 detections in April, 1 on May 3rd, and 1 on July 12th. These observed concentrations were greater than WSDA's aquatic plant assessment criterion (50% of the most sensitive EC_{50} for aquatic plants).

Lower Big Ditch

- 24 sampling events
- 31 unique analytes identified
- 239 total pesticide detections
- 1 detection exceeding assessment criteria

The detection of 4,4'-DDE, on July 20th (0.016 µg/L), was greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average) at Lower Big Ditch (Table 12).

Upper Big Ditch

- 24 sampling events
- 35 unique analytes identified
- 295 total pesticide detections
- 3 detections exceeding assessment criteria

On July 20th, there was a pyridaben detection of 0.454 µg/L, which is above WSDA's assessment criteria for both fish acute (0.360 µg/L) and invertebrates acute (0.265 µg/L) at Upper Big Ditch (Table 13). A single detection of bifenthrin on August 9th (0.034 µg/L) was greater than the most sensitive NOAEC value for invertebrates (0.0013 µg/L). Also on August 9th, a detection of methiocarb (0.124 µg/L) was greater than the most sensitive NOAEC for invertebrates (0.100 µg/L).

Upper Brender Creek

- 22 sampling events
- 18 unique analytes identified
- 89 total pesticide detections
- 54 detections exceeding assessment criteria

Pyriproxyfen, detected once at 0.321 µg/L, was found at a concentration that was greater than the most sensitive NOAEC for invertebrates (0.015 µg/L) at Upper Brender Creek (Table 14). There were 5 detections of chlorpyrifos (March-April, 0.031-1.03 µg/L) that were greater than WSDA's assessment criterion (25% of the most sensitive LC_{50} value for invertebrates). There were 9 detections of 4,4'-DDD with a mean concentration of 0.018 µg/L, 22 detections of 4,4'-DDE with a mean concentration of 0.030 µg/L, and 17 detections of 4,4'-DDT with a mean concentration of 0.027 µg/L. All individual detections of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT were greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average).

Clarks Creek

- 23 sampling events
- unique analytes identified
- 31 total pesticide detections

All pesticide detections at Clarks Creek were below the available pesticide assessment criteria and state water quality standards (Table 15).

Indian Slough

- 21 sampling events
- 38 unique analytes identified
- 188 total pesticide detections
- 5 detections exceeding assessment criteria

There were 2 detections of chlorpyrifos that were greater than WSDA's assessment criterion (25% of the most sensitive LC_{50} for invertebrates), 1 on September 7th (0.320 µg/L) and 1 on September 12th (0.049 µg/L) at Indian Slough (Table 16). Also, 1 detection of 4,4'-DDE on May 10th (0.013 µg/L) was greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average). On May 6th, 1 detection of simazine (0.397 µg/L) was greater than WSDA's aquatic plant assessment criterion (50% of the most sensitive EC_{50} for aquatic plants). Diazinon, detected once on March 29th (0.100 µg/L), was greater than WSDA's chronic invertebrate assessment criterion (50% of the most sensitive invertebrate NOAEC).

Marion Drain

- 25 sampling events
- 28 unique analytes identified
- 143 total pesticide detections
- 2 detections exceeding assessment criteria

The 1 detection of chlorpyrifos on April 4th (0.03 µg/L) was greater than WSDA's acute invertebrate assessment criterion (25% of the most sensitive LC_{50} value for invertebrates) at Marion Drain (Table 17). The single detection of malathion (0.063) µg/L) on June 14th was greater than 50% of the NRWQC chronic criteria (0.1 µg/L).

Mission Creek

- 23 sampling events
- 11 unique analytes identified
- 20 total pesticide detections
- 10 detections exceeding assessment criteria

On March 29th, 1 detection of chlorpyrifos (0.037 µg/L) was greater than WSDA's acute invertebrate assessment criterion (25% of the most sensitive LC_{50} value for invertebrates) at Mission Creek (Table 18). On March 22nd, chlorpyrifos was again detected (1.26 µg/L) and was greater than the LC_{50} value for invertebrates (0.100 µg/L). A single detection of 4,4'-DDT on May 18th (0.035 µg/L) and 7 detections of 4,4'-DDE between May and August (0.016-0.036 µg/L) were greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average).

Stemilt Creek

- 18 sampling events
- 13 unique analytes identified
- 32 total pesticide detections
- 2 detections exceeding assessment criteria

The single detection of chlorpyrifos (0.035 µg/L) that occurred on March 29th was greater than WSDA's acute invertebrate assessment criterion (25% of the most sensitive LC_{50} value for invertebrates) at Stemilt Creek (Table 20). A detection of malathion (0.098 µg/L) on June 1st was greater than 50% of the NRWQC chronic criteria (0.1 µg/L).

Snipes Creek

- 20 sampling events
- 18 unique analytes identified
- 66 total pesticide detections
- 6 detections exceeding assessment criteria

The 5 detections of chlorpyrifos (0.031- 0.269 µg/L), March through May, were greater than the most sensitive LC_{50} value for invertebrates (0.100 µg/L) at Snipes Creek (Table 19). Malathion (0.228 µg/L) detected on June 13th was greater than the NRWQC chronic criteria (0.1 µg/L).

Sulphur Creek Wasteway

- 22 sampling events
- 25 unique analytes identified
- 100 total pesticide detections
- 7 detections exceeding assessment criteria

All 3 detections of chlorpyrifos were greater than WSDA's acute invertebrate assessment criterion (25% of the most sensitive LC_{50} value for invertebrates) at Sulphur Creek Wasteway: 1 on March 21st (0.14 µg/L), 1 on March 28th (0.140 µg/L), and 1 on April 4th (0.042 µg/L) (Table 21). There were 4 detections of 4,4'-DDE, 1 on April 26th (0.016 µg/L), 2 in July (0.014 and 0.016 µg/L), and 1 on June 27th (0.016 µg/L) was greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average).

Special Site Summary: Lower Brender Creek

- 12 sampling events
- 1 unique analyte identified, 4,4’-DDE
- 9 total pesticide detections
- 9 detections exceeding assessment criteria

Lower Brender Creek was sampled for a subset of 8 analytes (4,4'-DDT, 4,4'-DDT degradates, and other legacy organochlorine pesticides) and sampled less frequently than the other monitoring sites. The purpose of these Lower Brender Creek sampling events were to compare the DDT concentrations upstream (Upper Brender Creek) and downstream (Lower Brender Creek) of a recently restored wetland. The mean concentration of the 4,4'-DDE detections was 0.003 µg/L, with a maximum of 0.004 µg/L, and a minimum of 0.003 µg/L. All individual detections of 4,4'-DDE were greater than the WAC chronic standard (0.001 µg/L, a 4-day average concentration not to be exceeded more than once every 3 years on the average).

Pesticide Calendars

Pesticide calendars provide a chronological overview of the pesticides detected during the 2016 monitoring season and a visual comparison to the WSDA assessment criteria. For specific values and information on the assessment criteria development please refer to Attachment 1 (Appendix B: Assessment Criteria for Pesticides).

Detection of a pesticide concentration above the 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.

Table 9 presents the color codes used in Table 10 through Table 21 to compare detected pesticide concentrations to WSDA assessment criteria. Detections are compared to criteria top-down (starting with Fish Acute) and once an exceedance is confirmed, the color is not changed. 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. The blank cells in the calendars often indicate no chemical was detected, but can also mean a chemical was detected below reportable sample quantitation limits or there was no chemical analysis in special cases. 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.

Table 9 – Exceedance descriptions

Calendar cell color	WSDA exceedance description
Red	Fish Acute Exceedance
Magenta	Endangered Species Acute Exceedance
Pink	Invertebrate Acute Exceedance
Dark orange	WAC Exceedance
Dark orange	NRWQC Exceedance
Orange	Fish Chronic Exceedance
Yellow	Invertebrate Chronic Exceedance
Green	Aquatic Plant Exceedance
Light blue	Detection did not exceed assessment criteria
Gray	No published criteria available
	Not detected / below the minimum detection level

Table 10 – Lower Bertrand Creek pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul				Aug				
Analyte Name	**Use ǂ**	16	22	30	5	13	19	26	3	10	17	26	8	14	22	29	6	12	19	26	3	10	17	24	29
2,4-D	H				0.299			0.080										0.064							
2,6-Dichlorobenzamide	D-H	0.051	0.074	0.068	0.115	0.037	0.036	0.056	0.088	0.055	0.035	0.062	0.074	0.061	0.049	0.091	0.087	0.149	0.098	0.086	0.095	0.079	0.077	0.072	0.082
Atrazine	H															0.055									
Azoxystrobin	F				0.013														0.006						
Boscalid	F		0.099		0.144	0.066	0.075	0.275	0.086	0.074	0.068	0.074	0.091	0.148	0.036	0.072	0.120	0.088	0.148	0.132	0.115	0.093	0.075	0.061	0.063
Bromacil	H									0.042	0.051	0.052	0.045			0.043	0.041		0.039	0.044	0.044	0.048	0.035	0.035	0.041
Chlorantraniliprole	I	0.004		0.004	0.008	0.004		0.005	0.254	0.153	0.122	0.069	0.057	0.047	0.033	0.017	0.010	0.027	0.014		0.004				
Cyprodinil	F							0.020											0.007						
Dacthal (DCPA)	H																						0.039	0.046	
Diazinon	I-OP			0.063	0.046	0.034		0.055																	
Dicamba	H				0.070			0.026																	
Dichlobenil	H		0.025	0.029	0.102	0.019	0.013	0.041	0.006	0.012	0.010		0.009												
Diuron	H			0.005	0.008	0.017	0.006	0.004								0.087		0.010	0.143		0.042	0.023	0.010	0.007	0.011
Fludioxonil	F													0.027		0.039	0.030		0.032	0.033	0.030				
Imidacloprid	I-N	0.007		0.016	0.026	0.022	0.021	0.020	0.015	0.014		0.018	0.011	0.028	0.026	0.011		0.016							
Isoxaben	H				0.003			0.002								0.032	0.013	0.075	0.022	0.006					
MCPA	H				0.358			0.054										0.085							
Malaoxon	D-OP			0.003																					
Malathion	I-OP													0.155											
Mecoprop (MCPP)	H		0.036	0.036	0.315			0.059										0.053							
Metalaxyl	F	0.073	0.072	0.135	0.351	0.093	0.090	0.135	0.070			0.095		0.085	0.060	0.067	0.059	0.053	0.064		0.063	0.056	0.055	0.052	0.057
Metolachlor	H	0.038	0.106	0.038	0.093	0.032		0.048																	
Monuron	H																		0.014	0.013	0.008	0.006			0.007
Myclobutanil	F								0.005						0.007			0.007							
DEET	IR							0.040																	
Oxadiazon	H																	0.048							
Oxamyl	I-C	0.084		0.135	0.098	0.071	0.085	0.111	0.040	0.098	0.041	0.089	0.101	0.117	0.113		0.113	0.084	0.061	0.098	0.114	0.131	0.121	0.100	0.147
Oxamyl oxime	D-C	0.080		0.131	0.101	0.211	0.321	0.160	0.233	0.212	0.183	0.135	0.094	0.151	0.232	0.283	0.222	0.192	0.266	0.291	0.211	0.214	0.220	0.291	0.267
Pentachlorophenol	WP																						0.030	0.038	
Propiconazole	F			0.035	0.171			0.065																	
Propoxur	I-C				0.008																				
Pyraclostrobin	F							0.011																	
Simazine	H				0.800			0.367	0.089	0.106	0.069			0.055				0.342							
Sulfentrazone	H								0.069	0.075	0.111	0.114	0.121	0.119		0.051	0.048		0.063	0.055	0.071	0.070	0.067		0.063
Terbacil	H				0.185			0.132																	
Tetrahydrophthalimide (THPI)	D-F																0.133		0.075	0.057					
Thiamethoxam	I-N			0.011	0.023	0.018	0.014	0.014	0.021	0.018	0.024	0.027	0.025	0.033	0.180	0.151	0.079	0.079	0.060	0.043	0.031	0.051	0.040	0.036	0.040
Triclopyr acid	H							0.047																	
Trifluralin	H				0.033																				
Precipitation	N/A	3.51	0.41	1.47	2.06	0.94	0.99	2.13	0.08	0.15	0.08	0.51	0.56	0.18	0.61	0.53	0.23	0.81	--	--	0.28	0.03	0.03	0.00	0.64
Streamflow	N/A	151.0	99.0	81.4	138.0	76.5	38.6	54.5	32.5	21.9	16.6	17.0	13.3	12.3	13.3	10.0	10.0	11.9	8.4	6.1	5.8	5.6	6.1	5.5	6.0
Total Suspended Solids	N/A	7	11	5	10	4	3	5	7	2	2	3	1	1	2	1	1	1	1	1	1	1	1	1	1

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L). The "--" signifies a sample or measurement was not collected.

Table 11 – Upper Bertrand Creek pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul				Aug				
Analyte Name	**Use ǂ**	16	22	30	5	13	19	26	3	10	17	26	8	14	22	29	6	12	19	26	3	10	17	24	29
2,4-D	H				0.360	0.518		0.073				0.034			0.039			0.060							
2,6-Dichlorobenzamide	D-H	0.048		0.050	0.111		0.068	0.094		0.084	0.038	0.038	0.077	0.040	0.075	0.106		0.179	0.081	0.057	0.044	0.037	0.032	0.032	0.028
Atrazine	H															0.175	0.079	0.063		0.028					
Azoxystrobin	F				0.012																				
Boscalid	F	0.075	0.121	0.088	0.180	0.066	0.109	0.408	0.150	0.352	0.130	0.106	0.159	0.116	0.066	0.092	0.080	0.113	0.088	0.070	0.072	0.059	0.059	0.054	0.060
Chlorantraniliprole	I			0.002		0.002		0.002	0.009	0.009	0.009				0.004			0.170	0.030		0.010				
Cyprodinil	F						0.007	0.031	0.008																
Dacthal (DCPA)	H											0.026												0.032	
Diazinon	I-OP							0.027																	
Dicamba	H				0.066	0.078		0.028																	
Dichlobenil	H		0.043	0.036	0.157	0.031	0.031	0.057	0.020	0.013	0.015	0.014	0.013	0.011	0.021	0.015		0.018		0.011					
Diuron	H				0.004																				
Fludioxonil	F								0.043	0.618															
Imidacloprid	I-N	0.011	0.025	0.017	0.024	0.014	0.051	0.028	0.029	0.029	0.037	0.055	0.055	0.129	0.080	0.077	0.036	0.060	0.028	0.031	0.011		0.011	0.007	
Isoxaben	H				0.003	0.002	0.006								0.817	0.303	0.107	0.661	0.101	0.041	0.020	0.011	0.007	0.007	0.006
MCPA	H				0.417	0.110	0.021	0.062	0.045	0.042					0.256			0.145							
Malaoxon	D-OP			0.003											0.004										
Mecoprop (MCPP)	H		0.075	0.052	0.284	0.530	0.051	0.079		0.020		0.024	0.017					0.066							
Metalaxyl	F			0.135	0.245	0.063	0.098	0.148	0.054					0.049		0.058	0.037								
Metolachlor	H	0.035	0.098	0.040	0.072			0.033																	
Myclobutanil	F		0.006				0.006		0.009						0.011	0.007	0.006	0.009							
DEET	IR							0.042		0.028					0.014			0.043	0.020						
Oxadiazon	H																	0.064	0.033	0.025					
Oxamyl	I-C	0.007	0.016	0.009	0.005	0.011	0.006	0.007	0.005	0.011	0.004	0.010	0.005	0.005	0.006			0.001							
Oxamyl oxime	D-C	0.011	0.026	0.015		0.051	0.048	0.014	0.039	0.038	0.036	0.021	0.023	0.027	0.018	0.029		0.016	0.027	0.014					
Pentachlorophenol	WP																							0.021	
Propiconazole	F		0.043	0.043	0.216	0.037	0.035	0.101	0.018									0.012							
Pyraclostrobin	F							0.018																	
Simazine	H				0.779		0.318	0.425	0.617		0.145	0.178	0.225	0.141			0.109	0.570							
Tebuthiuron	H									0.110															
Terbacil	H			0.071	0.136			0.126	0.092		0.088	0.110	0.107	0.080				0.050							
Thiamethoxam	I-N		0.012		0.017			0.013							0.010			0.007							
Triazine DIA degradate	D-H											0.009					0.012	0.046							
Triclopyr acid	H							0.076																	
Trifluralin	H				0.037																				
Precipitation	N/A	3.51	0.41	1.47	2.06	0.94	0.99	2.13	0.08	0.15	0.08	0.51	0.56	0.18	0.61	0.53	0.23	0.81	--	--	0.28	0.03	0.03	0.00	0.64
Streamflow	N/A	63.8	45.5	35.9	67.3	51.2	11.8	23.4	8.4	5.8	4.1	3.5	3.0	2.9	3.2	2.7	4.2	4.0	2.3	1.3	1.1	1.0	0.8	0.6	0.7
Total Suspended Solids	N/A	5	3	2	6	8	2	3	1	1	1	2	3	1	2	2	2	2	1	3	2	1	2	5	5

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L). The "--" signifies a sample or measurement was not collected.

Table 12 – Lower Big Ditch pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul			Aug				Sep	
Analyte Name	**Use ǂ**	15	23	29	6	12	20	26	4	10	18	25	7	15	21	28	5	13	20	9	15	23	30	7	12
2,4-D	H			0.123	0.176		0.050	0.257	0.042			0.070		0.261	0.493	0.143						0.039		0.837	0.152
2,6-Dichlorobenzamide	D-H	0.053	0.097	0.184	0.123	0.098	0.058	0.088	0.081					0.039		0.057					0.042		0.035	0.046	0.081
4,4'-DDE	D-OC																		0.016						
Atrazine	H															0.074									
Azoxystrobin	F	0.226	0.877	0.507	1.430	0.066	0.161	0.080	0.080	0.012	0.025	0.062	0.005	0.035	0.043	0.066		0.022			0.022			0.058	0.063
Bentazon	H	0.058		0.080																					
Boscalid	F		0.098			0.069	0.113		0.140	0.066	0.077	0.090		0.103	0.065	0.054	0.046			0.038	0.059	0.039	0.059	0.073	0.152
Bromoxynil	H							0.030																	
Chlorpropham	H		0.145		0.905							0.047													
Dicamba	H						0.027	0.082						0.029	0.336	0.053								0.219	0.039
Dichlobenil	H		0.044	0.047	0.025	0.007		0.018								0.014								0.015	
Difenoconazole	F	0.023	0.192	0.110	0.152	0.056	0.068	0.054	0.023														0.038		0.035
Dinotefuran	I-N		0.088	0.062	0.062	0.081	0.075	0.053	0.116	0.016		0.020		0.039	0.024	0.038	0.034	0.011			0.014		0.014	0.020	0.023
Diuron	H	0.025	0.025	0.034	0.024	0.019	0.021	0.040	0.014		0.025	0.007				0.011	0.006							0.005	
Fludioxonil	F		0.396	0.201	0.358	0.116	0.146	0.109	0.155	0.053	0.082	0.070	0.025	0.063	0.130	0.052	0.039	0.046	0.035	0.034	0.040	0.031	0.037	0.062	0.067
Imazapyr	H								0.013							0.064				0.027	0.013	0.005	0.012	0.032	0.017
Imidacloprid	I-N	0.011		0.010			0.013	0.022	0.006			0.016		0.022	0.046	0.077									
Isoxaben	H																							0.011	0.003
MCPA	H				0.034		0.031	0.057				0.045			0.049										
Mecoprop (MCPP)	H			0.044	0.048			0.017																	
Metalaxyl	F															0.241	0.138								
Metolachlor	H	0.105	0.051	0.078	0.055	0.052	0.131	0.271		0.032		0.056		0.053		0.130									0.023
Metribuzin	H											0.300													
Monuron	H			0.003	0.003	0.004	0.006	0.006																	
DEET	IR							0.041								0.024					0.022			0.026	0.022
Oxamyl oxime	D-C																				0.035				
Pentachlorophenol	WP	0.022	0.023	0.043		0.015		0.032				0.007													
Propiconazole	F						0.104	0.098	0.025						0.028										
Sulfentrazone	H							0.210																	
Sulfometuron methyl	H										0.010			0.018											
Tebuthiuron	H																								0.084
Thiamethoxam	I-N	0.026					0.057		0.017					0.029	0.012		0.024	0.005			0.017		0.018	0.027	0.043
Triadimefon	F														0.207										
Triclopyr acid	H			0.074	0.100			0.134	0.043			0.045		0.179	0.269	0.084				0.046	0.053			0.532	0.177
Precipitation	N/A	2.01	0.76	2.36	1.52	0.00	0.20	1.78	0.00	0.23	0.00	1.07	0.23	5.13	2.11	0.99	0.03	0.51	0.00	0.05	0.00	0.00	0.08	1.45	0.36
Streamflow	N/A	40.6	20.5	27.6	18.3	29.9	25.0	34.5	14.0	26.0	16.3	17.4	43.4	17.0	27.4	6.1	24.2	15.7	24.8	1.9	--	10.2	10.2	8.2	2.8
Total Suspended Solids	N/A	22	14	10	9	10	16	27	6	39	23	26	42	25	7	5	11	19	8	4	13	8	62	22	29

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L). The "--" signifies a sample or measurement was not collected.

Table 13 – Upper Big Ditch pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul			Aug				Sep	
Analyte Name	**Use ǂ**	15	23	29	6	12	20	26	4	10	18	25	7	15	21	29	5	13	20	9	15	23	30	7	12
2,4-D	H	0.244	0.159		0.086		0.065	0.111	0.052	0.168		0.066	0.071	0.299	0.130			0.095		0.174	0.067	0.056	0.052	0.237	0.088
2,6-Dichlorobenzamide	D-H	0.172	0.155	0.356	0.236	0.047	0.135	0.125	0.123	0.071		0.087	0.074	0.196		0.086	0.096	0.086	0.079	0.070	0.053	0.062	0.065	0.049	0.117
4-Nitrophenol	D-M					0.053			0.079																
Azoxystrobin	F		0.008	0.010	0.549	0.025	0.015	0.005	0.079	0.085	0.067	0.055	0.050	0.006	0.025	0.735		0.231	0.027		0.110	0.058		0.026	0.033
Bifenthrin	I-Py																			0.034					
Boscalid	F			0.089	0.598	0.191	0.124		0.194		0.383		0.289		0.035	0.127	0.625	0.265	0.115	0.288	0.262	0.109	0.100	0.060	0.099
Clopyralid	H												0.074	0.065											
Cyprodinil	F				0.011																		0.011		
Dicamba	H	0.023	0.061				0.029	0.044		0.023				0.047	0.048					0.047				0.083	
Dichlobenil	H	0.037	0.030	0.024	0.019		0.008	0.011	0.008	0.012	0.010		0.009	0.031	0.027	0.015									
Dinotefuran	I-N	0.176	0.188	0.514	0.336	0.610	0.304	0.359	0.365	0.792	0.128	0.148	0.157	0.067	0.278	0.176	0.342	0.094	0.162	0.092	0.040	0.039	0.046	0.036	0.033
Diuron	H		0.009	0.004	0.004	0.005	0.004	0.006							0.009					0.007				0.007	
Ethoprop	I-OP							0.035																	
Etridiazole	F				0.111								0.019											0.033	0.104
Fludioxonil	F		0.086	0.072	0.204	0.109	0.099	0.070	0.181		0.201		0.318	0.062	0.076	0.182	0.461	0.216	0.110	0.328	0.166	0.123	0.136	0.095	0.202
Imazapyr	H								0.023	0.026	0.024	0.024				0.014				0.012	0.021	0.031	0.027	0.026	0.024
Imidacloprid	I-N				0.106			0.007	0.014	0.032	0.017	0.010	0.013		0.012	0.036	0.063	0.018	0.012	0.056	0.096	0.017	0.019		
Isoxaben	H				0.003																	0.024	0.019	0.003	
Mecoprop (MCPP)	H	0.180			0.048			0.009		0.022				0.064	0.031					0.050				0.035	
Metalaxyl	F								0.057						0.087	0.991	0.094								
Methiocarb	I-C																			0.124					
Metolachlor	H									0.047					0.251										
Myclobutanil	F				0.008				0.006							0.005	0.023			0.012					
DEET	IR							0.031												0.023	0.023				
Oxamyl	I-C																		0.373	0.497	0.085	0.006	0.008		
Oxamyl oxime	D-C																		0.578	0.204	0.034	0.018			
Pentachlorophenol	WP	0.027				0.014								0.015											
Picloram	H																	0.165							
Propiconazole	F															0.011									
Pyraclostrobin	F				0.035	0.019					0.011						0.043			0.029	0.058	0.005	0.005		
Pyridaben	I																		0.454						
Tebuthiuron	H												0.137			0.083	0.079	0.073	0.085	0.088	0.094	0.110	0.118	0.081	0.182
Thiamethoxam	I-N				0.405	0.038	0.046		0.081	0.086	0.175	0.121	0.083		0.015	0.075	0.379	0.174	0.043	0.189	0.065	0.060	0.096	0.027	0.038
Triclopyr acid	H	0.077		0.046	0.055	0.036	0.045	0.091	0.054	0.111		0.057	0.069	0.298	0.090	0.057		0.104		0.127	0.105	0.086	0.067	0.266	0.140
Trifloxystrobin	F									0.032										0.019					
Precipiation	N/A	2.26	0.69	3.43	1.93	0.00	0.53	2.29	0.00	0.36	0.00	1.68	0.33	4.22	1.98	1.12	0.03	0.48	0.00	0.03	0.00	0.00	0.13	8.89	0.43
Streamflow	N/A	12.0	3.7	3.9	3.9	2.3	2.0	2.6	1.5	1.3	1.0	1.1	1.0	6.0	2.3	1.2	1.0	1.0	0.9	0.6	0.4	0.3	0.3	0.5	0.6
Total Suspended Solids	N/A	10	5	4	4	3	8	5	7	6	6	7	8	6	6	6	6	6	7	21	11	13	8	8	6

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable
Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 14 – Upper Brender Creek pesticide calendar

Month and Day		Mar		Apr				May				Jun				Jul				Aug			
Analyte Name	**Use ǂ**	22	29	5	12	19	27	3	10	18	25	1	14	21	28	6	12	19	26	3	9	16	23
2,4-D	H																				0.082		
2,6-Dichlorobenzamide	D-H														0.025	0.023		0.022	0.024		0.021	0.022	
4,4'-DDD	D-OC						0.024				0.024	0.024	0.025			0.016		0.015			0.017	0.017	0.003
4,4'-DDE	D-OC	0.039	0.024	0.036	0.021	0.028	0.026	0.029	0.034	0.016	0.030	0.048	0.043	0.041	0.029	0.033	0.030	0.027	0.024	0.023	0.039	0.029	0.018
4,4'-DDT	I-OC			0.029	0.025	0.026	0.029	0.026	0.035		0.035	0.039	0.044	0.015		0.026		0.026	0.024	0.025	0.029	0.026	0.007
Chlorpyrifos	I-OP	0.103	0.053	0.043	0.031		0.040																
Dacthal (DCPA)	H							0.029					0.024				0.030						
Diazinon	I-OP				0.043											0.030							
Difenoconazole	F		0.005		0.009	0.009																	
Diuron	H			0.004																			
Fenarimol	F	0.083						0.041				0.084			0.037				0.045		0.046		
Imidacloprid	I-N	0.006	0.009	0.010		0.012	0.008																
Myclobutanil	F						0.012																
DEET	IR																0.033					0.021	
Pentachlorophenol	WP																		0.017				
Phosmet	I-OP																0.031						
Piperonyl butoxide (PBO)	SY	0.079	0.049	0.079																			
Pyriproxyfen	I			0.321																			
Precipitation	N/A	0.08	0.00	0.18	0.00	1.93	0.00	0.00	0.05	0.28	1.85	0.00	0.05	1.27	0.03	0.00	0.63	0.41	0.00	0.00	0.03	0.00	0.00
Streamflow	N/A	4.1	3.8	3.7	3.2	2.9	6.7	3.7	2.2	4.2	4.2	3.7	4.1	3.2	2.4	3.2	3.5	6.4	1.5	2.5	5.5	3.7	2.8
Total Suspended Solids	N/A	58	43	79	24	33	152	37	53	39	31	67	68	41	34	40	37	60	20	18	62	40	33

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable
Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 15 – Clarks Creek pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul				Aug			
Analyte Name	**Use ǂ**	15	22	29	5	12	19	26	3	10	17	25	8	14	22	28	6	12	19	25	2	9	15	23
2,4-D	H								0.039															
2,6-Dichlorobenzamide	D-H		0.081		0.118	0.070	0.034		0.061	0.042	0.034	0.045	0.045	0.062	0.030	0.059	0.059	0.066	0.063	0.059	0.055	0.055	0.053	0.050
4-Nitrophenol	D-M	0.097						0.059																
Dacthal (DCPA)	H																					0.029		
Dichlobenil	H		0.021	0.007																				
Diuron	H							0.007																
Pentachlorophenol	WP	0.023	0.020																					
Triclopyr acid	H								0.022													0.041		
Precipitation	N/A	5.72	1.22	1.52	0.66	0.00	1.37	1.04	0.08	0.00	0.20	2.46	0.33	0.84	0.76	0.51	0.03	1.27	0.31	0.56	0.00	0.51	0.15	0.00
Streamflow	N/A	71.9	55.9	55.1	55.9	56.9	57.0	58.0	58.0	57.9	59.8	60.4	58.0	56.0	56.0	54.0	51.0	49.8	48.0	48.7	52.6	53.7	53.0	53.0
Total Suspended Solids	N/A	2	1	2	1	1	1	1	1	1	1	2	1	2	2	2	2	7	4	4	17	7	8	6

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 16 – Indian Slough pesticide calendar

Month and Day		Mar			Apr				May				Jun				Jul		Aug		Sep	
Analyte Name	**Use ǂ**	15	23	29	6	12	20	26	4	10	18	25	7	15	21	29	5	13	24	30	7	12
2,4-D	H		0.108		0.054		0.045	0.157				0.090			0.136	0.120					0.776	0.445
2,6-Dichlorobenzamide	D-H	0.154	0.116	0.219	0.181	0.103	0.103	0.183	0.095	0.049	0.081	0.113	0.070	0.078	0.144	0.133	0.133	0.088	0.031	0.028	0.175	0.339
4,4'-DDE	D-OC									0.013												
Azoxystrobin	F	0.022	0.026	0.020	0.145	0.015	0.007	0.028				0.005		0.005	0.007	0.008		0.006			0.050	0.024
Bentazon	H								0.064													
Boscalid	F									0.142												
Carbaryl	I-C							0.088													0.011	
Chlorpropham	H				0.104																	
Chlorpyrifos	I-OP																				0.032	0.049
Chlorsulfuron	H															0.043						
Clothianidin	I-N																				0.016	
Cyprodinil	F																				0.007	
Diazinon	I-OP			0.100	0.052																	
Dicamba	H		0.020																		0.226	0.158
Dichlobenil	H			0.010	0.037	0.007	0.007	0.026		0.017	0.013	0.017	0.012	0.011		0.021					0.047	0.029
Difenoconazole	F	0.009	0.009	0.011	0.011	0.014	0.008	0.017														
Diphenamid	H																0.021					
Diuron	H	0.044	0.015	0.027	0.029	0.009	0.009	0.011						0.003	0.058	0.031	0.017	0.012			0.522	0.229
Fludioxonil	F			0.045				0.044		0.026		0.025										0.042
Imazapyr	H								0.011	0.013						0.010					0.029	0.023
Imidacloprid	I-N	0.007						0.012													0.119	0.044
Isoxaben	H							0.022													0.011	
MCPA	H				0.388		0.829	0.159					0.055					0.071			0.543	0.284
Mecoprop (MCPP)	H		0.041					0.034				0.020									0.134	
Metolachlor	H	0.055		0.052	0.048	0.031	0.033	0.046				0.033			0.024						0.052	0.050
Metsulfuron-methyl	H																				0.062	0.027
Monuron	H			0.003	0.002	0.003	0.003	0.003														
DEET	IR																					0.023
Oxamyl	I-C															0.034						
Pentachlorophenol	WP	0.027		0.021		0.014																
Propiconazole	F	0.060	0.024	0.047	0.080	0.052	0.044	0.088	0.019				0.013	0.022	0.129	0.127		0.031			0.401	0.174
Simazine	H				0.397					0.196												
Sulfentrazone	H																			0.029		
Sulfometuron methyl	H														0.018							
Tebuthiuron	H										0.121					0.060	0.063		0.052	0.039		
Terbacil	H									0.099												
Thiamethoxam	I-N	0.027	0.014	0.024	0.021	0.012		0.012	0.009												0.048	0.021
Triclopyr acid	H		0.060	0.057	0.048		0.049	0.203				0.088			0.266	0.130					0.376	0.268
Precipitation	N/A	2.26	0.69	3.43	1.93	0.00	0.53	2.29	0.00	0.36	0.00	1.68	0.33	4.22	1.98	1.12	0.03	0.48	0.00	0.13	8.89	0.43
Streamflow	N/A	61.5	67.3	34.9	50.1	39.6	43.4	37.5	23.9	17.8	15.4	16.4	20.8	20.0	21.4	14.1	10.7	12.0	13.4	4.8	21.2	2.1
Total Suspended Solids	N/A	24	6	10	10	5	5	6	5	6	7	6	14	4	8	5	5	4	8	7	3	5

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 17 – Marion Drain pesticide calendar

Month and Day		Mar		Apr				May					Jun			Jul				Aug					Oct	Nov
Analyte Name	**Use ǂ**	21	28	4	11	18	26	2	9	17	24	31	13	20	27	5	11	18	27	2	8	15	22	29	31	7
2,4-D	H				0.027	0.031	0.049	0.071	0.045	0.090	0.195		0.081	0.050	0.059	0.095	0.071	0.045		0.042	0.039			0.051		
Atrazine	H																				0.018					
Azoxystrobin	F							0.007						0.008			0.012			0.024						
Bentazon	H	0.059						0.069	0.075	0.094	0.054	0.078	0.100	0.093	0.114	0.151	0.109	0.125	0.117	0.115	0.142	0.100	0.049	0.069	0.079	0.082
Boscalid	F														0.037	0.036		0.039		0.038						
Bromoxynil	H							0.043																		
Chlorantraniliprole	I		0.004			0.002	0.006	0.006	0.007		0.007	0.009	0.007	0.009			0.008		0.005	0.008			0.003		0.008	0.007
Chlorpyrifos	I-OP			0.031																						
Clothianidin	I-N																				0.022	0.022	0.014	0.015	0.032	0.031
Dacthal (DCPA)	H																								0.049	
Dicamba	H	0.022		0.020					0.019	0.038	0.019			0.026						0.037						
Difenoconazole	F		0.005		0.007																					
Diuron	H	0.007	0.009	0.013	0.008	0.015	0.033	0.010	0.007	0.006	0.003						0.007									
Fludioxonil	F									0.021																
Imidacloprid	I-N									0.008																
MCPA	H							0.029			0.029						0.030									
Malathion	I-OP															0.063										
Monuron	H																								0.003	
Myclobutanil	F									0.012	0.010				0.005		0.005			0.009	0.005					
DEET	IR																					0.020				
Pendimethalin	H						0.056	0.227	0.068	0.057	0.063	0.080	0.048													
Pentachlorophenol	WP																								0.027	0.026
Sulfentrazone	H							0.087																		
Terbacil	H						0.314	0.484	0.253	0.227	0.231	0.271	0.190			0.702	0.249	0.131	0.094	0.092	0.070	0.045		0.097		
Thiamethoxam	I-N													0.010			0.010	0.011	0.018	0.014	0.029	0.018	0.012	0.013	0.053	0.038
Triazine DEA degradate	D-H																								0.009	0.01
Triclopyr acid	H									0.026																
Trifluralin	H							0.025																		
Precipitation	N/A	0.00	0.00	0.00	0.33	0.41	0.18	0.00	0.00	1.37	0.13	0.00	0.05	0.23	0.00	0.00	0.20	0.03	0.10	0.00	0.18	0.28	0.36	0.08	0.33	0.13
Streamflow	N/A	247.7	187.1	256.5	--	255.7	162.2	145.4	122.7	151.0	146.6	75.6	24.0	35.9	23.6	25.0	26.2	21.3	26.1	42.2	62.2	59.0	62.7	69.6	177.8	173.4
Total Suspended Solids	N/A	14	10	33	28	21	13	14	14	17	12	4	2	3	2	3	3	3	3	5	16	6	5	6	11	10

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L). The "--" signifies a sample or measurement was not collected.

Table 18 – Mission Creek pesticide calendar

Month and Day		Mar		Apr				May				Jun				Jul				Aug				
Analyte Name	**Use ǂ**	22	29	5	12	19	27	3	10	18	25	1	14	21	28	6	12	19	26	3	9	16	23	29
2,4-D	H							0.068																
4,4'-DDE	D-OC									0.036							0.016	0.015	0.016	0.018		0.017		0.017
4,4'-DDT	I-OC									0.035														
Boscalid	F																						0.039	
Chlorpyrifos	I-OP	1.260	0.037																					
Dicamba	H							0.028																
Diuron	H			0.003																				
Imidacloprid	I-N												0.012							0.030				
DEET	IR																					0.022		
Piperonyl butoxide (PBO)	SY	0.696	0.052																					
Tetrachlorvinphos	I-OP																							0.1
Precipitation	N/A	0.08	0.00	0.18	0.00	1.93	0.00	0.00	0.05	0.28	1.85	0.00	0.05	1.27	0.03	0.00	0.63	0.41	0.00	0.00	0.03	0.00	0.00	0.00
Streamflow	N/A	99.0	85.6	149.0	126.0	116.0	69.5	58.4	48.2	48.3	28.5	24.1	20.7	17.1	11.6	10.3	4.9	17.3	39.3	7.2	14.4	6.6	7.0	4.1
Total Suspended Solids	N/A	23	14	119	123	42	39	19	15	8	13	6	6	7	8	6	6	599	113	34	179	26	11	25

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 19 – Snipes Creek pesticide calendar

Month and Day		Mar		Apr				May					Jun			Jul				Sep	
Analyte Name	**Use ǂ**	21	28	4	11	18	26	2	9	17	24	31	13	20	27	5	11	18	27	6	12
2,4-D	H					0.033	0.040		0.055	0.046	0.139	0.041	0.097	0.085	0.059	0.087	0.119	0.043	0.033	0.078	0.072
2,6-Dichlorobenzamide	D-H																		0.022		
Boscalid	F	0.062	0.050			0.099	0.075			0.067				0.015	0.050	0.038	0.044	0.044	0.036		
Carbaryl	I-C						0.011	0.060													
Chlorantraniliprole	I	0.005	0.003				0.003	0.006		0.009				0.009		0.005	0.007	0.008			
Chlorpyrifos	I-OP	0.269	0.098	0.060	0.033	0.031															
Diazinon	I-OP																	0.031			
Dicamba	H								0.030		0.060		0.027				0.039				
Dichlobenil	H	0.020															0.016				
Diuron	H	0.028	0.023		0.088	0.032					0.011										
Ethoprop	I-OP						0.044														
Isoxaben	H	0.004		0.004																	
MCPA	H					0.026					0.038										
Malathion	I-OP												0.228								
Methoxyfenozide	I						0.012														
Pyraclostrobin	F					0.019															
Thiamethoxam	I-N																0.021				
Triclopyr acid	H								0.029		0.056										
Precipitation	N/A	0.23	0.05	0.03	0.10	0.74	0.00	0.00	0.38	0.41	0.25	0.03	0.28	0.46	0.00	0.00	--	0.00	0.00	0.25	0.41
Streamflow	N/A	48.9	62.6	69.8	30.5	35.4	43.8	154.0	47.3	13.6	74.4	31.2	105.0	39.2	23.8	22.2	34.7	23.8	7.7	--	59.7
Total Suspended Solids	N/A	37	27	23	13	21	17	36	37	8	74	19	37	22	17	22	10	12	--	20	11

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable

Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L). The "--" signifies a sample or measurement was not collected.

Table 20 – Stemilt Creek pesticide calendar

Month and Day		Mar	Apr				May				Jun				Jul				Aug
Analyte Name	**Use ǂ**	29	5	12	19	27	3	10	18	25	1	14	21	28	6	12	19	26	3
2,4-D	H																0.147		
2,6-Dichlorobenzamide	D-H											0.048		0.033	0.027	0.026	0.030	0.046	0.041
Boscalid	F											0.129	0.016	0.054	0.040	0.043	0.046	0.041	0.040
Chlorpyrifos	I-OP	0.035																	
Chlorsulfuron	H													0.024				0.059	
Dacthal (DCPA)	H									0.023									
Diuron	H		0.003																
Imidacloprid	I-N											0.008							
Malathion	I-OP										0.098								
Myclobutanil	F															0.004			
Pentachlorophenol	WP	0.027	0.023	0.120	0.025	0.015													
Sulfentrazone	H																	0.027	
Triclopyr acid	H																	0.046	0.071
Precipitation	N/A	0.03	0.00	0.00	1.40	0.00	0.03	0.46	0.25	1.40	0.00	0.05	0.99	0.05	0.00	0.66	1.02	0.20	0.00
Streamflow	N/A	14.9	19.6	33.4	29.5	41.2	37.9	49.5	15.0	7.9	1.5	0.1	4.1	0.2	1.8	2.5	2.2	0.1	0.2
Total Suspended Solids	N/A	5	9	32	14	33	22	26	18	21	13	15	23	9	20	22	32	4	4

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable
Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Table 21 – Sulphur Creek Wasteway pesticide calendar

Month and Day		Mar			Apr				May					Jun			Jul				Sep		
Analyte Name	**Use ǂ**	14	21	28	4	11	18	26	2	9	17	24	31	13	20	27	5	11	18	25	6	12	19
2,4-D	H				0.074	0.033	0.043	0.040	0.066	0.067	0.195	0.197	0.138	1.590	0.087	0.147	0.090	0.134	0.092	0.059		0.064	0.062
2,6-Dichlorobenzamide	D-H	0.048																		0.020			
4,4'-DDE	D-OC							0.016								0.016		0.014	0.016				
Atrazine	H																		0.033				
Bentazon	H	0.062																					
Boscalid	F													0.092		0.043	0.052	0.046	0.048				
Bromacil	H															0.029	0.029			0.030	0.027		
Carbaryl	I-C							0.014															
Chlorantraniliprole	I		0.003	0.002					0.004	0.004			0.005	0.009	0.005			0.003					
Chlorpyrifos	I-OP		0.140	0.098	0.042																		
Dacthal (DCPA)	H																	0.037				0.045	
Dicamba	H				0.040				0.023	0.026	0.100	0.033	0.052	0.018	0.032	0.043	0.035					0.036	
Dichlobenil	H															0.013				0.016			
Difenoconazole	F					0.007																	
Diuron	H	0.077	0.017	0.109	0.107	0.020	0.033	0.061	0.020	0.047	0.024	0.019	0.006	0.009			0.027				0.077		
Fludioxonil	F																						0.020
Imazapyr	H								0.010	0.011	0.012	0.013									0.009		
Isoxaben	H						0.002																
MCPA	H								0.028										0.040				
Metolachlor	H												0.030										
Myclobutanil	F								0.057														
DEET	IR															0.021					0.019		
Terbacil	H																	0.034			0.028		0.051
Triclopyr acid	H										0.054	0.036											0.050
Trifluralin	H							0.039	0.024	0.030													
Precipiation	N/A	0.58	0.03	0.03	0.00	0.15	0.33	0.00	0.00	0.00	0.15	0.38	0.00	0.86	0.20	0.00	0.00	0.25	0.00	0.08	0.08	0.31	0.00
Streamflow	N/A	250.7	299.6	400.5	265.2	612.5	285.6	154.5	199.3	167.5	229.6	205.5	143.8	193.1	231.8	165.7	181.2	207.5	193.1	138.5	236.5	257.9	248.3
Total Suspended Solids	N/A	30	145	100	47	75	41	44	76	43	63	41	19	27	29	14	16	14	13	6	16	19	15

ǂ C: carbamate, D: degradate, F: fungicide, H: herbicide, I: insecticide, M: multiple, N: neonicotinoid, OC: organochlorine, OP: organophosphate, SY: synergist, WP: wood preservative, N/A: not applicable
Units for pesticide detections are in (µg/L), precipitation measurements are in (week total cm), streamflow measurements are in (cfs), and total suspended solids are in (mg/L).

Conventional Water Quality Parameters Summary

Table 22 provides an overview of the conventional water quality parameters at each site not including temperature. Measurements for pH, dissolved oxygen, and conductivity were collected in the field during all 282 sampling events. TSS (mg/L) was collected in the field by NRAS and analyzed by MEL. Streamflow measurements in cubic feet per second (cfs) were collected either by NRAS staff in the field or by USGS and US Bureau of Reclamation gauging stations.

Table 22 – Summary of conventional water quality parameters

Monitoring Site	Summary statistic	TSS (mg/L)	Stream discharge (cfs)	pH (s.u.)	Conductivity (µS/cm)	Dissolved oxygen (mg/L)
Upper Bertrand Creek	Sampling events	24	24	24	24	24
	Mean	3	14.53	7.23	205.55	9.38
	Minimum	1	0.59	6.90	105.20	6.55
	Maximum	8	67.35	7.59	243.60	11.92
Lower Bertrand Creek	Sampling events	24	24	24	24	24
	Mean	3	35.05	7.06	280.80	9.45
	Minimum	1	5.50	6.85	146.40	8.44
	Maximum	11	151.00	7.17	759.90	11.05
Indian Slough	Sampling events	21	21	21	21	21
	Mean	7	26.12	6.99	4557.38	8.42
	Minimum	3	2.14	6.61	273.80	4.73
	Maximum	24	67.26	8.20	20610.00	13.30
Clarks Creek	Sampling events	23	23	23	23	23
	Mean	3	55.68	6.97	226.18	9.82
	Minimum	1	48.00	6.67	148.60	8.34
	Maximum	17	71.90	7.37	233.00	12.52
Upper Big Ditch	Sampling events	24	24	24	24	24
	Mean	7	2.14	6.73	338.82	6.43
	Minimum	3	0.28	6.44	133.30	3.43
	Maximum	21	12.00	7.02	405.30	10.44
Lower Big Ditch	Sampling events	24	23	24	24	24
	Mean	19	20.09	6.90	405.34	6.85
	Minimum	4	1.91	6.38	50.50	2.60
	Maximum	62	43.36	7.43	876.00	13.64
Upper Brender Creek	Sampling events	22	23	21	21	22
	Mean	49	3.71	8.11	263.51	10.28
	Minimum	18	1.50	7.97	191.60	9.23
	Maximum	152	6.70	8.28	378.30	11.40
Lower Brender Creek	Sampling events	12	12	12	12	12
	Mean	6	4.30	7.54	356.15	7.57
	Minimum	3	1.18	7.42	260.20	6.43
	Maximum	10	6.66	7.69	452.70	9.52
Mission Creek	Sampling events	23	23	23	23	23
	Mean	63	44.05	8.31	253.61	10.46
	Minimum	6	4.05	7.90	193.10	9.31
	Maximum	599	149.00	8.55	302.00	11.85

Monitoring Site	Summary statistic	TSS (mg/L)	Stream discharge (cfs)	pH (s.u.)	Conductivity (µS/cm)	Dissolved oxygen (mg/L)
Stemilt Creek	Sampling events	18	18	18	18	18
	Mean	18	14.52	8.21	246.98	10.11
	Minimum	3	0.07	7.87	92.70	8.91
	Maximum	33	49.49	8.83	606.60	11.58
Marion Drain	Sampling events	25	25	26	26	26
	Mean	10	104.59	7.99	262.06	11.81
	Minimum	2	21.25	7.30	205.80	7.89
	Maximum	33	256.50	8.78	367.60	14.35
Sulphur Creek Wasteway	Sampling events	22	22	22	22	22
	Mean	41	239.45	8.34	323.27	10.08
	Minimum	6	138.48	7.84	235.90	8.83
	Maximum	145	612.50	8.81	877.60	10.88
Snipes Creek	Sampling events	20	20	21	21	21
	Mean	23	46.89	8.61	199.06	9.27
	Minimum	3	7.74	8.15	139.80	8.23
	Maximum	74	154.00	9.23	314.30	10.48

Within one site, differences in the number of weeks sampled for conventional water quality parameters, TSS, and streamflow were due to several factors: dangerously high flows preventing a flow measurement from being collected, weeks when streamflow was below an accurately measurable level, or field equipment malfunctions.

Total Suspended Solids

TSS samples were collected during all sampling events. TSS is monitored in streams because sediment entering streams can be a source of pesticide contamination to surface water through erosion and runoff from adjacent uplands. In particular, pesticides with low water solubility and a high affinity for soils (high Koc value), such as DDT, can enter stream systems, and are often particle bound (Anderson 2007), entering surface water through runoff and erosion of contaminated upland soils (Johnson et al., 1988; Joy and Patterson, 1997). Brender Creek, in particular, consistently has detectable levels of DDT and its associated degradates and relatively high TSS levels compared to other sites. The Washington State Department of Ecology collected orchard soil samples in 2003 in the Brender Creek watershed and estimated DDT levels at an average of 5.8 kg/hectare in the Brender Creek drainage due to historic use of the pesticide prior to its ban in 1972 (Anderson, 2007; Serdar and Era-Miller, 2004). According to the report, as much as 75% of the DDT in the surface water is particle bound, suggesting that much of the DDT contamination was due to runoff and erosion (Serdar and Era-Miller, 2004). This suggests that reducing runoff and erosion to streams, which reduces TSS levels, could also reduce DDT contamination of surface water, as well as other particle bound pesticides.

Land management practices that can be implemented to reduce runoff, erosion, and TSS loading to streams includes maintaining vegetated ground cover on land adjacent to streams. This is particularly important in watersheds where there is known pesticide contamination of upland soils. Land practices can include maintaining grass cover in orchards to retain upland soils, and is a common practice in the Brender and Mission Creek subbasins (Serdar and Era-Miller, 2004; personal observation). Riparian buffers can be planted/maintained along wetland/stream margins to reduce bank erosion and also filter or remove contaminants in runoff from adjacent uplands (Anderson, 2007). In 2016, WSDA collaborated with the Cascadia Conservation District to study the effects of a restored wetland between the Upper and Lower Brender Creek sites. The concentrations of Total DDT and TSS were consistently lower at the Lower Brender site than the Upper Brender site at each of 12 sampling events. The wetland in Brender Creek was found to be effective at retaining DDT contaminated suspended sediment.

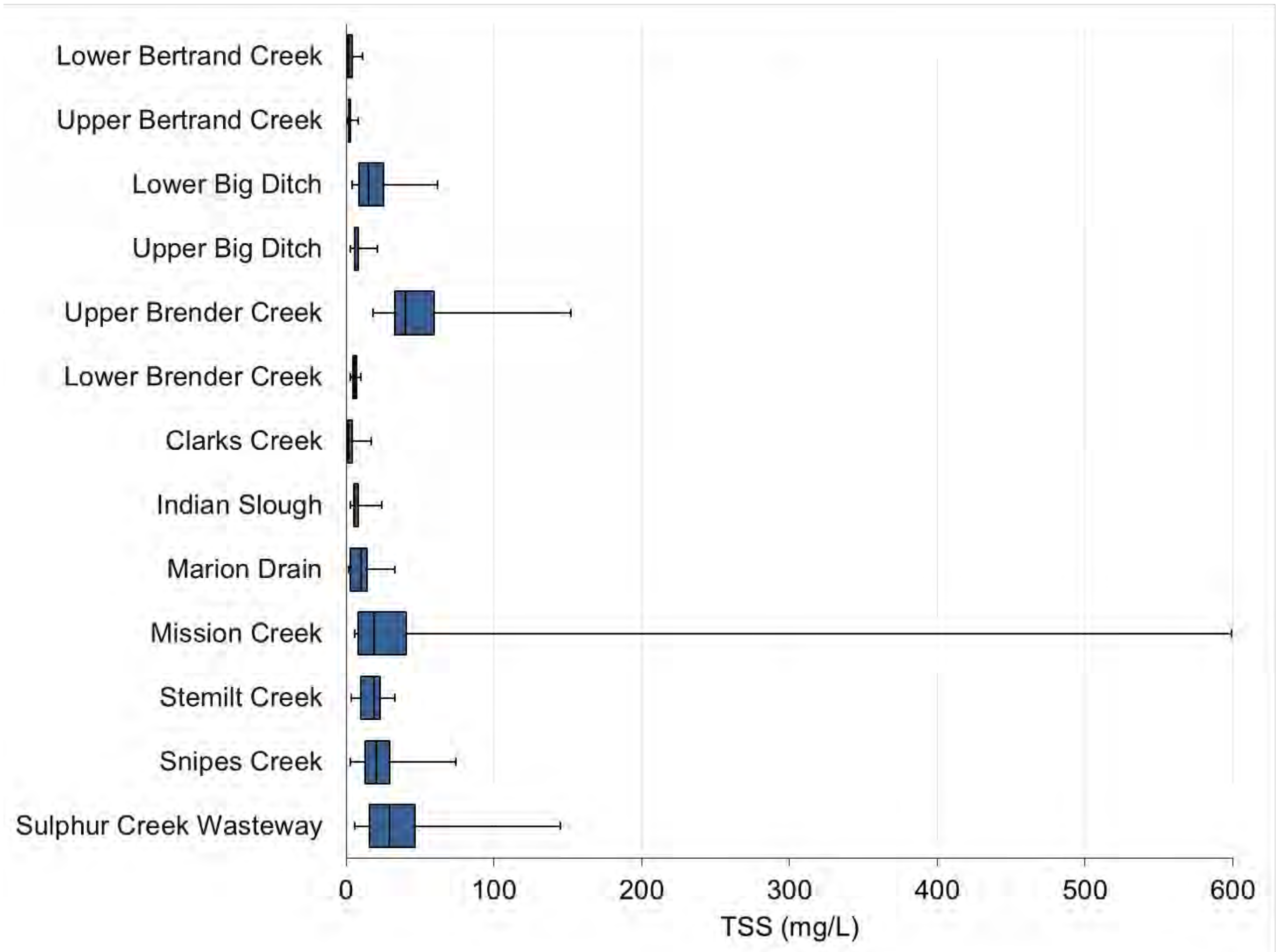

Figure 4 – Total suspended solid measurements with minimum, 25th percentile, median, 75th percentile, and maximum

Mission Creek had the highest TSS value of 599 mg/L with a seasonal average of 63 mg/L. Several TSS values at Mission Creek in 2016 were unusually high because of a landslide that deposited sediment into the creek's upper reaches in July. Upper Brender Creek followed with a maximum TSS value of 152 mg/L and average of 49 mg/L. The sites that had seasonal averages below 5 mg/L include Upper Bertrand Creek, Lower Bertrand Creek, and Clarks Creek. Data collected for TSS (mg/L) for each monitoring location are displayed in the pesticide calendars as well as a graphically in Figure 4.

Streamflow

Streams in Washington exhibit seasonal fluctuations in flow. Subbasins at high elevations and particularly on the eastern slopes of the Cascade Mountain Range, such as Mission Creek, are highly influenced by snowpack formed in the winter. Stream water levels and flows generally increase in the spring and early summer months due to seasonal rain events and melting snowpack (Hamlet and Lettenmaier, 2007). Streamflow in high-elevation subbasins like these typically decreases in the mid-late summer and fall months because of decreasing snow pack and reduced frequency of precipitation events. Due to milder temperatures and generally lower elevation, flow patterns of subbasins in western Washington, like Bertrand Creek, are more directly influenced by rain events and will often have higher flows during the typically wet winter months (Elsner et al., 2010). Subbasins located at mid-level elevations can be influenced by a combination of snow and rain events depending on seasonal temperatures and can experience 2 streamflow peaks, with 1 occurring in the winter due to rain/snow mix and a second peak in the spring or early summer when the snowpack melts (Hamlet and Lettenmaier, 2007; Elsner et al., 2010).

Sulphur Creek Wasteway had the highest maximum flow (612.50 cfs) and the highest average flow of 239.45 cfs. This sites streamflow is controlled in part by the fluctuation of water flow coming from irrigation canals, causing multiple peaks in streamflow throughout the monitoring season. Marion Drain had the second highest maximum flow (256.50 cfs) and average flow (104.59 cfs). Minimum streamflows below 1 cfs occurred at Upper Bertrand Creek, Upper Big Ditch, and Stemilt Creek. Lower Brender, Upper Brender, and Upper Big Ditch had the lowest maximum flows at 6.66 cfs, 6.70 cfs, and 12.00 cfs, respectively. Lower and Upper Brender Creek sites have very similar streamflows due to their close proximity to each other in the drainage (~0.5 miles apart). It should be noted that Indian Slough and Lower Big Ditch monitoring locations are tidally influenced, causing the sample timing of these sites to most often take place at low tide when the waterbodies were draining. Discharge at many of the monitoring sites can be influenced not only by precipitation but by irrigation flows, drains, and stormwater runoff too. Streamflow measurements for each monitoring site are displayed in the Pesticide Calendars as well as graphically in Figure 5.

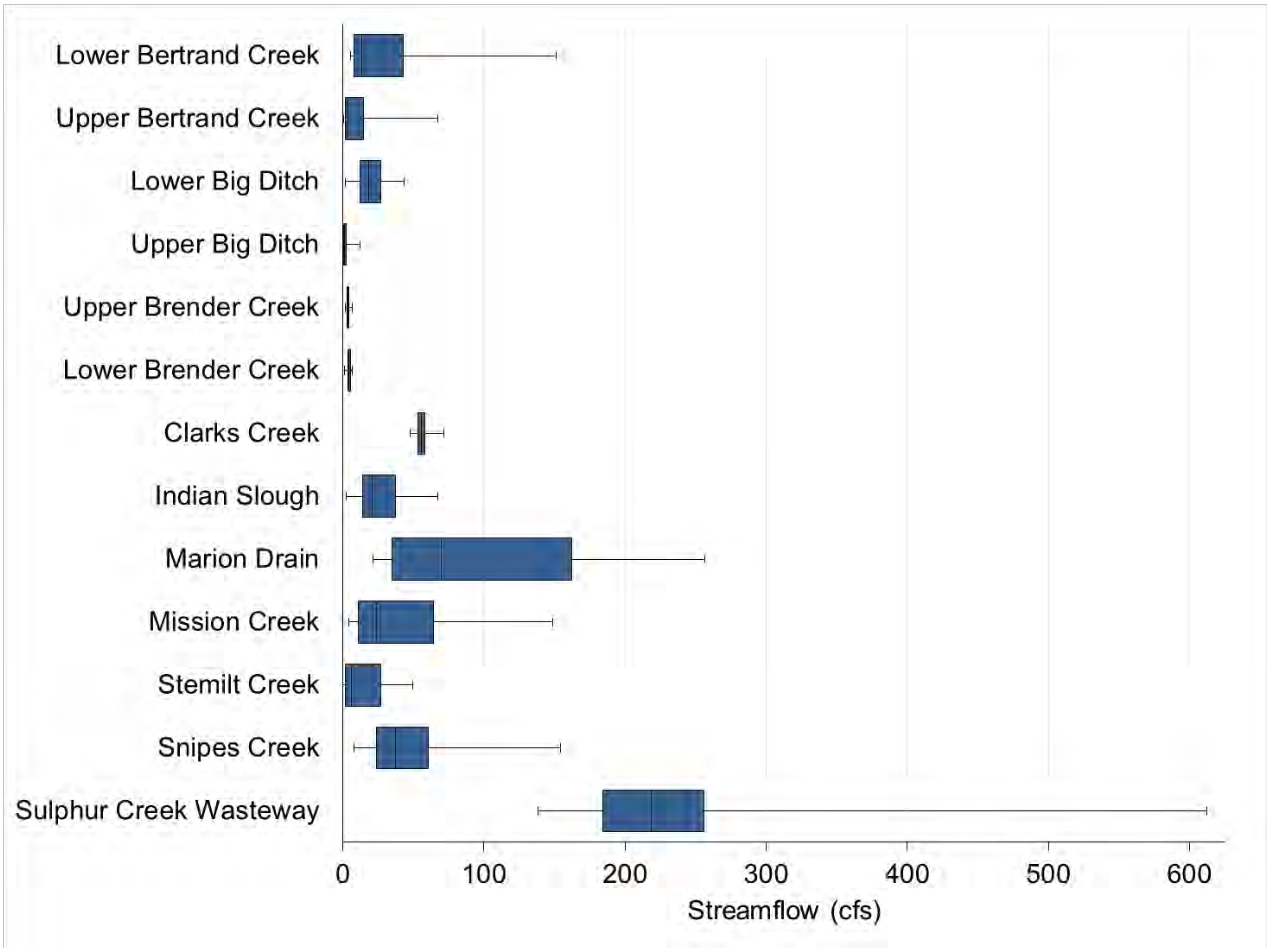

Figure 5 – Streamflow measurements with minimum, 25th percentile, median, 75th percentile, and maximum

Precipitation

Washington State University's AgWeatherNet weather monitoring network was used to supply daily precipitation data. Weather stations chosen were located in close proximity to monitoring sites. Weather station information (ID, latitude, and longitude) can be found in Appendix A: Monitoring Site Data. Summary statistics for daily precipitation between March 1st and September 30th are presented in Table 23. Seasonal precipitation consists of data collected for all days, including days with no measurable precipitation. This type of data gives insight into the local and regional climate of each site. Measurable precipitation events, the second analysis in Table 23, excludes days with no measurable precipitation. A higher mean value here can indicate larger storm events. Runoff of pesticides from adjacent streambanks will be greatest when a heavy rain follows soon after a pesticide application. Over-irrigation can also lead to pesticide runoff.

Table 23 – Summary of precipitation (cm) data between March 1st and September 30th, 2016

Monitoring Sites	Summary statistics	Seasonal precipitation	Precipitation from measurable events
Upper Bertrand Creek, Lower Bertrand Creek	Days	208	76
	Mean (cm/day)	0.114	0.311
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	2.134	2.134
Upper Big Ditch, Indian Slough	Days	214	73
	Mean (cm/day)	0.177	0.518
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	7.163	7.163
Lower Big Ditch	Days	214	69
	Mean (cm/day)	0.114	0.353
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	4.267	4.267
Clarks Creek	Days	214	75
	Mean (cm/day)	0.134	0.382
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	1.930	1.930
Brender Creek, Mission Creek	Days	214	28
	Mean (cm/day)	0.064	0.493
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	1.930	1.930
Marion Drain	Days	214	39
	Mean (cm/day)	0.034	0.188
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	1.143	1.143
Stemilt Creek	Days	214	34
	Mean (cm/day)	0.063	0.397
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	2.210	2.210
Snipes Creek	Days	212	32
	Mean (cm/day)	0.023	0.155
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	0.584	0.584
Sulphur Creek Wasteway	Days	214	34
	Mean (cm/day)	0.063	0.385
	Minimum (cm/day)	0.000	0.025
	Maximum (cm/day)	3.810	3.810

There were noticeable regional differences in mean seasonal precipitation between sites located east and west of the Cascade Mountains, with seasonal daily means at western sites ranging from 0.114 to 0.177 cm/day, and eastern sites ranging from 0.023 to 0.064 cm/day. The Cascade Mountain Range runs from north to south in Washington creating distinct differences in climatic conditions between western and eastern Washington, specifically differences in rainfall and temperature with western Washington averaging about 4 times as much rainfall yearly as eastern Washington (Elsner et al. 2010). The average of the seasonal daily means at weather stations near eastern Washington sites between March and September (0.049 cm/day) was approximately 36% of the average of the seasonal daily means at weather stations near western Washington sites (0.135 cm/day). In addition, there were nearly twice as many days with measurable precipitation at western sampling sites than there were at eastern sites. The greatest number of days with measurable rainfall (76 days) occurred at the Lynden weather station near the Bertrand Creek sites in western Washington. There were 39 days where rainfall was measured at the Toppenish weather station near Marion Drain, which was the greatest number of days with measurable rainfall at eastern Washington sites. In general, the seasonal daily maximum precipitation was comparable for eastern Washington sites and western Washington sites. Exceptions include a seasonal daily maximum precipitation of 7.16 cm on August 31st at Upper Big Ditch Creek and Indian Slough, and a seasonal daily maximum precipitation of 0.6 cm at Snipes Creek. Mean precipitation rates from measurable events were also comparable for all eastern and western Washington sites. Exceptions include Marion Drain and Snipes Creek, which were the only locations to average less than 0.2 cm/day of measurable precipitation, and Upper Big Ditch Creek and Indian Slough were the only sites to average above 0.5 cm/day.

Conventional Water Quality Parameter Exceedances

The aquatic life criteria of the Washington State water quality standards are location dependent and governed by aquatic life uses. Aquatic life uses are based on the presence of salmonid species, or the intent to provide protection for all indigenous fish and non-fish aquatic species.

Temperature Exceedances above the Aquatic Life Criteria

Continuous, 30-minute-interval temperature data was collected during the sampling season from March 7th through November 7th, 2016 at eastern Washington monitoring sites and from March 7th through September 26th, 2016 at western Washington monitoring sites. Table 24 provides a list of the time periods where the aquatic life temperature criteria were exceeded. Criteria are based on the designated aquatic life uses determined by WAC at each monitoring site. Water temperature criteria are listed in the standard as the highest allowable 7-day average of the daily maximum temperatures (7-DADMax).

Table 24 – Water temperatures exceeding the Washington State aquatic life criteria

Monitoring sites	Period of temperature exceedance (start - end)	Number of days	Maximum temperature during exceedance (ºC)	7-DADMax range (ºC)
Freshwater - Salmonid Spawning, Rearing, and Migration Habitat - (>17.5ºC) Exceedances:				
Western Washington Sites:				
Upper Bertrand Creek	June 2 - 9	8	21.2	17.8-19.6
	June 25 - July 5	11	19.7	17.7-19.0
	July 9 - August 28	51	21.2	17.6-20.4
Lower Bertrand Creek	July 22 - 30	9	18.6	17.6-18.0
Upper Big Ditch	June 4 - 7	4	19.2	17.7-17.9

Monitoring sites	Period of temperature exceedance (start - end)	Number of days	Maximum temperature during exceedance (ºC)	7-DADMax range (ºC)
Lower Big Ditch	July 18 - August 3	17	19.3	17.7-18.7
	August 10 -2 6	17	19.5	17.7-19.0
	April 17 - 24	8	22.7	17.6-19.9
	April 27 - May 25	29	31.9	17.6-20.1
	May 27 - June 9	14	22.0	17.6-20.3
	June 13 - September 9	100	26.7	17.6-25.8
Indian Slough	May 11 - 16	6	18.8	17.7-18.1
	May 31 - September 9	102	24.7	17.6-24.6
Eastern Washington Sites:				
Marion Drain	May 5 - 11	7	18.9	17.6-17.8
	May 27 - September 14	111	25.4	17.6-24.8
Snipes Creek	April 9 - 12	4	34.3	17.8-18.4
	April 16 - September 9	147	31.9	17.9-27.0
Sulphur Creek Wasteway	April 19 - September 16	151	25.0	17.7-24.3
Upper Brender Creek	July 25 - August 2	9	21.1	17.8-19.0
	August 13 - 19	7	19.1	17.9-18.5
Mission Creek	July 24 - August 6	13	21.0	17.6-20.1
	August 10 - 24	15	20.2	17.6-19.7
Stemilt Creek	June 4 -10	7	20.4	17.6-19.0
	June 26 - July 4	9	25.1	17.6-19.7
	July 13 - August 6	19	21.7	17.6-21.1
Freshwater - Core Summer Salmonid Habitat - (>16ºC) Exceedances:				
Clarks Creek	No Exceedances	0	N/A	N/A

There were 13 occasions when the water temperature exceeded the aquatic life temperature criteria at western Washington monitoring sites. The exceedance duration at western Washington sites (excluding Clarks Creek) varied from 4 days at Upper Big Ditch to as long as 102 days at Indian Slough. Water temperatures at Clarks Creek did not exceed aquatic life criteria. Lower Bertrand Creek had the second fewest days above temperature criteria at 9 days. Lower Big Ditch had the most consecutive days above temperature criteria with 151.

There were 12 occasions where the water temperature exceeded the aquatic life temperature criteria at eastern Washington monitoring sites. The exceedance duration at eastern sites varied from 4 days at Snipes Creek to 151 days at Sulphur Creek Wasteway. Upper Brender Creek had the fewest total days (16 days) above the temperature criteria, and Snipes Creek and Sulphur Creek Wasteway had the most days at 151 each.

For the following locations and dates, temperature data was obtained from other agencies with continuous temperature loggers on-site.

- Mission Creek, March 7 - September 31 (Washington State Department of Ecology)

Dissolved Oxygen Measurements Below the Acceptable Aquatic Life Criteria

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 the sampling day at an individual monitoring site. Table 25 provides a list of dates where dissolved oxygen was at levels that were below the aquatic life criteria.

Table 25 – Dissolved oxygen levels not meeting the WA. State aquatic life criteria

Monitoring sites	Dissolved oxygen measurement dates	Dissolved oxygen measurements outside of criteria (mg/L)
Freshwater - salmonid spawning, rearing, and migration habitat - (<8.0 mg/L) exceedances:		
Upper Bertrand Creek	July 26	7.10
	August 3, 10, 17, 24, 29	7.40, 7.23, 6.55, 6.74, 7.04
Upper Big Ditch	April 20, 26	6.91, 7.57
	May 4, 10, 18, 25	5.46, 7.14, 5.53, 5.72
	June 7, 21, 29	6.47, 6.38, 4.53
	July 5, 13, 20	4.95, 5.21, 6.73
	August 9, 15, 23, 30	4.37, 5.28, 5.08, 3.48
	September 7, 12	3.43, 5.21
Lower Big Ditch	March 23	7.53
	April 12, 20, 26	7.35, 5.98, 6.73
	May 4, 18	2.60, 7.34
	June 15, 13, 28	7.01, 2.95, 6.56
	July 5, 13, 20	4.27, 5.61, 4.70
	August 9, 15, 23, 30	4.96, 3.92, 6.72, 5.08
	September 7, 12	7.83, 6.64
Indian Slough	April 6	5.99
	May 4, 18, 25	7.84, 7.64, 7.56
	September 7, 12	4.73, 6.37
Marion Drain	July 18	7.89
Lower Brender Creek	April 19	7.09
	May 3, 18	7.92, 7.67
	June 1, 14, 28	7.20, 7.61, 6.55
	July 12, 26	6.91, 6.43
	August 9, 23	7.38, 7.21
Freshwater - core summer salmonid habitat - (<9.5 mg/L) exceedances:		
Clarks Creek	April 26	9.15
	May 25	9.31
	June 28	9.11
	July 12, 19, 25	8.34, 8.70, 8.92
	August 2, 9, 15, 23	8.78, 8.79, 9.04, 9.25

There were 58 individual occasions when dissolved oxygen levels could have been below the aquatic life criteria at western Washington monitoring sites. Of the 6 western Washington monitoring sites, Lower Bertrand Creek was the only site that could have met the dissolved oxygen criteria for the entire monitoring season.

During the 2016 monitoring season, 5 of the 7 eastern Washington monitoring sites could have been above the aquatic life criteria for dissolved oxygen for the entire season. Marion Drain and Lower Brender Creek were the only eastern sites where dissolved oxygen levels were below the aquatic life criteria, 1 time in Marion Drain and 10 times in Lower Brender Creek during the season.

pH Measurements Outside of the Acceptable Aquatic Life Criteria

The Washington State Water Quality Standards lists acceptable ranges for pH values for each aquatic life use category. Table 26 provides a list of occurrences where pH measurements were below or above the aquatic life criteria.

Table 26 – pH levels not meeting the Washington State aquatic life criteria

Monitoring sites	Dates of pH measurements	pH measurements outside of criteria (s.u.)
Freshwater – Salmonid Spawning, Rearing, and Migration – pH: 6.5 - 8.5:		
Upper Big Ditch	August 30	6.44
Lower Big Ditch	June 7	6.42
	July 20	6.38
Marion Drain	May 31	8.78
	June 13	8.68
	July 11	8.75
Snipes Creek	March 21	8.70
	April 4, 11, 18, 26	8.63, 9.10, 9.23, 8.73
	May 17, 31	8.57, 8.56
	June 27	8.70
	July 5, 11, 25, 27	9.18, 8.80, 8.85, 8.79
Sulphur Creek Wasteway	May 2, 17, 31	8.61, 8.62, 8.75
	June 13	8.81
	July 11	8.65
Mission Creek	July 6	8.55
Stemilt Creek	June 14	8.83

There were 3 occurrences where the pH measurement was outside of the range listed in the aquatic life pH criteria at 2 western Washington locations (UBD, LBD), and 22 occurrences were outside of the range listed at 5 eastern Washington locations (MI, SC, MA, SN, and SU).

Of the 13 sites, 4 western Washington monitoring sites (CC, UBC, LBC, and IS) and 2 eastern Washington monitoring sites (UBR and LBR) had pH measurements within the acceptable range listed for the aquatic life pH criteria during the 2016 monitoring season.

Conclusions

WSDA collected surface water monitoring data at 13 locations across eastern and western Washington in 2016. During the peak pesticide application season (March – November), staff collected samples 282 times. Samples taken from 12 of the monitoring sites were tested in a lab for 152 pesticide and pesticide-related chemicals. Samples from the 13th monitoring site, Lower Brender Creek in eastern Washington, were tested for 8 pesticides (including DDT and its breakdown products). This monitoring site was part of a small study on the effects of wetlands on DDT transport. The partial data from this unusual site is included in the statewide data summary below.

- Of 154 pesticides tested for, there were 76 unique pesticides detected.
- Pesticide active ingredients and pesticide breakdown products were positively detected 1,752 individual times.
- More pesticides were detected at western Washington sites than eastern Washington sites.
  - In western Washington, the 6 monitoring sites had 1,293 (74%) total pesticide detections in 140 sampling events.
  - In eastern Washington, the 7 monitoring sites (including the Lower Brender Creek) had 459 (26%) total pesticide detections in 142 sampling events.
- 2,6-dichlorobenzamide, a degradate of the herbicide dichlobenil, was the only pesticide detected in over 50% (137 detections) of sampling events it was tested for.
- Thiamethoxam and imidacloprid were the most frequently detected insecticides (78 and 74 times, respectively). These insecticides are both neonicotinoids.
- 2,4-D, diuron, and dichlobenil were the most frequently detected herbicides (101, 85, and 65 times, respectively).
- Boscalid, azoxystrobin, and fludioxonil were the most frequently detected fungicides (111, 60, and 59 times, respectively).

In 2016, mixtures of pesticides were commonly found at monitoring sites. There were 7 sites that had 2 or more pesticide detections at every sampling event during the entire field season. Although studies on the effects of pesticide mixtures are limited, there is evidence that indicates certain combinations of pesticides can have compounding adverse effects in aquatic systems (Broderius and Kahl, 1985).

In order to assess the potential effects of pesticide exposure to aquatic life and endangered species, detected pesticide concentrations were compared to WSDA's assessment criteria. Detections of these legacy and current-use pesticides above WSDA's criteria are considered exceedances. There were 108 exceedances at 12 monitoring locations. Of these, 90 (83%), occurred at monitoring sites in eastern Washington, and 18 (17%) occurred at monitoring sites in western Washington. Only 1 monitoring location, Clarks Creek in western Washington, had no exceedances.

Exceedances by current-use pesticides (excluding DDT and its degradates) are as follows:

- Out of 707 total herbicide detections, 9 detections exceeded criteria (1%).
- Out of 375 total fungicide detections, 0 detections exceeded criteria (0%).
- Out of 351 total insecticide detections, 28 detections exceeded criteria (8%).

The currently registered pesticides, bifenthrin, chlorpyrifos, diazinon, malathion, methiocarb, pyridaben, pyriproxyfen, and simazine, accounted for 1/3rd of the total exceedances (37 exceedances). Not every detection of these pesticides exceeded assessment criteria. Simazine was detected 19 times but only exceeded assessment criteria 9 times. A single detection of diazinon out of 10 total detections exceeded criteria. Every detection of bifenthrin, chlorpyrifos, malathion, methiocarb, pyridaben, and pyriproxyfen exceeded assessment criteria.

Detections of DDT and associated degradates accounted for the remaining 2/3^{rds} of the total exceedances across all monitoring sites (71 exceedances). Every detection of DDT exceeded assessment criteria. DDT was detected at 2 western Washington sites and 4 eastern Washington sites. At Upper Brender Creek there were 48 exceedances of DDT and associated degradates alone.

A registered pesticide that has exceeded assessment criteria at least once during the last 3 years is considered a WSDA Pesticide of Concern (POC). WSDA's POC list includes mostly insecticides with very low assessment criteria. All current-use pesticides exceeding assessment criteria in 2016 except pyriproxyfen were previously POCs. Pyriproxyfen will be added to the list in 2017 based on its exceedance this year. Even though DDT and its degradates exceeded assessment criteria, they are not considered POCs because they are legacy chemicals that have not been registered for use in the US since 1972.

When pesticide exceedances in surface water coincide with state water quality standard exceedances, there could be additive stress on aquatic life. All sites monitored for physical water quality parameters in 2016 exceeded at least 1 aquatic life criteria of the Washington State Water Quality Standards.

Generally speaking, pesticides are becoming more specific to the target organisms they are intended for. Insecticides usually have a low toxicity towards aquatic plants and vertebrates and a higher toxicity towards aquatic invertebrates. Meanwhile, herbicides and fungicides are often less toxic to fish and invertebrates but more toxic to aquatic plants. However, any pesticide at high enough concentrations in surface water can directly or indirectly effect ESA-listed salmonids. Invertebrates are the main food source of juvenile salmonids, and those invertebrates rely on aquatic plants to sustain their populations. If a pesticide is causing impairment to any organism, food webs and ecosystem functions can be potentially disrupted. Pesticide monitoring in Washington waterways is essential for understanding the fate and transport of pesticides that can cause water quality concerns. WSDA POCs should be given additional prioritization for management by WSDA and partners to ensure their concentrations are maintained or reduced below WSDA assessment criteria. WSDA will continue to implement the Pesticide Management Strategy as a way to identify and address specific pesticide issues, as well as promote public education and outreach efforts through presentations, reports, and watershed-specific fact sheets in order to support appropriate pesticide use.

Program Changes

Since 2003, each monitoring location has been sampled weekly or biweekly for the duration of the Washington growing season from March through September with few exceptions until this year. In order to optimize the use of WSDA resources, the sampling schedule will change prior to 2017 sampling. The sampling schedule will be tailored to each site based on past field data, pesticide use data, and agricultural land use data.

A tiered site selection guideline is also being developed to determine how frequently sites should be monitored, when a monitored site can be discontinued from the program, and when and how new sites should be selected. This refined approach will allow WSDA to diversify monitoring locations across the state.

Several site changes will be made prior to the start of the 2017 monitoring season. Changes in western Washington include the removal of the Clarks Creek monitoring site due to the lack of pesticide exceedances. Sites will be added: Burnt Bridge Creek in the Lower Columbia-Clatskanie subbasin and Woodland Creek in the Puget Sound subbasin. Both of these new monitoring locations are being selected to represent urban and residential land uses in regions not previously sampled by WSDA.

Site changes in eastern Washington for 2017 do not include any site removals. Crab Creek in the Lower Crab subbasin is being added to represent very diverse agricultural land uses and expands the monitoring further east where WSDA sampling has not taken place before. Naneum Creek in the Upper Yakima subbasin is being added to represent hay production (particularly timothy hay) and mixed agricultural land uses located in the heavily irrigated Kittitas Valley.

Continuous flow data will be collected by WSDA at all sites in 2017 that do not have a permanent gauging station. Hydrographs created from the flow data will be used to aid in analyzing pesticide movement in the environment throughout the Washington growing season.

Only carbendazim (chemical abstract number: 10605-21-7) will be added to the analyte list for the 2017 sampling season. A total of 9 analytes will be removed from the program prior to the start of the sampling season due to new use restrictions, changes in pesticide registration or lack of detections in surface water. The list of removed compounds and their associated chemical abstract numbers include diphenamid (957-51-7), 2,4’-DDD (53-19-0), 2,4’-DDE (3424-82-6), 2,4’-DDT (789-02-6), di-allate (avadex, 2303-16-4), endosulfan I (959-98-8), endosulfan II (33213-65-9), and endosulfan sulfate (1031-07-8).

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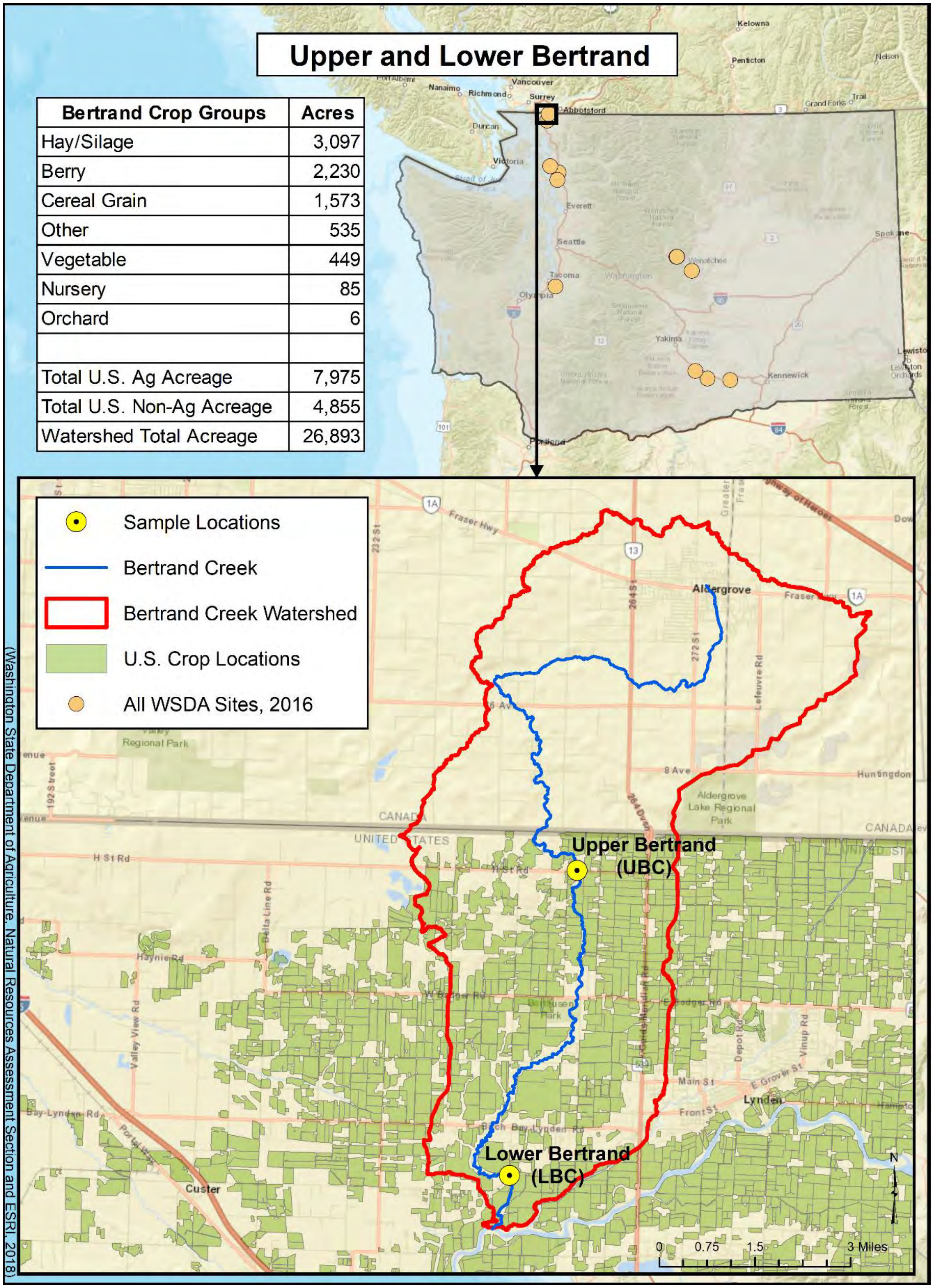
Appendix A: Monitoring Site Data

Watershed and Monitoring Site Maps

Table 27a – 2016 Monitoring site details

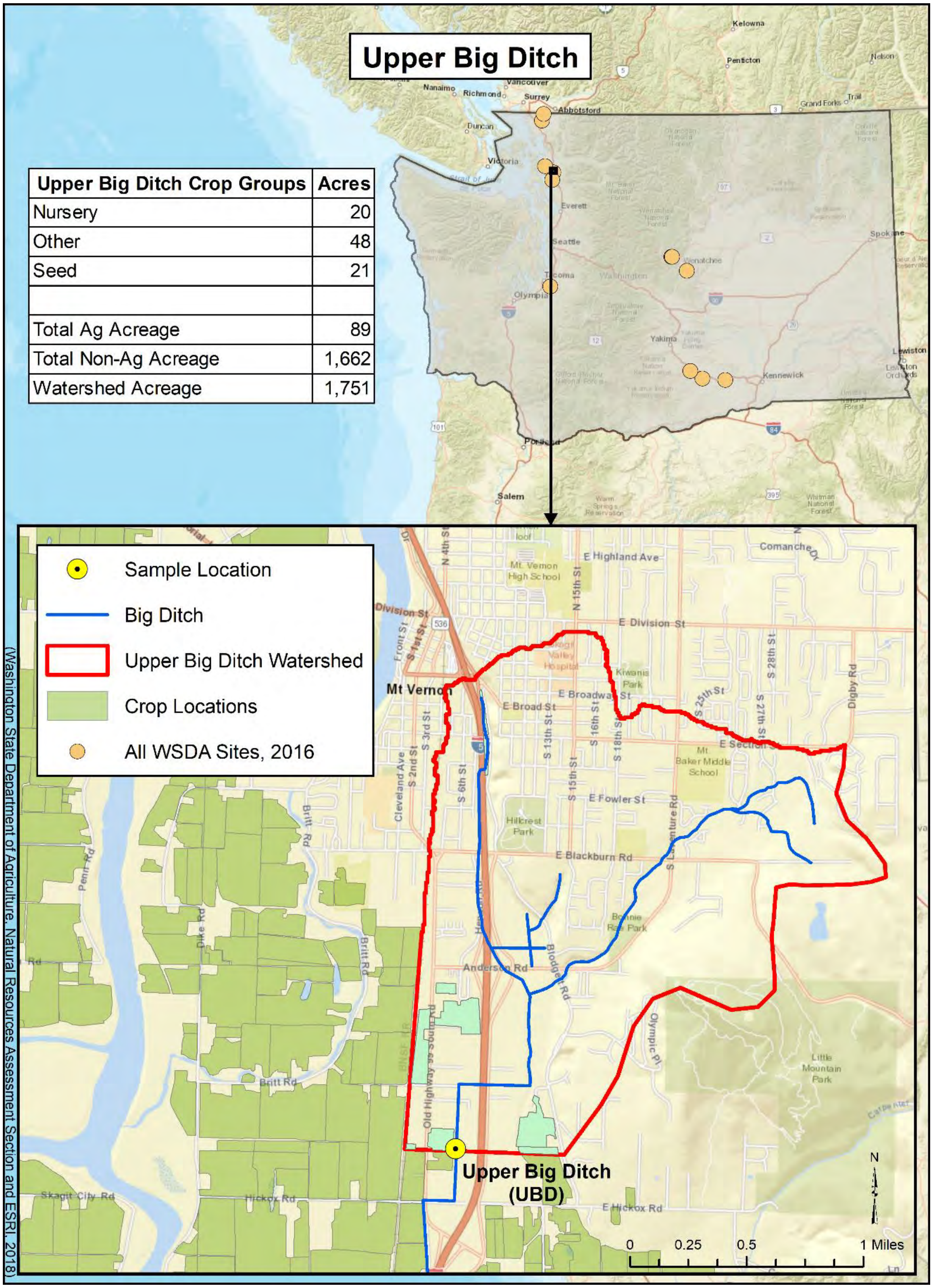
WRIA	Site name	Site ID	Duration	Latitude, longitude	Location description
WRIA 3: Lower Skagit-Samish	Lower Big Ditch	LBD	March-September	48.3085, -122.3474	Upstream side of bridge at Milltown Road.
	Upper Big Ditch	UBD	March-September	48.3882, -122.3330	Upstream side of bridge at Eleanor Lane.
	Indian Slough	IS	March-September	48.4506, -122.4650	Inside upstream side of tidegate at Bayview-Edison Road.
WRIA 1: Nooksack	Lower Bertrand	LBC	March-August	48.9241, -122.5300	Upstream side of the bridge over the creek on Rathbone Road. Parallel to staff gauge.
	Upper Bertrand	UBC	March-August	48.9935, -122.5105	Upstream side of the bridge over the creek on H Street Road.
WRIA 10: Puyallup	Clarks Creek	CC	March-August	47.1978, -122.3372	Downstream side of private bridge at the end of Tacoma Road.
WRIA 37: Lower Yakima	Marion Drain	MA	March-November	46.3307, -120.2000	About 50 meters upstream of bridge at Indian Church Road.
	Snipes Creek	SN	March-August	46.2332, -119.6774	About 30 meters downstream of the confluence of Snipes Creek and Spring Creek.
	Sulphur Creek Wasteway	SU	March-September	46.2510, -120.0200	Downstream side of bridge at Holaday Road.
WRIA 45: Wenatchee basin	Mission Creek	MI	March-August	47.5212, -120.4760	Downstream side of the bridge over the creek on Sunset HWY.
	Upper Brender	UBR	March-August	47.5211, -120.4863	Upstream side of culvert at Evergreen Drive and the footbridge.
	Lower Brender	LBR	March-August	47.5047, -120.4769	Downstream side of bridge over the creek on Sunset HWY.
WRIA 40: Alkali-Squilchuck basin	Stemilt Creek	SC	March-September	47.3748, -120.25	About 7 meters upstream of the bridge over the creek on Old West Malaga Road.

Datum in North American Datum (NAD) 83



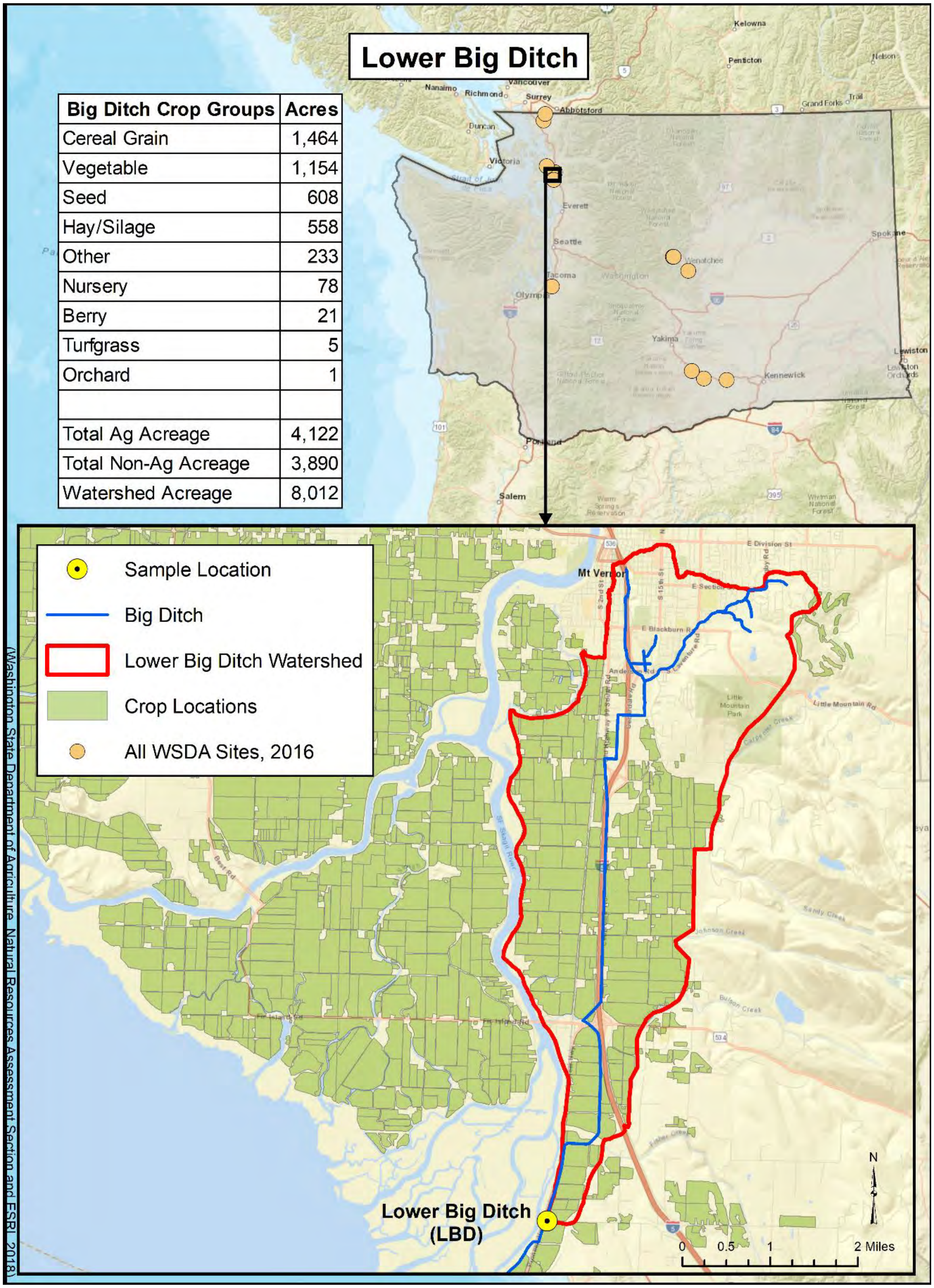
Bertrand Crop Groups	Acres
Hay/Silage	3,097
Berry	2,230
Cereal Grain	1,573
Other	535
Vegetable	449
Nursery	85
Orchard	6
Total U.S. Ag Acreage	7,975
Total U.S. Non-Ag Acreage	4,855
Watershed Total Acreage	26,893

Figure 6 – Upper and Lower Bertrand Creek



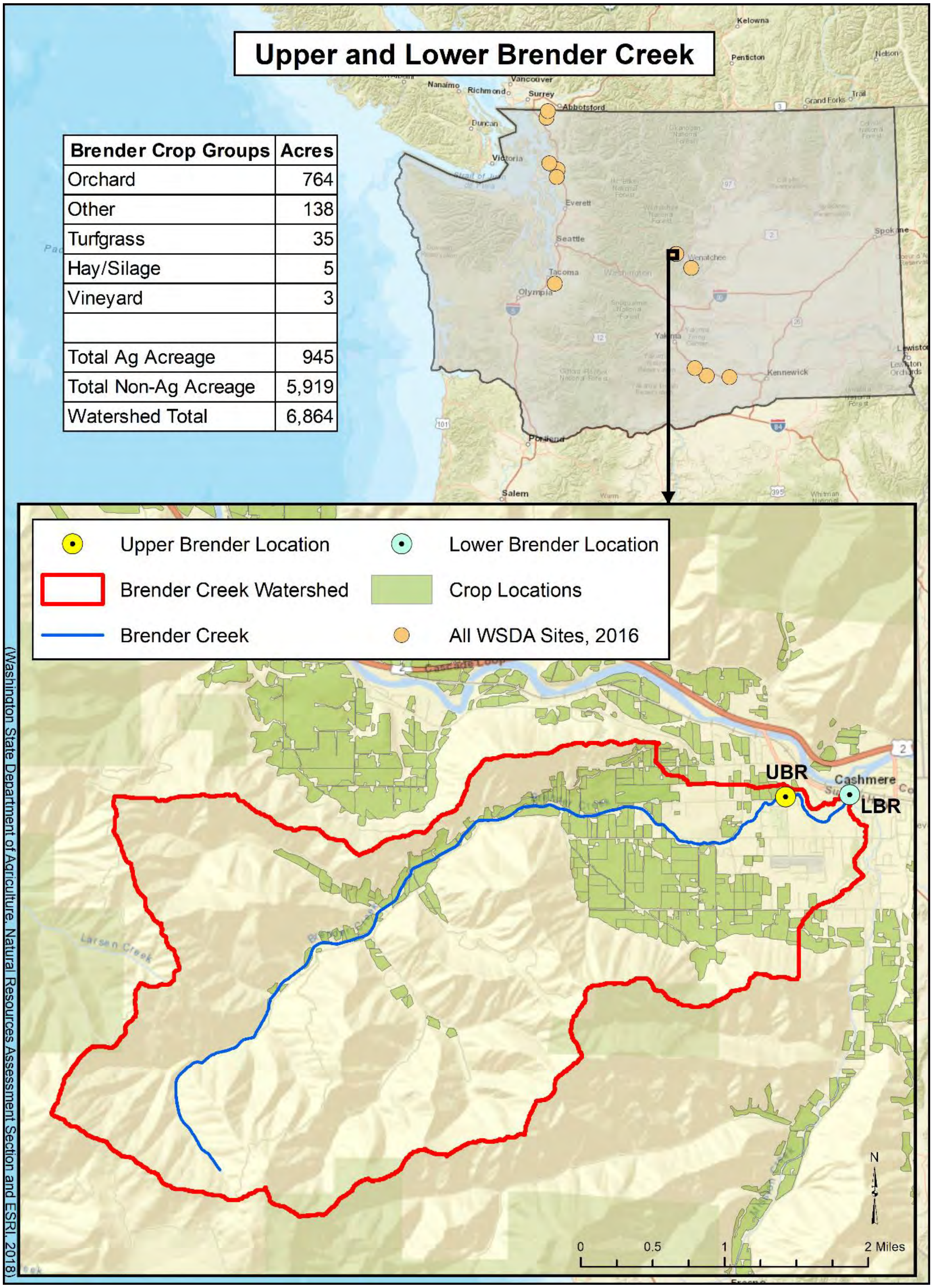
Upper Big Ditch Crop Groups	Acres
Nursery	20
Other	48
Seed	21
Total Ag Acreage	89
Total Non-Ag Acreage	1,662
Watershed Acreage	1,751

Figure 7 – Upper Big Ditch



Big Ditch Crop Groups	Acres
Cereal Grain	1,464
Vegetable	1,154
Seed	608
Hay/Silage	558
Other	233
Nursery	78
Berry	21
Turfgrass	5
Orchard	1
Total Ag Acreage	4,122
Total Non-Ag Acreage	3,890
Watershed Acreage	8,012

Figure 8 – Lower Big Ditch



Brender Crop Groups	Acres
Orchard	764
Other	138
Turfgrass	35
Hay/Silage	5
Vineyard	3
Total Ag Acreage	945
Total Non-Ag Acreage	5,919
Watershed Total	6,864

Figure 9 – Brender Creek

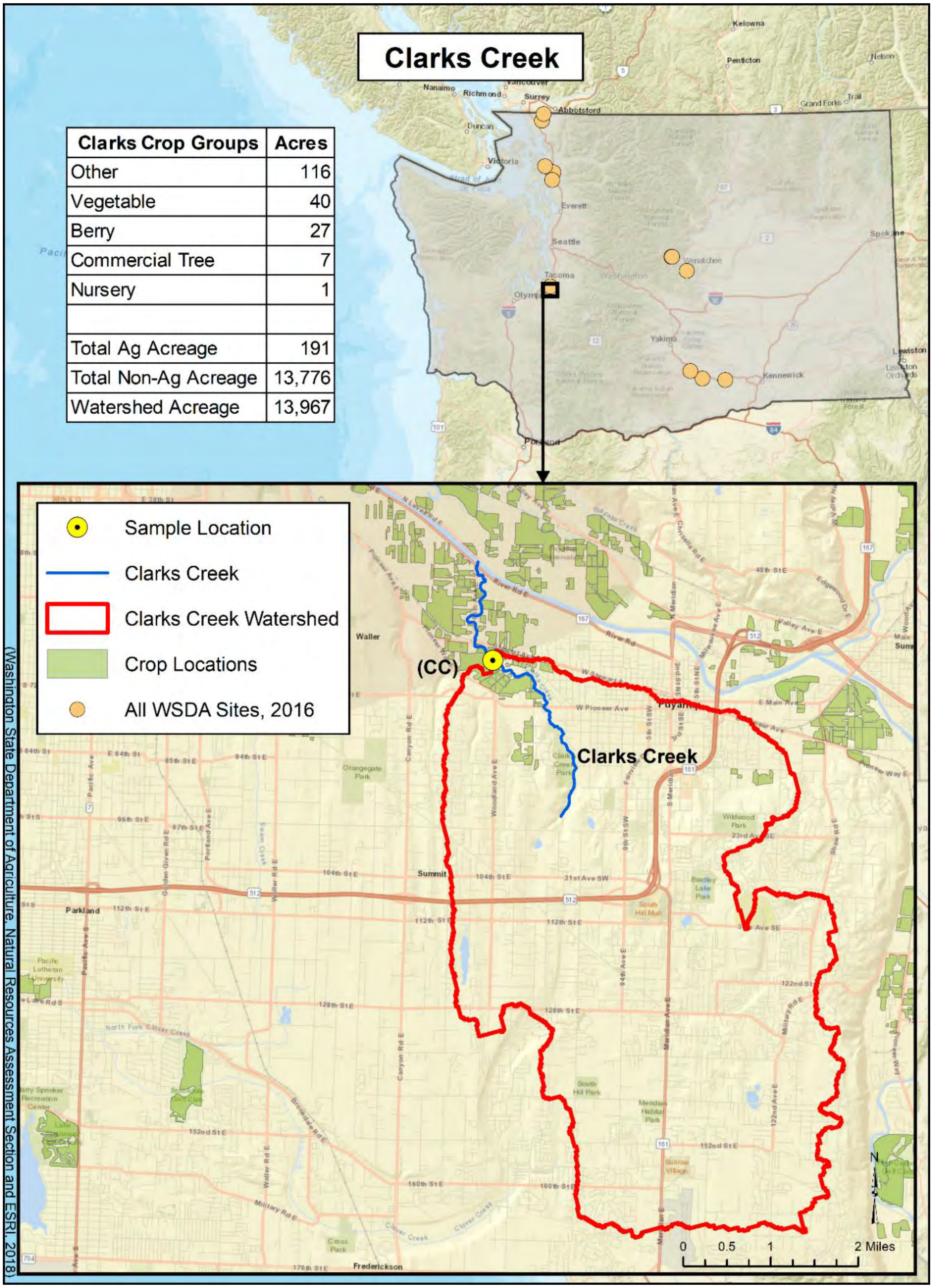
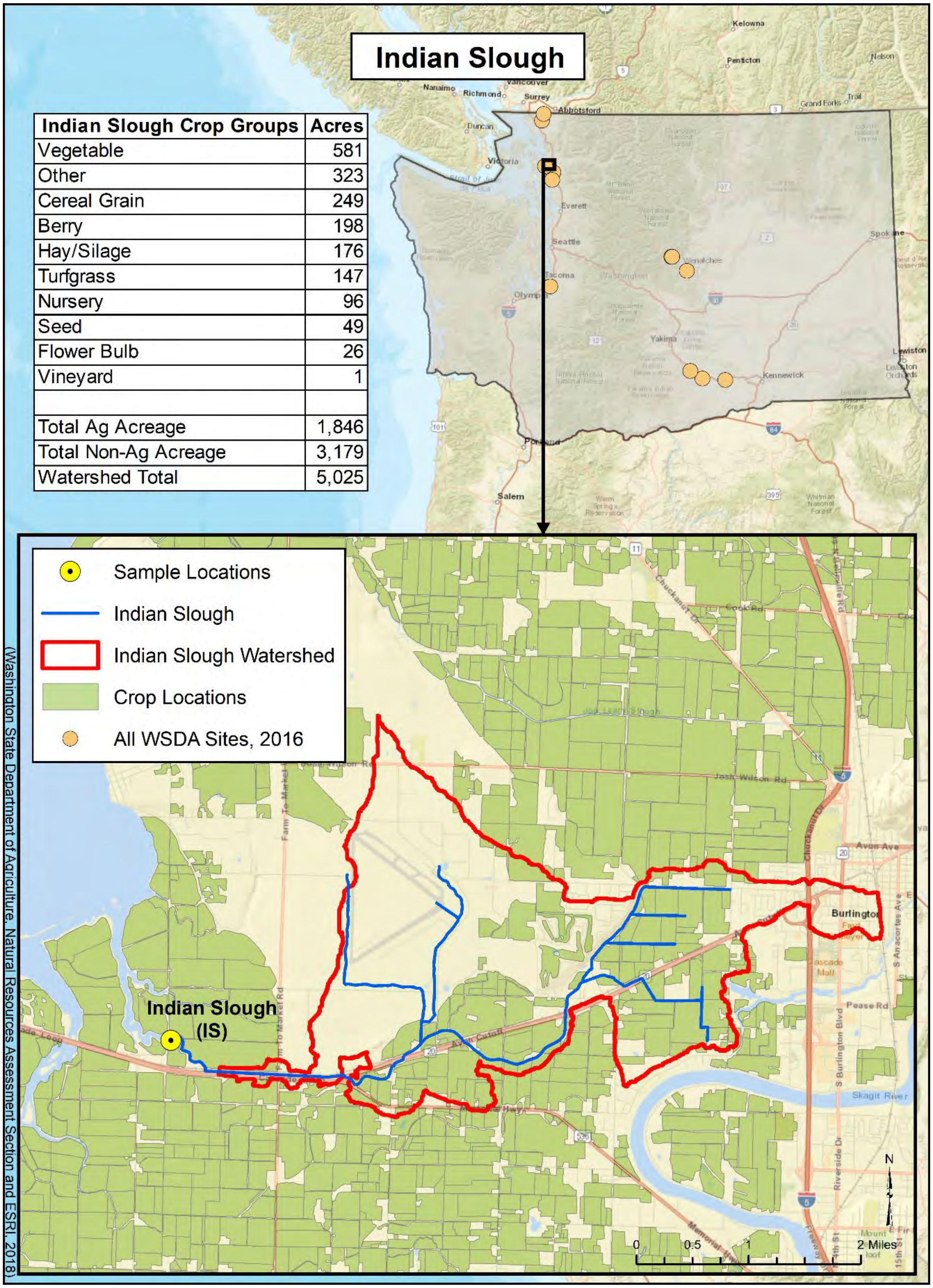
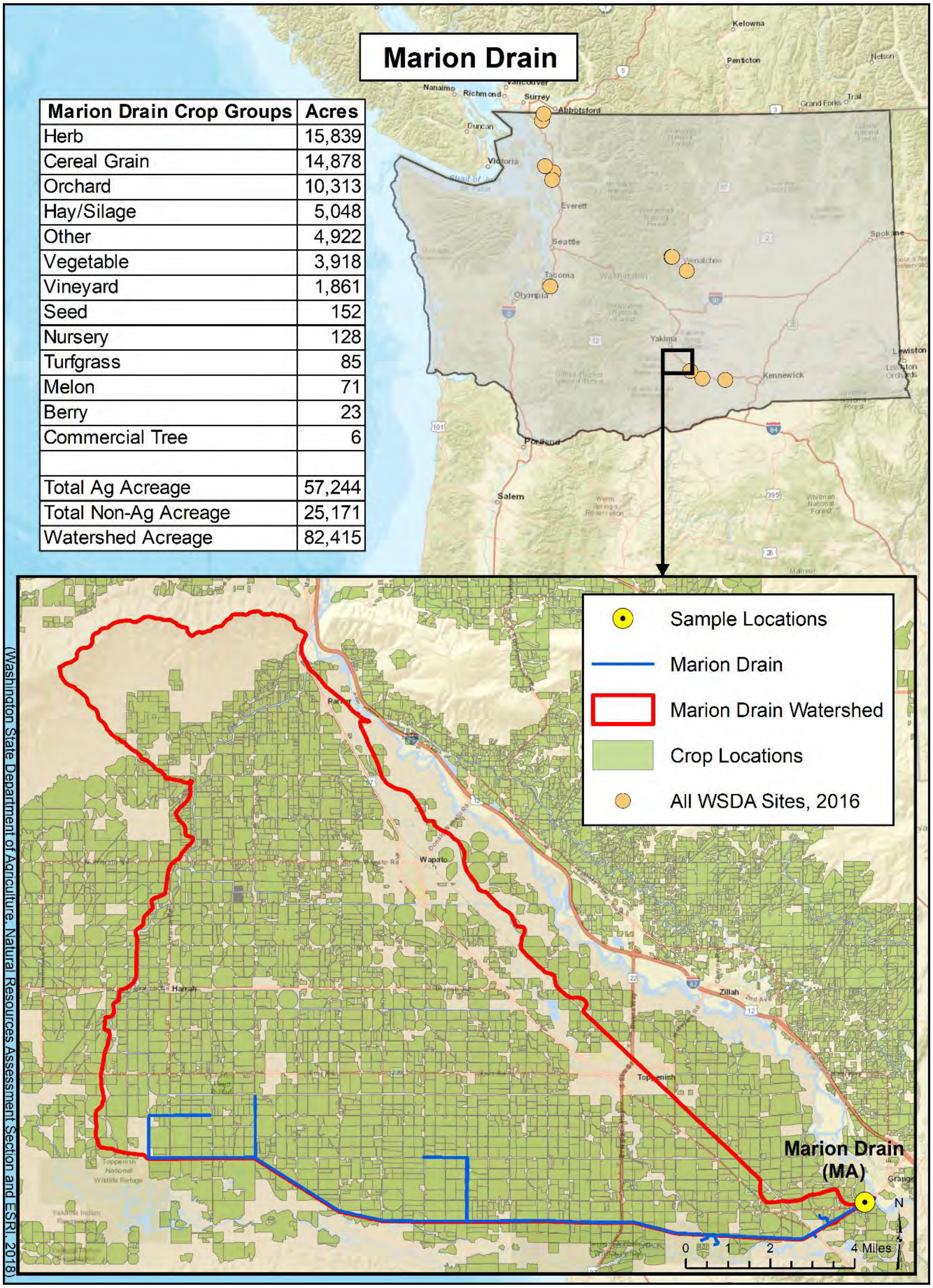


Figure 10 – Clarks Creek



Indian Slough Crop Groups	Acres
Vegetable	581
Other	323
Cereal Grain	249
Berry	198
Hay/Silage	176
Turfgrass	147
Nursery	96
Seed	49
Flower Bulb	26
Vineyard	1
Total Ag Acreage	1,846
Total Non-Ag Acreage	3,179
Watershed Total	5,025

Figure 11 – Indian Slough



Marion Drain Crop Groups	Acres
Herb	15,839
Cereal Grain	14,878
Orchard	10,313
Hay/Silage	5,048
Other	4,922
Vegetable	3,918
Vineyard	1,861
Seed	152
Nursery	128
Turfgrass	85
Melon	71
Berry	23
Commercial Tree	6
Total Ag Acreage	57,244
Total Non-Ag Acreage	25,171
Watershed Acreage	82,415

Figure 12 – Marion Drain

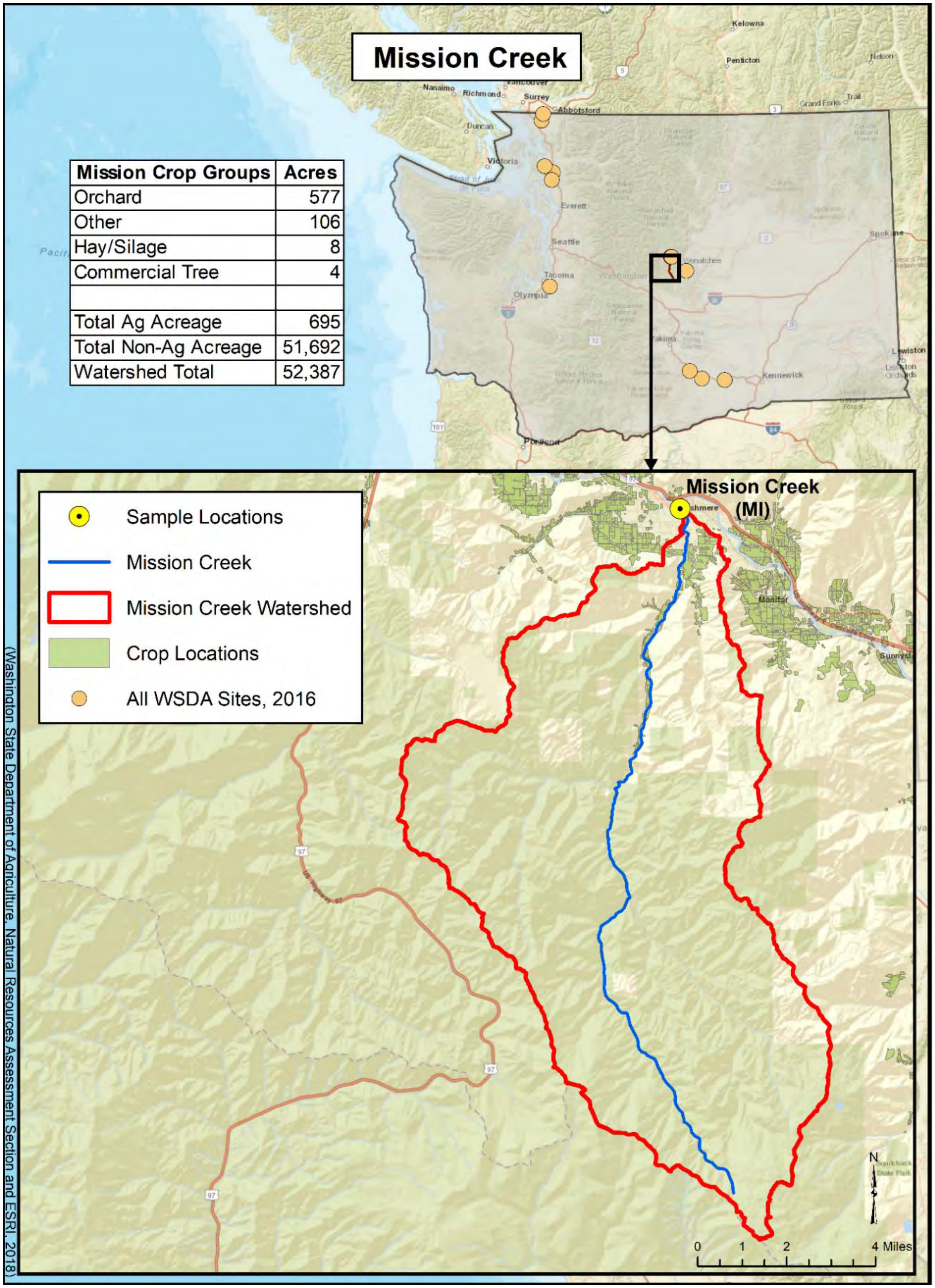
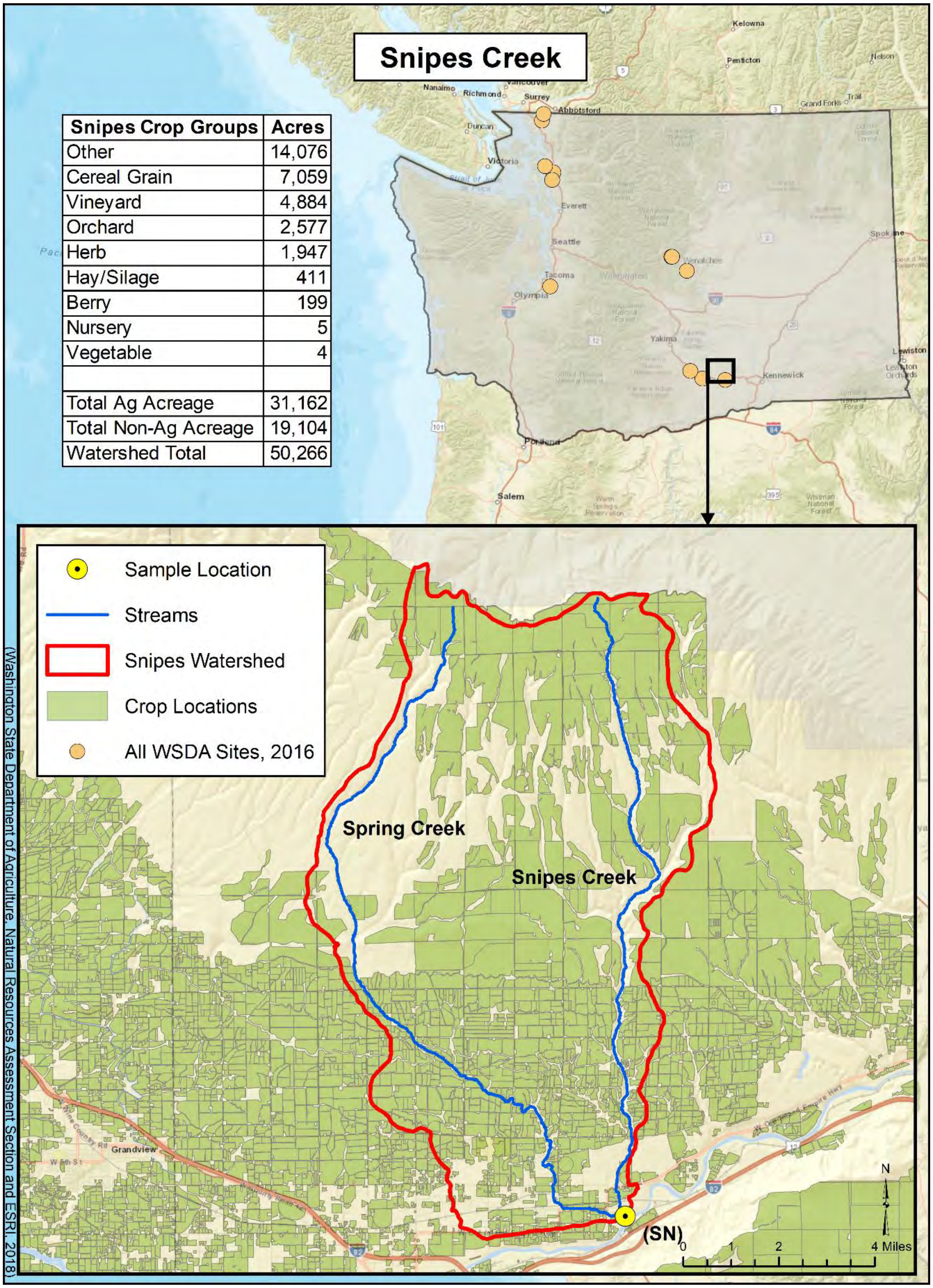


Figure 13 – Mission Creek



Snipes Crop Groups	Acres
Other	14,076
Cereal Grain	7,059
Vineyard	4,884
Orchard	2,577
Herb	1,947
Hay/Silage	411
Berry	199
Nursery	5
Vegetable	4
Total Ag Acreage	31,162
Total Non-Ag Acreage	19,104
Watershed Total	50,266

Figure 14 – Snipes Creek

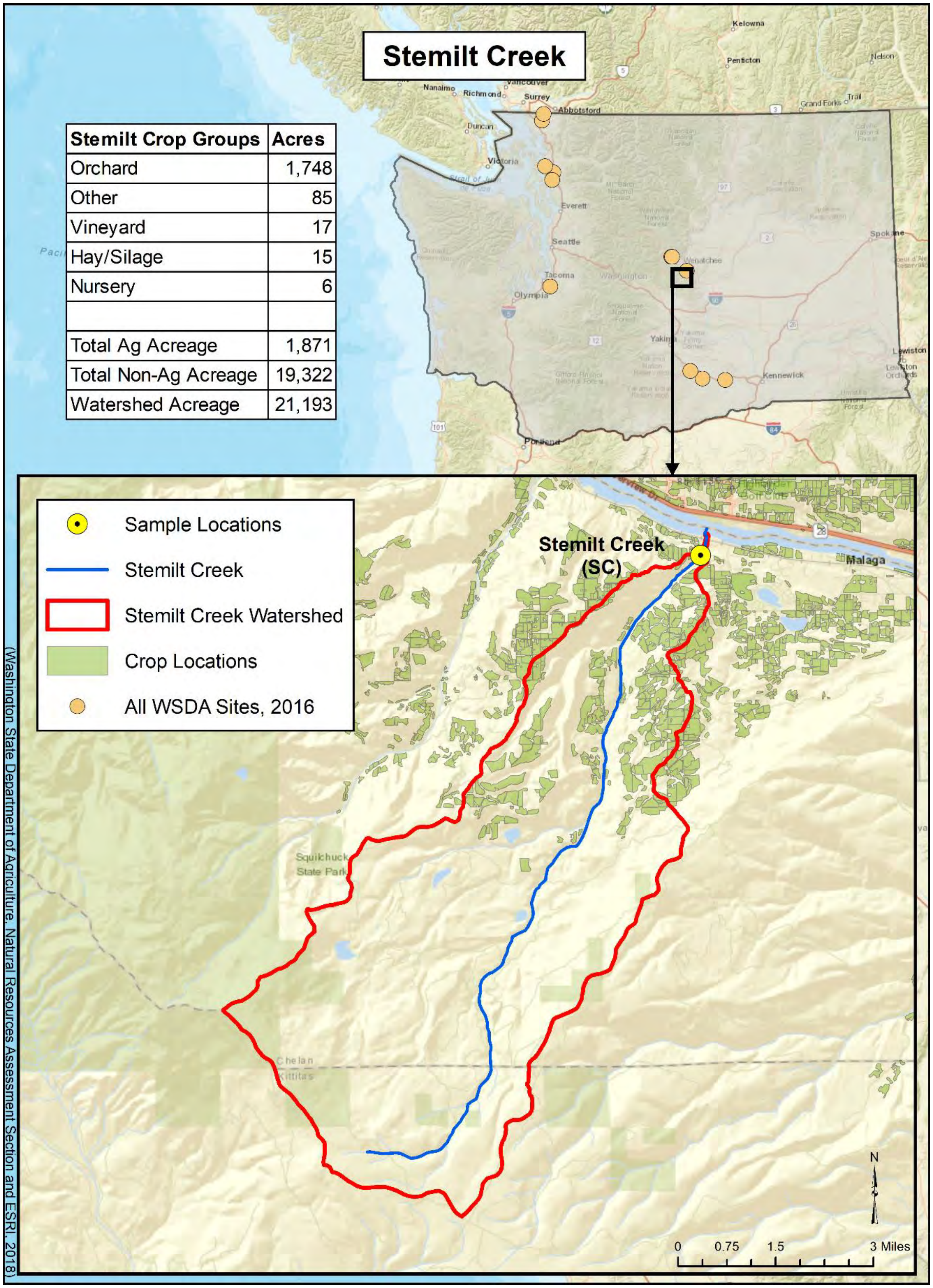


Figure 15 – Stemilt Creek

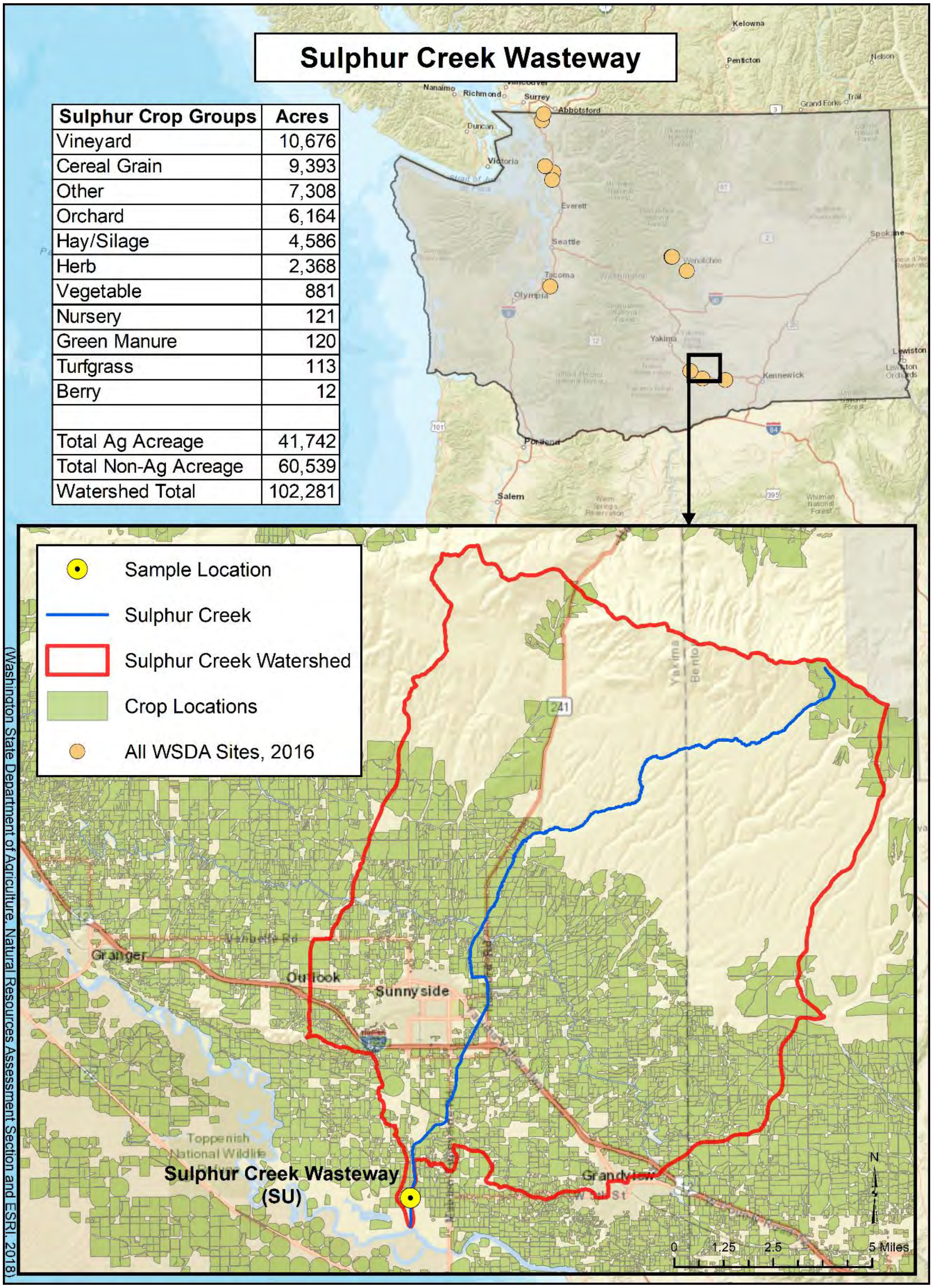


Figure 16 – Sulphur Creek Wasteway

Weather Station Locations

Precipitation data used in the Conventional Water Quality Parameters Summary section of this report was measured by WSU's AgWeatherNet weather stations. Each gauging station was chosen for its close proximity to each monitoring site's watershed area. Table 28a lists each monitoring site and its corresponding weather station.

Table 28a – Sites and associated AgWeatherNet weather stations

Subbasins & sites	Weather station name	Latitude & longitude of weather station
Nooksack:		
Upper & Lower Bertrand Creek	Lynden	48.94°, -122.51°
Lower Skagit-Samish:		
Upper Big Ditch & Indian Slough	WSU Mt Vernon	48.44°, -122.39°
Lower Big Ditch	Fir Island	48.36°, -122.42°
Puyallup:		
Clarks Creek	WSU Puyallup	47.19°, -122.33°
Wenatchee:		
Brender Creek & Mission Creek	N. Cashmere	47.51°, -120.43°
Alkali-Squilchuck:		
Stemilt Creek	Wenatchee Heights	47.37°, -120.31°
Lower Yakima:		
Marion Drain	Toppenish	46.37°, -120.39°
Snipes Creek	WSU Prosser	46.26°, -119.74°
Sulphur Creek Wasteway	Port of Sunnyside	46.28°, -120.01°

Appendix B: Assessment Criteria for Pesticides

This document is an appendix to the Ambient Monitoring for Pesticides in Washington State Surface Water: 2016 Technical Report. For this report, *Assessment Criteria* include data taken from studies determining hazards to non-target organisms and refer to acute and chronic hazard levels for fish, invertebrates, and aquatic plants. Various EPA derived risk assessments were reviewed to determine the most comparable and up-to-date toxicity guidelines for freshwater species.

WSDA applies a 0.5x safety factor to state and federal 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 1b. 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.

- Spp. refers to organisms used for testing, which are coded as follows:
  - Fish: BS-Bluegill Sunfish; BT-Brook Trout, BrT-Brown Trout, CC-Carp, FM-Fathead Minnow, LT-Lake Trout, ND-Not Described, RT-Rainbow Trout, SB-Striped Bass,
  - Invertebrates: ACR-Acute to Chronic Ratio, CR-Chironomus riparius, CT-Chironomus tentans (midge), DM-Daphnia magna, GF-Gammarus fasciatus (scud), HA-Hyalella azteca (amphipod), ND-Not Described, PC-Pteronarcys californica (stonefly),
  - Aquatic plants: AF-Anabaena flos-aquae, LG- Lemna gibba, LM-Lemna minor, ND-Not Described, NP-Navicula pelliculosa, SC-Pseudokirchneriella subcapitata formerly Selenastrum capricornutum (aka; Pseudokirchneria subcapitata), SP-Scenedesmus pannonicus.
- 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.
- Numbers are associated with the list of referenced studies included at the end of this addendum which are organized according to the reference.
- Only chemicals with WSDA Assessment Criteria are found in Table 1b. A list of all chemicals tested for in 2016 can be found in Attachment 2 (Appendix C: 2016 Quality Assurance Summary).

Table 1b – Freshwater assessment criteria (WSDA safety factors applied, µg/L)

	Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
1-Naphthol	35	350	50	RT/FM	10	175		DM	10	550	SC	10				
2,4-D[c]	10.7	107	39.6	BS	1	850	100	DM	1	165	LG	1				
2,4'-DDD													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
2,4'-DDE													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
2,4'-DDT													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
2,6-Dichlorobenzamide	3000	30000	5000	BS/RT	115	46000	160000	DM	115	50000	SP	115				
3-Hydroxycarbofuran	2.2	22	2.85	RT/BS	54, 60	0.5575	0.375	CD/DM	54							
4,4'-DDD													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
4,4'-DDE													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
4,4'-DDT													0.55[a]	0.0005[a]	0.55[a]	0.0005[a]
4-Nitrophenol	100	1000		RT	69	1250		DM	69							
Acetamiprid	250	2500	9600	RT/FM	101	5.25	1.05	CR/ACR	101	500	LG	101				
Acetochlor	9.5	95	65	RT	70	2050	11.05	DM	70	0.715	SC	70				
Alachlor	45	450	93.5	RT	2	1925	55	DM	2	0.82	SC	2				
Aldicarb	1.3	13	0.23	BS	3	5	1.5	CT	3	2500	LG	3				
Aldicarb Sulfone	1050	10500		RT	3	70	1.5	DM	3							
Aldicarb Sulfoxide	178.5	1785		RT	3	10.75	1.5	DM	3							
Aminomethylphosphoric acid	12475	124750		RT	39	170750		DM	39							
Atrazine	132.5	1325	32.5	RT/BT	4	875	70	DM	4	24.5	SC	4				
Azinphos-Ethyl	0.5	5		RT	71	1		DM	71							
Azinphos-methyl	0.0725	0.725	0.22	RT	5	0.2825	0.125	DM	5							0.005
Azoxystrobin	11.75	117.5	73.5	RT/FM	116	65	22	DM	116	24.5	NP	116				
Bifenazate	14.5	145		BS	103	125	75	DM	103	445	SC	103				
Bifenthrin	0.00375	0.0375	0.02	RT/FM	72	0.4	0.00065	DM	72							
Boscalid	67.5	675	58		94	266.5	395		94	670		94				

Pesticide	Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
Bromacil	900	9000	1500	RT	7	30250	4100	DM	7	3.4	SC	7				
Bromoxynil	0.725	7.25	9	RT/FM	8	2.75	1.25	DM	8	25.5	NP	83				
Captan	0.655	6.55	8.25	BrT/FM	73	2100	280	DM	73	985	SC	73				
Carbaryl	30	300	105	RT/FM	9, 10	1.4	0.75	DM	10	550	SC	10				
Carbofuran	2.2	22	2.85	RT/BS	54, 60	0.5575	4.9	CD/DM	54, 60							
Carboxin	57.5	575		RT	74	21100		DM	74	185	SC	74				
Chlorantraniliprole	29.75	297.5	55	BS/RT		1.775	2.235	DM		890	SC					
Chlorothalonil	1.0575	10.575	1.5	RT/FM	46	17	19.5	DM	46	95	SC	46				
Chlorpropham	75.25	752.5		RT	47	927.5		DM	47							
Chlorpyrifos	0.045	0.45	0.285	RT/FM	11, 12	0.025	0.02	DM	11				0.042	0.0205	0.0415	0.0205
Chlorsulfuron	7500	75000	16000	RT	117	92500	10000	DM	117	0.175	LG	117				
cis-Permethrin	0.01975	0.1975	0.15	BS/FM	58, 131	0.26	0.0195	DM	58							
Clopyralid	49200	492000		BS	64	28250		DM	64	3450	SC	64				
Clothianidin	2537.5	25375	4850	RT/FM	104	5.5	0.55	CR	104							
Cycloate	112.5	1125		RT	87	6000		DM	87							
Cyprodinil	6.025	60.25	115		96	80	4.1		96	1125		96				
DDT-Total													0.55	0.0005	0.55	0.0005
Dacthal (DCPA)	165	1650		RT	56	4505		DM	56							
Diazinon	2.25	22.5	0.4	RT/BT	13, 14	0.2	0.085	DM	13	1850	SC	13			0.085	0.085
Dicamba	700	7000		RT	15	25000		DM	15	30.5	AF	15				
Dichlobenil	123.25	1232.5	166.5	RT	16, 17	1550	280	DM	16	15	LG	16				
Dichlorprop	5350	53500	7350	RT	76	139500	37450	DM	76	38.5	NP	76				
Dichlorvos (DDVP)	4.575	45.75	2.6	LT/RT	75	0.0175	0.0029	DM	75	7000	ND	75				
Dicofol	1.325	13.25	1.375		97,98	35	9.5		98	2500						

	Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
Difenoconazole	20.25	202.5	4.35	RT/FM	118	192.5	2.8	DM	118	49	NP	118				
Dimethoate	155	1550	215	RT	18, 29	830	20	DM	29	18000	SC	29				
Dinotefuran	2477.5	24775		CC	105	242075	47650	DM	106	488000	SC	106				
Diphenamid	2425	24250		RT	59	14500		DM	59							
Disulfoton Sulfoxide	1500	15000		RT	19	16	0.765	DM	19							
Disulfoton sulfone	230	2300		RT	19	8.75	0.07	DM	19							
Dithiopyr	12.25	122.5	28	RT	88	425	40.5	DM	88							
Diuron	5	50	13.2	SB/FM	21, 22	40	100	GF/DM	21, 22	1.2	SC	21, 22				
EPN	3.575	35.75		RT	84											
Endosulfan I	0.02	0.2	0.05	RT	23	41.5	1	DM	23				0.11[b]	0.028[b]	0.11	0.028
Endosulfan II	0.02	0.2	0.05	RT	23	41.5	1	DM	23				0.11[b]	0.028[b]	0.11	0.028
Endosulfan Sulfate	0.035	0.35		RT	82	145		DM	23							
Eptam	350	3500		BS	24	1625	405	DM	24	700	SC	24				
Ethoprop	25.5	255	90	RT/FM	25	11	0.4	DM	25							
Etoxazole	9.25	92.5	7.5	RT	107	1.825	0.065	DM	107	25.95	NP	107				
Etridiazole	30.25	302.5	60	RT	119	770	185	DM	119	36	SC	119				
Fenamiphos	1.7	17	1.9	RT	77	0.325	0.06	DM	77							
Fenarimol	52.5	525	435	RT	67	1700	56.5	DM	67		SC	67				
Fipronil	6.15	61.5	3.3	RT	78	47.5	4.9	DM	78	70	SC	78				
Fipronil Sulfide	2.075	20.75	3.3	ND	78	25	0.055	DM/ND	78	70	ND					
Fipronil Sulfone	0.975	9.75	0.335	RT/ND	78	7.25	0.0185	DM/ND	78	70	ND					
Fludioxonil	11.75	117.5	9.5	RT/FM	121	225	9.5	DM	121							
Hexachlorobenzene	0.75	7.5	1.84	RT	26	7.5	8	DM	26	15	SC	26				
Hexazinone	4500	45000	8500	RT/FM	27, 28	37900	10000	DM	27	3.5	SC	27				
Imazapic	2500	25000	48000	RT/FM	108	25000	48000	DM	108	3.11	LM	108				

		Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
Imazapyr	2500	25000	59000	RT/FM	109	25000	48550	DM	109	9	LM	109				
Imidacloprid	2075	20750	600	RT	61	17.25	650	CT/DM	61	5000	ND	61				
Isoxaben	25	250	200	RT	120	325	345	DM	120	5	LG	120				
Linuron	75	750	2.79	RT	48	30	0.045	DM	48	33.5	SC	49				
Malaoxon	0.82	8.2	4.3	RT	31	0.1475	0.03	DM	31	1200		99				
Malathion	0.82	8.2	4.3	RT	31	0.1475	0.0175	DM	31	1200		99				0.05
MCPA	19	190	6000		100	45	5500		100	10	SC	32				
Mecoprop (MCPP)	3120	31200		RT	65	25000	25400	DM	65; 93	7	SC	93				
Metalaxyl	460	4600	4550	RT/FM	51	3000	635	DM	51	50000	SC	51				
Methiocarb	10.9	109	25	ND	30	1.75	0.05	ND	30							
Methomyl	21.5	215	28.5	RT/FM	57, 50	1.25	0.35	DM	57							
Methoxychlor	0.475	4.75		BT	102	0.35		PC	102							
Methoxyfenozide	105	1050	265	FM	110	12.5	3.15	CR	110	1700	SC	110				
Metolachlor	95	950	1250	RT	33	275	0.5	DM	33	4	SC	33				
Metribuzin	1050	10500	1500	RT	52	1050	645	DM	52	5.95	NP	52				
Metsulfuron-methyl	2287.5	22875	14800	RT	125	22550	850	DM	125	0.32	LG	125				
Myclobutanil	60	600	490	BS/FM	122	2750		DM	122	415	SC	122				
N,N-Diethyl-m-toluamide	1875	18750		RT	123	18750		DM	123							
Napropamide	160	1600	550	RT	80	3575	550	DM	80	1700	SC/LM	80				
Norflurazon	202.5	2025	385	RT	34	3750	500	DM	34	4.85	SC	34				
Oryzalin	81.5	815	230	RT	85	375	179	DM	85	26	SC	85				
Oxadiazon	30	300	16.5	RT/FM	124	545	16.5	DM	124	4	SC	124				
Oxamyl	105	1050	385	RT	62	45	6	DM/ACR	62	60	SC	62				
Oxamyl oxime	105	1050	385	RT	62	45	6	DM/ACR	62	60	SC	62				
Oxyfluorfen	6.25	62.5	19	RT/FM	35	20	6.5	DM	35	0.145	SC	35				
Pendimethalin	3.45	34.5	3.15	RT/FM	37	70	7.25	DM	37	2.7	SC	37				

	Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
Pesticide	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
Pentachlorophenol	0.375	3.75	5.5	RT	38	112.5	120	DM	38	25	SC	38	4.1	2.6	3.95	3.05
Phosmet	5.75	57.5	1.5	RT	79	1.5	0.4	DM	79	75	SC	79				
Picloram	137.5	1375	275	RT	53	8600	5900	DM	53	17450	SC	53				
Piperonyl butoxide	47.5	475	20	RT	81	127.5	15	DM	81							
Prodiamine	0.325	3.25		BS	89	3.25	0.75	DM	89							
Prometon	300	3000	4750	RT/FM	68	6425	1750	DM	68	49	SC	68				
Prometryn	72.75	727.5	310	RT/FM	126	2425	500	DM	126	0.52	NP	126				
Propargite	2.95	29.5	8	RT/FM	40	18.5	4.5	DM	40	33.1	SC	40				
Propazine	109.5	1095	280	BS/FM	20	1330	23.5	DM	20	12.45	NP	20				
Propiconazole	21.25	212.5	47.5	RT/FM	127	325	130	DM	127	10.5	ND	127				
Propoxur	92.5	925		RT	63	2.75		DM	63							
Propyzamide	1800	18000	3850	RT	66	1400	300	DM	66	2000	AF	66				
Pyraclostrobin	0.155	1.55	1.175	RT	128	3.925	2	DM	128	0.75	NP	128				
Pyridaben	0.018	0.18	0.0435	RT	129	0.1325	0.022	DM	129	8.1	LG	129				
Pyrimethanil	252.5	2525	10	RT	130	750	500	DM	130	900	ND	130				
Pyriproxyfen	8.25	82.5	2.15		90	100	0.0075		90	0.090		90				
Simazine	160	1600	480	FM	41, 36	250	20	DM/ACR	41	0.307	SC	41				
Sodium Bentazon	4750	47500	4915	RT/FM	6	15575	50600	CR/DM	6	2250	SC	6				
Spirotetramat	35.25	352.5	267	RT/FM	91	165	1000	CR/DM	91	2025		91				
Sulfentrazone	2345	23450	1475	RT	132	15100	100	DM	132	15.5	SC	132				
Sulfometuron methyl	3700	37000		RT	133	37500	48500	DM	133	0.225	LG	133				
Sulfoxaflor	9675	96750	330	RT/FM	111	100000	25250	DM	111	40600	NP	111				
Tebuthiuron	2650	26500	4650	FM	42	74250	10900	DM	42	65	LG	42				
Tefluthrin	0.0015	0.015	0.002		92	0.0175	0.004		92							
Terbacil	1155.5	11555	600	RT	43	16250	320	DM	43	5.5	NP	43				
Tetrahydrophthalimide	3000	30000		RT	73	28250		DM	73							

Pesticide	Fish					Invertebrate				Aquatic Plant			WAC		NRWQC	
	Endangered Species Acute	Acute	Chronic	Spp.	Ref.	Acute	Chronic	Spp.	Ref.	Acute	Spp.	Ref.	Acute	Chronic	CMC	CCC
Thiacloprid	630	6300	459	BS/RT	112	9.45	0.485	HA/ACR	112	22500	SC	112				
Thiamethoxam	2500	25000	10000	BS/RT	113	8.75	25000	CT	113	4500	LM	113				
Total Cypermethrin	0.00975	0.0975	0.07		95	0.105	0.195		95							
trans-Permethrin	0.0725	0.725	0.15		58	0.025	0.0195		58	0.0195		58				
Triadimefon	102.5	1025	20.5	RT	55	400	26	DM	55	855	SC	55				
Triclopyr acid	2925	29250	52000	RT/FM	86, 44	33225	40350	DM	86	16250	SC	86				
Triclosan	7.2	72		RT	114	97.5		DM	114	0.35	LG	114				
Trifloxystrobin	0.3575	3.575	2.15	RT	134	6.325	1.38	DM	134	18.55	SC	134				
Trifluralin	1.09	10.9	1.09	RT	45	62.75	1.2	DM	45	3.76	SC	45				

CMC: Criteria Maximum Concentration
CCC: Criteria Continuous Concentration
[a] Criteria is specific to total DDT but is used here for individual metabolites as well.
[b] Criteria is specific to endosulfan but is used here for individual metabolites as well.
[c] 2,4-D criteria in this table are in acid equivalents. Toxicity values for the individual forms of 2,4-D are available in the referenced document.

Assessment Criteria Reference Documents

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Appendix C: 2016 Quality Assurance Summary

Data Qualification

Data Qualifiers

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, 2016), Manchester Environmental Lab's data qualification criteria and professional judgement. The Manchester Environmental Lab (MEL) provides a list of data qualifiers and their definitions in Table 1c that are used for sample analysis of pesticides and total suspended solids (TSS).

Table 1c – 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.

Evaluating Replicates and Standard Recoveries

Performance measures are used to determine when data should be qualified. Percent recovery is used to assess bias in an analysis; a known amount of chemical is added to a sample before analysis and compared to the amount detected during analysis. Systematically low percent recoveries show analytical bias. Relative percent difference (RPD) is used to assess analytical precision; the difference between replicate pairs (matrix spike duplicates, laboratory control sample duplicates, and field replicates) is compared. When RPDs and percent recoveries are outside control limits, analytical results may be qualified. These control limits may be specified by the EPA method or provided by the lab. Control limits for RPD and percent recovery are presented in Table 2c.

Table 2c – Performance measures for quality assurance and quality control

Analytical method	Use	Analyte/Parameter	RPD control limit (%)	Recovery lower limit (%)	Recovery upper limit (%)
Conductivity	N/A	Specific Conductivity	≥ 20	95	105
GCMS-Herbicides	Degradate	3,5-Dichlorobenzoic Acid	≥ 40	40	130
GCMS-Herbicides	Degradate	4-Nitrophenol	≥ 40	40	130
GCMS-Herbicides	Herbicide	2,4-D	≥ 40	40	130
GCMS-Herbicides	Herbicide	Bentazon	≥ 40	40	130
GCMS-Herbicides	Herbicide	Bromoxynil	≥ 40	40	130
GCMS-Herbicides	Herbicide	Clopyralid	≥ 40	40	130
GCMS-Herbicides	Herbicide	Dacthal	≥ 40	40	130
GCMS-Herbicides	Herbicide	Dicamba	≥ 40	40	130
GCMS-Herbicides	Herbicide	Dichlorprop	≥ 40	40	130
GCMS-Herbicides	Herbicide	MCPA	≥ 40	40	130
GCMS-Herbicides	Herbicide	MCPP	≥ 40	40	130
GCMS-Herbicides	Herbicide	Picloram	≥ 40	40	130
GCMS-Herbicides	Herbicide	Triclopyr	≥ 40	40	130
GCMS-Herbicides	Wood Preservative	Pentachlorophenol	≥ 40	40	130
GCMS-Pesticides*	Antimicrobial	Triclosan	≥ 40	30	130
GCMS-Pesticides*	Degradate	Tetrahydrophthalimide	≥ 40	50	150
GCMS-Pesticides*	Degradate	Fipronil Disulfinyl	≥ 40	30	130
GCMS-Pesticides*	Degradate	Fipronil Sulfide	≥ 40	30	130
GCMS-Pesticides*	Degradate	Fipronil Sulfone	≥ 40	30	130
GCMS-Pesticides*	Degradate	2,4'-DDD	≥ 40	29	132
GCMS-Pesticides*	Degradate	2,4'-DDE	≥ 40	37	127
GCMS-Pesticides*	Degradate	4,4'-DDD	≥ 40	49	143

Analytical method	Use	Analyte/Parameter	RPD control limit (%)	Recovery lower limit (%)	Recovery upper limit (%)
GCMS-Pesticides*	Degradate	4,4'-DDE	≥ 40	40	140
GCMS-Pesticides*	Degradate	Endosulfan Sulfate	≥ 40	77	142
GCMS-Pesticides*	Degradate	2,6-Dichlorobenzamide	≥ 40	30	140
GCMS-Pesticides*	Fungicide	Boscalid	≥ 40	50	150
GCMS-Pesticides*	Fungicide	Captan	≥ 40	10	219
GCMS-Pesticides*	Fungicide	Chlorothalonil (Daconil)	≥ 40	57	227
GCMS-Pesticides*	Fungicide	Etridiazole	≥ 40	30	150
GCMS-Pesticides*	Fungicide	Fenarimol	≥ 40	30	130
GCMS-Pesticides*	Fungicide	Fludioxonil	≥ 40	30	150
GCMS-Pesticides*	Fungicide	Metalaxyl	≥ 40	56	153
GCMS-Pesticides*	Fungicide	Pentachloronitrobenzene	≥ 40	30	150
GCMS-Pesticides*	Fungicide	Triadimefon	≥ 40	61	178
GCMS-Pesticides*	Herbicide	Acetochlor	≥ 40	30	130
GCMS-Pesticides*	Herbicide	Alachlor	≥ 40	13	184
GCMS-Pesticides*	Herbicide	Atrazine	≥ 40	13	178
GCMS-Pesticides*	Herbicide	Benefin	≥ 40	44	151
GCMS-Pesticides*	Herbicide	Bromacil	≥ 40	55	181
GCMS-Pesticides*	Herbicide	Chlorpropham	≥ 40	53	181
GCMS-Pesticides*	Herbicide	Cycloate	≥ 40	49	151
GCMS-Pesticides*	Herbicide	Di-allate (Avadex)	≥ 40	30	130
GCMS-Pesticides*	Herbicide	Dichlobenil	≥ 40	34	153
GCMS-Pesticides*	Herbicide	Diphenamid	≥ 40	52	170
GCMS-Pesticides*	Herbicide	Dithiopyr	≥ 40	30	130
GCMS-Pesticides*	Herbicide	Eptam	≥ 40	41	159
GCMS-Pesticides*	Herbicide	Ethalfluralin (Sonalan)	≥ 40	6	243
GCMS-Pesticides*	Herbicide	Flumioxazin	≥ 40	30	150
GCMS-Pesticides*	Herbicide	Fluroxypyr-meptyl	≥ 40	30	150
GCMS-Pesticides*	Herbicide	Hexazinone	≥ 40	41	183
GCMS-Pesticides*	Herbicide	Metolachlor	≥ 40	55	180
GCMS-Pesticides*	Herbicide	Metribuzin	≥ 40	30	130
GCMS-Pesticides*	Herbicide	Napropamide	≥ 40	70	180
GCMS-Pesticides*	Herbicide	Norflurazon	≥ 40	70	168
GCMS-Pesticides*	Herbicide	Oryzalin	≥ 40	10	277
GCMS-Pesticides*	Herbicide	Oxadiazon	≥ 40	30	150
GCMS-Pesticides*	Herbicide	Oxyfluorfen	≥ 40	42	154
GCMS-Pesticides*	Herbicide	Pendimethalin	≥ 40	39	163
GCMS-Pesticides*	Herbicide	Prodiamine	≥ 40	30	130
GCMS-Pesticides*	Herbicide	Prometon	≥ 40	55	164
GCMS-Pesticides*	Herbicide	Prometryn	≥ 40	60	165
GCMS-Pesticides*	Herbicide	Pronamide (Kerb)	≥ 40	63	169
GCMS-Pesticides*	Herbicide	Pyraflufen-ethyl	≥ 40	30	150
GCMS-Pesticides*	Herbicide	Simazine	≥ 40	72	192
GCMS-Pesticides*	Herbicide	Simetryn	≥ 40	44	171
GCMS-Pesticides*	Herbicide	Sulfentrazone	≥ 40	30	150
GCMS-Pesticides*	Herbicide	Tebuthiuron	≥ 40	10	235
GCMS-Pesticides*	Herbicide	Terbacil	≥ 40	27	237

Analytical method	Use	Analyte/Parameter	RPD control limit (%)	Recovery lower limit (%)	Recovery upper limit (%)
GCMS-Pesticides*	Herbicide	Treflan (Trifluralin)	≥ 40	41	174
GCMS-Pesticides*	Herbicide	Triallate	≥ 40	52	128
GCMS-Pesticides*	Herbicide	Triclopyr-butoxyl	≥ 40	30	150
GCMS-Pesticides*	Insect Repellent	N,N-Diethyl-m-toluamide (DEET)	≥ 40	30	150
GCMS-Pesticides*	Insecticide	Bifenazate	≥ 40	50	150
GCMS-Pesticides*	Insecticide	Chlorethoxyfos	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Etoxazole	≥ 40	50	150
GCMS-Pesticides*	Insecticide	Prallethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Pyridaben	≥ 40	30	150
GCMS-Pesticides*	Insecticide	Pyriproxyfen	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Tefluthrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Tetramethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	2,4'-DDT	≥ 40	25	118
GCMS-Pesticides*	Insecticide	4,4'-DDT	≥ 40	42	148
GCMS-Pesticides*	Insecticide	Endosulfan I	≥ 40	58	195
GCMS-Pesticides*	Insecticide	Endosulfan II	≥ 40	58	160
GCMS-Pesticides*	Insecticide	Kelthane	≥ 40	10	265
GCMS-Pesticides*	Insecticide	Chlorpyriphos	≥ 40	52	152
GCMS-Pesticides*	Insecticide	Coumaphos	≥ 40	10	487
GCMS-Pesticides*	Insecticide	Diazinon	≥ 40	59	168
GCMS-Pesticides*	Insecticide	Dichlorvos (DDVP)	≥ 40	27	169
GCMS-Pesticides*	Insecticide	Dimethoate	≥ 40	48	217
GCMS-Pesticides*	Insecticide	Ethoprop	≥ 40	10	263
GCMS-Pesticides*	Insecticide	Imidan	≥ 40	32	203
GCMS-Pesticides*	Insecticide	Malathion	≥ 40	50	147
GCMS-Pesticides*	Insecticide	Methyl Chlorpyrifos	≥ 40	50	144
GCMS-Pesticides*	Insecticide	Naled	≥ 40	10	220
GCMS-Pesticides*	Insecticide	Phorate	≥ 40	12	130
GCMS-Pesticides*	Insecticide	Tetrachlorvinphos	≥ 40	70	196
GCMS-Pesticides*	Insecticide	Fipronil	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Bifenthrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	cis-Permethrin	≥ 40	17	201
GCMS-Pesticides*	Insecticide	Cyfluthrin	≥ 40	30	150
GCMS-Pesticides*	Insecticide	Cypermethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Deltamethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Fenvalerate	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Phenothrin	≥ 40	20	130
GCMS-Pesticides*	Insecticide	Tau-fluvalinate	≥ 40	30	150
GCMS-Pesticides*	Insecticide	Tralomethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	trans-Permethrin	≥ 40	30	130
GCMS-Pesticides*	Insecticide	Propargite	≥ 40	30	130
GCMS-Pesticides*	Synergist	Piperonyl Butoxide	≥ 40	30	130
GCMS-Pesticides*	Synergist	MGK264	≥ 40	49	193
LCMS-Pesticides	Degradate	Aldicarb Sulfoxide	≥ 40	40	130
LCMS-Pesticides	Degradate	Methomyl oxime	≥ 40	40	130

Analytical method	Use	Analyte/Parameter	RPD control limit (%)	Recovery lower limit (%)	Recovery upper limit (%)
LCMS-Pesticides	Degradate	Oxamyl oxime	≥ 40	40	130
LCMS-Pesticides	Degradate	Malaoxon	≥ 40	40	130
LCMS-Pesticides	Degradate	Desisopropyl Atrazine	≥ 40	40	130
LCMS-Pesticides	Degradate	Desethylatrazine	≥ 40	40	130
LCMS-Pesticides	Fungicide	Azoxystrobin	≥ 40	40	130
LCMS-Pesticides	Fungicide	Cyprodinil	≥ 40	40	130
LCMS-Pesticides	Fungicide	Difenoconazole	≥ 40	40	130
LCMS-Pesticides	Fungicide	Fenbuconazole	≥ 40	40	130
LCMS-Pesticides	Fungicide	Myclobutanil	≥ 40	40	130
LCMS-Pesticides	Fungicide	Propiconazole	≥ 40	40	130
LCMS-Pesticides	Fungicide	Pyraclostrobin	≥ 40	40	130
LCMS-Pesticides	Fungicide	Pyrimethanil	≥ 40	40	130
LCMS-Pesticides	Fungicide	Trifloxystrobin	≥ 40	40	130
LCMS-Pesticides	Fungicide	Zoxamide	≥ 40	40	130
LCMS-Pesticides	Herbicide	Chlorsulfuron	≥ 40	40	130
LCMS-Pesticides	Herbicide	Diuron	≥ 40	40	130
LCMS-Pesticides	Herbicide	Imazapic	≥ 40	40	130
LCMS-Pesticides	Herbicide	Imazapyr	≥ 40	40	130
LCMS-Pesticides	Herbicide	Isoxaben	≥ 40	40	130
LCMS-Pesticides	Herbicide	Linuron	≥ 40	40	130
LCMS-Pesticides	Herbicide	Metsulfuron-methyl	≥ 40	40	130
LCMS-Pesticides	Herbicide	Monuron	≥ 40	40	130
LCMS-Pesticides	Herbicide	Sulfometuron methyl	≥ 40	40	130
LCMS-Pesticides	Insecticide	Chlorantraniliprole	≥ 40	40	130
LCMS-Pesticides	Insecticide	Methoxyfenozide	≥ 40	40	130
LCMS-Pesticides	Insecticide	Spirotetramat	≥ 40	40	130
LCMS-Pesticides	Insecticide	Diflubenzuron	≥ 40	40	130
LCMS-Pesticides	Insecticide	Baygon	≥ 40	40	130
LCMS-Pesticides	Insecticide	Carbaryl	≥ 40	40	130
LCMS-Pesticides	Insecticide	Methiocarb	≥ 40	40	130
LCMS-Pesticides	Insecticide	Methomyl	≥ 40	40	130
LCMS-Pesticides	Insecticide	Oxamyl	≥ 40	40	130
LCMS-Pesticides	Insecticide	Acetamiprid	≥ 40	40	130
LCMS-Pesticides	Insecticide	Clothianidin	≥ 40	40	130
LCMS-Pesticides	Insecticide	Dinotefuran	≥ 40	40	130
LCMS-Pesticides	Insecticide	Imidacloprid	≥ 40	40	130
LCMS-Pesticides	Insecticide	Thiacloprid	≥ 40	40	130
LCMS-Pesticides	Insecticide	Thiamethoxam	≥ 40	40	130
GC-ECD-Pesticides	Degradate	2,4'-DDD	≥ 40	59	129
GC-ECD-Pesticides	Degradate	2,4'-DDE	≥ 40	58	131
GC-ECD-Pesticides	Degradate	4,4'-DDD	≥ 40	59	116
GC-ECD-Pesticides	Degradate	4,4'-DDE	≥ 40	53	114
GC-ECD-Pesticides	Insecticide	2,4'-DDT	≥ 40	49	121
GC-ECD-Pesticides	Insecticide	4,4'-DDT	≥ 40	51	116
GC-ECD-Pesticides	Insecticide	Aldrin	≥ 40	24	96
GC-ECD-Pesticides	Insecticide	Dieldrin	≥ 40	47	114

Analytical method	Use	Analyte/Parameter	RPD control limit (%)	Recovery lower limit (%)	Recovery upper limit (%)
TSS	N/A	Total Suspended Solids	≥ 20	80	120

* Indicates that limits are analyte-specific control limits. All other limits are default limits specified by the EPA method.

Method Reporting Limits

MEL reports the method reporting limit (MRL) which is the lowest concentration used in the initial calibration for each analyte. The MRL is adjusted for each individual sample according to sample volume and dilution (if needed). Results outside the calibration range may be qualified as estimates (J). Mean MRL (calculated for each individual sample in 2016) and standard deviation are presented in Table 3c.

Table 3c – Mean performance of method reporting limits (MRL) in µg/L

CAS Number	Analyte	Use	Analytical method	Mean MRL	Standard deviation
94-75-7	2,4-D	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
53-19-0	2,4'-DDD	Degradate	GC-ECD-Pesticides	2.51E-03	3.32E-05
53-19-0	2,4'-DDD	Degradate	GCMS-Pesticides	3.31E-02	4.51E-04
3424-82-6	2,4'-DDE	Degradate	GC-ECD-Pesticides	2.51E-03	3.32E-05
3424-82-6	2,4'-DDE	Degradate	GCMS-Pesticides	3.31E-02	4.51E-04
789-02-6	2,4'-DDT	Insecticide	GC-ECD-Pesticides	2.51E-03	3.32E-05
789-02-6	2,4'-DDT	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
2008-58-4	2,6-Dichlorobenzamide	Degradate	GCMS-Pesticides	3.31E-02	4.50E-04
51-36-5	3,5-Dichlorobenzoic Acid	Degradate	GCMS-Herbicides	6.01E-02	7.02E-04
72-54-8	4,4'-DDD	Degradate	GC-ECD-Pesticides	2.51E-03	3.32E-05
72-54-8	4,4'-DDD	Degradate	GCMS-Pesticides	3.31E-02	4.51E-04
72-55-9	4,4'-DDE	Degradate	GC-ECD-Pesticides	2.51E-03	3.32E-05
72-55-9	4,4'-DDE	Degradate	GCMS-Pesticides	3.31E-02	4.51E-04
50-29-3	4,4'-DDT	Insecticide	GC-ECD-Pesticides	2.51E-03	3.32E-05
50-29-3	4,4'-DDT	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
100-02-7	4-Nitrophenol	Degradate	GCMS-Herbicides	6.01E-02	7.02E-04
135410-20-7	Acetamiprid	Insecticide	LCMS-Pesticides	1.43E-02	4.96E-03
34256-82-1	Acetochlor	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
15972-60-8	Alachlor	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
1646-87-3	Aldicarb Sulfoxide	Degradate	LCMS-Pesticides	1.00E-02	1.40E-06
309-00-2	Aldrin	Insecticide	GC-ECD-Pesticides	2.51E-03	3.32E-05
1912-24-9	Atrazine	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
131860-33-8	Azoxystrobin	Fungicide	LCMS-Pesticides	1.43E-02	4.96E-03
114-26-1	Baygon	Insecticide	LCMS-Pesticides	1.34E-02	4.73E-03
1861-40-1	Benefin	Herbicide	GCMS-Pesticides	3.63E-02	6.65E-03

CAS Number	Analyte	Use	Analytical method	Mean MRL	Standard deviation
25057-89-0	Bentazon	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
149877-41-8	Bifenazate	Insecticide	GCMS-Pesticides	5.02E-02	6.19E-04
82657-04-3	Bifenthrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
188425-85-6	Boscalid	Fungicide	GCMS-Pesticides	1.00E-01	1.22E-03
314-40-9	Bromacil	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
1689-84-5	Bromoxynil	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
133-06-2	Captan	Fungicide	GCMS-Pesticides	3.31E-02	4.51E-04
63-25-2	Carbaryl	Insecticide	LCMS-Pesticides	3.40E-02	2.60E-02
500008-45-7	Chlorantraniliprole	Insecticide	LCMS-Pesticides	1.00E-02	1.40E-06
54593-83-8	Chlorethoxyfos	Insecticide	GCMS-Pesticides	3.35E-02	2.44E-03
1897-45-6	Chlorothalonil (Daconil)	Fungicide	GCMS-Pesticides	3.31E-02	4.51E-04
101-21-3	Chlorpropham	Herbicide	GCMS-Pesticides	3.39E-02	4.88E-03
2921-88-2	Chlorpyriphos	Insecticide	GCMS-Pesticides	3.36E-02	7.39E-03
64902-72-3	Chlorsulfuron	Herbicide	LCMS-Pesticides	3.86E-02	9.91E-03
54774-45-7	cis-Permethrin	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
1702-17-6	Clopyralid	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
210880-92-5	Clothianidin	Insecticide	LCMS-Pesticides	5.69E-02	3.99E-02
56-72-4	Coumaphos	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
1134-23-2	Cycloate	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
68359-37-5	Cyfluthrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
52315-07-8	Cypermethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
121552-61-2	Cyprodinil	Fungicide	LCMS-Pesticides	1.00E-02	1.40E-06
1861-32-1	Dacthal	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
1007-28-9	Desisopropyl Atrazine	Degradate	LCMS-Pesticides	2.75E-02	1.70E-02
52918-63-5	Deltamethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
6190-65-4	Desethylatrazine	Degradate	LCMS-Pesticides	2.46E-02	1.85E-02
2303-16-4	Di-allate (Avadex)	Herbicide	GCMS-Pesticides	3.31E-02	4.51E-04
333-41-5	Diazinon	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
1918-00-9	Dicamba	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
1194-65-6	Dichlobenil	Herbicide	GCMS-Pesticides	3.31E-02	4.51E-04
120-36-5	Dichlorprop	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
62-73-7	Dichlorvos (DDVP)	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
60-57-1	Dieldrin	Insecticide	GC-ECD-Pesticides	2.51E-03	3.32E-05
119446-68-3	Difenoconazole	Fungicide	LCMS-Pesticides	1.27E-02	6.84E-03
35367-38-5	Diflubenzuron	Insecticide	LCMS-Pesticides	7.00E-02	4.06E-06
60-51-5	Dimethoate	Insecticide	GCMS-Pesticides	3.83E-02	7.86E-03
165252-70-0	Dinotefuran	Insecticide	LCMS-Pesticides	1.43E-02	4.96E-03
957-51-7	Diphenamid	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
97886-45-8	Dithiopyr	Herbicide	GCMS-Pesticides	3.37E-02	3.21E-03
330-54-1	Diuron	Herbicide	LCMS-Pesticides	1.34E-02	4.73E-03

CAS Number	Analyte	Use	Analytical method	Mean MRL	Standard deviation
959-98-8	Endosulfan I	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
33213-65-9	Endosulfan II	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
1031-07-8	Endosulfan Sulfate	Degradate	GCMS-Pesticides	3.31E-02	4.51E-04
759-94-4	Eptam	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
55283-68-6	Ethalfluralin (Sonalan)	Herbicide	GCMS-Pesticides	3.63E-02	6.65E-03
13194-48-4	Ethoprop	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
153233-91-1	Etoxazole	Insecticide	GCMS-Pesticides	5.02E-02	6.17E-04
2593-15-9	Etridiazole	Fungicide	GCMS-Pesticides	5.02E-02	6.19E-04
60168-88-9	Fenarimol	Fungicide	GCMS-Pesticides	3.31E-02	4.50E-04
114369-43-6	Fenbuconazole	Fungicide	LCMS-Pesticides	1.43E-02	4.96E-03
51630-58-1	Fenvalerate	Insecticide	GCMS-Pesticides	3.61E-02	6.42E-03
120068-37-3	Fipronil	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
205650-65-3	Fipronil Disulfinyl	Degradate	GCMS-Pesticides	1.00E-01	1.22E-03
120067-83-6	Fipronil Sulfide	Degradate	GCMS-Pesticides	1.00E-01	1.22E-03
120068-36-2	Fipronil Sulfone	Degradate	GCMS-Pesticides	1.00E-01	1.22E-03
131341-86-1	Fludioxonil	Fungicide	GCMS-Pesticides	5.02E-02	6.19E-04
103361-09-7	Flumioxazin	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
81406-37-3	Fluroxypyr-meptyl	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
51235-04-2	Hexazinone	Herbicide	GCMS-Pesticides	5.02E-02	6.19E-04
104098-48-8	Imazapic	Herbicide	LCMS-Pesticides	6.05E-02	3.76E-02
81334-34-1	Imazapyr	Herbicide	LCMS-Pesticides	8.51E-02	2.47E-02
138261-41-3	Imidacloprid	Insecticide	LCMS-Pesticides	1.43E-02	4.96E-03
732-11-6	Imidan	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
82558-50-7	Isoxaben	Herbicide	LCMS-Pesticides	1.00E-02	1.40E-06
115-32-2	Kelthane	Insecticide	GCMS-Pesticides	3.01E-01	3.57E-03
330-55-2	Linuron	Herbicide	LCMS-Pesticides	7.00E-02	4.06E-06
1634-78-2	Malaoxon	Degradate	LCMS-Pesticides	1.00E-02	1.40E-06
121-75-5	Malathion	Insecticide	GCMS-Pesticides	3.31E-02	4.50E-04
94-74-6	MCPA	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
93-65-2	MCPP	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
57837-19-1	Metalaxyl	Fungicide	GCMS-Pesticides	3.31E-02	4.51E-04
2032-65-7	Methiocarb	Insecticide	LCMS-Pesticides	3.00E-02	4.99E-06
16752-77-5	Methomyl	Insecticide	LCMS-Pesticides	1.00E-02	1.40E-06
13749-94-5	Methomyl oxime	Degradate	LCMS-Pesticides	7.14E-02	2.48E-02
161050-58-4	Methoxyfenozide	Insecticide	LCMS-Pesticides	1.00E-02	1.40E-06
5598-13-0	Methyl Chlorpyrifos	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
51218-45-2	Metolachlor	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
21087-64-9	Metribuzin	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
74223-64-6	Metsulfuron-methyl	Herbicide	LCMS-Pesticides	3.28E-02	1.49E-02
113-48-4	MGK264	Synergist	GCMS-Pesticides	5.02E-02	6.19E-04

CAS Number	Analyte	Use	Analytical method	Mean MRL	Standard deviation
150-68-5	Monuron	Herbicide	LCMS-Pesticides	1.34E-02	4.73E-03
88671-89-0	Myclobutanil	Fungicide	LCMS-Pesticides	1.00E-02	1.40E-06
134-62-3	N,N-Diethyl-m-toluamide	Insect Repellent	GCMS-Pesticides	5.02E-02	6.19E-04
300-76-5	Naled	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
15299-99-7	Napropamide	Herbicide	GCMS-Pesticides	5.02E-02	6.19E-04
27314-13-2	Norflurazon	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
19044-88-3	Oryzalin	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
19666-30-9	Oxadiazon	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
23135-22-0	Oxamyl	Insecticide	LCMS-Pesticides	1.00E-02	1.40E-06
30558-43-1	Oxamyl oxime	Degradate	LCMS-Pesticides	1.00E-02	1.40E-06
42874-03-3	Oxyfluorfen	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
40487-42-1	Pendimethalin	Herbicide	GCMS-Pesticides	3.63E-02	6.65E-03
82-68-8	Pentachloronitrobenzene	Fungicide	GCMS-Pesticides	5.02E-02	6.19E-04
87-86-5	Pentachlorophenol	Wood Preservative	GCMS-Herbicides	6.01E-02	7.02E-04
26002-80-2	Phenothrin	Insecticide	GCMS-Pesticides	3.31E-02	4.51E-04
298-02-2	Phorate	Insecticide	GCMS-Pesticides	3.01E-01	3.57E-03
1918-02-1	Picloram	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
51-03-6	Piperonyl Butoxide (PBO)	Synergist	GCMS-Pesticides	1.00E-01	1.22E-03
23031-36-9	Prallethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
29091-21-2	Prodiamine	Herbicide	GCMS-Pesticides	5.02E-02	6.19E-04
1610-18-0	Prometon	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
7287-19-6	Prometryn	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
23950-58-5	Pronamide (Kerb)	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
2312-35-8	Propargite	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
60207-90-1	Propiconazole	Fungicide	LCMS-Pesticides	1.71E-02	4.56E-03
175013-18-0	Pyraclostrobin	Fungicide	LCMS-Pesticides	1.75E-02	5.28E-03
129630-19-9	Pyraflufen-ethyl	Herbicide	GCMS-Pesticides	5.02E-02	6.19E-04
121-21-1	Pyrethrins	Insecticide	GCMS-Pesticides	7.93E-02	2.48E-02
96489-71-3	Pyridaben	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
53112-28-0	Pyrimethanil	Fungicide	LCMS-Pesticides	1.00E-02	1.40E-06
95737-68-1	Pyriproxyfen	Insecticide	GCMS-Pesticides	5.02E-02	6.19E-04
122-34-9	Simazine	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
1014-70-6	Simetryn	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
203313-25-1	Spirotetramat	Insecticide	LCMS-Pesticides	2.07E-02	9.99E-03
122836-35-5	Sulfentrazone	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
74222-97-2	Sulfometuron methyl	Herbicide	LCMS-Pesticides	1.43E-02	4.96E-03
102851-06-9	Tau-fluvalinate	Insecticide	GCMS-Pesticides	5.02E-02	6.19E-04
34014-18-1	Tebuthiuron	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04

CAS Number	Analyte	Use	Analytical method	Mean MRL	Standard deviation
79538-32-2	Tefluthrin	Insecticide	GCMS-Pesticides	5.02E-02	6.19E-04
5902-51-2	Terbacil	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
961-11-5	Tetrachlorvinphos	Insecticide	GCMS-Pesticides	5.02E-02	6.20E-04
27813-21-4	Tetrahydrophthalimide	Degradate	GCMS-Pesticides	1.00E-01	1.22E-03
7696-12-0	Tetramethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
111988-49-9	Thiacloprid	Insecticide	LCMS-Pesticides	1.00E-02	1.40E-06
153719-23-4	Thiamethoxam	Insecticide	LCMS-Pesticides	1.43E-02	4.96E-03
66841-25-6	Tralomethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
61949-77-7	trans-Permethrin	Insecticide	GCMS-Pesticides	1.00E-01	1.22E-03
1582-09-8	Treflan (Trifluralin)	Herbicide	GCMS-Pesticides	3.31E-02	4.50E-04
43121-43-3	Triadimefon	Fungicide	GCMS-Pesticides	3.31E-02	4.50E-04
2303-17-5	Triallate	Herbicide	GCMS-Pesticides	3.31E-02	4.51E-04
55335-06-3	Triclopyr	Herbicide	GCMS-Herbicides	6.01E-02	7.02E-04
64700-56-7	Triclopyr-butoxyl	Herbicide	GCMS-Pesticides	1.00E-01	1.22E-03
3380-34-5	Triclosan	Antimicrobial	GCMS-Pesticides	1.00E-01	1.22E-03
141517-21-7	Trifloxystrobin	Fungicide	LCMS-Pesticides	1.94E-02	1.00E-02
156052-68-5	Zoxamide	Fungicide	LCMS-Pesticides	1.00E-02	1.40E-06

Analytical Quality Assurance and Quality Control Samples

Quality assurance (QA) and quality control (QC) samples assure consistency and accuracy throughout sample collection, sample analysis, and the data reporting process. For this project, QA/QC samples used in pesticide analysis 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. Method blanks and split sample duplicates are used as QA/QC samples for TSS and conductivity.

In 2016, QA/QC samples were 12% of all the samples collected in the field. There were 154 QA/QC samples in total which included 49 field replicates, 44 field blanks, 48 MS/MSD samples and 13 conductivity check samples and replicates.

Field Replicate Results

Field replicate samples are collected in order to assess the potential for variation in sample homogeneity and the entire process of sampling and analysis. During 2016, 4% of pesticide and TSS samples were field replicates, which were evaluated using RPD. There were 71 consistently identified pairs for pesticide analysis and 11 consistently identified pairs for TSS analysis (Table 4c). Consistent identification refers to analytes identified in both the original sample and field replicate with unqualified or qualified J and E results.

Table 4c presents the results and relative percent difference for analytes consistently identified in both the grab sample and replicate sample.

Table 4c – Consistently detected field replicate pairs

Sample date	Parameter	Site ID	Mean	MRL (µg/L)	RPD (%)	Sample and replicate sample details
4/6	2,4-D	LBD	0.123	0.06	0	(0.123 ug/L and 0.123 ug/L)
4/27	2,4-D	UBD	0.065	0.059	3	(0.064 ug/L J and 0.066 ug/L J)
4/27	2,4-D	IS	0.045	0.06	13	(0.042 ug/L J and 0.048 ug/L J)
4/12	2,4-D	SU	0.074	0.06	0	(0.074 ug/L J and 0.074 ug/L J)
9/22	2,4-D	SU	0.064	0.059	28	(0.073 ug/L and 0.055 ug/L J)
7/13	2,6-Dichlorobenzamide	LBC	0.091	0.033	4	(0.093 ug/L and 0.089 ug/L)
5/27	2,6-Dichlorobenzamide	UBC	0.038	0.033	5	(0.039 ug/L and 0.037 ug/L)
4/28	2,6-Dichlorobenzamide	LBD	0.089	0.033	28	(0.101 ug/L and 0.076 ug/L)
7/13	2,6-Dichlorobenzamide	UBD	0.086	0.033	9	(0.09 ug/L and 0.082 ug/L)
5/21	2,6-Dichlorobenzamide	CC	0.042	0.034	12	(0.039 ug/L and 0.044 ug/L)
5/12	2,6-Dichlorobenzamide	IS	0.095	0.033	43	(0.074 ug/L and 0.115 ug/L)
5/12	4,4'-DDE	UBR	0.029	0.033	11	(0.027 ug/L J and 0.03 ug/L J)
8/10	4,4'-DDE	MI	0.018	0.034	6	(0.018 ug/L J and 0.017 ug/L J)
5/12	4,4'-DDT	UBR	0.027	0.033	4	(0.026 ug/L J and 0.027 ug/L J)
7/13	Atrazine	LBC	0.055	0.033	7	(0.053 ug/L and 0.057 ug/L)
4/7	Azoxystrobin	LBC	0.013	0.01	0	(0.013 ug/L and 0.013 ug/L)
7/23	Azoxystrobin	LBD	0.022	0.02	5	(0.021 ug/L and 0.022 ug/L)
7/28	Azoxystrobin	UBD	0.027	0.02	4	(0.026 ug/L and 0.027 ug/L)
8/10	Azoxystrobin	MA	0.024	0.02	4	(0.024 ug/L and 0.023 ug/L)
4/7	Baygon	LBC	0.008	0.01	13	(0.007 ug/L J and 0.008 ug/L J)
4/6	Bentazon	LBD	0.080	0.061	9	(0.076 ug/L and 0.083 ug/L)
7/13	Boscalid	LBC	0.072	0.1	6	(0.074 ug/L J and 0.07 ug/L J)
5/27	Boscalid	UBC	0.106	0.099	36	(0.125 ug/L and 0.087 ug/L J)
7/13	Boscalid	UBD	0.127	0.1	0	(0.127 ug/L and 0.127 ug/L)
7/13	Bromacil	LBC	0.044	0.033	7	(0.042 ug/L and 0.045 ug/L)
8/10	Chlorantraniliprole	MA	0.008	0.01	13	(0.008 ug/L J and 0.007 ug/L J)
4/11	Chlorpyriphos	SN	0.061	0.033	5	(0.062 ug/L and 0.059 ug/L)
4/27	Dicamba	UBD	0.030	0.059	3	(0.03 ug/L J and 0.029 ug/L J)
3/31	Dicamba	MA	0.023	0.06	4	(0.022 ug/L J and 0.023 ug/L J)
9/22	Dicamba	SU	0.036	0.059	17	(0.039 ug/L J and 0.033 ug/L J)
5/27	Dichlobenil	UBC	0.014	0.033	0	(0.014 ug/L J and 0.014 ug/L J)
4/28	Dichlobenil	LBD	0.018	0.033	11	(0.017 ug/L J and 0.019 ug/L J)
7/13	Dichlobenil	UBD	0.015	0.033	21	(0.016 ug/L J and 0.013 ug/L J)
7/23	Dinotefuran	LBD	0.011	0.02	10	(0.011 ug/L J and 0.01 ug/L J)
7/28	Dinotefuran	UBD	0.162	0.02	0	(0.162 ug/L and 0.162 ug/L)
4/7	Diuron	LBC	0.008	0.01	13	(0.007 ug/L J and 0.008 ug/L J)
4/28	Fludioxonil	LBD	0.109	0.05	2	(0.108 ug/L and 0.11 ug/L)
7/13	Fludioxonil	UBD	0.183	0.05	1	(0.183 ug/L and 0.182 ug/L)
5/24	Fludioxonil	MA	0.021	0.05	0	(0.021 ug/L J and 0.021 ug/L J)

Sample date	Parameter	Site ID	Mean	MRL (µg/L)	RPD (%)	Sample and replicate sample details
4/7	Imidacloprid	LBC	0.026	0.01	4	(0.026 ug/L and 0.025 ug/L)
6/14	Imidacloprid	UBC	0.055	0.01	13	(0.058 ug/L and 0.051 ug/L)
7/28	Imidacloprid	UBD	0.012	0.02	9	(0.011 ug/L J and 0.012 ug/L J)
4/7	Isoxaben	LBC	0.003	0.01	40	(0.003 ug/L J and 0.002 ug/L J)
4/27	MCPA	IS	0.829	0.06	19	(0.749 ug/L and 0.909 ug/L)
4/6	MCPP	LBD	0.045	0.061	2	(0.045 ug/L J and 0.044 ug/L J)
7/13	Metalaxyl	LBC	0.067	0.033	2	(0.066 ug/L and 0.067 ug/L)
7/13	Metalaxyl	UBD	0.991	0.033	1	(0.998 ug/L and 0.984 ug/L)
4/28	Metolachlor	LBD	0.271	0.033	7	(0.281 ug/L and 0.261 ug/L)
8/10	Myclobutanil	MA	0.009	0.01	0	(0.009 ug/L J and 0.009 ug/L J)
4/28	N,N-Diethyl-m-toluamide	LBD	0.041	0.05	7	(0.039 ug/L J and 0.042 ug/L J)
4/7	Oxamyl	LBC	0.098	0.01	1	(0.097 ug/L and 0.098 ug/L)
6/14	Oxamyl	UBC	0.005	0.01	0	(0.005 ug/L J and 0.005 ug/L J)
7/28	Oxamyl	UBD	0.373	0.01	11	(0.353 ug/L and 0.393 ug/L)
4/7	Oxamyl oxime	LBC	0.101	0.01	8	(0.097 ug/L and 0.105 ug/L)
6/14	Oxamyl oxime	UBC	0.023	0.01	0	(0.023 ug/L and 0.023 ug/L)
7/28	Oxamyl oxime	UBD	0.578	0.01	8	(0.601 ug/L and 0.554 ug/L)
5/24	Pendimethalin	MA	0.057	0.033	11	(0.06 ug/L and 0.054 ug/L)
4/7	Propiconazole	LBC	0.171	0.02	2	(0.169 ug/L and 0.172 ug/L)
5/27	Simazine	UBC	0.179	0.033	4	(0.175 ug/L and 0.182 ug/L)
7/13	Sulfentrazone	LBC	0.051	0.1	6	(0.049 ug/L J and 0.052 ug/L J)
4/28	Sulfentrazone	LBD	0.211	0.099	0	(0.21 ug/L J and 0.211 ug/L J)
7/13	Tebuthiuron	UBD	0.083	0.033	1	(0.083 ug/L and 0.082 ug/L)
5/27	Terbacil	UBC	0.110	0.033	12	(0.116 ug/L and 0.103 ug/L)
5/24	Terbacil	MA	0.227	0.033	14	(0.211 ug/L and 0.242 ug/L)
4/7	Thiamethoxam	LBC	0.023	0.01	4	(0.022 ug/L and 0.023 ug/L)
7/23	Thiamethoxam	LBD	0.005	0.02	22	(0.004 ug/L J and 0.005 ug/L J)
7/28	Thiamethoxam	UBD	0.043	0.02	12	(0.04 ug/L and 0.045 ug/L)
8/10	Thiamethoxam	MA	0.014	0.02	0	(0.014 ug/L J and 0.014 ug/L J)
7/29	Total Suspended Solids	UBC	3	1 mg/L	0	(3 mg/L and 3 mg/L)
7/1	Total Suspended Solids	LBD	5	1 mg/L	0	(5 mg/L and 5 mg/L)
5/27	Total Suspended Solids	UBD	6.5	3 mg/L	15	(7 mg/L and 6 mg/L)
9/15	Total Suspended Solids	UBD	5.5	4 mg/L	18	(6 mg/L and 5 mg/L)
3/31	Total Suspended Solids	UBR	43	6 mg/L	5	(44 mg/L and 42 mg/L)
6/3	Total Suspended Solids	LBR	6	1 mg/L	0	(6 mg/L and 6 mg/L)
7/28	Total Suspended Solids	CC	4	1 mg/L	0	(4 mg/L and 4 mg/L)
5/20	Total Suspended Solids	IS	7	4 mg/L	29	(6 mg/L and 8 mg/L)
5/4	Total Suspended Solids	MA	13.5	1 mg/L	7	(13 mg/L and 14 mg/L)
5/12	Total Suspended Solids	MI	15	1 mg/L	0	(15 mg/L and 15 mg/L)
8/8	Total Suspended Solids	SC	3.5	1 mg/L	29	(3 mg/L and 4 mg/L)

Sample date	Parameter	Site ID	Mean	MRL (µg/L)	RPD (%)	Sample and replicate sample details
4/6	Triclopyr	LBD	0.075	0.061	9	(0.078 ug/L and 0.071 ug/L)
4/27	Triclopyr	UBD	0.046	0.06	2	(0.046 ug/L J and 0.045 ug/L J)
4/27	Triclopyr	IS	0.049	0.06	12	(0.046 ug/L J and 0.052 ug/L J)

For pesticides, the mean RPD of the consistently identified replicate pairs was 8%. For TSS, the mean RPD of the consistently detected replicates was 9%.

Only 1 of the 71 consistently identified replicate pairs for pesticides exceeded the 40% RPD criterion (2,6-dichlorobenzamide, May 4th, IS). There were no RPD exceedances for the 11 replicate pairs for TSS. The 2,6-dichlorobenzamide results were not requalified because the RPD has limited effectiveness in assessing variability at low levels (Mathieu, 2006). When concentrations are low the RPD may be large even though the actual difference between the pairs is low. The remaining data for pesticide and TSS field replicates are of acceptable data quality.

In 2016, there were 14 inconsistently identified replicate pairs for pesticides and 1 inconsistently identified replicate pair for TSS (Table 5c). The majority of the inconsistently identified pairs were detections between the MRL and the method detection limit (below which the laboratory is unable to distinguish between instrument response due to the presence of analytes or background noise). The RPD also exceeded the 40% criterion for 13 of the 15 replicate pairs. Most of these replicate pairs consist of a J-qualified detection and a U- or UJ-qualified detection with the value replaced with the MRL.

There were no sample detections requalified due solely to inconsistent field replicate results. Consistently and inconsistently paired replicate values were averaged for comparisons to pesticide assessment criteria and water quality standards.

Table 5c – Inconsistent field replicate detections (µg/L)

Sample date	Parameter	Site ID	Mean	Reporting limit	RPD (%)	Sample and replicate sample details
6/7	Azoxystrobin	IS	0.008	0.01	50	(0.01 ug/L U and 0.006 ug/L J)
3/21	Bentazon	MA	0.059	0.06	3	(0.058 ug/L J and 0.06 ug/L U)
4/5	Chlorantraniliprole	LBC	0.008	0.01	67	(0.005 ug/L J and 0.01 ug/L U)
5/10	Chlorantraniliprole	LBR	0.007	0.01	86	(0.01 ug/L U and 0.004 ug/L J)
8/24	Dacthal	LBC	0.046	0.06	57	(0.033 ug/L J and 0.059 ug/L UJ)
9/12	Dacthal	SU	0.045	0.059	67	(0.03 ug/L J and 0.06 ug/L U)
4/4	Dicamba	SU	0.040	0.06	104	(0.06 ug/L UJ and 0.019 ug/L J)
7/13	Diuron	LBD	0.008	0.01	50	(0.01 ug/L U and 0.006 ug/L J)
5/3	Fenarimol	LBR	0.041	0.033	39	(0.049 ug/L and 0.033 ug/L U)
6/29	Fludioxonil	LBC	0.039	0.05	56	(0.028 ug/L J and 0.05 ug/L U)
3/29	Pentachlorophenol	LBD	0.043	0.06	87	(0.024 ug/L J and 0.061 ug/L U)

Sample date	Parameter	Site ID	Mean	Reporting limit	RPD (%)	Sample and replicate sample details
8/24	Pentachlorophenol	LBC	0.039	0.06	106	(0.018 ug/L J and 0.059 ug/L UJ)
6/7	Propiconazole	IS	0.013	0.01	46	(0.016 ug/L and 0.01 ug/L U)
7/13	Propiconazole	LBD	0.015	0.02	76	(0.02 ug/L U and 0.009 ug/L J)
6/14	Total Suspended Solids	CC	1.500	2 mg/L	67	(2 mg/L U and 1 mg/L)

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 2016, there were no detections in the 44 field blank samples collected for TSS and pesticide analysis. It is unlikely that samples are becoming contaminated during field operations.

Matrix Spike/Matrix Spike Duplicate Results

MS/MSD results assess the potential for matrix interactions or interaction between analytes that can affect analytical results. In 2016, almost all analytes tested for during the season were used to spike MS/MSDs, although MEL rotated between 2 spike mixtures for the GCMS-Pesticides analytical method to avoid coelution of analytes. Summary MS/MSD results for each analyte are shown in

Table 6c, with mean, maximum, and minimum percent recovery as well as RPD of MS and MSD samples.

Table 6c – Summary of MS/MSD results

Analyte	Number of MS/MSD recoveries	Mean recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD (%)	Max. RPD (%)	Min. RPD (%)
<u>LCMS-Pesticides:</u>							
Acetamiprid	12	92	105	84	4	12	0.7
Aldicarb Sulfoxide	12	91	106	79	7	13	3
Azoxystrobin	12	103	129	87	4	11	1
Baygon	12	87	111	69	3	7	0.4
Carbaryl	12	58	98	18	11	18	4
Chlorantraniliprole	12	89	107	78	5	13	0.05
Chlorsulfuron	12	74	106	54	4	13	1
Clothianidin	12	73	94	53	6	13	1
Cyprodinil	12	99	115	84	5	14	1
Desisopropyl Atrazine	12	57	91	37	10	24	2
Desethylatrazine	12	62	91	45	4	11	0.1
Difenoconazole	12	94	120	74	6	10	0.9
Diflubenzuron	12	78	97	63	9	14	4
Dinotefuran	12	93	107	86	5	12	1
Diuron	12	94	110	84	5	15	1
Fenbuconazole	12	77	108	58	7	16	2

Analyte	Number of MS/MSD recoveries	Mean recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD (%)	Max. RPD (%)	Min. RPD (%)
Imazapic	12	81	92	66	6	10	3
Imazapyr	12	76	87	67	6	12	1
Imidacloprid	12	88	97	77	6	10	2
Isoxaben	12	106	136	87	6	14	0.8
Linuron	12	97	117	79	9	18	3
Malaoxon	12	58	96	20	10	19	5
Methiocarb	12	57	110	19	13	23	3
Methomyl	12	89	104	80	4	13	0.2
Methomyl oxime	12	99	137	81	5	11	1
Methoxyfenozide	12	105	136	89	5	16	0.3
Metsulfuron-methyl	12	74	102	55	5	13	0.7
Monuron	12	92	108	87	4	11	0.3
Myclobutanil	12	85	113	73	5	13	0.02
Oxamyl	12	48	100	9	16	28	5
Oxamyl oxime	12	135	170	108	9	26	0.3
Propiconazole	12	96	140	75	7	20	3
Pyraclostrobin	12	101	127	88	4	12	0.6
Pyrimethanil	12	99	110	89	7	14	0.3
Pyriproxyfen	12	87	111	53	8	13	3
Spirotetramat	12	64	99	29	9	19	0.2
Sulfometuron methyl	12	94	107	87	4	11	0.9
Thiacloprid	12	87	97	78	4	10	0.9
Thiamethoxam	12	84	94	73	4	10	0.04
Trifloxystrobin	12	94	123	66	4	9	0.4
Zoxamide	12	85	112	76	4	16	0.3
GCMS-Herbicides:							
2,4-D	12	68	118	33	13	20	7
3,5-Dichlorobenzoic Acid	12	73	106	44	6	14	0.5
4-Nitrophenol	12	75	144	26	16	55	2
Bentazon	12	89	131	58	5	10	0.2
Bromoxynil	12	76	108	49	6	12	1
Clopyralid	12	34	63	20	16	32	2
Dacthal	12	97	131	72	5	9	2
Dicamba	12	68	110	44	8	26	2
Dichlorprop	12	85	129	58	6	11	2
MCPA	12	74	125	43	8	23	0.5
MCPP	12	86	127	62	5	11	1
Pentachlorophenol	12	76	103	53	3	8	1
Picloram	12	65	139	20	29	63	3
Triclopyr	12	83	133	55	8	17	2
GC-ECD-Pesticides:							
2,4'-DDD	2	103	110	96	14	14	14
2,4'-DDE	2	97	106	88	18	18	18
2,4'-DDT	2	99	105	92	14	14	14
4,4'-DDD	2	102	108	96	12	12	12
4,4'-DDE	2	100	106	93	14	14	14

Analyte	Number of MS/MSD recoveries	Mean recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD (%)	Max. RPD (%)	Min. RPD (%)
4,4'-DDT	2	95	102	87	16	16	16
Aldrin	2	79	81	76	6	6	6
Dieldrin	2	109	114	103	10	10	10
GCMS-Pesticides:							
2,4'-DDD	12	76	101	63	9	13	6
2,4'-DDE	12	69	89	57	5	10	1
2,4'-DDT	12	80	110	65	8	15	2
4,4'-DDD	12	80	108	64	12	29	3
4,4'-DDE	12	70	92	55	9	14	2
4,4'-DDT	12	84	121	62	6	15	0.5
Acetochlor	10	144	234	93	7	13	0.9
Alachlor	10	109	135	96	5	15	0.5
Atrazine	10	92	113	80	6	15	0.4
Benefin	12	102	143	78	9	25	0.04
Bifenazate	8	146	179	129	7	18	1
Bifenthrin	10	92	119	70	11	18	2
Boscalid	8	115	145	84	6	9	1
Bromacil	10	115	129	99	3	6	0.6
Captan	12	65	104	14	6	17	0.06
Chlorothalonil (Daconil)	12	76	100	61	6	11	1
Chlorpropham	10	108	121	91	3	6	0.9
Chlorpyriphos	12	100	131	78	2	4	0.1
cis-Permethrin	12	91	116	78	5	11	1
Coumaphos	12	129	189	91	6	9	1
Cycloate	10	78	97	45	10	20	6
Cyfluthrin	10	103	137	52	8	14	2
Cypermethrin	10	97	136	51	11	19	3
Di-allate (Avadex)	12	93	107	71	9	25	0.6
Diazinon	12	107	129	84	9	18	2
Dichlobenil	12	85	102	67	14	34	0.3
Dichlorvos (DDVP)	12	107	129	82	14	33	4
Dimethoate	8	121	153	90	5	10	0.1
Diphenamid	10	95	111	81	6	12	1
Endosulfan I	12	78	102	57	10	16	4
Endosulfan II	12	74	105	56	11	17	4
Endosulfan Sulfate	12	53	83	29	11	19	3
Eptam	10	96	113	72	11	32	3
Ethalfluralin (Sonalan)	12	118	161	90	7	13	0.6
Ethoprop	12	105	141	82	11	22	3
Etridiazole	10	136	158	119	5	8	0.02
Fenarimol	10	119	132	103	6	16	3
Fenvalerate	12	98	125	77	10	20	3
Fipronil	10	176	248	142	6	12	3
Fipronil Disulfinyl	10	111	136	92	3	9	0.4
Fipronil Sulfide	10	99	109	91	4	5	3
Fipronil Sulfone	10	115	126	104	3	6	0.6

Analyte	Number of MS/MSD recoveries	Mean recovery (%)	Maximum recovery (%)	Minimum recovery (%)	Mean RPD (%)	Max. RPD (%)	Min. RPD (%)
Fludioxonil	10	95	112	84	6	11	0.5
Flumioxazin	10	112	134	92	11	19	8
Fluroxypyr-meptyl	10	96	112	73	6	12	1
Hexazinone	10	94	104	76	6	13	0.9
Imidan	12	127	186	87	5	12	1
Kelthane	8	135	209	103	9	17	5
Malathion	10	125	149	102	5	7	1
Metalaxyl	12	103	138	76	9	23	0.8
Methyl Chlorpyrifos	12	102	132	78	5	9	1
Metolachlor	10	113	134	100	2	8	0.3
Metribuzin	10	145	184	106	8	25	0.4
MGK264	10	102	116	86	7	12	2
N,N-Diethyl-m-toluamide	10	104	124	88	4	5	3
Naled	12	101	131	74	11	26	4
Napropamide	10	101	114	80	5	7	3
Norflurazon	10	109	133	86	5	9	0.5
Oxadiazon	10	89	103	70	6	11	1
Oxyfluorfen	12	121	178	92	4	7	3
Pendimethalin	12	112	144	85	3	8	0.7
Pentachloronitrobenzene	10	112	126	97	7	12	2
Phenothrin	12	81	111	62	5	14	0.4
Phorate	12	109	138	76	9	23	0.8
Piperonyl Butoxide	10	111	121	94	4	7	2
Prometon	10	110	140	80	4	9	1
Prometryn	10	103	122	89	4	7	0.8
Pronamide (Kerb)	10	99	114	73	3	9	0.04
Propargite	12	90	121	69	7	19	0.8
Pyraflufen-ethyl	10	117	130	98	6	8	1
Pyridaben	10	116	135	96	6	11	0.8
Simazine	10	94	108	82	7	15	2
Simetryn	10	98	116	86	5	12	0.3
Sulfentrazone	10	147	164	134	6	14	1
Tau-fluvalinate	10	133	163	104	8	14	3
Tebuthiuron	10	112	164	52	4	6	1
Terbacil	10	143	173	111	3	11	0.5
Tetrachlorvinphos	12	100	138	72	5	10	0.9
Tetrahydrophthalimide	8	70	113	20	28	50	0.1
Treflan (Trifluralin)	10	106	115	96	3	6	0.4
Triadimefon	10	110	128	92	6	12	2
Triallate	12	88	103	75	12	29	2
Triclopyr-butoxyl	10	99	117	79	7	12	2

There were a total of 1,562 results (781 MS/MSD pairs) from MS and MSD recoveries. Overall, the mean recovery was 94% with a standard deviation of 28%. RPDs for those 781 MS/MSD pairs were below the 40% RPD control limit 99% of the time. The mean RPD for paired MS/MSD recoveries that were below the 40% RPD control limit was 7% with a standard deviation of 6%. The mean RPD for paired MS/MSD recoveries that were equal to or above the 40% RPD control limit was 57% with a standard deviation of 5%.

Table 7c describes the frequency of MS/MSD recoveries that were above or below the laboratory control limits set for each analyte. Table 7c also shows how often recoveries for each analyte were outside of the control limits and the number of detections from all grab samples throughout the season for each analyte.

Table 7c – Frequency of MS/MSD recoveries falling outside of the laboratory control limits

Analyte	Recoveries outside control limits (%)	MS/MSD samples (n)	MS/MSD recoveries above control limits	MS/MSD recoveries below control limits	Lower control limit (%)	Upper control limit (%)	Total number of detections in 2016
2,4-D	8	12	0	1	40	130	103
2,4'-DDD	0	2	0	0	59	129	0
2,4'-DDD	0	12	0	0	29	125	0
2,4'-DDE	0	2	0	0	58	131	0
2,4'-DDE	0	12	0	0	37	116	0
2,4'-DDT	0	2	0	0	49	121	0
2,4'-DDT	0	12	0	0	25	118	0
3,5-Dichlorobenzoic Acid	0	12	0	0	40	130	0
4,4'-DDD	0	2	0	0	59	116	9
4,4'-DDD	0	12	0	0	49	143	9
4,4'-DDE	0	2	0	0	53	114	45
4,4'-DDE	0	12	0	0	40	130	45
4,4'-DDT	0	2	0	0	51	116	18
4,4'-DDT	8	12	1	0	42	120	18
4-Nitrophenol	33	12	2	2	40	130	4
Acetamiprid	0	12	0	0	40	130	0
Acetochlor	40	10	4	0	30	130	0
Alachlor	0	10	0	0	16	181	0
Aldicarb Sulfoxide	0	12	0	0	40	130	0
Aldrin	0	2	0	0	24	96	0
Atrazine	0	10	0	0	13	172	8
Azoxystrobin	0	12	0	0	40	130	60
Baygon	0	12	0	0	40	130	1
Benefin	0	12	0	0	50	151	0
Bentazon	8	12	1	0	40	130	24
Bifenazate	38	8	3	0	50	150	0
Bifenthrin	0	10	0	0	30	130	1
Boscalid	0	8	0	0	50	150	111
Bromacil	0	10	0	0	55	181	17
Bromoxynil	0	12	0	0	40	130	2
Captan	0	12	0	0	10	219	0
Carbaryl	17	12	0	2	40	130	5
Chlorantraniliprole	0	12	0	0	40	130	59
Chlorothalonil (Daconil)	0	12	0	0	57	227	0
Chlorpropham	0	10	0	0	53	181	4

Analyte	Recoveries outside control limits (%)	MS/MSD samples (n)	MS/MSD recoveries above control limits	MS/MSD recoveries below control limits	Lower control limit (%)	Upper control limit (%)	Total number of detections in 2016
Chlorpyriphos	0	12	0	0	52	152	19
Chlorsulfuron	0	12	0	0	40	130	3
cis-Permethrin	0	12	0	0	17	201	0
Clopyralid	75	12	0	9	40	130	2
Clothianidin	0	12	0	0	40	130	7
Coumaphos	0	12	0	0	10	487	0
Cycloate	10	10	0	1	49	151	0
Cyfluthrin	0	10	0	0	50	150	0
Cypermethrin	10	10	1	0	30	130	0
Cyprodinil	0	12	0	0	40	130	8
Dacthal	8	12	1	0	40	130	13
Desisopropyl Atrazine	17	12	0	2	40	130	3
Desethylatrazine	0	12	0	0	40	130	2
Di-allate (Avadex)	0	12	0	0	30	130	0
Diazinon	0	12	0	0	59	168	10
Dicamba	0	12	0	0	40	130	48
Dichlobenil	0	12	0	0	34	153	65
Dichlorprop	0	12	0	0	40	130	0
Dichlorvos (DDVP)	0	12	0	0	27	169	0
Dieldrin	0	2	0	0	47	114	0
Difenoconazole	0	12	0	0	40	130	23
Diflubenzuron	0	12	0	0	40	130	0
Dimethoate	0	8	0	0	65	217	0
Dinotefuran	0	12	0	0	40	130	42
Diphenamid	0	10	0	0	52	170	1
Diuron	0	12	0	0	40	130	86
Endosulfan I	8	12	0	1	58	195	0
Endosulfan II	50	12	0	6	72	146	0
Endosulfan Sulfate	92	12	0	11	77	140	0
Eptam	0	10	0	0	41	159	0
Ethalfluralin (Sonalan)	0	12	0	0	6	243	0
Ethoprop	0	12	0	0	10	263	2
Etridiazole	20	10	2	0	50	150	4
Fenarimol	20	10	2	0	30	130	6
Fenbuconazole	0	12	0	0	40	130	0
Fenvalerate	0	12	0	0	30	130	0
Fipronil	100	10	10	0	30	130	0
Fipronil Disulfinyl	10	10	1	0	30	130	0
Fipronil Sulfide	0	10	0	0	30	130	0
Fipronil Sulfone	0	10	0	0	30	130	0
Fludioxonil	0	10	0	0	50	150	59
Flumioxazin	0	10	0	0	50	150	0
Fluroxypyr-meptyl	0	10	0	0	50	150	0
Hexazinone	0	10	0	0	41	183	0
Imazapic	0	12	0	0	40	130	0

Analyte	Recoveries outside control limits (%)	MS/MSD samples (n)	MS/MSD recoveries above control limits	MS/MSD recoveries below control limits	Lower control limit (%)	Upper control limit (%)	Total number of detections in 2016
Imazapyr	0	12	0	0	40	130	29
Imidacloprid	0	12	0	0	40	130	75
Imidan	0	12	0	0	32	203	1
Isoxaben	8	12	1	0	40	130	34
Kelthane	0	8	0	0	10	265	0
Linuron	0	12	0	0	40	130	0
Malaoxon	25	12	0	3	40	130	3
Malathion	10	10	1	0	50	147	4
MCPA	0	12	0	0	40	130	31
MCPP	0	12	0	0	40	130	30
Metalaxyl	0	12	0	0	56	149	38
Methiocarb	33	12	0	4	40	130	1
Methomyl	0	12	0	0	40	130	0
Methomyl oxime	17	12	2	0	40	130	0
Methoxyfenozide	8	12	1	0	40	130	1
Methyl Chlorpyrifos	0	12	0	0	50	144	0
Metolachlor	0	10	0	0	55	180	37
Metribuzin	60	10	6	0	30	130	1
Metsulfuron-methyl	0	12	0	0	40	130	2
MGK264	0	10	0	0	49	193	0
Monuron	0	12	0	0	40	130	16
Myclobutanil	0	12	0	0	40	130	24
N,N-Diethyl-m-toluamide	0	10	0	0	50	150	21
Naled	0	12	0	0	10	220	0
Napropamide	0	10	0	0	70	180	0
Norflurazon	0	10	0	0	70	168	0
Oxadiazon	0	10	0	0	50	150	4
Oxamyl	42	12	0	5	40	130	43
Oxamyl oxime	42	12	5	0	40	130	45
Oxyfluorfen	17	12	2	0	51	153	0
Pendimethalin	0	12	0	0	39	163	7
Pentachloronitrobenzene	0	10	0	0	50	150	0
Pentachlorophenol	0	12	0	0	40	130	25
Phenothrin	0	12	0	0	22	130	0
Phorate	17	12	2	0	12	130	0
Picloram	33	12	1	3	40	130	1
Piperonyl Butoxide	0	10	0	0	30	130	5
Prometon	0	10	0	0	55	164	0
Prometryn	0	10	0	0	62	165	0
Pronamide (Kerb)	0	10	0	0	63	169	0
Propargite	0	12	0	0	30	130	0
Propiconazole	8	12	1	0	40	130	31
Pyraclostrobin	0	12	0	0	40	130	11
Pyraflufen-ethyl	0	10	0	0	50	150	0
Pyridaben	0	10	0	0	50	150	1

Analyte	Recoveries outside control limits (%)	MS/MSD samples (n)	MS/MSD recoveries above control limits	MS/MSD recoveries below control limits	Lower control limit (%)	Upper control limit (%)	Total number of detections in 2016
Pyrimethanil	0	12	0	0	40	130	0
Pyriproxyfen	0	12	0	0	40	130	2
Simazine	0	10	0	0	72	192	19
Simetryn	0	10	0	0	61	171	0
Spirotetramat	17	12	0	2	40	130	0
Sulfentrazone	20	10	2	0	50	150	18
Sulfometuron methyl	0	12	0	0	40	130	3
Tau-fluvalinate	40	10	4	0	50	150	0
Tebuthiuron	0	10	0	0	10	235	18
Terbacil	0	10	0	0	27	237	30
Tetrachlorvinphos	0	12	0	0	70	196	1
Tetrahydrophthalimide	38	8	0	3	50	150	3
Thiacloprid	0	12	0	0	40	130	0
Thiamethoxam	0	12	0	0	40	130	78
Treflan (Trifluralin)	0	10	0	0	58	174	6
Triadimefon	0	10	0	0	61	178	1
Triallate	0	12	0	0	52	128	0
Triclopyr	8	12	1	0	40	130	55
Triclopyr-butoxyl	0	10	0	0	50	150	0
Trifloxystrobin	0	12	0	0	40	130	2
Zoxamide	0	12	0	0	40	130	0

The percentage of analyte recoveries from MS\MSD samples that were above, below, or fell within the laboratory control limits are as follows:

- 4% of analyte recoveries fell below the control limits for MS/MSD samples,
- 92% of analyte recoveries were within the control limits for MS/MSD samples,
- 4% of analyte recoveries were above the control limits for MS/MSD samples.

Some analytes tend to be associated with a higher frequency of MS/MSD recoveries that are outside of the control limits due to effects that are associated with the sample matrix and not method. Percentages of MS/MSD sample recoveries that were reported as above or below the control limits that were associated with analytes frequently outside of the control limits were:

- 1% of recoveries from MS/MSDs were associated with analytes that were outside of the control limits between 50% and 74% of the time,
- 1% of recoveries from MS/MSDs were associated with analytes that were outside of the control limits between 75% and 99% of the time,
- 1% of recoveries from MS/MSDs were associated with analytes that were outside of the control limits 100% of the time.

Laboratory Duplicates

MEL uses split sample duplicates to evaluate the precision of TSS and conductivity analyses. In 2016 there were 97 laboratory duplicate pairs for TSS and 20 duplicate pairs for conductivity (Table 8c). Of the TSS duplicate pairs, 2 were qualified “U”, leaving 95 pairs with RPD calculated. No field TSS or conductivity samples were requalified due solely to RPD exceedances. Overall, laboratory duplicate results were of acceptable data quality.

Table 8c – Laboratory duplicate results

Parameter	Results	RPD control limit (%)	Pairs that exceeded the RPD limit	Percentage outside the RPD limit (%)
Specific Conductivity	20	20	0	0%
Total Suspended Solids	95	20	16	17%

Laboratory Blanks

MEL uses laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. Lab blanks also provide a method to measure the response of an analytical process to the analyte at a theoretical concentration of zero, helping to determine at what concentration samples can be distinguished from background noise. If lab blank detections occur, the sample MRL may be increased, and detections may be qualified as estimates. Table 9c lists the analyte detections that occurred in the laboratory blanks. Of the 11 detections, 4 were less than 5 times the method detection limit (MDL) and below the MRL.

Table 9c – Analyte detections in laboratory blanks

Analysis date	Analytical method	Analyte	Result (µg/L)	MRL (µg/L)	MDL (µg/L)	Qualifier
6/10	GCMS-Pesticides	Fenarimol	0.045	0.033	0.021	
6/17	GCMS-Pesticides	Fenarimol	0.029	0.033	0.021	J
7/6	GCMS-Pesticides	Metribuzin	0.187	0.033	0.016	
7/11	LCMS-Pesticides	Propiconazole	0.007	0.02	0.005	J
7/22	LCMS-Pesticides	Sulfometuron methyl	0.018	0.02	0.007	J
8/10	GCMS-Pesticides	Metribuzin	0.162	0.033	0.016	
8/16	GCMS-Pesticides	Triclosan	0.031	0.1	0.062	J
8/23	GCMS-Pesticides	Metribuzin	0.159	0.033	0.016	
8/30	GCMS-Pesticides	Metribuzin	0.163	0.033	0.016	
9/2	GCMS-Pesticides	Metribuzin	0.152	0.033	0.016	
9/20	GCMS-Pesticides	Metribuzin	0.103	0.033	0.016	J

Surrogates

Surrogates are analytes used to assess recovery for a group of structurally related chemicals. Surrogates specific the list of analytes are spiked into all field samples received at MEL. For instance, triphenyl phosphate is a surrogate for organophosphate insecticides. Summary statistics for surrogate recoveries are presented in Table 10c.

Table 10c – Pesticide surrogates

Analytes by structurally related group	Analytical method	Number of results	Mean recovery (%)	Results within control limits (%)	Lower Control Limit	Upper Control Limit
Carbamate pesticides:						
Carbaryl C13	LCMS-Pesticides	410	100	100.0	40	130
Acid-derivitizable herbicides:						
2,4,6-Tribromophenol	GCMS-Herbicides	394	72	99.0	40	130
2,4-Dichlorophenylacetic acid	GCMS-Herbicides	394	79	98.7	40	130
Nitrogen containing pesticides:						
1,3-Dimethyl-2-nitrobenzene	GCMS-Pesticides	408	93	98.5	41	135
Decachlorobiphenyl (DCB)	GC-ECD-Pesticides	54	63	100.0	35	96
Chlorinated pesticides:						
4,4'-DDE-13C12	GCMS-Pesticides	418	68	99.5	20	117
Decachlorobiphenyl (DCB)	GCMS-Pesticides	418	47	100.0	13	98
Dibutylchlorendate	GC-ECD-Pesticides	54	75	100.0	21	110
Tetrachloro-m-xylene	GC-ECD-Pesticides	54	47	98.1	14	96
Organophosphate pesticides:						
Chlorpyrifos-D10	GCMS-Pesticides	418	89	99.5	30	178
Triphenyl phosphate	GCMS-Pesticides	418	89	99.5	45	137
Chlorine and nitrogen containing pesticides:						
Trifluralin-D14	GCMS-Pesticides	418	68	99.3	26	180
Atrazine-D5	GCMS-Pesticides	418	85	99.3	45	167

In 2016, the overall mean recovery for surrogates was 78% and the surrogate recoveries meeting control limits mean was 99%.

Laboratory Control Samples

Laboratory control samples and laboratory control sample duplicates are generated by MEL by adding analytes at known concentrations to purified water free of all organics. An LCS/LCSD pair is extracted and analyzed with every batch of field samples and other QC samples. They are used to evaluate method performance for a specific analyte and to check for bias and precision of the lab's extraction and analytical processes. Detections from a batch may be qualified based on low recovery and/or high RPD between the paired LCS and LCSD.

Table 11c presents the mean, minimum, and maximum percent recovery for the LCS and LCSD for 3 types of analysis, as well as the RPD between the LCS and the paired LCSD for 2016.

Table 11c – Summary statistics for LCS/LCSD recoveries and RPD

Analytical method and analyte	Number of LCS/LCSD recoveries	Mean recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Mean RPD (%)	Minimum RPD (%)	Maximum RPD (%)
LCMS-Pesticides:							
Acetamiprid	30	102	85	127	4	0.3	20
Aldicarb Sulfoxide	30	100	76	121	4	0.3	15
Azoxystrobin	30	100	75	121	5	0.02	13
Baygon	30	97	84	114	4	0.004	13
Carbaryl	30	97	53	113	6	0.1	53
Chlorantraniliprole	29	100	78	143	5	0.03	16
Chlorsulfuron	30	76	23	103	6	0.6	20
Clothianidin	30	96	71	146	4	0.2	17
Cyprodinil	30	95	60	112	6	0.2	30
Desisopropyl Atrazine	29	95	50	209	6	0.2	22
Desethylatrazine	29	87	53	154	4	0.1	28
Difenoconazole	30	85	48	127	8	0.1	23
Diflubenzuron	30	86	64	113	9	0.03	27
Dinotefuran	30	102	73	131	4	0.04	12
Diuron	30	97	82	114	3	0.2	13
Fenbuconazole	30	83	50	121	6	0.6	18
Imazapic	30	93	61	126	7	0.04	42
Imazapyr	30	99	74	137	5	0.01	27
Imidacloprid	30	100	78	126	5	0.7	17
Isoxaben	30	101	73	133	5	0.1	14
Linuron	30	99	67	127	11	1	36
Malaoxon	30	93	54	110	6	0.2	50
Methiocarb	30	95	42	113	8	1	66
Methomyl	30	101	84	122	3	0.1	11
Methomyl oxime	30	95	65	131	7	0.1	29
Methoxyfenozide	30	103	78	122	5	0.4	16
Metsulfuron-methyl	30	72	13	115	5	1	17
Monuron	30	96	81	114	4	0.1	12
Myclobutanil	30	88	66	115	5	0.4	15
Oxamyl	30	100	78	127	5	0.1	17
Oxamyl oxime	30	102	78	141	5	0.1	17
Propiconazole	30	87	59	124	6	0.1	18

Analytical method and analyte	Number of LCS/LCSD recoveries	Mean recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Mean RPD (%)	Minimum RPD (%)	Maximum RPD (%)
Pyraclostrobin	30	118	70	340	7	0.2	21
Pyrimethanil	30	97	75	114	6	0.3	23
Pyriproxyfen	29	106	53	248	9	0.6	27
Spirotetramat	29	89	47	136	12	0.1	53
Sulfometuron methyl	30	90	44	112	5	0.3	13
Thiacloprid	30	99	84	128	4	0.4	20
Thiamethoxam	30	102	76	129	4	0.1	11
Trifloxystrobin	30	97	56	139	7	0.1	25
Zoxamide	30	86	52	118	5	0.4	17
GCMS-Herbicides:							
2,4-D	30	66	8	113	14	0.6	62
3,5-Dichlorobenzoic Acid	30	69	11	116	13	0.1	48
4-Nitrophenol	30	84	30	141	19	0.9	59
Bentazon	30	97	61	141	9	1	24
Bromoxynil	30	82	60	121	9	0.3	38
Clopyralid	30	41	6	78	13	0.8	58
Dacthal	30	100	62	149	8	0.1	24
Dicamba	30	71	20	114	12	0.3	56
Dichlorprop	30	84	35	126	9	0.03	34
MCPA	30	72	15	116	13	0.5	69
MCPP	30	86	50	133	10	0.2	29
Pentachlorophenol	30	82	58	115	10	0.2	36
Picloram	30	55	8	132	22	0.6	102
Triclopyr	30	82	16	150	12	0.5	80
GC-ECD-Pesticides:							
2,4'-DDD	12	81	32	96	14	0.9	74
2,4'-DDE	12	80	34	104	17	0.3	71
2,4'-DDT	12	80	33	98	13	0.2	69
4,4'-DDD	12	85	33	104	15	0.7	81
4,4'-DDE	12	79	34	93	14	0.8	71
4,4'-DDT	12	79	32	98	15	2	72
Aldrin	12	56	24	74	19	5	77
Dieldrin	12	82	29	102	16	3	83
GCMS-Pesticides:							
2,4'-DDD	15	73	49	91	11	3	58
2,4'-DDE	15	70	50	100	13	0.1	44
2,4'-DDT	15	78	47	113	11	0.6	34
4,4'-DDD	15	76	49	95	11	2	63
4,4'-DDE	15	69	49	105	16	1	46
4,4'-DDT	15	80	53	116	11	0.7	37
Acetochlor	15	103	0	202	7	1	22
Alachlor	15	88	5	121	17	1	160
Atrazine	15	81	0	106	6	0.8	29

Analytical method and analyte	Number of LCS/LCSD recoveries	Mean recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Mean RPD (%)	Minimum RPD (%)	Maximum RPD (%)
Benefin	15	91	49	137	11	0.2	48
Bifenazate	6	97	41	141	7	4	10
Bifenthrin	15	79	42	107	10	2	35
Boscalid	6	111	91	130	5	2.0	16
Bromacil	15	88	5	126	17	0.09	161
Captan	15	67	8	123	14	0.2	66
Chlorothalonil (Daconil)	15	75	35	104	15	1	85
Chlorpropham	15	87	0	119	6	0.1	32
Chlorpyriphos	15	87	48	129	11	0.2	48
cis-Permethrin	15	87	66	125	11	1	25
Coumaphos	15	101	46	157	10	0.1	45
Cycloate	15	76	0	104	13	0.2	25
Cyfluthrin	15	80	42	125	10	2	25
Cypermethrin	15	85	44	141	13	2	32
Di-allate (Avadex)	15	91	47	132	16	4	74
Diazinon	15	96	47	144	11	1	53
Dichlobenil	15	81	39	109	15	1	87
Dichlorvos (DDVP)	15	95	56	134	13	1	65
Dimethoate	14	98	33	141	15	0.2	85
Diphenamid	15	83	3	103	16	0.7	169
Endosulfan I	15	73	40	107	13	0.2	59
Endosulfan II	15	78	36	104	13	0.7	63
Endosulfan Sulfate	15	57	17	86	15	1	46
Eptam	15	83	0	116	18	4.0	42
Ethalfluralin (Sonalan)	15	101	43	160	12	0.09	46
Ethoprop	15	94	52	137	14	3	51
Etridiazole	15	95	5	146	21	0.3	159
Fenarimol	15	93	8	122	13	0.4	136
Fenvalerate	15	88	57	125	14	4	28
Fipronil	15	120	5	226	5	0.3	22
Fipronil Disulfinyl	15	90	4	123	9	1	38
Fipronil Sulfide	15	88	5	105	6	0.03	11
Fipronil Sulfone	15	90	7	117	6	0.4	15
Fludioxonil	15	86	5	111	15	0.7	154
Flumioxazin	15	85	0	122	8	0.7	20
Fluroxypyr-meptyl	15	88	32	114	10	2	54
Hexazinone	15	85	4	115	14	0.01	161
Imidan	15	97	38	166	15	0.02	58
Kelthane	6	109	85	165	3	0.2	6
Malathion	15	98	5	139	17	0.4	167
Metalaxyl	15	97	45	159	12	0.4	54
Methyl Chlorpyrifos	15	88	45	131	12	0.3	67
Metolachlor	15	89	4	120	16	0.3	168

Analytical method and analyte	Number of LCS/LCSD recoveries	Mean recovery (%)	Minimum recovery (%)	Maximum recovery (%)	Mean RPD (%)	Minimum RPD (%)	Maximum RPD (%)
Metribuzin	15	95	5	185	21	1	160
MGK264	15	86	5	116	19	0.4	167
N,N-Diethyl-m-toluamide	15	81	7	118	17	0.3	141
Naled	15	93	37	145	16	0.7	86
Napropamide	15	87	5	115	16	0.006	156
Norflurazon	15	92	6	126	16	0.4	160
Oxadiazon	15	81	7	104	7	0.8	19
Oxyfluorfen	15	102	49	164	13	0.4	45
Pendimethalin	15	95	58	142	11	1	52
Pentachloronitrobenzene	15	84	5	119	19	0.2	161
Phenothrin	15	69	49	103	10	2.0	29
Phorate	15	117	47	406	15	0.06	62
Piperonyl Butoxide	15	101	11	128	13	0.9	134
Prometon	15	92	4	130	17	0.2	171
Prometryn	15	89	5	125	17	0.5	163
Pronamide (Kerb)	15	85	5	114	17	0.8	163
Propargite	15	82	44	110	10	0.2	34
Pyraflufen-ethyl	15	94	10	127	13	0.2	121
Pyridaben	15	97	33	127	8	1.0	45
Simazine	15	80	0	101	8	0.06	29
Simetryn	15	83	0	120	7	1.0	24
Sulfentrazone	15	104	0	146	8	0.08	30
Tau-fluvalinate	15	99	63	134	9	0.4	24
Tebuthiuron	15	83	5	147	25	1	156
Terbacil	15	99	0	158	7	0.2	30
Tetrachlorvinphos	15	88	31	146	11	0.1	56
Tetrahydrophthalimide	6	61	14	125	30	0.2	52
Treflan (Trifluralin)	15	82	8	112	18	0.5	138
Triadimefon	15	87	0	120	8	0.8	32
Triallate	15	84	45	126	13	0.7	76
Triclopyr-butoxyl	15	84	9	109	15	1	140

There were a total of 5,898 results (2,932 LCS/LCSD pairs) from LCS and LCSD recoveries. Overall, the mean recovery was 89% with a standard deviation of 25%. RPDs for those 2,932 LCS/LCSD pairs were below the 40% RPD control limit 96% of the time. The mean RPD for paired LCS/LCSD recoveries that were below the 40% RPD control limit was 7% with a standard deviation of 7%. The mean RPD for paired LCS/LCSD recoveries that were equal to or above the 40% RPD control limit was 78% with a standard deviation of 43%.

Table 12c describes the frequency of LCS and LCSD recoveries that were above or below the laboratory control limits set for each analyte. Table 12c also shows how often recoveries for each analyte were outside of the control limits and the number of detections from all grab samples throughout the sampling season for each analyte.

Table 12c – Frequency of LCS/LCSD recoveries falling outside of the laboratory control limits

Analytical method and analyte	Number of LCS/LCSD recoveries	Recoveries outside control limits (%)	Recoveries above control limits	Recoveries below control limits	Total number of detections in 2016
2,4-D	30	27	0	8	101
2,4'-DDD	12	8	0	1	0
2,4'-DDD	15	0	0	0	0
2,4'-DDE	12	8	0	1	0
2,4'-DDE	15	0	0	0	0
2,4'-DDT	12	8	0	1	0
2,4'-DDT	15	0	0	0	0
3,5-Dichlorobenzoic Acid	30	27	0	8	0
4,4'-DDD	12	8	0	1	9
4,4'-DDD	15	27	0	4	9
4,4'-DDE	12	8	0	1	45
4,4'-DDE	15	0	0	0	45
4,4'-DDT	12	8	0	1	18
4,4'-DDT	15	0	0	0	18
4-Nitrophenol	30	17	2	3	4
Acetamiprid	30	0	0	0	0
Acetochlor	15	33	4	1	0
Alachlor	15	7	0	1	0
Aldicarb Sulfoxide	30	0	0	0	0
Aldrin	12	0	0	0	0
Atrazine	15	7	0	1	8
Azoxystrobin	30	0	0	0	60
Baygon	30	0	0	0	1
Benefin	15	0	0	0	0
Bentazon	30	7	2	0	24
Bifenazate	6	33	0	2	0
Bifenthrin	15	0	0	0	1
Boscalid	6	0	0	0	111
Bromacil	15	13	0	2	17
Bromoxynil	30	0	0	0	2
Captan	15	53	0	8	0
Carbaryl	30	0	0	0	5
Chlorantraniliprole	29	7	2	0	59
Chlorothalonil (Daconil)	15	147	0	22	0
Chlorpropham	15	20	0	3	4
Chlorpyriphos	15	20	0	3	19
Chlorsulfuron	30	13	0	4	3
cis-Permethrin	15	0	0	0	0
Clopyralid	30	93	0	28	2
Clothianidin	30	10	3	0	7
Coumaphos	15	7	0	1	0
Cycloate	15	13	0	2	0
Cyfluthrin	15	0	0	0	0
Cypermethrin	15	7	1	0	0

Analytical method and analyte	Number of LCS/LCSD recoveries	Recoveries outside control limits (%)	Recoveries above control limits	Recoveries below control limits	Total number of detections in 2016
Cyprodinil	30	0	0	0	8
Dacthal	30	7	2	0	12
Deisopropyl Atrazine	29	34	10	0	3
Desethylatrazine	29	14	4	0	2
Di-allate (Avadex)	15	7	1	0	0
Diazinon	15	27	1	3	10
Dicamba	30	7	0	2	47
Dichlobenil	15	7	0	1	65
Dichlorprop	30	3	0	1	0
Dichlorvos (DDVP)	15	0	0	0	0
Dieldrin	12	8	0	1	0
Difenoconazole	30	0	0	0	23
Diflubenzuron	30	0	0	0	0
Dimethoate	14	7	0	1	0
Dinotefuran	30	7	2	0	42
Diphenamid	15	27	0	4	1
Diuron	30	0	0	0	85
Endosulfan I	15	127	0	19	0
Endosulfan II	15	27	0	4	0
Endosulfan Sulfate	15	180	0	27	0
Eptam	15	13	0	2	0
Ethalfluralin (Sonalan)	15	0	0	0	0
Ethoprop	15	7	0	1	2
Etridiazole	15	40	5	1	4
Fenarimol	15	7	0	1	6
Fenbuconazole	30	0	0	0	0
Fenvalerate	15	0	0	0	0
Fipronil	15	80	11	1	0
Fipronil Disulfinyl	15	7	0	1	0
Fipronil Sulfide	15	7	0	1	0
Fipronil Sulfone	15	7	0	1	0
Fludioxonil	15	7	0	1	59
Flumioxazin	15	20	0	3	0
Fluroxypyr-meptyl	15	0	0	0	0
Hexazinone	15	20	0	3	0
Imazapic	30	0	0	0	0
Imazapyr	30	3	1	0	29
Imidacloprid	30	0	0	0	74
Imidan	15	7	0	1	1
Isoxaben	30	3	1	0	32
Kelthane	6	0	0	0	0
Linuron	30	0	0	0	0
Malaoxon	30	0	0	0	3
Malathion	15	20	1	2	4
MCPA	30	7	0	2	30

Analytical method and analyte	Number of LCS/LCSD recoveries	Recoveries outside control limits (%)	Recoveries above control limits	Recoveries below control limits	Total number of detections in 2016
MCPP	30	3	1	0	30
Metalaxyl	15	20	2	1	35
Methiocarb	30	0	0	0	1
Methomyl	30	0	0	0	0
Methomyl oxime	30	3	1	0	0
Methoxyfenozide	30	0	0	0	1
Methyl Chlorpyrifos	15	7	0	1	0
Metolachlor	15	20	0	3	36
Metribuzin	15	33	4	1	1
Metsulfuron-methyl	30	27	0	8	2
MGK264	15	20	0	3	0
Monuron	30	0	0	0	16
Myclobutanil	30	0	0	0	24
N,N-Diethyl-m-toluamide	15	7	0	1	21
Naled	15	0	0	0	0
Napropamide	15	53	0	8	0
Norflurazon	15	47	0	7	0
Oxadiazon	15	7	0	1	4
Oxamyl	30	0	0	0	43
Oxamyl oxime	30	13	4	0	45
Oxyfluorfen	15	27	4	0	0
Pendimethalin	15	0	0	0	7
Pentachloronitrobenzene	15	7	0	1	0
Pentachlorophenol	30	0	0	0	25
Phenothrin	15	7	1	0	0
Phorate	15	53	8	0	0
Picloram	30	47	1	13	1
Piperonyl Butoxide	15	7	0	1	5
Prometon	15	13	0	2	0
Prometryn	15	20	0	3	0
Pronamide (Kerb)	15	47	0	7	0
Propargite	15	0	0	0	0
Propiconazole	30	0	0	0	31
Pyraclostrobin	30	33	10	0	11
Pyraflufen-ethyl	15	7	0	1	0
Pyridaben	15	0	0	0	1
Pyrimethanil	30	0	0	0	0
Pyriproxyfen	29	38	11	0	2
Simazine	15	67	0	10	19
Simetryn	15	13	0	2	0
Spirotetramat	29	7	2	0	0
Sulfentrazone	15	47	6	1	18
Sulfometuron methyl	30	0	0	0	3
Tau-fluvalinate	15	7	1	0	0
Tebuthiuron	15	73	10	1	18

Analytical method and analyte	Number of LCS/LCSD recoveries	Recoveries outside control limits (%)	Recoveries above control limits	Recoveries below control limits	Total number of detections in 2016
Terbacil	15	13	0	2	30
Tetrachlorvinphos	15	93	0	14	1
Tetrahydrophthalimide	6	83	0	5	3
Thiacloprid	30	0	0	0	0
Thiamethoxam	30	0	0	0	78
Treflan (Trifluralin)	15	7	0	1	6
Triadimefon	15	20	0	3	1
Triallate	15	27	0	4	0
Triclopyr	30	13	2	2	54
Triclopyr-butoxyl	15	7	0	1	0
Trifloxystrobin	30	10	3	0	2
Zoxamide	30	0	0	0	0

Analyte recoveries from LCS and LCSD samples were within the control limits 93% of the time. Out of all the analyte recoveries, 2% were above the upper control limits and 5% were below the lower control limits for LCS and LCSD samples.

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

Field Data Quality Control Measures

In eastern Washington, a Hach HydroLab MS5 field meter was calibrated the morning of the first field day of the week according to manufacturer's specifications, using Ecology's *Standard Operating Procedure for Hydrolab® DataSonde® and MiniSonde® Multiprobes* (Swanson, 2010). In western Washington, a YSI ProDSS field meter was calibrated the evening before, or the morning of the first field day of the week according to manufacturer's specifications described in the *YSI ProDSS User Manual* (YSI, 2014). Both field meters were post-checked, using known standards, at the end of the sampling week.

Dissolved oxygen (DO) meter results were compared to results from grab samples analyzed using the Winkler laboratory titration method. DO grab samples for Winkler titrations were collected and analyzed according to the SOP (Ward, 2016). Winkler grab samples were collected at the first sampling site each day and at the last sampling site each day. Additionally, a replicate Winkler grab sample was collected per week at either the beginning or the end of one of the sampling days.

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

Streamflow measurements were taken with OTT MF pro flow meters and top-setting wading rods for both eastern and western Washington monitoring sites. Each flow meter was calibrated the morning of the first day of the week as described in the *OTT MF pro Basic User Manual* (OTT, 2015). A replicate streamflow measurement was taken once a week at a randomly selected site for each flow meter.

Measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler DO comparisons are described in Anderson and Sargeant (2009). Data that did not meet MQOs were qualified.

Field Data Collection Performance

The field meters met MQOs for laboratory conductivity comparisons for all monitoring locations for eastern Washington and all but 1 site for western Washington locations (Table 13c). The conductivity MQO exceedance occurred at Upper Bertrand Creek during the first week of sampling on March 16th, 2016, with a laboratory conductivity result of 155.0 µS/cm compared to the field meter reading of 105.20 µS/cm, resulting in RSD of 19%. Despite the exceedance, all post sampling calibration checks passed MQOs. For the first week of sampling the YSI ProDSS was calibrated on a linear scale using 2 conductivity standards, 1 standard with a conductivity value of 10,000 µS/cm, and the second standard with a value of 100 µS/cm. The large difference in conductivity of the standards, and the conductivity of Bertrand Creek being on the lower end of the conductivity spectrum may have resulted in the RSD exceedance. A follow-up conductivity sample was collected on May 3rd, 2016 with a laboratory conductivity result of 218.0 µS/cm compared to the field meter reading of 212.7 µS/cm (1% RSD). After the first week of sampling and through the rest of the sampling season the YSI ProDSS was calibrated on a linear scale using conductivity standards of 1,000 µS/cm, and 100 µS/cm. The calibration range of 100 µS/cm to 1,000 µS/cm covers all expected monitoring site conductivities.

Table 13c – Quality control results for conventional water qualiter parameter replicates

Replicate meter parameter	MQO	Western Washington		Eastern Washington	
		Mean	Maximum	Mean	Maximum
Winkler and meter DO	10% RSD	3% RSD	16% RSD	1% RSD	3% RSD
Replicate Winkler's for DO	±0.2 mg/L	0.1 mg/L	0.3 mg/L	0.1 mg/L	0.5 mg/L
Conductivity (field meter vs. laboratory)	10% RSD	4% RSD	19% RSD	2% RSD	3 % RSD
Streamflow	10% RSD	2% RSD	15% RSD	3% RSD	12% RSD

During 2016, no MQO exceedances occurred between the Hach Hydrolab MS5 field meter and DO Winkler analysis in eastern Washington. YSI ProDSS meter results exceeded MQOs for DO Winkler comparisons 1 time in western Washington for the following location:

- Indian Slough, 16% RSD, August 30, 2016 (Winkler: 9.56 mg/L and field meter: 13.30 mg/L)

Field notes from the August 30th sampling event at Indian Slough state that DO readings were fluctuating rapidly. Field notes from a sampling event 2 weeks later state that readings were changing rapidly with small vertical changes of the field meter probes position in the water column. Indian Slough is tidally influenced and contains thick aquatic vegetation, resulting in a stratified water column, particularly during periods of low flow (4.80 cfs on August 30th, 2016). Winkler and DO results for Indian Slough for the August 30th sample event were reported and qualified as estimates for the listed date.

2016 Winkler replicate values for both eastern and western Washington locations met the MQOs with the exception of the following locations and dates:

Eastern Washington

- Snipes Creek, difference 0.49 mg/L, June 20 (8.89 mg/L and 8.40 mg/L)
- Upper Brender Creek, difference 0.27 mg/L, July 6 (9.94 mg/L and 9.67 mg/L)
- Sulphur Creek, difference 0.23 mg/L, September 12 (9.39 mg/L and 9.16 mg/L)

Western Washington

- Upper Bertrand Creek, difference 0.22 mg/L, April 19 (10.71 mg/L and 10.49 mg/L)
- Upper Bertrand Creek, difference 0.26 mg/L, April 26 (10.11 mg/L and 9.84 mg/L)
- Lower Bertrand Creek, difference 0.30 mg/L, July 19 (8.68 mg/L and 8.98 mg/L)
- Upper Bertrand Creek, difference 0.22 mg/L, August 10 (6.90 mg/L and 6.68 mg/L)

The 2016 streamflow replicate results for both the eastern and western Washington sites met MQO (Table 13) except for the following site visits:

- Stemilt Creek, 11% RSD, June 14, 2016 (0.08 cfs and 0.10 cfs)
- Lower Brender Creek, 12% RSD, July 26, 2016 (1.18 cfs and 0.93 cfs)
- Upper Big Ditch, 15% RSD, August 9, 2016 (0.62 cfs and 0.84 cfs)
- Upper Big Ditch, 12% RSD, September 7, 2016 (0.47 cfs and 0.37 cfs)

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

Field Audit

The purpose of the field audit was to ensure sampling methodologies were consistent for all field teams. For field audits, both the western and eastern Washington field teams met at a surface water monitoring site. The teams measured general water quality parameters, streamflow, and Winkler grab samples. Results and methods were compared to ensure field teams were using consistent sampling methodologies resulting in comparable data.

On September 14th, 2016, a field audit was conducted at Mission Creek in the town of Cashmere in Chelan County, Washington. The Westside team calibrated their YSI ProDSS Multi-Meter on September 12th, 2016 in Olympia, Washington, at the Natural Resources Building in the Entomology lab. The Eastside team calibrated their Hach Hydrolab MS5 field meter on September 12th, 2016 at the WSDA Yakima office in the NRAS lab, located in Yakima, Washington. Both teams met to perform the field audit simultaneously. Results are displayed in Table 14c.

Table 14c – Conventional water quality parameter and flow data from field audit

Equipment and location	Temperature (°C)	pH (s.u.)	Conductivity (µS/cm)	DO (mg/L)	DO (% sat.)	Streamflow (cfs)
Field meter – West	10.40	8.21	309.9	10.95	98.0	
Field meter – East	10.46	8.38	303.5	10.96	101.1	
Winkler – West				10.41		
Winkler – East				10.40		
Flow – West						3.78
Flow – East						3.61

All meter results were acceptable based on the Measurement Quality Objectives described in Anderson and Sargeant (2009). Table 14c shows the MQO's for conventional field parameters.

Quality Assurance Summary References

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