Washington State Department of Agriculture

WSDA Report

Assessment of Herbicides in Surface Water in the Hoh River Watershed

June 2018

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1. Abstract

The Natural Resources Assessment Section (NRAS) of the Washington State Department of Agriculture (WSDA) monitors surface water for pesticides each year during the growing season. This data is used by WSDA, as well as other state and federal agencies, to evaluate pesticide presence in surface water. However, WSDA has not yet monitored a watershed where the primary land use is managed timber production. Testing water in a timber dominated watershed is valuable because data of this type is limited. To begin collecting this information, WSDA conducted a pilot, seasonal study of herbicides in the Hoh River watershed. NRAS planned and executed this project with collaboration from the Hoh Tribe, the Washington State Department of Natural Resources (DNR), and private timber companies. The goal of this project was to conduct an initial surface water assessment of herbicides commonly used in timber production in a watershed with managed timber. Additional goals included developing relationships with partners in forestry and identifying future research needs. The area selected was the Hoh River watershed on the northwest coast of Washington State.

The Hoh watershed is predominantly rural, with federal lands and managed timber production as the primary land uses. Four tributaries to the Hoh River were selected for analysis and sites were sampled 6 times; 1 background sample in July 2017 and 5 consecutive weekly samples in August and early September 2017. Samples were analyzed for the presence of herbicides commonly used in timber production: glyphosate, glufosinate-ammonium, AMPA (aminomethylphosphonic acid), imazapyr, triclopyr, metsulfuron methyl, and sulfometuron methyl. On 4 of the 6 sampling dates at least 1 herbicide was detected. There were detections of glyphosate, glufosinate-ammonium, and AMPA. All detected concentrations were below levels known to negatively affect aquatic life, they were less than 1% of the established aquatic life benchmarks maintained by the Environmental Protection Agency (EPA).

Potential herbicide uses in this region are not limited to the timber industry, and may also include roadside weed control, noxious weed control, and applications by private land owners. Samples were collected during the time period herbicides are likely to be used and the driest time period in the region. It is unknown whether samples were collected before, during, or after timber applications. Therefore, the source of the herbicide detections is unknown. Follow up studies should plan sampling efforts in conjunction with known herbicide applications when possible in order to connect detections to specific land uses. WSDA anticipates that this study is a first step towards future collaboration with the timber industry with a goal of better understanding the relationship between existing herbicide use practices and actual environmental exposure.

2. Background

WSDA has a well-established monitoring program for pesticides in surface water that spans across many of Washington's mixed land uses. WSDA is the state lead agency for pesticide regulation in Washington as delegated by EPA under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). WSDA responds to pesticide detections according to procedures laid out in the EPA-approved Washington State Pesticide Management Strategy (Cook and Cowles, 2009). The strategy requires WSDA to review pesticide detections in surface water and compare concentrations to aquatic life benchmarks established by EPA.

In 2015, the Hoh Tribe contacted EPA to discuss potential herbicide sampling in the Hoh River watershed. EPA recommended the collaboration between the Hoh Tribe and WSDA's NRAS to complete this project. The final project was designed by NRAS staff and the Hoh Tribe. Based on land ownership, collaborators identified private timber companies and DNR as the primary land owners and potential herbicide users. Other potential herbicide uses in the area include roadside and right-of-way weed control, noxious weed control, and use by rural landowners. NRAS identified regions likely to have timber harvested in 2017 within the Hoh watershed by working with partners at DNR and private timber companies. NRAS worked with the Hoh Tribe to identify sampling sites on tributaries to the Hoh River.

The sampling sites selected were all located within the Hoh River watershed in the northwest corner of Washington State on the Olympic Peninsula. The Hoh River originates at the Hoh Glacier on Mount Olympus. The river flows west through Olympic National Park and eventually into the Pacific Ocean. Collectively, the 4 subbasins selected drain approximately 26.28 square miles of land, which is about 9% of the total Hoh River watershed area (~298 square miles). With a mean annual precipitation of 140-165 inches in the region many tributaries to the Hoh River are dominated by rainfall. The basin supports all 5 species of Pacific salmon (Chinook, sockeye, Coho, pink, chum), steelhead, and cutthroat trout (Northwest Indian Fisheries Commission, 2016).

The primary land uses within the watershed are commercial forestry and protected (National Park). From 1996 to 2010, 24 square miles of forest land were harvested in the Hoh Tribe's Area of Concern (includes Hoh River watershed) (Northwest Indian Fisheries Commission, 2016). Historically, herbicide uses such as those described above have been used in the Hoh watershed for commercial timber harvest.

3. Project Design and Scope

One goal of this project was to successfully complete WSDA's first sampling in a managed-timber-dominated watershed. Through the execution and completion of this project, relationships were developed between WSDA and the private forestry industry, the Hoh tribe, and DNR. In addition, the project was designed to sample watersheds where herbicide use was likely, during the time period when herbicides are commonly used in the timber industry. Information from this project will be used to make an initial assessment of herbicide concentrations in the sampled tributaries to the Hoh River, identify additional research needs, and plan next steps. However, this project was extremely limited in scope. The results cannot be used to assess the effects of specific application practices or to make assessments of areas outside the sampled tributaries.

3.1. General Approach

NRAS and the Hoh Tribe designed this project to assess herbicide concentrations downstream of timber harvest areas in the Hoh River watershed during the time when herbicide applications are expected by collecting surface water samples in tributary streams. Background samples were collected by NRAS staff to analyze conditions before anticipated herbicide applications (mid-July). NRAS sampled surface water from these selected streams weekly for 5 weeks during the time when herbicide applications are expected (August 9th-September 5th). Collected samples were sent to the Washington State Department of Ecology Manchester Environmental Laboratory (MEL) in Port Orchard for analysis.

3.2. Site Selection and Study Area

To select sites for this project, NRAS worked with DNR and private timber companies to identify regions within the watershed that were likely to have herbicide applications in 2017. NRAS worked with the Hoh Tribe to identify specific sampling sites within the actively harvested area. Four sites downstream of expected herbicide applications were selected for sample collection and herbicide analysis. All of the streams selected for sampling are tributaries to the Hoh River and are located between the mouth and the South Fork Hoh River (Figure 1, Table 1).

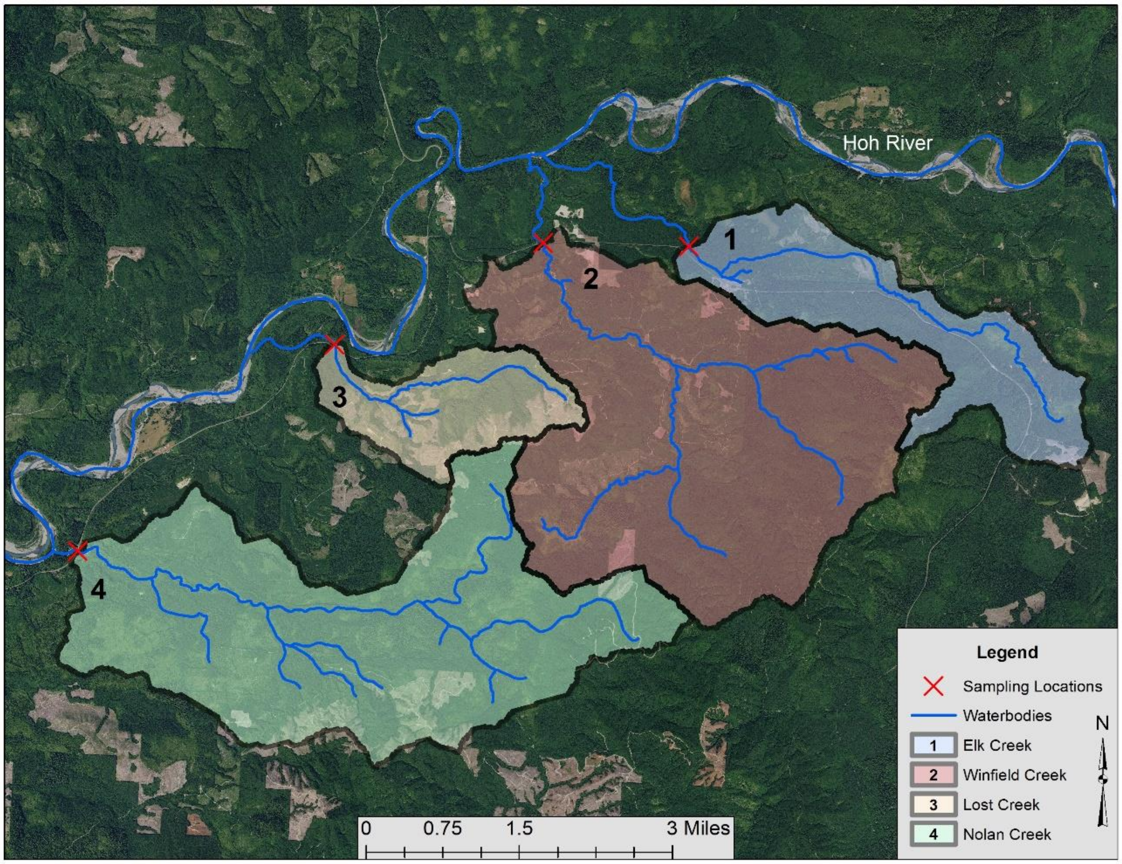

Figure 1: Map of Sampling Locations

Table 1: Profile of Watersheds Draining to Sampling Sites

WATERSHED	SIZE	FISH POPULATIONS SUPPORTED*	OWNERSHIP	LAND USE NOTES
Elk Creek (1)	3.74 mi^2	Resident cutthroat trout, coho salmon, and presumed winter steelhead	76.8% State 22.8% Private timber 0.4% Nonprofit	Forestry dominates. About 99% of state land is DNR-managed timber
Winfield Creek (2)	10.74 mi^2	Resident cutthroat trout; fall, spring, and summer Chinook salmon; coho salmon, and winter steelhead	54.1% State 41.3 % Private timber 4.6 % Nonprofit	About 99% of state land is DNR-managed timber
Lost Creek (3)	2.11 mi^2	Resident cutthroat trout, coho salmon, and presumed winter steelhead	66.7 % Private timber 31.0 % Non-profit 2.3 % State	Timber harvest less common on nonprofit land
Nolan Creek (4)	9.69 mi^2	Resident cutthroat trout, fall Chinook salmon, and winter steelhead.	48.9% State 34.5% Private timber 16.6% Nonprofit	Majority of state and private land is managed timberland

*(WDFW, 2017)

3.3. Herbicides of Interest

At WSDA's request, DNR provided herbicide application records from its Olympic Region (which contains the Hoh River watershed) from 2014-2016. This information was used to determine which herbicides are most likely used in the region. The list of herbicides was then shared with timber industry partners for confirmation prior to finalization. The herbicides (and one breakdown product) most regularly used by DNR for vegetation management were selected as analytes for this study. These were: glyphosate, glufosinate-ammonium, AMPA (a breakdown product of glyphosate), imazapyr, triclopyr, sulfometuron methyl, and metsulfuron methyl. The herbicides are considered slightly toxic or practically non-toxic to fish, with half-lives ranging from approximately 2.4 days to 6 months (EPA, 2009, 2011, 2012, 2014, and 2014b).

4. Field methods

All field data for this project was collected in accordance with WSDA's Standard Operating Procedure for Water Quality and Pesticide Monitoring Programs (Bischof, 2017). A summary of these procedures is presented here. All field data was collected on paper field forms and transferred into WSDA's surface water monitoring database on a weekly basis.

4.1. Water sample collection

Sampling staff collected all water samples wearing nitrile gloves following standard procedures (vertically-integrated quarter-point sampling). At each sampling event, water samples were collected for analysis by 3 methods: glyphosate, carbamates, and total suspended solids (TSS). Samples were collected, preserved when necessary, and immediately placed on ice to keep samples below 4 ºC. Glyphosate samples were preserved with 1:1 HCl and carbamates were preserved with acetic acid. The samples were transported to MEL within 24 hours of collection. The laboratory analyzed the samples for imazapyr, triclopyr, metsulfuron methyl, sulfometuron methyl, glyphosate, glufosinate-ammonium, and AMPA.

Field quality assurance/quality control (QA/QC) samples collected were field blank samples, duplicates, and MS/MSDs (matrix spike/matrix spike duplicate). Of the total samples collected, 10% were field QA/QC samples, which were prepared according to a predetermined QA/QC schedule. To generate field blanks, laboratory-grade deionized water was transported to the field and poured into prepared sample containers at each site. They were submitted blind to the lab for analysis. Blanks were used to determine the risk of sample contamination in the field, the quality of sample handling and the condition of the sample containers supplied by the laboratory. Duplicates were 2 sets of sample containers filled with the same composited water sample from the same sampling site. They were used to determine both field and laboratory precision. The relative percent difference (RPD) has been calculated for each duplicate set and was used to give a rough estimate of overall precision. Like blanks, duplicates were not identified and were submitted blindly to the laboratory for analysis. MS/MSD samples were collected alongside field samples and were not submitted blindly to the laboratory. MS/MSD results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery; this measure is the best overall indicator of accuracy and reproducibility in the sampling process. Field blanks, duplicates, and MS/MSD samples were stored and handled with the normal samples for shipment to the laboratory.

4.2. General water chemistry

General water chemistry was collected at all site visits to provide background information on stream health. Field equipment was calibrated in a laboratory according to the manufacturer’s procedures prior to data collection. A Hach Hydrolab multiparameter water quality meter was placed into the stream immediately upon arrival at each site to allow the sensors to equilibrate to stream conditions. Temperature, conductivity, dissolved oxygen (DO), and pH were recorded at all sites during each sampling event. In addition to the regularly scheduled sampling events, background water chemistry was recorded on 6/29/2017 to assess general stream conditions prior to the start of timeframe that herbicide applications are expected. DO QA samples were collected and preserved with manganous sulfate monohydrate and alkali-iodine-azide in the field to confirm readings from the multiparameter meter. DO was determined in a lab by performing Winkler titrations.

4.3. Volumetric flow measurements

OTT MF Pro Flow meters were used to collect one volumetric flow measurement at each sampling event. At one site each week, a duplicate flow measurement was conducted for quality assurance purposes. Detailed procedures can be found in Bischof 2017.

4.4. Limitations and assumptions

The goal of this project was to conduct an initial surface water assessment of herbicides commonly used in timber production in a watershed with managed timber. Additional goals included developing relationships with partners in forestry and identifying future research needs. This project was designed to assess off-target movement of herbicides into nearby streams, and was limited in geographic scope and sample collection timing, which affects the conclusions that can be drawn from this research.

Timing of data collection

DNR provided WSDA with herbicide application records from the Olympic Region from 2014-2016 to assist in the planning for this project. WSDA used this information to identify the best time period for sample collection. It was assumed that private timber companies would follow a similar timeline for herbicide application. However, there is no certainty that applications took place in conjunction with water quality sampling. Herbicide concentrations or the number of detections may have been different if WSDA was able to collect samples in conjunction with the known schedule of forestry herbicide applications.

Regional specific data

Data for this project was collected in four tributaries to the Hoh River on the Olympic Peninsula. Both forestry practices and watershed hydrology vary regionally. Data from this project should only be used as an initial assessment for the Hoh River watershed and should not be used to make conclusions about other regions.

Non-forestry uses

WSDA consulted with DNR and private timber companies to select herbicides to screen for in water samples. In addition to forest management, some of these herbicides are commonly used in roadside spraying and for noxious weed control. Because of these various uses, it is impossible to associate herbicide detections with a specific use practice or application event.

For example, on August 23, 2017 WSDA staff were conducting a site visit at Elk Creek when several people working for a local nonprofit organization entered the stream wearing backpack sprayers. The crew was using Aquaneat™ (active ingredient: glyphosate) for noxious weed control in the riparian area of the stream. At WSDA's request, the crew suspended the application until water samples were collected. However, it is possible that glyphosate detected in those samples was deposited as a result of that application rather than a forestry application.

4.5. Analytical methods and data quality control

MEL completed the analysis using modified EPA methods. Triclopyr, imazapyr, metsulfuron-methyl, and sulfometuron-methyl were analyzed using MEL's "Pesticides by HPLC-MS/MS analysis (EPA Method 8321B)." Glyphosate, glufosinate-ammonium, and AMPA were analyzed using MEL's "Glyphosate by HPLC-MS/MS analysis (EPA Method 8321B)." Method performance evaluations included quality control samples, analyzed with every batch to ensure sample data integrity. Internal laboratory spikes and duplicates were all part of the laboratory quality assurance program. Analytical precision was estimated from duplicate sample analysis and duplicate spiked sample analyses. Analytical bias was estimated from matrix spikes and matrix spike duplicates. Mean percent recoveries of spiked sample analyses provided an estimate of bias due to matrix interference.

5. Results and discussion

In this report the term “sampling event” is used to describe a time that a sample was collected at one site; there were 24 total sampling events for this project. The term “sampling date” describes the time that all sites were visited and sampled on one date; there were a total of 6 sampling dates for this project.

5.1. Conventional water quality parameters and exceedances

Table 2 provides an overview of the conventional water quality parameters observed during this study. Measurements of streamflow, temperature, pH, DO, and conductivity were collected in the field during all sampling events. Due to an equipment malfunction, no DO or conductivity data was collected on 7/12/2017; those parameters have one fewer data point than pH and temperature. TSS was collected in the field and analyzed by MEL.

Table 2: Summary of conventional water quality parameters

Site	Summary Statistic	TSS (mg/L)	Temperature (°C)	Conductivity (µS/cm)	pH (SU)	DO (mg/L)	Flow (CFS)
Nolan Creek	Sampling Events	6	7	6	7	6	6
	Mean	<1*	16.6	49.8	6.85	9.29	1.99
	Minimum	<1*	13.6	35.0	6.69	8.86	1.21
	Maximum	<1*	18.5	55.5	7.06	10.33	4.06
Lost Creek	Sampling Events	6	7	6	7	6	6
	Mean	2	13.5	54.5	7.08	9.94	0.57
	Minimum	1	12.7	45.2	6.92	9.46	0.34
	Maximum	3	15.0	57.9	7.32	10.50	1.08
Elk Creek	Sampling Events	6	7	6	7	6	6
	Mean	3	13.7	43.8	7.20	9.83	1.96
	Minimum	1	12.4	38.2	7.01	9.36	1.66
	Maximum	6	15.7	46.2	7.44	10.38	2.68
Winfield Creek	Sampling Events	6	7	6	7	6	6
	Mean	<1*	14.5	48.1	6.84	9.40	5.00
	Minimum	<1*	13.2	42.0	6.58	9.08	3.59
	Maximum	<1*	15.2	51.1	7.12	9.77	8.60

*<1 values are assigned where all laboratory results were below the minimum reporting limit of 1 mg/L

The aquatic life criteria of the Washington State Water Quality Standards are location dependent based on 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. Exceedances of temperature and dissolved oxygen criteria are listed and explained below. There were no exceedances of aquatic life criteria for pH at any sampling event.

5.1.1 Temperature exceedances

Criteria are based on the designated aquatic life uses at each monitoring location and are listed in the standard as the highest allowable 7-day average of the daily maximum temperatures.

Temperature data was collected using a multiparameter water quality meter at each sampling event; continuous temperature data was not collected. Point data was compared to the state criteria (7-day average of the daily maximum). The Hoh River and its tributaries are designated as core summer salmonid habitat from the mouth to the South Fork Hoh River, which has an established aquatic life temperature criteria of 16 °C (Ecology, 2016). It should be noted that there are some limitations in comparing point data to 7-day average of the daily maximum as the criteria is developed based on a longer exposure than one point measurement. It is possible that comparing point measurements to the criteria could result in missing an exceedance. Table 3 lists all exceedances of aquatic life temperature criteria for the project.

Table 3: Exceedances of aquatic life temperature criteria

Monitoring Site	Date of Exceedance	Temperature (°C)
Nolan Creek	7/12/2017	17.0
	8/9/2017	18.5
	8/16/2017	16.2
	8/23/2017	16.8
	8/29/2017	17.0
	9/6/2017	17.2

There are several potential reasons why Nolan Creek temperature readings exceeded the core summer salmonid habitat temperature criteria while other sites did not. Due to project planning logistics, Nolan Creek was consistently sampled in the afternoon (between 12pm and 2pm) while other sites were sampled earlier in the morning. Additionally, Nolan Creek is one of the larger systems studied in this project with a wider channel and therefore receives limited shading from streamside vegetation which could result in increased stream temperatures.

5.1.2 Dissolved Oxygen

Aquatic life criteria for dissolved oxygen are listed as the 1-day minimum for each aquatic life stage. The Hoh River and tributaries are designated as core summer salmonid habitat from the mouth to the South Fork Hoh River, which has an established aquatic life dissolved oxygen criteria of 9.5 mg/L (Ecology, 2016). All sites evaluated in this study are located between the mouth and the South Fork Hoh River. Table 4 lists all exceedances of the dissolved oxygen criteria for this project (an exceedance of this criteria is any number **below** the established criteria of 9.5 mg/L). Only point measurements of dissolved oxygen data were collected for this project; it is possible that the one day minimum for these streams was lower than the point measurement, resulting in an exceedance that was not identified in this study.

Table 4: Exceedances of aquatic life dissolved oxygen criteria

Monitoring Site	Date of Exceedance	Dissolved Oxygen (mg/L)
Nolan Creek	8/9/2017	9.00
	8/16/2017	9.46
	8/23/2017	9.09
	8/29/2017	8.97
	9/6/2017	8.86
Lost Creek	9/6/2017	9.46
Elk Creek	8/29/2017	9.45
	9/6/2017	9.36
Winfield Creek	8/9/2017	9.33
	8/23/2017	9.34
	8/29/2017	9.08
	9/6/2017	9.11

Dissolved oxygen readings were taken from a well-mixed portion of the stream expected to be representative of the aquatic life conditions at that location. The dissolved oxygen criteria for other life stages (salmonid spawning, rearing, or migration) is 8 mg/L and was not exceeded for any sampling event.

5.2. Herbicide detections

A total of 24 sampling events (6 sampling events at each of the 4 sites) were completed for this project. Triclopyr, imazapyr, sulfometuron methyl, and metsulfuron methyl were not detected in any of the samples collected. There were positive detections for glyphosate, glufosinate-ammonium and aminomethylphosphonic acid (AMPA) at 3 of the 4 sites sampled. All detections of glufosinate-ammonium and one detection of AMPA were qualified by MEL with a “J.” Detections qualified with a “J” occur when an analyte was positively identified, but the associated numerical value is the approximate concentration of the analyte in the sample. Additional information on laboratory QA can be found in Appendix B.

There were a total of 13 positive detections for all sampling events. There were 4 detections of glyphosate, 7 detections of glufosinate-ammonium, and 2 detections of AMPA. Table 5 summarizes the average and maximum concentrations detected for each analyte.

Table 5: Summary of herbicide detections

Analyte	Number of Detections	Sampling Events	Average Concentration (µg/L)	Maximum Concentration (µg/L)
Glyphosate	4	24	0.084	0.266
AMPA	2	24	0.012	0.015
Glufosinate-ammonium	7	24	0.015	0.058
Imazapyr	0	24	-	-
Triclopyr	0	24	-	-
Sulfometuron-methyl	0	24	-	-
Metsulfuron-methyl	0	24	-	-

No herbicides were detected in the background samples collected on 7/12/2018. There were herbicide detections in 4 out of the 5 sampling dates collected in August and September. There were no herbicide detections on 8/16/2018. The most detections (5) occurred on 8/23/2018. There were 5 sampling events with 2 herbicide detections. Table 6 displays all of the positive herbicide detections from this project.

Table 6: All Herbicide Detections

Date	Location	Herbicide	Concentration (µg/L)
8/9/2017	Nolan Creek	Glufosinate-ammonium	0.008
	Nolan Creek	Glyphosate	0.01
8/23/2017	Nolan Creek	Glufosinate-ammonium	0.058
	Nolan Creek	Glyphosate	0.032
	Lost Creek	Glufosinate-ammonium	0.008
	Elk Creek	Glufosinate-ammonium	0.01
	Elk Creek	Glyphosate	0.266
8/29/2017	Elk Creek	AMPA	0.015
	Elk Creek	Glufosinate-ammonium	0.003
	Elk Creek	Glyphosate	0.027
9/6/2017	Nolan Creek	Glufosinate-ammonium	0.008
	Elk Creek	AMPA	0.008
	Elk Creek	Glufosinate-ammonium	0.008

During the project, no herbicides were detected at Winfield Creek and only one herbicide was detected at Lost Creek (glufosinate-ammonium on 8/23/2017).

At Nolan and Elk Creeks, at least one herbicide was detected in half of the sampling events. Both sites had 3 detections of glufosinate-ammonium and 2 detections of glyphosate.

The highest detected concentration of glyphosate was at Elk Creek on 8/23/2017, the sampling event that WSDA observed a noxious weed control crew entering the site. It is possible that the presence or activity of this crew contributed to this glyphosate detection.

5.3. Comparison to Aquatic Life Benchmarks

WSDA compared herbicide detections to aquatic life benchmarks to determine whether a system or its organisms are at risk from herbicide exposure. EPA's freshwater fish aquatic life benchmark for glyphosate is 21.5 mg/L (EPA, 2009). Detections of glyphosate, glufosinate-ammonium, and AMPA were compared to this benchmark to assess the potential for effects on aquatic life. The maximum detected concentration from this study was 0.266 µg/L (glyphosate), which is approximately 0.0012% of the aquatic life benchmark. With a maximum detection of much less than 1% of a benchmark, risks to aquatic life are considered low.

5.4. Comparison to previous studies

Due to the high analytical cost, WSDA does not routinely sample for glyphosate as part of the ambient surface water monitoring program. Glyphosate sampling was conducted in 2015 as a special project, with samples tested for glyphosate from all ambient surface water monitoring sites (14) during the typical use period (April – May) (WSDA, 2017). These samples were analyzed for glyphosate, AMPA, and glufosinate-ammonium. Land use in these watersheds were primarily agriculture or urban. There were several notable differences between the two projects that may have contributed to differing concentrations and detection frequencies. The 2015 study had a much larger sample size, samples were collected from a broad range of locations with variable land use, and samples were collected in the springtime. Table 7 displays the maximum concentration detected and the detection frequency from the 2015 glyphosate monitoring and this study.

Table 7: Comparison with 2015 WSDA data

	WSDA 2015 Data		Hoh Watershed Data	
Analyte	Maximum Concentration (µg/L)	Detection Frequency (%)	Maximum Concentration (µg/L)	Detection Frequency (%)
Glyphosate	1.5	77	0.266	17
AMPA	0.38	65	0.015	8
Glufosinate-ammonium	0.28	7	0.058	29

Maximum concentrations detected for all 3 analytes were higher in the 2015 project than this project, but still considerably lower than any level of concern. Detection frequency was much higher for glyphosate and AMPA for the 2015 sampling, while there was a higher detection frequency for glufosinate-ammonium in the Hoh watershed sampling. Several factors may have contributed to differences in herbicide concentrations and detection frequency including timing of sampling, land use characteristics, local and regional meteorology, and location.

5.5. Field quality control

All field data was reviewed and checked against established measurement quality objectives (MQOs) for quality assurance purposes. There were no exceedances of MQOs in the meter calibration data or field data collected for this project. A more detailed explanation of the field QA/QC procedure and results can be found in Appendix A.

5.6. Laboratory quality control

Quality assurance samples were collected alongside grab samples in the field and analyzed. Quality control samples were generated by the laboratory for every batch of field samples submitted. QA and QC samples assure consistency and accuracy throughout sample collection, sample analysis, and the data reporting process.

For this project, QA samples included: field replicates, field blanks, and matrix spike and matrix spike duplicates. Laboratory control samples (LCS), LCS duplicates (LCSD), surrogate spikes, and method blanks are included as QC samples in each batch of samples analyzed for pesticides as are method blanks and split sample duplicates for each batch of TSS. QA results can be found in Appendix B.

6. Conclusions and recommendations

The goal of this project was to conduct an initial surface water assessment of herbicides commonly used in timber production in a watershed with managed timber. Additional goals included developing relationships with partners in forestry and identifying future research needs. Four tributaries were selected for sampling and a total of 6 samples were taken at each tributary site, one background sample in July and 5 consecutive weekly samples in August and September. Field sampling involved collecting water samples, taking general water chemistry readings with a multiparameter probe, and volumetric flow measurements. There were a total of 13 herbicide detections over all 24 sampling events. There were 4 detections of glyphosate, 7 detections of glufosinate-ammonium, and 2 detections of AMPA. Glufosinate-ammonium is not known for use in forestry, but is commonly used in roadside spray operations. These detections were at 3 of the 4 sites; there were no herbicide detections at Winfield Creek. All detections were much lower than 1% of the established aquatic life benchmark, resulting in low risk to aquatic life.

One of the primary limitations to this study is the timing of data collection. Samples were collected during the time period herbicides are likely to be used and the driest time period in the region. It is unknown whether samples were collected before, during, or after timber applications. Therefore, the source of the herbicide detections is unknown; these herbicides are used for a number of purposes and there is no certainty the detections are a result of forestry applications.

Future studies in the area should be planned in partnership with applicators to ensure that samples are taken in conjunction with forestry applications. Additionally, sampling immediately following the first fall rain event would capture potential herbicide runoff and should also be considered.

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Appendix A. Field parameter QA

Multiparameter water quality meters were calibrated each week, on either the evening before or the morning of the first field day of the week. Calibration procedures followed the manufacturer's guidelines and WSDA NRAS Standard Operating Procedure: Water Quality and Water Monitoring Programs (Bischof, 2017). Field meters were post-checked, using known standards, at the end of the sampling week to ensure calibration had been maintained during field work.

Water samples analyzed with the Winkler method were used to check the quality of dissolved oxygen measurements from the multiparameter meters. Grab samples were collected, at a minimum, at the first and last sampling site each day. In addition, 1 replicate grab sample was collected each week. These samples were preserved in the field with manganous sulfate monohydrate reagent and alkali-iodine-azide reagent, and transported to the lab for analysis of dissolved oxygen content by titration. Titrations were conducted according to the methods described in Ecology's Standard Operating Procedures (Ward, 2007).

The measurement quality objectives (MQOs) for meter post-checks, replicates, and Winkler DO comparisons used are described in Anderson and Sargeant (2009). Depending on the parameter, the MQO is defined as a percentage of the relative standard deviation (RSD) or a defined value with the same units of the parameter.

A1. Field data collection performance

The Hach Hydrolab multiparameter meter met MQOs for dissolved oxygen at all sampling locations. Winkler replicate values also met the MQOs for all samples. QA results for dissolved oxygen are displayed in Table 8.

Table 8: Quality control results for field meters and Winkler replicates

Replicate Meter Parameter	MQO	Average	Maximum
Winkler and meter DO	10% RSD	0.99% RSD	4.33% RSD
Replicate Winklers	±0.2 mg/L	0.02 mg/L	0.03 mg/L
Streamflow	10% RSD	4.3% RSD	9.52% RSD

Acceptance of Hydrolab field meter results were based on the Measurement Quality Objectives described in Anderson and Sargeant (2009). The MQOs for conventional field parameters are shown in Table 9. All parameters for field meter calibrations fell within specified criteria.

Table 9: Measurement quality objectives for conventional parameters measured by field meters or determined by a standard method

Parameter	Method/Equipment	Field Replicate MQO	Accuracy
Discharge Volume	OTT MF pro flow meter	10% RSD	0.015 m/s
Water Temperature	Hydrolab MiniSonde®	±0.2° C	+/- 0.10° C
Conductivity	Hydrolab MiniSonde®	10% RSD	+/- 0.001 mS/cm
pH	Hydrolab MiniSonde®	10% RSD	+/- 0.2 s.u.
Dissolved Oxygen	Hydrolab MiniSonde®	10% RSD	+/- 20 mV
Dissolved Oxygen	SM4500OC	±0.2 mg/L	+/- 0.1 mg/L

A2. References

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Appendix B. Results summary for QA/QC samples

B1. Quality assurance sample performance

For this project, 10% of all the samples collected in the field were QA samples. There were 6 QA samples total (1 replicate, 3 field blanks, and 2 MS/MSD samples).

B1.1. Field replicates results

Precision between replicate pairs was calculated using the relative percent difference (RPD) statistic. The RPD is calculated by dividing the absolute value of the difference between the replicates by their mean, then multiplying by 100 for a percent value. When both replicates are qualified as detections the result is considered consistent. If one replicate is qualified as a detection and one is not, the result is considered inconsistent. There was a single pair of results that were inconsistently detected during this project (Table 10). For the TSS replicates collected at Lost Creek on 8/16/18 one result was a detection ("D") and the other result was below the detection limit of 1 mg/L ("U"). It is very likely that the results for this pair of samples were inconsistently detected because the concentrations of TSS in the sample was close to the detection limit.

Table 10: Inconsistent field replicate detections

Sample Date	Parameter	Site-ID	Reporting Limit	Units	Sample and Replicate Sample Details
8/16/2017	TSS	Lost Creek	1	mg/L	1 mg/L "D" & 1 mg/L "U"

B1.2. Field blank results

Field blank detections indicate the potential for sample contamination in the field or laboratory and the potential for false detections due to analytical error. There were no detections in any of the blank QA samples collected for this project.

B1.3. Matrix spike/matrix spike duplicate (MS/MSD) results

MS/MSD results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. This measure is the best overall indicator of accuracy and reproducibility in the sampling process.

Table 11 presents the mean, maximum, and minimum percent recovery for the MS/MSDs for the all parameters measured in the herbicide samples as well as the RPD for the MS/MSDs.

Table 11: Summary statistics for MS/MSD recoveries and RPD

Parameter Name	Number of Results	Average Recovery %	Max Recovery %	Min Recovery %	Mean RPD	Max RPD	Min RPD
AMPA	2	104.5	118	91	26	26	26
Glufosinate-ammonium	2	206.5	211	202	4	4	4
Glyphosate	2	109	118	100	17	17	17
Imazapyr	8	74	77	71	8	8	8
Metsulfuron-methyl	8	23.5	30	17	57	57	57
Sulfometuron methyl	8	79	79	79	0.5	0.5	0.5
Triclopyr	8	65	67	63	6	6	6

Table 12 reports the frequency of MS/MSD recoveries that were above or below the laboratory control limits set for each analyte. Table 12 also shows how often recoveries for each analyte were outside of the control limits and the number of detections from grab samples for each analyte.

Table 12: Frequency of MS/MSD recoveries falling outside of the laboratory control limits

Analyte	Total Percent Recoveries Outside Control Limit	MS/MSD Recovery Below Control Limit	MS/MSD Recovery Above Control Limit	Lower Control Limit (%)	Upper Control Limit (%)	Total Detections
AMPA	0	0	0	40	130	2
Glufosinate-ammonium	100	0	2	40	130	7
Glyphosate	0	0	0	40	130	4
Imazapyr	0	0	0	40	130	0
Metsulfuron-methyl	100	8	0	40	130	0
Sulfometuron methyl	0	0	0	40	130	0
Triclopyr	0	0	0	40	130	0

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. All detections of an analyte within an analytical batch were be qualified as estimates ("J") whenever MS/MSD recoveries for that analyte fall above or below the upper and lower control limit respectively.

B2. Quality control sample performance

Quality control samples were analyzed by the laboratory to assure consistency and accuracy of sample analysis and to assess the accuracy and precision of the results.

B2.1. Laboratory duplicates

MEL used laboratory split sample duplicates to ensure consistency of TSS samples. There were 15 laboratory duplicate pairs for TSS. All laboratory duplications fell below the RPD criteria.

B2.2. Laboratory blanks

MEL used laboratory blanks to assess the precision of equipment and the potential for internal laboratory contamination. If lab blank detections occur, the sample LPQL may be increased, and detections may be qualified as estimates. No analytes were detected above the detection limit in the laboratory blanks.

B2.3. Surrogates

Surrogates are analytes spiked into field samples at the laboratory. Surrogates were used to assess recovery for a group of structurally related analytes. Summary statistics for surrogate recoveries are presented in Table 13.

Table 13: Pesticide surrogates

Method	Surrogate	Average Recovery (%)	Number of Recoveries	Percentage within Control Limits
LCMSMS-Pesticides	Carbaryl C13	95	51	98
LCMSMS-Glyphosate	AMPA-C13N15	100	31	71
LCMSMS-Glyphosate	AMPA-C13N15	74	14	100
LCMSMS-Glyphosate	Glyphosate-C13N15	30	31	45.2
LCMSMS-Glyphosate	Glyphosate-C13N15	65	14	100

Some results for the surrogate analysis exceeded the control limits for the QA process. Surrogate recoveries that are not within specific control limits requires all related sample data to be qualified as estimates (qualified with a “J”).

B2.4. Laboratory control samples

Laboratory control samples (LCS) were created in the laboratory before beginning the sample extraction process by the addition of analytes at known concentrations to purified water free of all organics. These samples were then subjected to extraction and analysis conditions alongside the field samples and other QC samples. They were used to evaluate accuracy of pesticide residue recovery for a specific analyte. Detections may be qualified based on low recovery and/or high RPD between the paired LCS and LCS duplicate (LCSD).

Table 14 displays average recovery and percentage of samples outside the recovery limits for the LCS and LCSD for the three types of analyses.

Table 14: Summary statistics for LCS/LCSD recoveries and RPD

Method	Analyte	Number of Results	Average Recovery	Percentage Outside Recovery Limits
LCMSMS-Pesticides	Imazapyr	12	72.8	0
LCMSMS-Pesticides	Metsulfuron-methyl	12	37.3	50
LCMSMS-Pesticides	Sulfometuron methyl	12	84.2	0
LCMSMS-Pesticides	Triclopyr	12	59.8	16.7
LCMSMS-Glyphosate	AMPA	12	100.2	0
LCMSMS-Glyphosate	Glufosinate-ammonium	12	174.3	83.3
LCMSMS-Glyphosate	Glyphosate	12	104.6	0
TSS	Total Suspended Solids	8	95	0

Each time the RPD statistic or analyte recoveries fell outside of the control limits for a given analyte all detections from field samples associated with that analytical batch were qualified as estimates.