Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams 2006-2008 Triennial Report

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Cover photos: Skagit Valley tulip crop, and Paul Anderson conducting pesticide sampling in Browns Slough (photos by Paul Anderson and Chris Burke).

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams

2006-2008 Triennial Report

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Abstract

The Washington State Departments of Agriculture and Ecology are conducting a multi-year monitoring study to characterize pesticide concentrations in selected salmon-bearing streams during a typical pesticide-use period.

Monitoring is being conducted in five basins:

- Thornton Creek in the Cedar-Sammamish basin representing urban land use.
- Lower Skagit-Samish basin representing western Washington agricultural practices.
- Lower Yakima basin representing irrigated agriculture.
- Wenatchee and Entiat basins representing tree fruit agriculture.

During the 2006-2008 monitoring period, the majority of detected pesticides met water quality standards or assessment criteria.

Over the three years, 71 pesticides were detected. Of these, six insecticides did not meet a water quality standard or assessment criterion: permethrin, chlorpyrifos, diazinon, azinphos-methyl, malathion, and endosulfan. The other pesticide that did not meet a water quality standard was total DDT, which has not been registered for use in the United States since 1972.

For all monitoring sites, co-occurrence of insecticides with a similar mode of action (acetylcholinesterase inhibitors) rarely occurred.

The only significant trend found in pesticide levels was a decrease in the number of herbicide detections in Thornton Creek during 2006-2008 as compared to 2003-2005.

None of the sites sampled in 2006-2008 met water quality standards for temperature. In addition, Thornton Creek and the Skagit-Samish agricultural drainages did not meet water quality standards for dissolved oxygen.

High water temperatures and low dissolved oxygen levels are of concern for the fisheries resource in Indian Slough, Browns Slough, and Big Ditch in the Skagit-Samish basin. Temperature levels for the lower Yakima sites during some periods are of concern for steelhead fisheries.

Pesticide concentrations found in this 2006-2008 study likely do not directly affect salmonids. Pesticide concentrations at some sites may affect aquatic invertebrate populations which serve as a prey base for salmonids.

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Executive Summary

The Washington State Departments of Agriculture and Ecology are conducting a multi-year monitoring study to characterize pesticide concentrations in selected salmon-bearing streams during a typical pesticide-use period. This monitoring project began in 2003 in the lower Yakima and Cedar-Sammamish basins. As the project progressed, additional sampling areas were added in the lower Skagit-Samish, Wenatchee, and Entiat basins. This report describes findings for 2006-2008. Reports from previous years and more information about this project can be found at: www.ecy.wa.gov/programs/eap/toxics/pesticides.htm.

Sample Design

From 2006 through 2008, monitoring was conducted in five basins: an urban area and an agricultural area in western Washington and three agricultural areas in eastern Washington (Figure ES1). Thornton Creek in the Cedar-Sammamish basin has been sampled since 2003, and represents urban land use. The lower Skagit-Samish basin has been sampled since 2006, and represents western Washington agricultural practices. The lower Yakima basin has been sampled since 2003, and represents eastern Washington irrigated agriculture. The Wenatchee and Entiat basins have been sampled since 2007, and represent eastern Washington tree fruit agriculture.

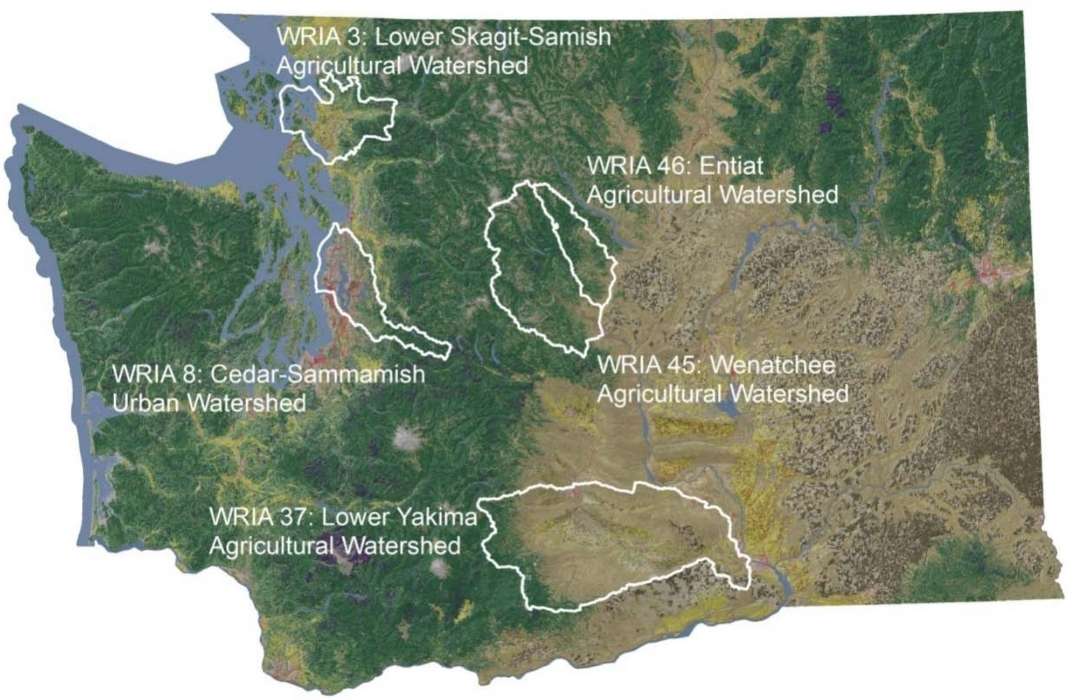


Figure ES1. State map showing locations of urban and agricultural project areas.

WRIA – Water Resource Inventory Area.

Weekly sampling occurred during the typical pesticide-use period, March through September. Over 160 pesticides and degradate compounds were analyzed. Additional parameters included total suspended solids, temperature, dissolved oxygen, pH, conductivity, and streamflow measurements. To determine if water quality concentrations were healthy for aquatic life, monitoring data were compared to pesticide registration toxicity criteria, and EPA National Recommended Water Quality Criteria (NRWQC), referred to as *assessment criteria*. Data were also compared to the Washington State numeric water quality standards, referred to as *water quality standards*. Trends in water quality parameters were examined, and water quality conditions were compared to salmon habitat requirements.

Results

Pesticide Results

For 2006-2008, the majority of pesticide detections met (did not exceed) an assessment criteria or water quality standard. Over these three years, 64 current-use pesticides and seven legacy pesticides and degradate compounds were detected: 34 herbicides, 23 insecticides, eight degradate compounds, five fungicides, and one wood preservative.

Of the 74 pesticides or degradates detected, six currently registered pesticides did not meet an assessment criteria or water quality standard. Also DDT (not registered for use in the United States since 1972) and its associated degradates did not meet water quality standards. The pesticides that did not meet (exceeded) assessment criteria or water quality standards are:

- Permethrin exceeded the EPA Endangered Species Level of Concern (ESLOC) in Thornton Creek once (Cedar-Sammamish basin).
- Chlorpyrifos exceeded the marine acute and chronic water quality standard twice in both 2007 and 2008 in Browns Slough (lower Skagit-Samish basin). Chlorpyrifos also exceeded the freshwater water quality standard (acute and chronic) in Sulphur Creek Wasteway (four times), Marion Drain (eight times), and lower Spring Creek (four times). Chlorpyrifos exceeded the ESLOC for fish once in Spring Creek and Sulphur Creek Wasteway (lower Yakima basin).
- Diazinon exceeded the marine acute and chronic NRWQC for invertebrates twice in 2007 in Browns Slough (lower Skagit-Samish basin).
- Azinphos-methyl exceeded the chronic NRWQC eight times in Spring Creek and three times in Sulphur Creek Wasteway in 2006 (lower Yakima basin).
- Malathion exceeded the chronic NRWQC in Marion Drain once in 2007 (lower Yakima basin).
- Total DDT exceeded the chronic water quality standard in Spring Creek (three times) and Sulphur Creek Wasteway (five times) in the lower Yakima basin as well as in Brender Creek (during all sample events but one) in the Wenatchee basin.
- Endosulfan exceeded the chronic water quality standard and the ESLOC for fish 14 times in Brender Creek and once in Peshastin and Mission Creeks as well as once in the Wenatchee River (Wenatchee basin).

Conventional Parameters

None of the sites consistently met water temperature standards during the 2006-2008 monitoring. Dissolved oxygen samples were collected in 2008. The only areas to meet the dissolved oxygen water quality standard were the lower Yakima and Wenatchee-Entiat sites.

During 2006-2008, most sites fell below or exceeded (did not meet) the pH standard. The sites east of the Cascade Mountains tended toward exceedances of the pH standard, while the sites west of the mountains tended to fall below the standard.

Conclusions

During the 2006-2008 monitoring period:

- Data analysis showed the major factor in pesticide detections is season of the year and timing of application for specific crops.
- The majority of detected pesticides met (did not exceed) a water quality criteria.
- For all sites, co-occurrence of acetylcholinesterase-inhibiting insecticides rarely occurred.
- Thornton Creek in the Cedar-Sammamish WRIA had one exceedance of an assessment criterion for permethrin, an insecticide.
- A statistically significant decrease in herbicide detections has occurred in Thornton Creek over the last six years (Figure ES2).
- In the Skagit-Samish basin, with the exception of a few exceedances in Browns Slough, pesticide concentrations did not exceed water quality standards or assessment criteria. High water temperatures and low dissolved oxygen levels are of concern for the fisheries resource in Indian Slough, Browns Slough, and Big Ditch.
- The lower Yakima sites had the greatest number of pesticide detections that did not meet (exceeded) water quality standards or assessment criteria. The greatest concern is for chronic to acute risk for aquatic invertebrates which are part of the prey base for salmonids
- In late June through August, water temperatures at the lower Yakima sites may present a thermal blockage to steelhead migration; also, elevated temperatures may make fish more susceptible to pesticide toxicity (Mayer and Ellersick, 1986 as referenced in Burke et al., 2006).
- In the lower Yakima basin, an increase in total suspended solids was observed at the upstream Spring Creek site while the downstream site showed a decreasing trend in total suspended solids.
- Endosulfan levels in the Wenatchee basin from mid-March through May indicate chronic aquatic health concerns and are above the ESLOC for fish.

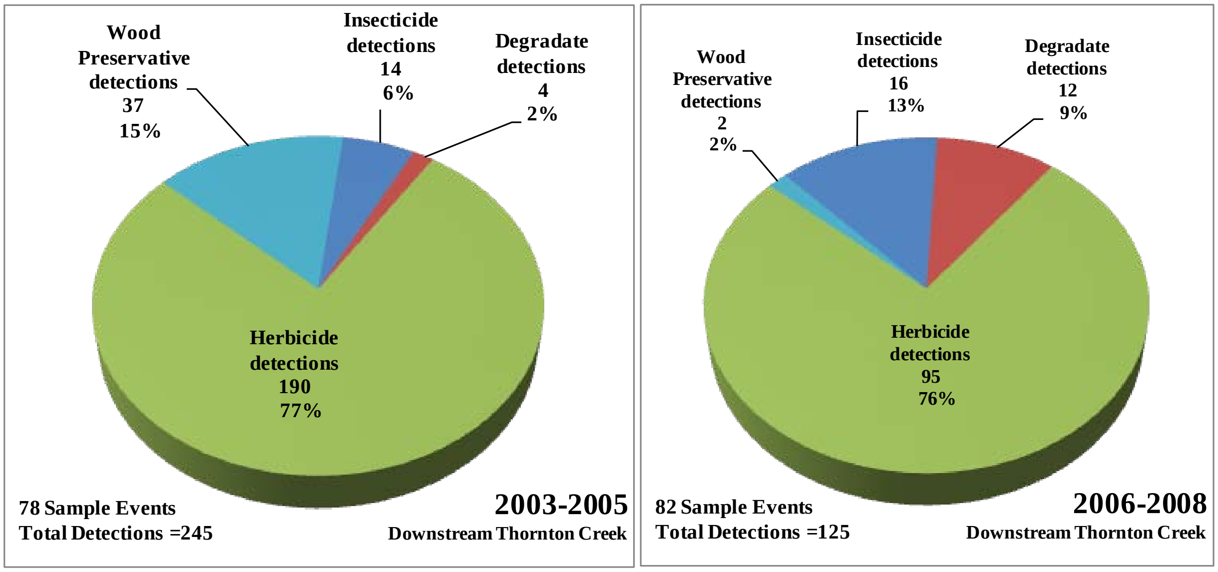


Figure ES2. Pesticide distribution at the downstream Thornton Creek site for the 2003-2005 and 2006-2008 periods.

Recommendations

- Conduct intensive weekly sampling during periods when the greatest number of detections occurs for organophosphate insecticides.
- Install an additional continuous temperature monitoring device in Browns Slough to determine if influx of warmer water is from upstream or downstream sources.
- Explore opportunities to evaluate the effects of monitored pesticide concentrations and mixtures on aquatic invertebrates and salmonids, including the effects of other environmental stressors such as temperature and dissolved oxygen in laboratory toxicity testing.
- WSDA should continue to work with agricultural stakeholders to explore mitigation measures for endosulfan concentrations found in surface water in the Wenatchee basin. Monitoring will continue to assess the effectiveness of mitigation measures.
- Continue efforts to resolve the issue of blank detections in the carbamate analysis.
- Evaluate the need for adding new pesticides to the monitoring program.

Introduction

The Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) are conducting a multi-year monitoring study to evaluate pesticide concentrations in surface water. The study assesses pesticide presence in salmon-bearing streams during a typical pesticide-use season.

The data collected are used by WSDA, the U.S. Environmental Protection Agency (EPA), the National Atmospheric and Oceanic Administration (NOAA) Fisheries Service, and U.S. Fish and Wildlife Service to refine exposure assessments for pesticides that are registered for use in Washington State.

Understanding the fate and transport of pesticides allows regulators to assess potential impacts to endangered salmon species while minimizing the economic impacts to agriculture.

This monitoring project has been ongoing since 2003. As the project progressed, additional sampling areas were added. Currently four types of land-use areas are monitored for this study: an urban area and three agricultural areas. The urban subbasin was chosen due to land-use characteristics, history of pesticide detections, pre-spawning mortality of coho salmon, and habitat use by salmon. The agricultural areas were chosen because they support several salmonid populations, produce a variety of agricultural commodities, and have a high percentage of cultivated land area.

Monitoring areas and time frames are:

1. Thornton Creek, located in the Cedar-Sammamish basin (WRIA[1] 8) represents an urban land-use area. Two to three sites have been sampled on this creek since 2003.

2. Four subbasins of the lower Skagit-Samish basin (WRIA 3) were selected to represent western Washington agricultural land-use practices. The Samish River, Big Ditch, Browns Slough, and Indian Slough have been sampled since 2006.

3. Three subbasins of the lower Yakima basin (WRIA 37) were selected to represent eastern Washington irrigated agricultural land-use practices. Marion Drain, Sulphur Creek Wasteway, and Spring Creek have been sampled since the start of the project in 2003.

4. Four subbasins of the Wenatchee basin (WRIA 45) and one subbasin in the Entiat basin (WRIA 46) were selected to represent central Washington agricultural tree fruit practices. The Wenatchee River, Mission Creek, Peshastin Creek, and Brender Creek in WRIA 45; and the Entiat River in WRIA 46 have been sampled since 2007.

Figure 1 shows the locations of the four project areas encompassing these five WRIAs.

[1] Water Resource Inventory Area

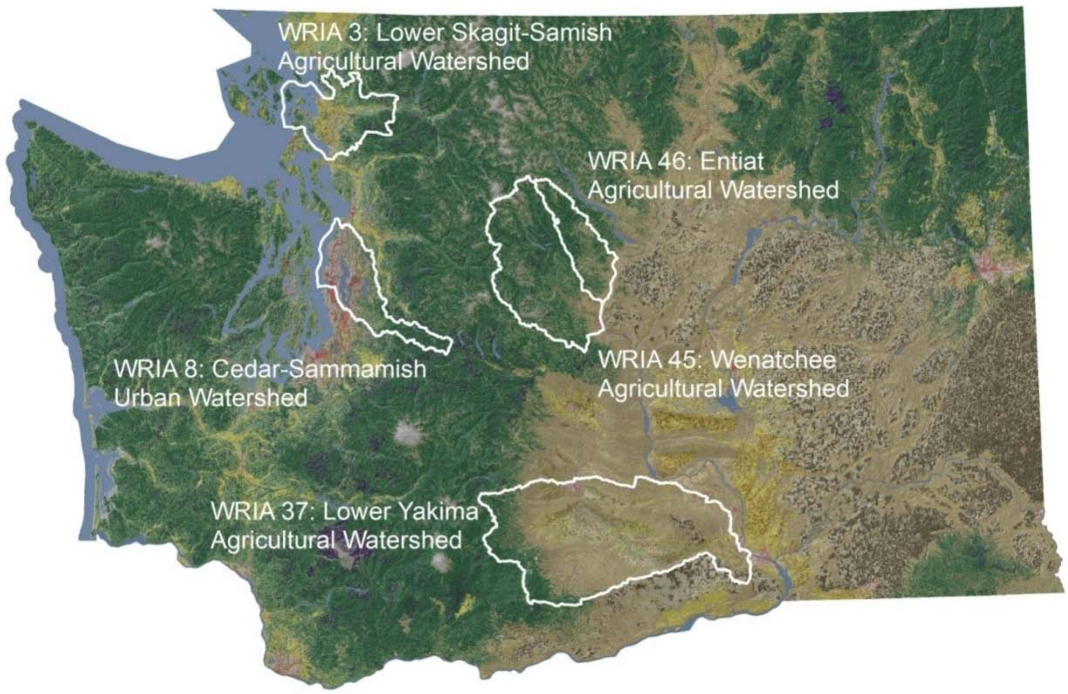


Figure 1. State map showing locations of urban and agricultural project areas.

Detected pesticide concentrations are evaluated against toxicity criteria used for pesticide registration under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA), EPA National Recommended Water Quality Criteria (NRWQC), and Washington State water quality standards. In addition, monitoring data are compared to salmonid life history and habitat use.

Results of the first three years of monitoring (2003-2005) are presented in Burke et al. (2006). Annual data summary reports for 2006 and 2007 are presented in Anderson et al. (2007) and Anderson and Dugger (2008) respectively.

During the last three-year monitoring period (2006-2008), samples were analyzed for approximately 160 currently registered and historical-use pesticides and degradates. These compounds were selected based on pesticide use, toxicity to non-target organisms, transport potential, and cost of analysis. Conventional water quality parameters were also measured to better understand factors influencing pesticide toxicity, fate and transport, and general water quality. Conventional water quality parameters measured include total suspended solids (TSS), pH, conductivity, temperature, and streamflow. In 2008 dissolved oxygen (DO) measurements were added.

Study Area

Basin Descriptions

Cedar-Sammamish Basin (WRIA 8): Thornton Creek

Thornton Creek drains a 12.1 square mile watershed before flowing into Lake Washington and ultimately Puget Sound. Thornton Creek sample stations are presented in Figure 2 and described in Appendix B. Subbasins of Thornton Creek include the mainstem, North Branch, and South Branch (Maple Leaf Creek). The headwaters of the North Branch originate near Ronald Bog. The North Branch drains approximately 4,400 acres within the municipalities of Shoreline and Seattle. The South Branch originates west of Interstate-5 near North Seattle Community College and drains approximately 2,300 acres. Thornton Creek and its tributaries flow over 15 miles before entering the northern end of Lake Washington at Matthews Beach Park (Thornton Creek Watershed Characterization Report, 2000; Kerwin, 2001; Homer et al., 2004).

Thornton Creek basin is a fully developed urban basin. Population density in the basin is on the order of 600-1000 people per square mile. In addition to dense residential development, there are large shopping malls, commercial development, and an interstate freeway bisecting the basin. Impervious surface covers approximately 50% of the basin. Existing land use consists of 53% residential, 23% roads, 9% commercial and industrial, 4% parks and golf courses, 4% schools, and 4% vacant (Kerwin, 2001). Land-use coverages are presented in Appendix C.

The climate of the Thornton Creek watershed is typical of the mild, mid-latitude coastal climate of the Pacific Northwest, moderated by marine air from the Pacific Ocean. In the summer, temperatures range from the 70- 90 °F during the day, then drop to the 60s (°F) at night. In the winter, temperatures average in the 40s (°F) during the day, and 30s (°F) at night, with occasional cold spells and temperatures in the low 20s (°F). Precipitation in the watershed averages 34.9 inches per year. Thornton Creek and its tributaries flow year-round, and groundwater provides much of the base flow. Flows average 11.2 cubic feet per second (cfs) near the mouth (Kerwin, 2001).

Table 1 presents the 1996-2007 monthly average streamflow for the pesticide-use season, as well as the 1992-2008 monthly average precipitation.

Table 1. 1996-2007 monthly average streamflow (cfs) for Thornton Creek at USGS Station 12128000[1] and 1992-2008 monthly average precipitation (inches) for Thornton Creek at King County's Brugger's Bog (site code 35U)[2].

Years	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct
1996-2007 cfs	12.8	12.7	9.6	7.9	5.7	4.7	4.0	5.2	8.8
1992-2008 inches	3.3	3.5	2.9	2.0	1.7	1.1	1.1	1.5	3.3

cfs – cubic feet per second.
[1] – located in Thornton Creek at RM 0.25.
[2] - located at 19547 25th Ave NE, Seattle.

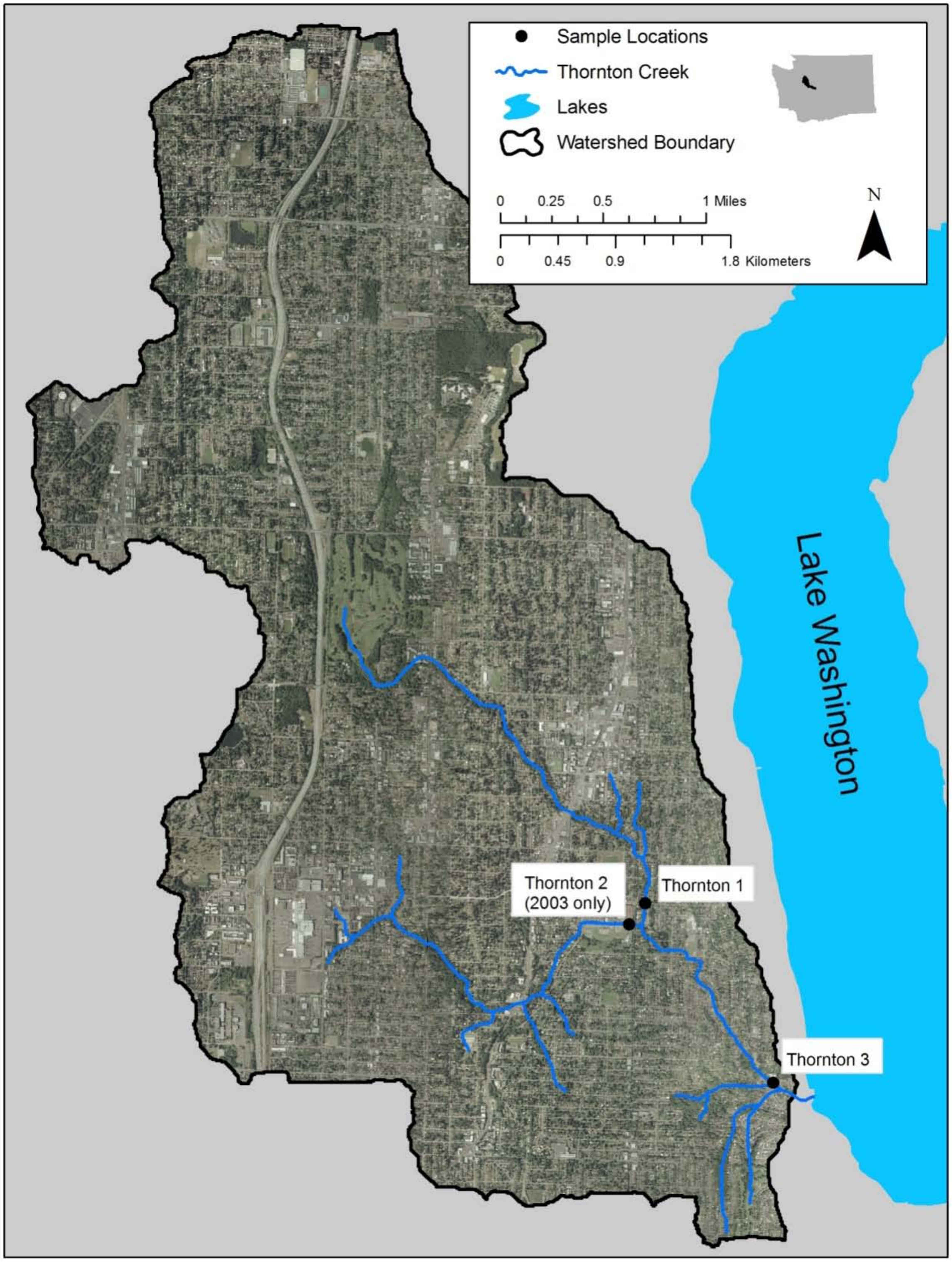


Figure 2. Sampling stations in Thornton Creek in the Cedar-Sammamish basin.

Salmonid Fishery

Several salmonid surveys have been conducted in this area, primarily in the mainstem of Thornton Creek. Salmonid species present in the creek include chinook, coho, and sockeye salmon, coastal cutthroat trout, steelhead, and rainbow trout (Kerwin, 2001).

According to the StreamNet (2009) fisheries database, migrating chinook and sockeye are present at both the upstream and downstream sites, and migrating coho are present at the downstream site.

Thornton Creek is within the Puget Sound Chinook Salmon Evolutionary Significant Unit (ESU) and the Puget Sound Bull Trout Distinct Population Segment (DPS), both designated threatened status. As of March 29, 2006, the Puget Sound Steelhead DPS has been proposed for threatened status (71FR15666). Puget Sound coho are an Endangered Species Act (ESA) Species of Concern.

Table 2 presents the life cycle for fall chinook in Thornton Creek during the pesticide-use period. Black indicates periods of use, and white represent periods of little or no use. Coho spawn in October, and fry emerge in February. Juveniles spend over a year in the stream and out migrate in April and May (Foley, 2009).

Table 2. General life cycle of Thornton Creek fall chinook during the pesticide-use period.

Life Stage	March	April	May	June	July	August	Sept	October
Spawning Run*								
Spawning								
Incubation								
Emergence								
Fry Colonization								
0+ Summer Rearing								
Juvenile Outmigration								

Factors contributing to salmonid decline include poor habitat and water quality. Water quality concerns include high temperatures, low dissolved oxygen, possibly heavy metals, as well as pesticides and poly-aromatic hydrocarbons in sediments (Kerwin, 2001).

Lower Skagit-Samish Basin (WRIA 3)

The lower Skagit-Samish basin is located in Skagit County in northwest Washington (Figure 1). Agricultural land use dominates the western portion of the basin, largely supporting cropland and pasture. The eastern uplands are predominantly forested, with some scattered residential development (Zalewsky and Bilhimer, 2004).

The estuarine deltas within the basin include the Samish River, Padilla Bay Slough estuaries, Swinomish Channel, North Fork Skagit River, Central Skagit Slough estuaries, South Fork Skagit River, and the Douglas Slough deltas. Many of these estuaries are in or near lands used for agriculture. Agriculture is concentrated in the Samish delta, northeast and south Padilla Bay deltas, the Skagit delta, and along parts of the Swinomish Channel. Industrial land use is primarily along the northern Fidalgo Bay shoreline, March Point, and near Bayview. Central Padilla Bay is primarily rural, whereas public lands surround the lower South Fork Skagit River (Smith, 2009).

Since the late 1800s, hydrology in the lower Skagit-Samish watershed has changed significantly to facilitate water transportation, land reclamation, and flood attenuation. Many of the freshwater wetlands and estuary area in the lower Skagit-Samish basin were diked and drained via tidal sloughs and ditches to reclaim land for agriculture (Collins, 1998).

The intensity of agriculture and importance of the salmon habitat make this area a good index watershed for evaluating pesticides associated with western Washington agricultural practices. Monitoring of four drainages in the Skagit-Samish basin began in 2006 as described in Burke and Anderson (2006).

The four monitored drainages in the Skagit-Samish watershed include:

- Samish River at river mile (RM) 4.6 (drains to Samish Bay).
- Indian Slough above tidegate (drains to Padilla Bay).
- Browns Slough downstream of tidegate (drains to Skagit Bay).
- Big Ditch upstream of tidegates (drains to Skagit Bay).

Figure 3 presents the locations of the six sample sites. Appendix B describes sampling locations and duration of sampling for each site.

Sample sites are characterized by a unique combination of agricultural practices, history of pesticide residue detection, and salmonid habitat. All sites represent a reach which drains agricultural lands and has hydraulic and salmonid connectivity to the outlying estuaries. Connectivity is altered by tidegates, although many are modified to allow fish passage. Big Ditch and Indian Slough sites are located upstream of their respective tidegates, and Browns Slough site is located on the seaward side of the Fir Island Road tidegate.

The climate in the lower Skagit-Samish basin is mild with cool, dry summers and mild, wet winters. The majority of annual precipitation occurs between October and March (Zalewsky and Bilhimer, 2004). Average minimum and maximum temperatures and average total precipitation by month are presented in Table 3 (Western Regional Climate Center, 2009).

Table 3 also presents mean monthly streamflow for the Samish River near Burlington, Washington at RM 10.3 (USGS, 2009). Highest air temperatures are seen in July and August. Average annual precipitation is 32.3 inches, with the heaviest rainfall November through January.

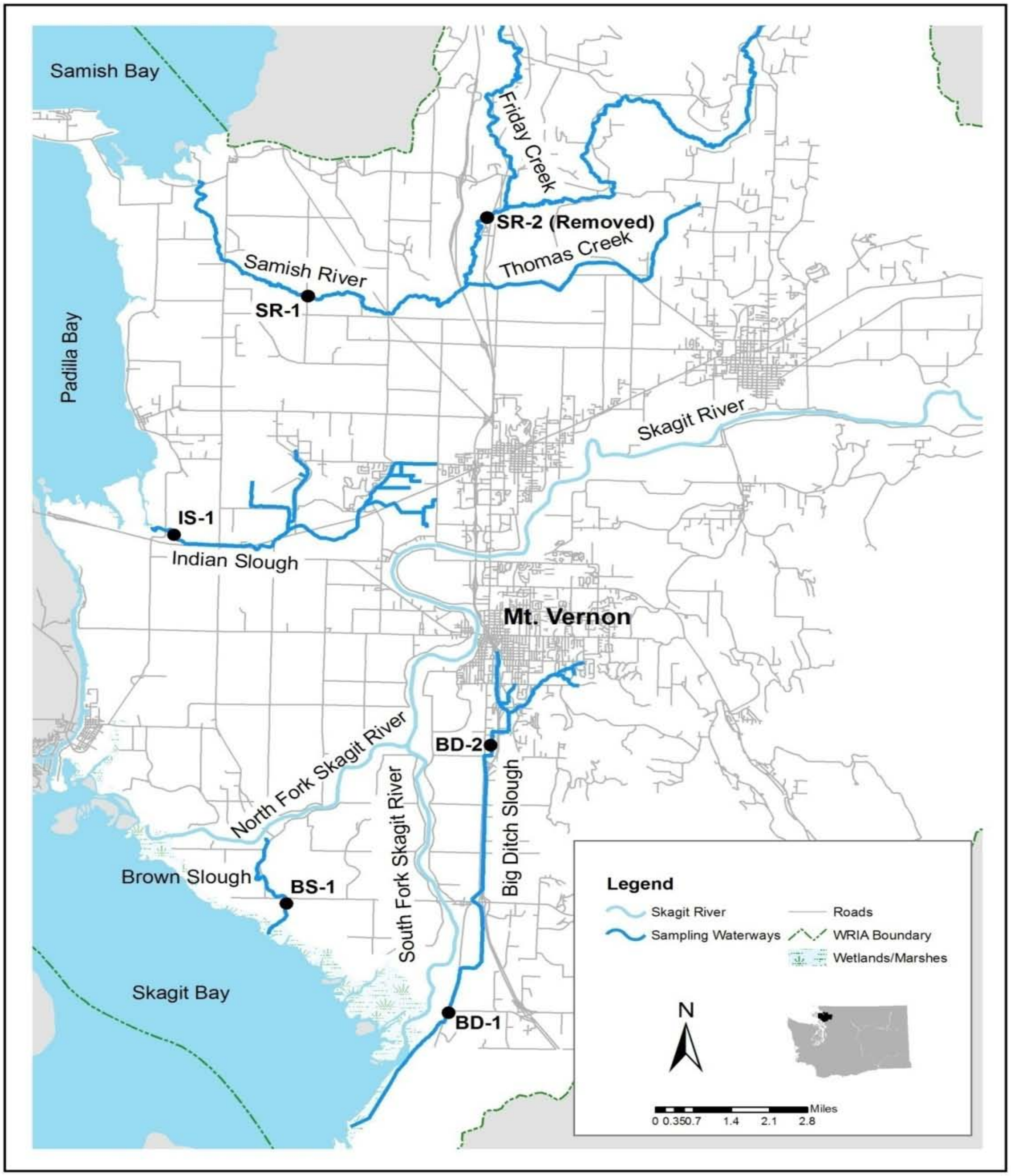


Figure 3. Sampling locations in the Lower Skagit-Samish basin.

Table 3. Average maximum and minimum temperatures and average precipitation for Mount Vernon weather station for 1956-2005 and average monthly streamflow at Samish River near Burlington for 1943-2007.

Average monthly totals	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Maximum temperature (°F)	45.5	49.2	52.8	57.7	63.9	68.6	73.2	73.8	68.6	59.4	50.7	45.9	59.1
Minimum temperature (°F)	33.6	35.1	37.1	39.9	44.7	48.8	50.6	50.9	47.0	41.9	37.8	34.6	41.8
Total precipitation (in.)	4.0	2.8	2.7	2.4	2.2	1.8	1.2	1.5	1.8	3.2	4.4	4.08	32.3
Monthly flow for Samish RM 10.3 (cfs)	514	447	350	280	172	106	58.0	38.7	46.4	145	336	448	244

Agricultural Land Use

All of the Skagit-Samish sites have a portion of their area in agricultural production. The most intensively cultivated subbasins are Browns Slough, Big Ditch, and Indian Slough (Table 4). Appendix C includes crop area and land-use estimates for the Skagit-Samish subbasins. Land coverage statistics presented are estimates due to the low topographic relief which makes accurate basin delineation difficult.

Table 4. Skagit-Samish subbasin summary land-use statistics.
All values are approximate.

Subbasin	Watershed Area (acres)	Cropped Area (acres)	Percent Cropped
Big Ditch	8000	4000	50%
Browns Slough	3400	3200	92%
Indian Slough	5000	1600	33%
Samish River	65000	4000	6%

Appendix C crop totals shows that a variety of agricultural commodities are produced in the Big Ditch drainage subbasin. Major crops include potatoes, wheat, hay, and corn. Land-use immediately upstream of the upper Big Ditch site is largely industrial. Browns Slough subbasin is mostly agricultural (92%). Major crops include potatoes, wheat, cucumber, peas, and corn. Major crops in the Indian Slough subbasin include hay, potatoes, wheat, blueberries, and sod. Samish River basin has the least cropped area acreage. Major crops include hay, potatoes, corn, and wheat.

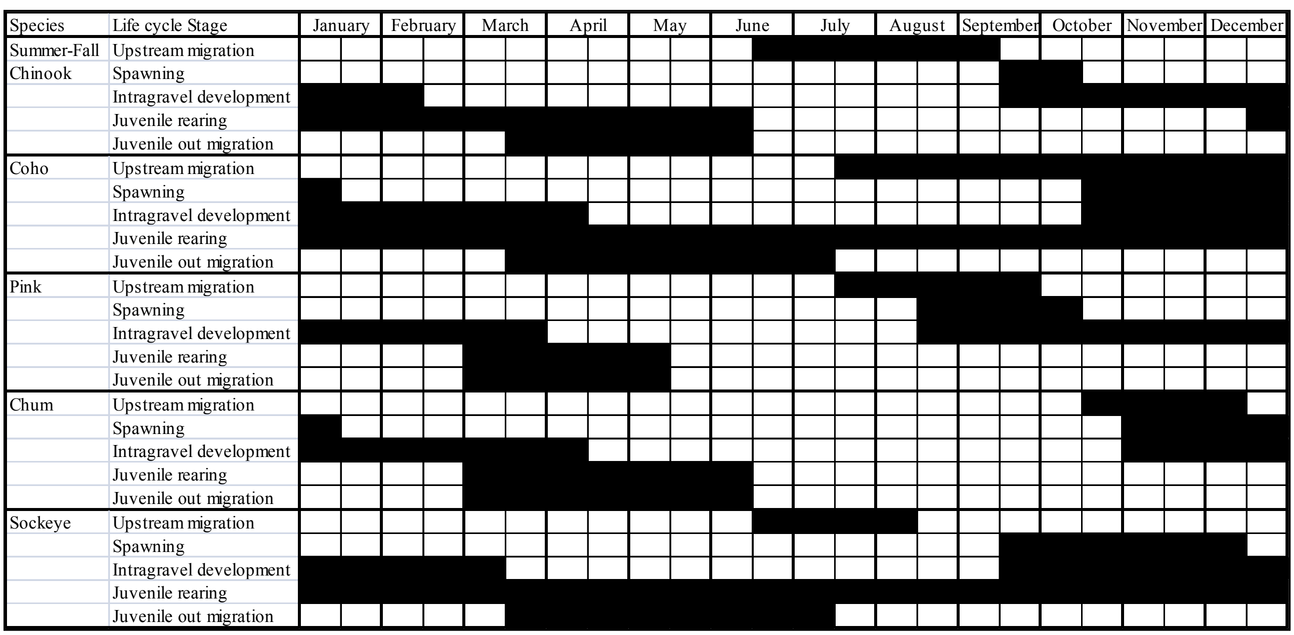
Salmonid Fishery

The Skagit-Samish supports several Puget Sound salmonid populations, described in Table 5. Table 6 summarizes the life phases and periods when salmonids are present in the Skagit-Samish basins (Washington Department of Fisheries, 1975). Black indicates periods of use, and white areas represent periods of little or no use.

Table 5. Salmonid presence and use of the Skagit-Samish sample sites.
(StreamNet, 2009; Burke and Anderson, 2006.)

Species	Big Ditch	Browns Slough	Indian Slough	Samish River
Fall chinook	--	Presence	Presence	Presence
Coho	Rearing	Presence	Presence	Rearing
Fall chum	--	Presence	--	Presence
Pink	--	Presence	--	Presence
Sockeye	--	--	--	Rearing
Bull trout	--	--	--	Presence
Winter steelhead	--	--	--	Rearing

Table 6. Timing of freshwater life phases for salmon in the Skagit-Samish basins.
(Washington Department of Fisheries, 1975.)



Salmonid habitat use is classified according to the highest level of habitat supported. The greatest value is placed on spawning habitat, followed by rearing, and then documented presence (occupation) of a fish species. All sites represent freshwater salmonid habitats; Browns Slough also includes wetland, and estuarine habitats.

The Samish River is well known for coho production; coho are found throughout the lower 27.5 miles of mainstem, the entire length of Friday Creek, and in most tributaries. In addition, chinook, steelhead, and chum have been recorded up to RM 25.2 in the mainstem Samish River, as well as in several tributaries. Pink and sockeye salmon have been recorded to about RM 10 in the Samish River (Smith, 2009).

Lower Yakima Basin (WRIA 37)

The Yakima River subbasin is located in south-central Washington and includes most of Yakima and Kittitas counties as well as small portions of Benton and Klickitat Counties. Most of the Yakama Nation Reservation is located within the subbasin (Figure 1).

The Yakima River drains an area of 6,155 square miles and contains about 1,900 river miles of perennial streams. Originating near the crest of the Cascade Range above Keechelus Lake, the Yakima River flows 214 miles southeastward to its confluence with the Columbia River.

The rainy season is November through January, when about half the annual precipitation occurs. Snowfall in the lower Yakima valley ranges from 20 to 25 inches, and from 75 inches at 2,500 feet to over 500 inches at the summit of the Cascades. Mountain snowpack provides most of the water for irrigated agriculture and streamflow (Haring, 2001).

The economic base of the Yakima basin is irrigated agriculture. The Yakima basin is among the leading agricultural areas in the United States. Livestock production and forestry are also important contributors to the area's economy. The major industries in the basin are related primarily to the processing of agricultural and forest products. The Yakama Nation Reservation in southern Yakima County comprises 25% of the bi-county area (Haring, 2001).

The Yakima and Naches Rivers supply irrigation water to approximately 339,000 acres of cropland in the lower Yakima valley. Most of the water in the Yakima River system is managed by the U.S. Bureau of Reclamation. Water distribution from canals to farm is primarily managed by irrigation districts. During the summer, the quality of agricultural return flows largely determines water quality in surface waters.

Irrigated agriculture in the Yakima subbasin is represented by three drainages:

- Marion Drain
- Sulphur Creek Wasteway
- Spring Creek

Figure 4 presents the locations of the six lower Yakima sample sites. Appendix B describes sampling locations and duration of sampling for each site.

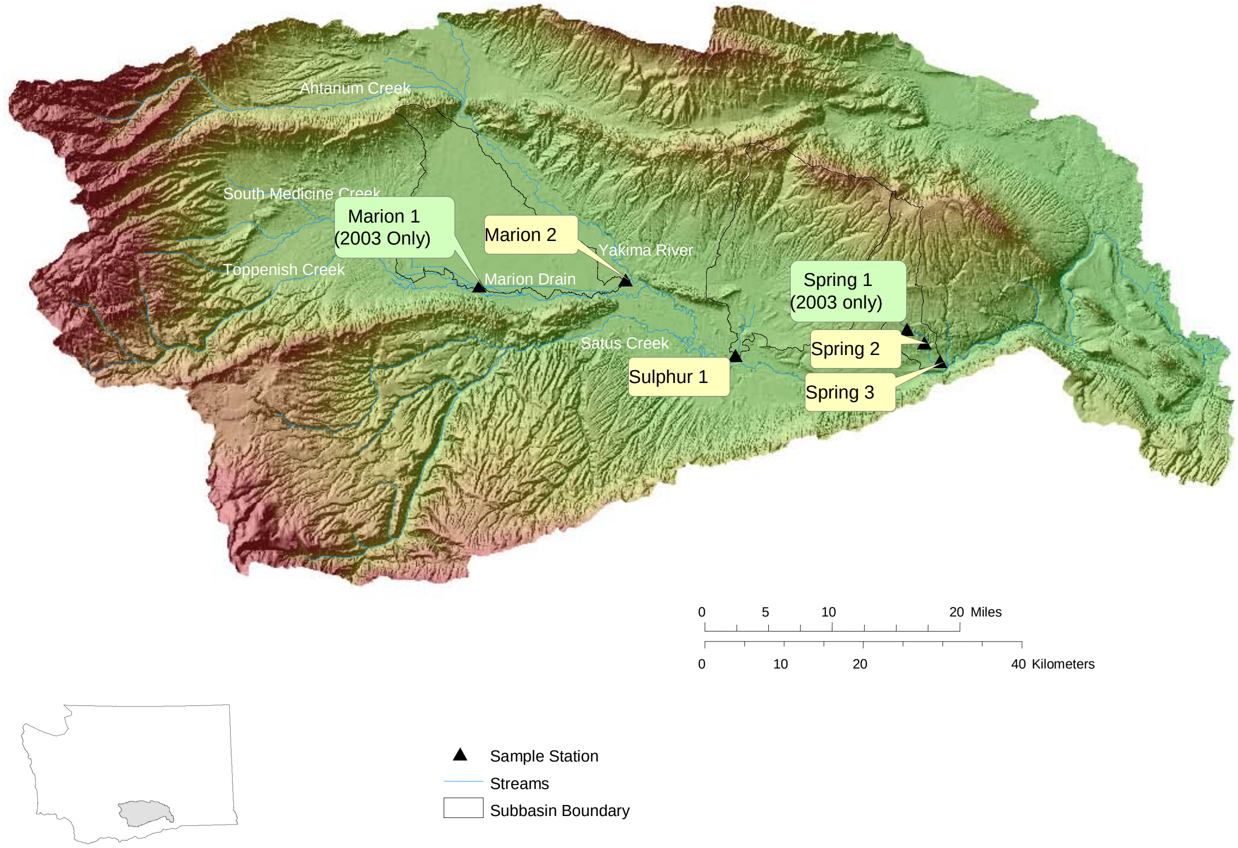


Figure 4. Sampling stations in Marion Drain, Sulphur Creek Wasteway, and Spring Creek in the Lower Yakima basin.

Marion Drain discharges into the Yakima River 2.2 miles upstream of the mouth of Toppenish Creek at RM 82.6. Marion Drain is a 19-mile-long drainage ditch with a watershed area of approximately 80,500 acres, collecting water from Harrah Drain, Toppenish Creek, Wanity Slough, and groundwater extrusion, all within the Yakama Nation lands. The Marion Drain watershed includes the communities of Harrah, Toppenish, Wapato, White Swan, and other unincorporated towns.

Sulphur Creek Wasteway is a highly channelized agricultural conveyance that discharges into the Yakima River at RM 61.0. Approximately 34% of the 103,000 acre watershed is in agricultural production. The Sulphur Creek Wasteway drainage includes the city of Sunnyside.

Spring Creek discharges to the Yakima River at RM 41.8. The Spring Creek drainage is 27,400 acres with 50% cropped area.

Agricultural Land Use

The Yakima sites represent irrigated cropland agriculture. Estimated crop area and land use by subbasin is presented in Appendix C. It is estimated about 66% of the Marion Drain subbasin is in agricultural production with major crops being hops, corn, apples, wheat, and a variety of vegetables. A total of 34% of the Sulphur Creek Wasteway drainage is in agricultural production; major crops include grapes, apples, corn, hay, and a variety of vegetable crops. The Spring Creek subbasin has about 50% of its area in agricultural production with major crops being wheat, grapes, apples, and hops.

Salmonid Fishery

The monitored drainages support a diverse assortment of salmonid species including fall chinook, spring chinook, coho, and summer steelhead. Of the fisheries, Mid-Columbia steelhead are designated threatened and have been documented in all three drainages. The Yakima River supports ESA-listed Upper Columbia River summer/fall chinook (river-type), Mid-Columbia River spring chinook (ocean-type), and Mid-Columbia River bull trout (Burke et al., 2006).

Table 7 presents the life phases and periods steelhead are present in the Yakima basin (Haring, 2001; Kohr, 2009).

Table 7. General life history of the Yakima basin summer steelhead during the March-October monitoring period (Haring, 2001; modification Kohr, 2009).

Life Stage	March	April	May	June	July	August	September	October
Spawning Run					1			
Incubation								
Emergence							2	
Fry Colonization								
0+ Summer Rearing								
0+ Winter Migration								
1+ Smolt Outmigration								
Overwintering	December through February. No pesticide sampling during this period.							

	Periods of heaviest use.
	Periods of moderate use.
Blank	Periods of little or no use.

1: Few out-migrating kelts during this month.

2: Higher elevation tributary use.

The majority of summer discharge in Marion Drain, Sulphur Creek Wasteway, and Spring Creek is comprised of irrigation return flows. Upstream migration of adult salmonids generally requires an environmental cue in the form of an "attraction flow" which provides a chemical or other type of signal to the fish that upstream conditions are suitable for migration and spawning.

So, bypasses and water diversions can present false migration pathways, which interfere with spawning and limit the success of salmonid populations.

For example, Marion Drain is a constructed conveyance which intercepts a portion of historical groundwater flow to Toppenish Creek. As a result, Marion Drain steelhead are likely ancestral Toppenish Creek fish. Marion Drain provides spawning habitat for fall chinook, summer steelhead, and resident fish. Coho have been observed in the drain (Burke et al., 2006).

Fish distribution in Sulphur Creek Wasteway includes spawning coho; however, suitable spawning gravels and low velocity habitat for emerging fry are rare. Salmonids are attracted to Sulphur Creek Wasteway by the high volume of irrigation return flows. Summer steelhead and fall and spring chinook presence have been documented in the Sulphur Creek Wasteway (Burke et al., 2006).

In November 2007, construction began on a fish barrier designed to prevent adult salmonids from entering Sulphur Creek Wasteway. Construction was completed in March 2008. The barrier was a cooperative project between the Yakama Nation, Rosa-Sunnyside Board of Joint Control, and Washington Department of Fish and Wildlife.

Fish distribution in the lower reach of Spring Creek includes spawning coho and rearing spring chinook. Coho, spring and fall chinook, and summer steelhead presence have been documented in the lower reach (Burke et al., 2006).

Wenatchee/Entiat Basin (WRIAs 45 and 46)

The Wenatchee River drains a portion of the east slopes of the Cascade Mountains in north-central Washington within Chelan County (Figure 1). The river flows generally in a southeasterly direction, emptying into the Columbia River at the City of Wenatchee. The Wenatchee River basin encompasses about 1,371 square miles. Wenatchee Lake is the source of the Wenatchee River. Major tributaries include the Chiwawa River and Icicle, Nason, Chumstick, Peshastin, and Mission Creeks. The primary land uses within the Wenatchee River subbasin are forestry, wilderness, agriculture, range, residential, and recreation.

The federal government is the largest landowner in the subbasin, with approximately 671,220 acres, 76% of the subbasin. Only 17% of the land is privately owned. Privately owned land occurs mostly in the low-lying valley bottoms and in the southern portion of the subbasin next to the Wenatchee River and along its major tributaries (Andonaegui, 2001).

The Wenatchee and Entiat watersheds support diverse salmon populations and produce a variety of agricultural commodities. Agriculture in the basins is dominated by orchard crops. Because previous studies showed pesticide detections in surface water, the Wenatchee-Entiat was added as an index watershed for evaluation of eastern Washington tree fruit agricultural practices (see Appendix F). Sampling of the Wenatchee-Entiat began in 2007 as described in Dugger et al. (2007).

Sampling is conducted at five sites in the Wenatchee-Entiat basin:

- Wenatchee River at RM 2.8
- Mission Creek at RM 3.1
- Brender Creek at RM 0.7
- Peshastin Creek at RM 0.1
- Entiat River at RM 1.4

Figure 5 presents the locations of the five sample sites. Appendix B describes sampling locations and duration of sampling for each site.

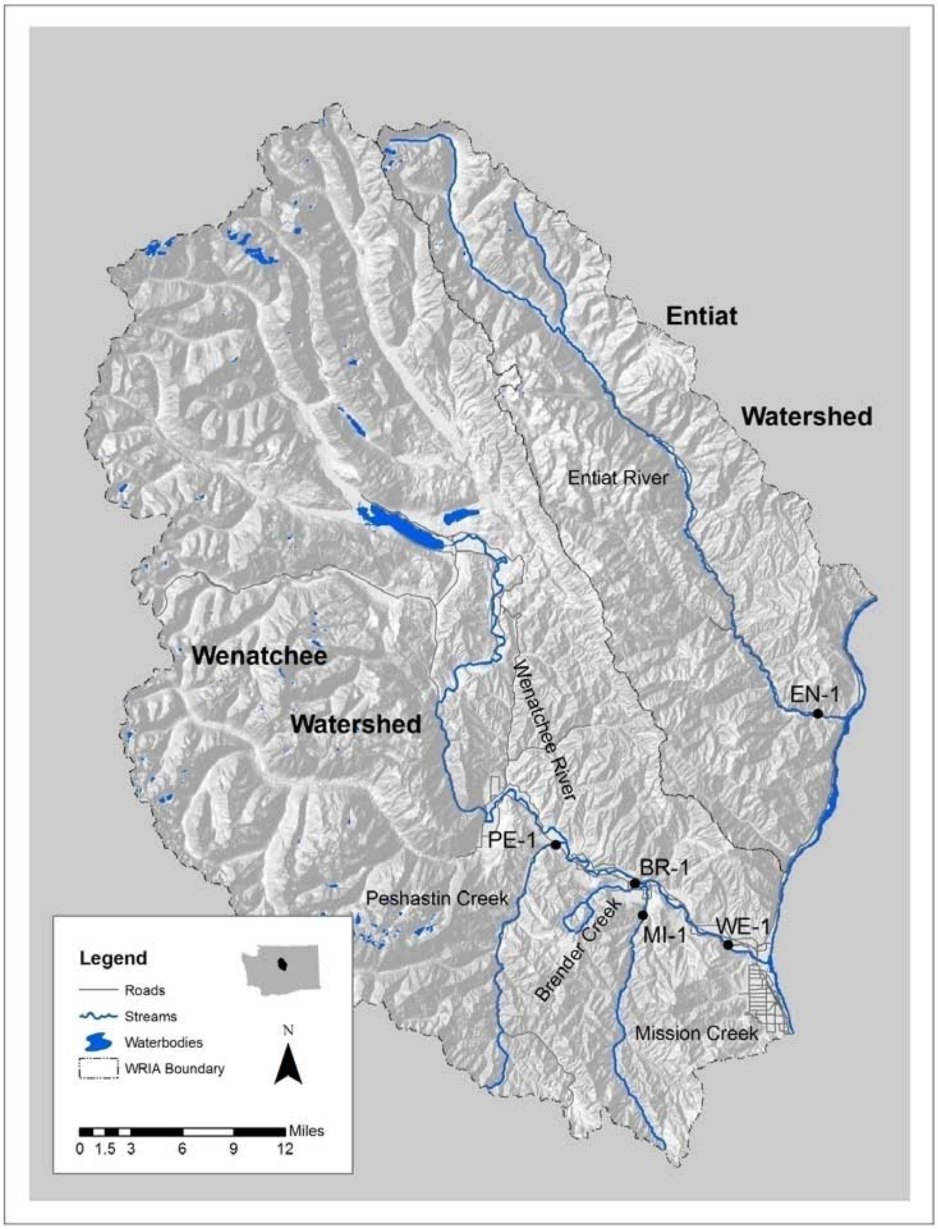


Figure 5. Location of sampling sites in the Wenatchee and Entiat basins.

The sampling sites are located to minimize the influence of residential areas. Brender Creek and the Wenatchee River have the highest percentage of cropped area among the five selected drainages. Brender Creek receives a substantial amount of flow from the Peshastin Canal, at times greater than 50% (Rickel, 2009). Brender Creek discharges into Mission Creek downstream of the confluence with Yaksum Creek. Peshastin and Mission Creeks discharge into the Wenatchee River, and the Wenatchee and Entiat Rivers discharge to the Columbia River.

In the Wenatchee basin, most precipitation occurs in late fall and winter. In the upper watershed, the Cascade Mountain area is characterized by heavy precipitation and snow, nearly 150 inches annually. Most of the precipitation occurs during the winter months as snow. Temperatures at Wenatchee range from a January average of 26 °F to a July average of 73 °F. As air masses move east toward the Columbia Basin, moisture progressively decreases, resulting in arid conditions within the lowermost region of the watershed. In contrast to the mountainous areas, the City of Wenatchee receives only 8.5 inches or less of precipitation annually, with maximum summer temperatures averaging 95-100 °F (Andonaegui, 2001). For the Wenatchee River at Monitor, the highest average monthly streamflows occur in May and June during spring snowmelt (Table 8) (USGS, 2008a).

Table 8. Average, maximum, and minimum streamflows (cfs) for the Wenatchee River at Monitor, 1963-2008 (USGS, 2008a).

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Mean	1067	2155	1982	1811	1954	2399	3939	8051	8818	4339	1437	788
Max.	3095	9636	6983	4309	5447	6853	7260	12970	17020	9880	3985	1628
Min.	346	426	556	527	518	995	1634	3565	2273	1015	425	301

Peshastin Creek is a tributary to the Wenatchee River, originating at Blewett Pass and flowing in a northeasterly direction for 15.4 miles before entering the Wenatchee River at RM 17.9, downstream of the town of Peshastin. Although it is one of the major subbasins in the Wenatchee basin in terms of size, Peshastin Creek contributes only 4% of the summer low flow in the Wenatchee River. The lower portion of the Peshastin Creek subbasin is more arid, with annual precipitation levels ranging from 80 inches in the upper elevations to 15 inches at the mouth of Peshastin Creek. The area in agricultural production is 0.6 percent (Andonaegui, 2001; Dugger et al., 2007).

The Mission Creek subbasin is 93 square miles (59,609 acres). Mission Creek flows 9.4 miles before discharging to the Wenatchee River at RM 10.4 at the town of Cashmere. The average annual precipitation is 19 inches with the Mission Creek subbasin. Mission Creek contributes only 1% of the average annual flow of the Wenatchee River. Approximately 0.5% of the acreage in Mission Creek is in agricultural production. Brender Creek enters Mission Creek at RM 0.2, within the town of Cashmere, just upstream of the mouth of Mission Creek. Approximately 12% of the Brender Creek subbasin is in agricultural production (Andonaegui, 2001; Dugger et al., 2007)

Flow characteristics in Mission and Brender Creeks are complicated by (1) diversions of surface water from Mission Creek, and (2) the influence of irrigation waters conveyed from Icicle and Peshastin Creeks into Mission and Brender Creeks. While reaches in both creeks have historically gone dry, currently Brender Creek has year-round flow due to irrigation return flows from the Peshastin Irrigation District (Andonaegui, 2001). At times Brender Creek receives more than 50% of its flow from the Peshastin Canal (Rickel, 2009).

The Entiat River basin is located in north-central Washington in Chelan County. It originates in a glaciated basin near the crest of the Cascade Mountains and flows southeasterly, meeting the Columbia River near the town of Entiat, about 20 miles upstream from Wenatchee. The drainage area is about 268,000 acres of which approximately 224,000 acres (84%) are in public ownership, primarily national forest. There are 1,300 acres of orchard land in the lower valley.

Mean annual precipitation in the Entiat basin ranges from 90 inches in the moist, alpine-type higher elevations to less than 10 inches in the arid shrub steppe of the lowest elevations. Most winter precipitation falls as snow; however, rain is not unusual. During the summer, mean temperatures in the lower Entiat watershed usually range from 60-70 °F, decreasing to the 50s (°F) at higher elevations (Andonaegui, 1999).

As with the Wenatchee River, the highest average monthly streamflows seen in the Entiat River occur in May and June during spring snowmelt (Table 9) (USGS, 2008b).

Table 9. Average, maximum, and minimum streamflows (cfs) for the Entiat River near Entiat, 1996-2008 (USGS, 2008b).

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Mean	149	207	164	176	176	271	572	1447	1614	700	241	136
Max.	301	508	316	330	290	623	1090	2277	2674	1682	655	232
Min.	89.4	99.7	101	108	92.1	125	165	673	497	213	93.5	71.2

Agricultural Land Use

The Wenatchee and Entiat basins produce a variety of agricultural products with orchard crops (tree fruit) being the major agricultural commodity. Appendix C has estimates of crop and land-use areas. In the Peshastin subbasin, the major crops are pears, apples, and cherries. Pears are the major products in the Mission Creek subbasin. Brender Creek has the greatest area in agricultural production (10%) with major crops being pears, apples, and cherries. Approximately 1% of the Wenatchee basin is in production with pear and apple orchards covering 0.9% of the basin.

Salmonid Fishery

A summary of salmonid distribution and use is presented in Table 10. Salmonid distribution and habitat is classified according to the highest level of habitat supported. The greatest value is placed on spawning habitat, followed by rearing and migration. Habitat is classified for the reach where the sample station is located; higher quality habitat may be available in the upper watershed. Tables 11, 12, and 13 present the life phases and periods when salmonid species are present in the lower Wenatchee River, and Peshastin and Mission Creeks (EES Consulting Inc. and Thomas R. Payne & Associates, 2005). Entiat River salmonid life phases and periods of use are presented in Table 14 (Chelan County Conservation District, 2004). Periods of heaviest fish use are in black, periods of moderate use are in gray, and periods of little or no use are in white.

Table 10. Salmonid presence and use for the Wenatchee-Entiat sample sites.
(StreamNet, 2009; Burke, 2006.)

Species	Wenatchee River	Mission Creek	Brender Creek	Peshastin Creek	Entiat River
Spring chinook	Rearing	Rearing	--	Rearing	Rearing
Summer chinook	Spawning	Spawning	Presence	--	Presence
Coho	--	--	--	--	Spawning
Sockeye	Rearing	--	--	--	Presence
Bull trout	Rearing	--	--	Presence	Presence
Summer steelhead	Rearing	Spawning	Presence	Rearing	Spawning

Table 11. Timing of salmonid life phases in the lower Wenatchee basin.
(EES Consulting, Inc. and Thomas R. Payne & Associates, 2005.)

Species	Life Stage	October	November	December	January	February	March	April	May	June	July	August	September
Spring	Spawning												
Chinook	Incubation												
	Rearing												
	In-migration												
Summer	Spawning												
Chinook	Incubation												
	Rearing												
	In-migration												
Steelhead	Spawning												
	Incubation												
	Rearing												
	In-migration												
Bull Trout	Spawning												
	Incubation												
	Rearing												

Table 12. Timing of salmonid life phases in the Peshastin Creek basin.
(EES Consulting, Inc. and Thomas R. Payne & Associates, 2005.)

Species	Life Stage	October	November	December	January	February	March	April	May	June	July	August	September
Spring	Spawning												
Chinook	Incubation												
	Rearing												
	In-migration												
Steelhead	Spawning												
	Incubation												
	Rearing												
	In-migration												
Bull Trout	Spawning												
	Incubation												
	Rearing												

Table 13. Timing of salmonid life phases in the Mission Creek basin.

(EES Consulting, Inc. and Thomas R. Payne & Associates, 2005.)

Species	Life Stage	October	November	December	January	February	March	April	May	June	July	August	September
Spring	Spawning												
Chinook	Incubation												
	Rearing												
	In-migration												
Summer	Spawning												
Chinook	Incubation												
	Rearing												
	In-migration												
Steelhead	Spawning												
	Incubation												
	Rearing												
	In-migration												

Table 14. Timing of salmonid life phases in Entiat River basin.

(Chelan County Conservation District, 2004.)

Species	Life Stage	January	February	March	April	May	June	July	August	September	October	November	December
Late Run	Spawning												
Chinook	Incubation												
	Emergence												
	Fry Colinization												
	0-Age Active Rearing												
	0-Age Migrant												
	Prespawning migrant + Holding												
Spring	Spawning												
Chinook	Incubation												
	Emergence												
	Fry Colinization												
	0-Age Active Rearing												
	0-Age Migrant												
	1-Age Transient Rearing												
	Prespawning migrant + Holding												
Steelhead	Spawning												
	Incubation												
	Emergence												
	Fry Colinization												
	0-Age Active Rearing												
	0-Age Migrant												
	1-Age Resident Rearing												
	1-Age Transient Rearing												
	2+-Age Transient Rearing												
	Prespawning migrant + Holding												

Study Design and Methods

Study design and methods for this study are described in the Quality Assurance (QA) Project Plan (Johnson and Cowles, 2003), subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007, and Anderson and Sargeant, 2009), and the first triennial report (Burke et al., 2006). Study design and methods are much the same as during the 2003-2005 monitoring period. Major changes to the program for 2006-2008 are described below.

Sample Sites and Sampling Frequency

Sampling sites and frequency have varied over the past six years. The 2003 effort was primarily exploratory and focused on different sampling regimes that would yield the most useful results. Sampling sites and frequency for 2003-2005 are described in the first triennial report (Burke et al., 2006). Using an adaptive approach, monitoring subsequent to 2003 was adjusted to focus on periods with the maximum likelihood of detecting pesticide residues. Sampling sites in the first three years varied slightly and are also described in Burke et al. (2006). For the 2006-2008 period, the sampling regimes and sites were as follows:

2006

The Skagit-Samish basin study area was added. Five sites were sampled including two sites on the Samish River and sites on Indian Slough, Brown Slough, and Big Ditch. Detail on site locations can be found in the 2006 Annual Report (Anderson et al., 2007). The Skagit-Samish sites were sampled for 29 weeks from the first week in March into the second week in September.

Thornton Creek and the lower Yakima basin sites were monitored weekly for 24 weeks, from the first week in April through the second week in September. The upstream sites on Thornton and Spring Creeks were only sampled every other week due to budget constraints. Marion Drain sampling was extended through the end of October due to historic organophosphate detections during this period.

2007

The Wenatchee/Entiat basin study area was added. Site selection was based on the presence of both tree fruit agriculture and salmonid presence in the basin. Five sites were sampled including sites on the Wenatchee River, Mission Creek, Peshastin Creek, Brender Creek, and the Entiat River. Detail on site locations can be found in the 2007 Annual Report (Anderson and Dugger, 2008).

For 2007, sampling began in February, approximately one month earlier than in past years, and continued through the second week in September, for a total of 31 weekly sample events at most sites. As in 2006, the upstream sites on Thornton Creek and Spring Creek were sampled every other week. From September 5 to the end of the sample season, the Mission Creek site was dry. During this period, water samples and measurements were collected at a site 0.6 miles upstream.

In 2007, the upstream site on the Samish River was discontinued, and the site was moved to an upstream site on Big Ditch. As in 2006, Marion Drain sampling extended through October.

In conjunction with this project, staff conducted an intensive 22-day pesticide sampling effort in Marion Drain during the spring of 2007 to compare daily and weekly sampling frequencies using conventional grab samples and passive sampling devices. A full report for this monitoring project can be found at: www.ecy.wa.gov/biblio/0803020.html (Dugger et al., 2008).

2008

For 2008, sampling began the second week of March and continued through the second week of September for a total of 27 weekly sample events at most sites. As in 2007, the upstream site on Thornton Creek and Spring Creek were sampled every other week, and Marion Drain sampling was extended through the end of October.

From August 19 through September 8, 2008, the Mission Creek site had very little flow or was dry. For this reason, a new sampling site was used upstream 0.6 miles on these dates.

Field Procedures

Field procedures are defined in the QA Project Plans (Johnson and Cowles, 2003; Burke et al., 2006). Any changes to the original plan are documented in the first triennial report and yearly monitoring reports (Burke et al., 2006; Anderson et al., 2007; and Anderson and Dugger, 2008) and in QA Project Plan addendums (Burke and Anderson, 2006; Dugger et al., 2007; and Anderson and Sargeant, 2009).

Field methods are a direct application or modification of USGS or EPA procedures. Surface water samples were collected by hand-compositing grab samples from quarter-point transects across each stream. In situations where streamflow was vertically integrated, a one-liter transfer container was used to dip and pour water from the stream into sample containers. Otherwise samples were collected using depth integrating equipment. Sample/transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA, 1990). After collection, all samples were labeled and preserved according to the QA Project Plan (Johnson and Cowles, 2003).

Temperature, pH, and conductivity were measured in the field using Environmental Assessment Program sampling protocols (Swanson, 2007). In 2008, dissolved oxygen (DO) was also measured (grab samples) by Winkler Titration following Environmental Assessment Program protocol (Ward, 2007). Continuous, 30-minute interval, temperature data were collected year-round from 2006-2008. Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Wagner et al., 2000; USGS, 2006a).

Discharge for sites other than Sulphur Creek Wasteway, Wenatchee River, and Entiat River are measured using a Marsh-McBirney flow meter and top-setting wading rod, as described in the USGS method for "Measurement of Discharge by Conventional Current-Meter Method" (Rantz et al., 1983). Discharge data for Sulphur Creek Wasteway was obtained from an adjacent

U.S. Bureau of Reclamation gaging station, "SUCW – Sulphur Creek Wasteway at Holaday Road near Sunnyside". Wenatchee and Entiat River discharge was obtained from USGS at the Wenatchee River at Monitor (Station 12462500) and Entiat River near Entiat (Station 12452990). Fifteen-minute discharges were available during the sampling period. The record closest to the actual sampling time was used in lieu of field measurements.

Laboratory Analyses

Manchester Environmental Laboratory (MEL) analyzed all pesticide and total suspended solids (TSS) samples. Laboratory methods for the 2006-2008 period are presented in Table 15. The methods employed in 2003-2005 differed for certain pesticide analysis, as described in Burke et al. (2006). A list of target analytes for 2006-2008 is presented in Appendix D, Table D-3. Laboratory methods are also discussed in the QA Project Plans (Johnson and Cowles, 2003, amended in Burke et al., 2006), and monitoring reports (Anderson et al., 2004; Burke et al., 2005).

Table 15. Summary of laboratory methods, 2006-2008.

Analyte	Analytical Methods[1]		
	Extraction	Analysis	Reference
Pesticides[2]	3510	GC/MS	8270
Herbicides	8151	GC/MS	8270
Carbamates	3535M	HPLC	8321 AM
Total Suspended Solids	n/a	Gravimetric	EPA 160.2

[1]All analytical methods refer to EPA SW 846, unless otherwise noted.
[2]Pesticides refers to all forms tested unless indicated otherwise.
GC: gas chromatograph.
HPLC: high performance liquid chromatography.
MS: mass spectrometry.
n/a: not applicable.

The 2006-2008 changes in laboratory methods include:

- In 2006, carbamate analyses and confirmation for the herbicides diuron and linuron were by Liquid Chromatography coupled with Mass Spectrometry (LCMS; EPA SW 846 method 3535M for solid phase extraction and 8321AM modified). Previous laboratory analysis used High Performance Liquid Chromatography (HPLC; EPA Method (modified) 8318/531.1M) or Gas Chromatography coupled with mass Spectrometry (GCMS; EPA Method (modified) 3510/8270M).
- In 2007, MEL changed the reporting limits for carbamates. MEL determined that reporting limits had been too low, which increased the chance of false positives. The change in reporting limits was documented in the MEL Week 18 case narrative (April 30-May 4, 2007). Changes in the reporting limits are documented in the 2007 data summary (Anderson and Dugger, 2008).
- In 2008, imidacloprid (a neonicotinoid insecticide) analysis was added to the pesticide analysis profile.

Laboratory and Field Data Quality

Laboratory Data Quality

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. The QA/QC protocol employs diverse application of blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSD). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. Highlights of laboratory and field data quality are presented below; for a detailed discussion refer to Appendix D.

Laboratory Blanks

Very few laboratory blank detections occurred for the pesticide GCMS or for the herbicide analysis (Appendix D, Table D-9). There were several laboratory blank detections for the low-level carbamate and imidacloprid analysis.

Carbamate Field Blank Detections

Across basins, field blank detections of certain carbamate compounds indicated problems with select carbamate parameters: 1-napthol, aldicarb sulfone, and aldicarb sulfoxide. During 2009 an anomaly in the analytical method for carbamate pesticides was identified. This analytical anomaly caused false positive identification of these compounds. Data for these parameters are not reported. Although QA/QC criteria were met for all reported carbamate values, there is a possibility of some false positives.

During the same period there were also occasional laboratory blank detections for carbamate compounds: seven detections of promecarb, five detections of oxamyl, two detections of aldicarb, and one detection of methomyl and oxamyl oxime. There was also one detection of the neonicotinoid, imidacloprid. All detections were below the year's lower practical quantification limits (LPQL) with the exception of six promecarb detections and one aldicarb, oxamyl, and oxamyl oxime detection.

Field Blanks

Field blank detections indicate the potential for sample contamination in the field and laboratory and the potential for false detections due to analytical error. No field blank contamination was detected in 2006.

In 2007, dichlobenil was found in one field blank at a concentration higher than the sample and above the LPQL. Thus dichlobenil was qualified as tentatively undetected (UJ) in the associated sample. In addition, one TSS field blank was contaminated; the TSS concentration for that site was qualified as an estimate.

In 2008, promecarb contamination was found in three field blanks above the LPQL. Promecarb was not found in the associated samples. Thus, no sample detections were qualified.

Replicate Results

Replicate sampling tests the reproducibility or precision of sampling results. Field replicate sampling frequency increased from 4% of samples in 2006 to 8% of samples in 2008. During 2006-2008, 3% of the replicate analysis pairs had a detection (number value) in at least one replicate. When a sample and its replicate have results below detection limits, that is a valid result but it does not tell us how precise results are. When the sample and the replicate have a detected value (number value), then we can compare the values to determine how reproducible our results are.

For instances where detections occurred in both the sample and its replicate, the average relative percent difference (RPD) was low, 11% (Appendix D, Table D-6). Similarly, the median pooled relative standard deviation (RSD) of all replicates was 8%. This variation is lower than our 2003-2005 results (14%; Burke et al., 2006). This variation is also lower than the USGS National Water Quality Assessment (NAWQA) median pooled RSD of 15% at concentrations < 0.01 µg/L and 12% at concentrations near 0.1 µg/L (Martin, 2002). This indicates that data obtained for this study have good reproducibility or precision.

Surrogates and Matrix Spikes

Surrogates are used to evaluate recovery for a group of compounds. Except for dioxocarb, the majority of surrogate recoveries fell within the control limits established by MEL. Dioxocarb was used as a surrogate for carbamate pesticides in early 2006. For this period, all carbamate analyses were qualified as estimates. Carbaryl-C13 then replaced dioxocarb as the carbamate surrogate. Carbaryl-C13 was not an option as a surrogate until MEL transitioned to the LC/MS analysis, as it was impossible to distinguish Carbaryl-C13 from the native carbaryl compound when using HPLC. After making the instrument change, Carbaryl-C13 proved to be a better surrogate than dioxocarb when evaluating recovery of the carbamate compounds.

Matrix Spike/Matrix spike duplicates (MS/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. The average recovery of matrix-spiked compounds was 83%, and the average RPD between MS/MSD pairs was 17%. For most compounds, the recovery and RPDs of MS/MSD pairs showed acceptable performance, and were within defined limits for the project. Results with an average RPD outside the ± 40% criteria, the data were qualified as estimates.

Field Data Quality

Field meters were calibrated at the beginning of the field day according to manufacturers' specifications, using Ecology standard operating procedures (Swanson, 2007). Meters were post- checked at the end of the field day using known standards. DO meter results were compared to Winkler laboratory titration results from grab samples. Dissolved oxygen meter readings failed the QC objectives, varying from the more accurate Winkler titration results by greater than 10% RSD. Meter DO data were therefore discarded. All reported DO concentrations are obtained from grab samples and Winkler titration measurements.

To determine comparability of field methods, a side-by-side field audit was conducted on July 10, 2008. Comparison of field meter results for temperature, conductivity, streamflow, and Winkler DO measurements met established criteria. The pH results varied more than expected, but results remained within QC requirements for the meters +/- 0.2 standard units (s.u.), with a difference of 0.4 s.u. between the meters.

Data Analysis Methods

Field and laboratory data were compiled and organized using Excel® spreadsheet software and Access® data base software (Microsoft Corporation, 2001). Water quality results from field and laboratory work were also entered into Ecology's Environmental Information Management (EIM) database (www.ecy.wa.gov/eim).

Protocols for Analysis of Pesticide Data

The following guidelines were used in reporting and analyzing data for this report:

Pesticide Detections

Laboratory data were qualified as needed, and qualifiers are described in Table 16. A positive pesticide detection included un-qualified values and values qualified with a J or E. Values qualified with NJ, U, or UJ were considered non-detects.

Table 16. Definitions of data qualifiers.

Qualifier	Definition
No qualifier	The analyte was detected at the reported concentration. Data are not qualified.
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.
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 QC 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.

MEL, 2000, 2008; EPA, 1999, 2007.

Comparison to Assessment Criteria and Water Quality Standards

Non-detect values (U, UJ, N, NJ) were not used for comparison to assessment criteria or water quality standards. When summing compound totals (such as total DDT, total endosulfan), the Toxic Studies Unit Guidance was used (Ecology, 2008). Non-detects (U, UJ) were assigned a value of zero (as in the guidance). Unlike the guidance, NJ values (tentatively identified compounds) were also assigned a value of zero.

Data Analysis

Graphs, plots, mass balance calculations, and some statistical analyses are made using Excel® software. For statistical trend analysis, WQHYDRO software (Aroner, 2002) is used.

Replicate Values

Field and laboratory replicates were obtained to determine data quality. For comparison to assessment criteria and water quality standards, and for data analysis purposes, field and laboratory replicates were arithmetically averaged. If the sample value or the replicate value was a non-detect value while the other value was a detection, then the detected value was used.

When a laboratory replicate was performed on a field replicate, the laboratory replicate mean was calculated before the field replicate mean.

For select statistical analysis, NJ qualified data were used when detected pesticide values were not available. When this occurred, it is specified in the statistical test description.

Statistical Analysis

Summary Statistics

For this 2006-2008 study, the laboratory analyzed samples for over 160 pesticide and degradate compounds. For a majority of compounds, concentrations were below the analytical reporting limit of the laboratory and were reported as “less than” the reporting limit. These “less-than” reporting limit values make it difficult to analyze data statistically. Substituting a value of zero or a value half the detection limit is not defensible, and results may vary depending on the substituted value selected.

For estimating summary statistics, the Kaplan-Meier estimate is used. Helsel (2005) describes several methods for estimating summary statistics for data sets which include a large portion of non-detect data and data sets where reporting limits vary. Helsel (2005) recommends the Kaplan-Meier estimate for non-parametric estimation of summary statistics. While the Kaplan-Meier estimate is fundamental to survival data analysis, it is often overlooked when a left or right censored data arises in other settings (Helsel, 2005). For Kaplan-Meier analysis, NJ (analyte was tentatively identified) qualified data values were used. The Excel® worksheet for computing Kaplan-Meier was downloaded from the Practical Statistics web-site (Helsel, 2009). U and UJ qualified values were considered values less than the detection limit and were treated as such.

Correlations

Correlation analysis was used to examine the association between pesticide concentrations and variables such as TSS, flow, and rainfall (day of rainfall, the sum of day of rainfall and previous 24-hour rainfall, previous 24-hour rainfall, and previous 48-hour rainfall). A two-tailed, Kendall's tau-b, a non-parametric correlation coefficient, was used to test for correlation between parameters. Non-detect values (U, or UJ qualified) were assigned a pesticide concentration of zero. NJ qualified data were used in this test. For pesticides and TSS, the data were first graphed and visually inspected to select data for analysis. Selected periods during the sample season were tested where appropriate. Some pesticides are only seen during a select period; this minimizes the number of non-detect data in the analysis.

Differences in Number of Detections

To determine if pesticide detections have decreased over time, a statistical test procedure for testing differences between two proportions is used (Zar, 1984). Pesticide groups (herbicide, insecticide, and degradate compounds) were tested individually using a two-tailed test. Qualified data (N, NJ, U, UJ) were not considered detections for this test.

Assessment Criteria and Washington State Water Quality Standards

Assessment of pesticide effects to endangered salmonid species is evaluated by comparing detected pesticide concentrations against three criteria:

- Pesticide registration toxicity and risk assessment criteria.
- EPA National Recommended Water Quality Criteria (NRWQC).
- Washington State water quality standards for the protection of aquatic life (WAC 173-201A).

The EPA and Washington State aquatic life criteria are based on evaluating the effects of a single chemical on a specific species (often non-salmonid) and do not take into account the effects of multiple chemicals or pesticide mixtures on an organism.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix E. Numeric exceedances of values in Appendix E do not necessarily indicate that the water quality criteria have been exceeded. There is typically a temporal duration of exposure criteria in addition to numeric criteria for a water quality standard. In this report, pesticide registration toxicity and risk assessment criteria, and EPA NRWQC will be referred to as *assessment criteria*. Washington State numeric water quality standards for pesticides will be referred to as *water quality standards*.

Pesticide Registration Toxicity Criteria

The EPA uses risk quotients (RQ) to assess the potential risk of a pesticide to non-target organisms. A RQ is calculated by dividing the environmental concentration by either an acute or chronic toxicity value, which gives an evaluation of exposure over toxicity. The resulting RQ is a unitless value that is compared to Levels of Concern (LOC). The LOCs set by EPA are presented in Table 17 and are used to assess the potential risk of a pesticide to non-target organisms.

The endangered species LOC (0.05 for aquatic species) is used as a comparative value to assess potential risk to threatened or endangered salmonids. The endangered species RQ can also be expressed as 1/20th of the acute Lethal Concentration 50 (LC_{50}) for aquatic organisms. To assess the potential risk of a pesticide to salmonids, the LC_{50} for rainbow trout is commonly used as a surrogate species. Thus the endangered species LOC presented in subsequent tables are 1/20th of the rainbow trout LC_{50}. When available, the endangered species LOC for specific salmonids is also presented.

Table 17. Risk quotient criteria for direct and indirect effects on aquatic organisms.

Test Data	Risk Quotient	Presumption
Acute LC_{50}	>0.5	Potentially high acute risk.
	>0.1	Risk that may be mitigated through restricted use classification.
	>0.05	Endangered species may be affected acutely, including sublethal effects.
Chronic NOEC	>1	Chronic risk; endangered species may be affected chronically, including reproduction and effects on progeny.
Acute invertebrate LC_{50}	>0.5	May be indirect effects on T&E fish through food supply reduction.
Aquatic plant acute LC_{50}	>1	May be indirect effects on aquatic vegetative cover for T&E fish.

(Turner, 2003).
NOEC - No observable effect concentration.
T&E – Threatened and endangered.

Acute toxicity is calculated by standardized toxicity tests using lethality as the measured criteria. A properly conducted test will use a sensitive (representative) species, at a susceptible life stage (usually young, though not immature). The test also will subject the test species to a pesticide under a range of concentrations (minimum: no effect, 50% and 100% mortality). The dose response curve may be calculated, and the LC_{50}, lethal concentration to cause mortality in 50% of test species will be derived. For fish, the lethality test is conducted over 96 hours at a constant concentration. Acute invertebrate toxicity is normally calculated over 48 hours, with the criteria being mortality or immobility (LC_{50}, or Effective Concentration - EC_{50} for immobility). Acute toxicity testing for aquatic plants is conducted over 96 hours, and the criterion is reduction in growth (EC_{50}).

Chronic fish tests normally use reproductive effects or effect to offspring as the criteria. The dose response curve is evaluated to determine a no observable effect concentration (NOEC). The chronic toxicity test is longer than the 96-hour acute test (21 day for fish, 14 days for invertebrates, 5 to 60 days for plants) to simulate exposure resulting from a persistent chemical, or effect of repeated applications.

Toxicity values such as those used for pesticide registration are determined from continuous exposure over time (e.g., LC_{50} freshwater fish acute toxicity tests are run for 96 hours at a constant concentration). When comparing the monitoring data either to the aquatic life criteria or directly to the toxicity criteria, one must consider the duration of exposure as well as the numeric toxicity value. For pesticide registration criteria, it is not possible to determine if an aquatic life criterion has been exceeded based solely on an individual sample because the sampling frequency is usually weekly which does not allow for assessment of the temporal component of the criteria.

National Recommended Water Quality Criteria

The NRWQC are established by the EPA Office of Water for the protection of aquatic life, as established under the Clean Water Act (33 U.S.C. 1251 et. seq.). The pesticide criteria established under the Clean Water Act are closely aligned with invertebrate acute and chronic toxicological criteria. States often adopt the NRWQC as their promulgated (legal) standards. The NRWQC was updated in 2006, and those criteria are used in this report (EPA 2006).

Washington State Water Quality Standards

Pesticides

Washington State water quality standards are established in the Washington Administrative Code (WAC), Chapter 173-201A. Washington State water quality standards include numeric pesticide criteria for the protection of aquatic life.

The aquatic life criteria are designed to protect for both short-term (acute) and long-term (chronic) effects of chemical exposure. The criteria are primarily intended to avoid direct lethality to fish and other aquatic life within the specified exposure periods. The chronic criteria for a number of the chlorinated pesticides are to protect fish-eating wildlife from adverse effects due to bioaccumulation.

The exposure periods assigned to the acute criteria are expressed as: (1) an instantaneous concentration not to be exceeded at any time, or (2) a one-hour average concentration not to be exceeded more than once every three 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 four-day average concentration not to be exceeded more than once every three years on the average. For 303(d) listing purposes, measurements of instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards for both acute and chronic criteria, unless additional measurements are available to calculate averages (Ecology, 2006).

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix E.

Water Quality Standards for Temperature, pH, and Dissolved oxygen

Washington State water quality standards for conventional water quality parameters are set forth in Chapter 173-201A of the WAC. 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 in this study.

Why are Conventional Water Quality Parameters Important for Fish?

Temperature

Water temperature affects the physiology and behavior of fish and other aquatic life. Salmonids require cool, well-oxygenated water to survive. Many laboratory studies have shown that elevated water temperatures can have a number of negative effects on salmonids such as the following (Ecology, 2000):

- Decreased supply of oxygen: Higher water temperatures lower the availability of dissolved oxygen by reducing its solubility. When dissolved oxygen levels are low, fry emerge late, are smaller and less healthy, and have reduced survival rates due to predation, disease, and starvation.
- Disrupted metabolism: Elevated temperatures accelerate the metabolism, respiration, and oxygen demands of fish and other aquatic life.
- Increased susceptibility to toxins: The toxicity of many substances to salmonids intensifies as water temperature rises.
- Increased vulnerability to disease: Many fish diseases spread more rapidly at higher water temperatures. A substantial amount of research demonstrates that many fish diseases become considerably more virulent at water temperatures over 16 °C. Additionally, salmonids are weakened by higher temperatures and are more susceptible to disease; even if infected fish do not die from the disease, they are more susceptible to predation and are less able to compete for food.

Water temperature levels fluctuate over the day and night in response to changes in climatic conditions and river flows. Since the health of aquatic species is tied predominantly to the pattern of maximum temperatures, the criteria for temperature is expressed as the highest 7-day average of the daily maximum temperatures (7-DADMax) occurring in a waterbody.

Dissolved Oxygen

Aquatic organisms are very sensitive to reductions in the level of dissolved oxygen in the water. The health of fish and other aquatic species depends on maintaining an adequate supply of oxygen dissolved in the water. Oxygen levels affect growth rates, swimming ability, susceptibility to disease, and the relative ability to endure other environmental stressors and pollutants. While direct mortality due to inadequate oxygen can occur, the state designed the criteria to maintain conditions that support healthy populations of fish and other aquatic life.

Oxygen levels can fluctuate over the day and night in response to changes in climatic conditions as well as the respiratory requirements of aquatic plants and algae. Since the health of aquatic species is tied predominantly to the pattern of daily minimum oxygen concentrations, the criteria are the lowest one-day minimum oxygen concentrations that occur in a waterbody (Ecology, 2002; Carter, 2008).

pH

pH is a measure of how acidic or alkaline the water is. Optimal pH levels to support fish and wildlife should range from 6.5 to 9.0. A pH of 7 is neutral. pH can affect the solubility of metal compounds. The solubility of many metal compounds changes greatly with pH; generally a reduction in pH increases the solubility of heavy metals. When more metals are dissolved in the water, aquatic life may absorb them faster. Therefore, a lower pH (more acidic) may make these metals more toxic to aquatic life (Carter, 2008).

Numeric Water Quality Standards

Thornton Creek Beneficial uses include *Core Summer Salmonid Habitat* and *Extraordinary Primary Contact Recreation*. The numeric water quality standards for temperature, dissolved oxygen, and pH in Thornton Creek are described in Table 18. This table also includes supplemental spawning and incubation criteria for temperature during the September 15 - May 15 period.

Table 18. Freshwater water quality standard for temperature, dissolved oxygen, and pH for core summer salmonid habitat use and *Extraordinary Primary Contact Recreation.*

Parameter	Condition	Value
Temperature	Highest 7- DADMax	16º C. Thornton Creek has *Supplemental Spawning and Incubation* criteria: During the September 15 - May 15, period highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	9.5 mg/L.
pH	--	Range within 6.5 – 8.5, with a human-caused variation within the above range of < 0.2 units.

DADMax: Daily average of the daily maximum temperature.

Skagit-Samish basins: Beneficial uses for the Samish River, Indian Slough, Big Ditch, and Browns Slough include: *Salmonid Spawning, Rearing, and Migration Habitat* and *Primary Contact Recreation*. The Samish River, Indian Slough, and Big Ditch sites are freshwater and must meet the water quality standards described in Table 19. The site on Browns Slough is marine water and must meet the water quality standards described in Table 20.

Lower Yakima basin: Beneficial uses for Marion Drain, Sulphur Creek Wasteway, and Spring Creek include: *Salmonid Spawning, Rearing, and Migration Habitat*. The freshwater water quality standard described in Table 19 applies to these sites.

Wenatchee-Entiat basins: Beneficial uses for the Wenatchee River, Brender Creek, Mission Creek, Spring Creek, and Entiat River include: Salmonid Spawning, Rearing, and Migration. The water quality standard described in Table 19 applies to these sites. In addition, during the October 1 – May 15 period, the Wenatchee River has a Supplemental Spawning and Incubation criteria for temperature described in Table 19.

Table 19. Freshwater water quality standard for temperature, dissolved oxygen, and pH for salmonid spawning, rearing, and migration habitat.

Salmonid Spawning, Rearing and Migration Habitat – Primary Contact Recreation		
Parameter	Condition	Value
Temperature	Highest 7- DADMax	17.5º C. The Wenatchee River site has Supplemental Spawning and incubation criteria: during the October 1- May 15 period highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	8 mg/L.
pH	--	Range within 6.5 – 8.5, with a human-caused variation within the above range of < 0.5 units.

Table 20. Marine water quality standard for temperature, dissolved oxygen, and pH, beneficial use of aquatic life excellent.

Temperature Highest 7- DADMax	Dissolved Oxygen Lowest 1-day minimum	pH Must be within the range:
16°C (60.8°F).	6.0 mg/L.	7.0 – 8.5, with a human-caused variation within the above range of < 0.5 units.

Historical Information Review

Pesticide residues have historically been detected at project sites, or sites with similar land-use. Appendix F contains a summary of previous pesticide related studies and a summary of pertinent findings. Appendix F also includes a summary of 303(d) listings for each of the project areas. The 303(d) list is a list of surface waters in the state for which beneficial uses are impaired by pollutants.

For the project, *Surface Water Monitoring Program for Pesticides in Salmonid Bearing Streams,* several reports are available. These include the 2003-2005 triennial report describing the first three years of sampling (2003-2005), annual data summary reports, and an intensive sampling report on Marion Drain. All of these reports can be found on the following web sites: www.ecy.wa.gov/programs/eap/toxics/pesticides.htm. or http://agr.wa.gov/PestFert/natresources/SWM/default.aspx#2007FinalReport

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Results

This study investigated pesticide occurrence in salmonid-bearing streams during a typical pesticide-use season. Basins and monitoring locations were chosen with a likely combination of off-site pesticide transport and use by salmonids.

The following sections discuss the 2006-2008 results in terms of pesticide detection frequency, seasonal patterns, exceedances of assessment criteria and water quality standards, and factors potentially affecting pesticide concentrations.

Where possible, the 2006-2008 results are compared to the findings from the 2003-2005 monitoring program Results for the 2003-2005 monitoring can be found in *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2003-2005* (Burke et al., 2006).

Monitoring results for all sites from 2003-2008 are available through Ecology's EIM system, www.ecy.wa.gov/eim/.

Cedar-Sammamish Basin (WRIA 8): Thornton Creek

Monitoring sites in Thornton Creek have changed over the six-year project period, 2003-2008. Sampling during 2006-2008 has consistently included two sites on Thornton Creek (Figure 2): an upstream site (Thornton 1.1) monitored since 2004, and a downstream site near the mouth (Thornton 3) monitored since 2003. During 2006-2008, 41 sample events were conducted at the upstream site and 81 conducted at the downstream site.

Pesticide Detections and Concentrations

Pesticide Detections

A summary of pesticide detections for both the upstream and downstream Thornton Creek sites is presented in Appendix G, Table G-1. Because sampling periods differ over the six years, a direct comparison of detection frequency between years may be misleading. Table G-1 includes the average lower practical quantitation limit (ALPQL). The ALPQL is a three-year average of the lowest concentration that can be accurately measured by year. Compounds detected below this level are qualified as estimates. For most of the pesticide compounds, few detections were noted.

Comparison to Assessment Criteria and Water Quality Standards

The 2006-2008 pesticide data were compared to assessment criteria and water quality standards. Detailed summaries of the monitoring results can be found in pesticide calendars presented in Appendix H. Highlights of findings are summarized below.

Pesticide calendars for Thornton Creek (Appendix H, Tables H-2 – H-7) present a chronological overview of detections. The only exceedance of water quality criteria for pesticides occurred in April 2007: the upstream site exceeded the EPA Endangered Species Level of Concern (ESLOC) for cis-permethrin, a pyrethroid insecticide. The ESLOC is $1/20^{th}$ of the acute toxicity criteria. No violations in state water quality standards for pesticides were observed.

Statistical Analysis

Statistical comparison was performed on concentrations of five of the most commonly detected herbicides: dichlobenil, prometon, triclopyr, 2,4-D, and mecoprop (MCPP), using a non-parametric test, Kaplan-Meir. No statistical difference was found between the two monitoring periods, 2003-2005 and 2006-2008.

While there is no difference in concentrations of the more commonly seen herbicides, the number of herbicide detections has decreased. Table 21 presents the number of detections by pesticide type for both monitoring periods. For most compounds, detection limits improved greatly during 2006-2008, but the number of herbicide detections decreased (Table 21).

Table 21. Distribution of Pesticides Detected during 2003-2005 and 2006-2008.

Types of Pesticides	2003-2005	2006-2008	2003-2005	2006-2008
	Downstream Site (TC3)		Upstream Site (TC 1.1) Includes 2 upstream sites sampled in 2005.	
Insecticide detections	14	16	21	13
Degradate compound detections	4	12	4	3
Herbicide detections	190	95	131	39
Wood preservative detections	37	2	40	1
Total	245	125	196	56

Using a statistical test of proportions, the ratio of detections and no detection of the different pesticide groups (herbicides, insecticides, and degradate compounds) was compared. The results of the test showed the only group with a significant decrease in detections between the 2003-2005 and 2006-2008 periods was herbicides (two-tailed; $\alpha<0.001$). The other pesticide groups showed no statistical difference in detection frequency between the two time periods.

Pesticide Distribution and Detections

The distribution of detections by pesticide group has not changed dramatically from 2003-2005 to 2006-2008 (Figure 6). Herbicides are the most frequently detected group, accounting for over 70% of detections. Insecticides make up a smaller fraction of detections.

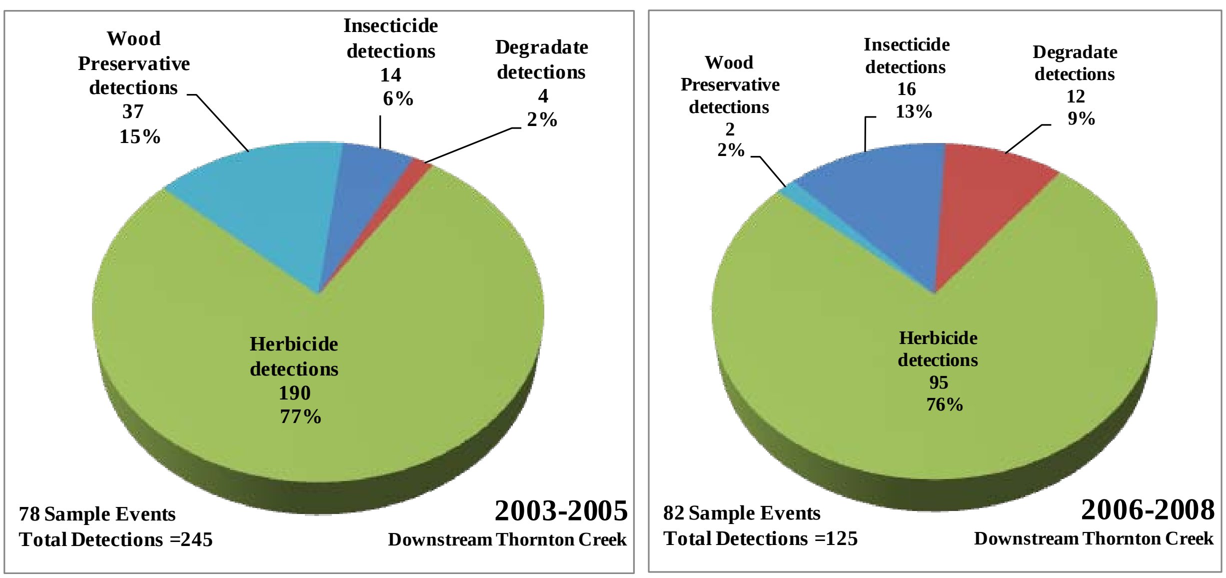


Figure 6. Pesticide distribution at the downstream Thornton Creek site, 2003-2005 and 2006-2008.

Pesticide distribution at the upstream and downstream sites is similar. Dichlobenil is the most frequently detected herbicide occurring during 39-56% of sample events upstream and 56-63% of sample events at the downstream site. Other frequently detected herbicides include 2,4-D, mecoprop (MCPP), prometon, and triclopyr. These results are similar to the 2003-2005 results for herbicides.

A greater number of pentachlorophenol (wood preservative) detections were seen during the 2003-2005 period. Changes in pentachlorophenol detections may be due to changes in the analytical method. In 2007, the laboratory changed from liquid-liquid phase extraction to solid-phase extraction. The laboratory's reporting procedures changed in 2007 as well, affecting when pentachlorophenol is reported. The laboratory no longer reported estimated pentachlorophenol values below the method detection limit.

More detections of pesticide degradate compounds were seen during 2006-2008 (Figure 6). These differences are also likely due to changes in laboratory methods. In 2005 and 2006, the laboratory added analysis for additional degradate compounds including several carbamate degradates.

Figure 7 presents insecticide detections for upstream and downstream Thornton Creek during 2006-2008. Insecticides with the same mode of action, acetylcholinesterase inhibitors, are displayed as stacked bars in the graph. The most frequently detected insecticides include the organophosphate diazinon and the carbamate insecticides carbaryl and methomyl (Figure 7). Diazinon detections decreased from 2003-2005 to 2006-2008, from 15 to 6 detections respectively. This is likely due to diazinon not being registered for residential use since 2004.

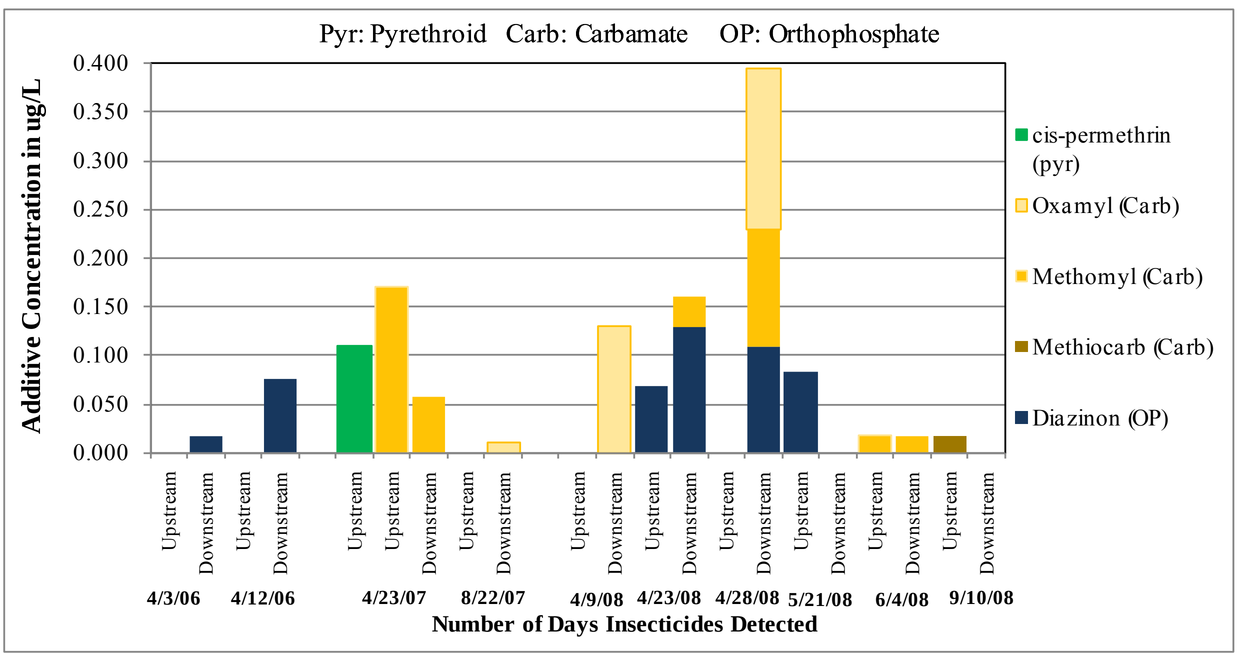


Figure 7. Cumulative total amount for insecticide detections, upstream and downstream Thornton Creek sites, 2006-2008.

More carbamate insecticide detections were seen during 2006-2008. Once again this is likely due to a change in laboratory methods. Changes in insecticide use may have occurred as well, but this is difficult to distinguish from changing laboratory methodology. The average lower practical quantification limits (ALPQL) for carbamates were much higher during 2003-2005 (0.10 – 0.19 µg/L). In addition, Thornton Creek was not sampled for carbamates in 2004. During 2006-2008, the ALPQL range for carbamates decreased by approximately half, from 0.02 – 0.10 µg/L.

There was one detection of a pyrethroid insecticide (cis-permethrin) in 2007. Limited laboratory analysis for pyrethroids began that year.

During 2006-2008, multiple insecticide detections on the same day rarely occurred (Figure 7). At the upstream site during one sample event, a carbamate and pyrethroid insecticide were detected on the same day (these insecticides have different modes of action). At the downstream site, an organophosphate (diazinon) and a carbamate were detected on the same day during two sample events.

In general, analytical methodology for detecting pesticides has improved but fewer herbicide detections are seen. Increased detection of degradate compounds is likely due to degradate compounds being added to the analysis list at MEL. Decreased detections of wood preservative may be due to changes in lab methodology and reporting. Streamflow is likely not a factor in detecting pesticides (higher flows dilute pesticide concentrations); a t-test showed no statistical difference in flow rates for the two time periods.

Comparison of Pesticide Detections at the Upstream and Downstream Thornton Creek Sites

A comparison between upstream and downstream detections depends partly on the mobility and persistence of pesticides in the environment. These are determined by the chemical and physical properties of the pesticide. Fate and transport of pesticides varies greatly depending on the compound. Highly soluble compounds, those with high water solubility or low K_{OC} tend to move from the land at relatively high rates. Other factors affecting environmental fate include chemical half life, pattern and extent of chemical use, and physical or hydrologic characteristics of the drainage basin (Carpenter et al., 2008).

The two Thornton Creek sites are about 1.2 miles apart. Flow at the upstream site is generally half the flow of the downstream site. Travel time from the upstream to downstream site averages about 4-5 hours depending on flow velocities. Due to field scheduling, sampling was not timed based on expected water movement and capturing upstream water at the downstream site.

During 2006-2008, upstream and downstream sites were sampled on the same day on 41 occasions. The same compounds were infrequently detected at both sites on the same day. Figures 8 and 9 show the instream loads for compounds detected at both sites. Figure 8 presents loading for herbicides, and Figure 9 presents loading for insecticides.

Dichlobenil and 2,4-D detections occurred most frequently at both the upstream and downstream sites, 13 and 14 times respectively (Figure 8). Dichlobenil and 2,4-D are among the most frequently detected herbicides in Thornton Creek. For insecticides, upstream and downstream detections on the same day are rarely seen (Figure 9). These results suggest specific sources near the sampling site rather than upstream inputs, were primarily responsible for detection.

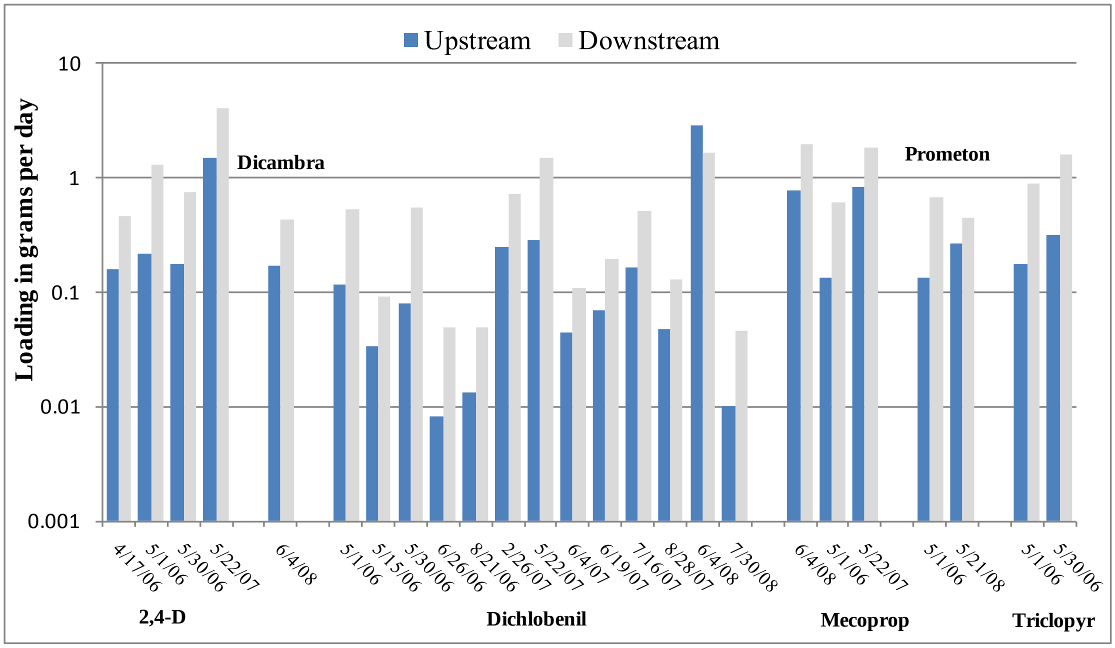


Figure 8. Herbicide loading at the upstream and downstream Thornton Creek sites for the days when both sites had detections.

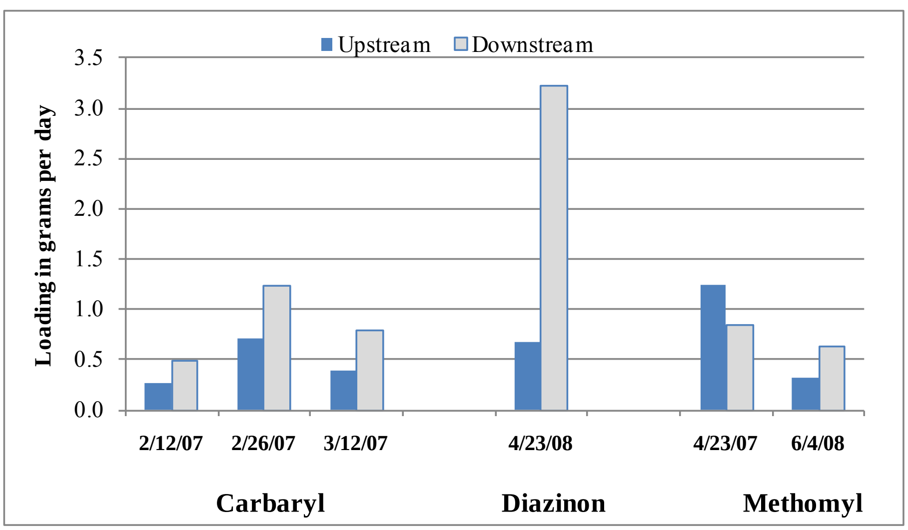


Figure 9. Insecticide loading at the upstream and downstream Thornton Creek sites for the days when both sites had detections.

Factors Affecting Pesticide Detections

Environmental Factors

A statistical test for correlation coefficient (Kendall's tau-b) was used to determine if there was a relationship between some of the more commonly seen pesticides (dichlobenil, 2,4-D, mecoprop, prometon, or triclopyr) and environmental factors such as flow and rainfall. Data from all six years (2003–2008) were compared for the downstream Thornton Creek site.

Dichlobenil, mecoprop, and 2,4-D had a positive, but extremely weak, relationship with some rainfall comparisons (Kendall's tau= 0.2, p=< 0.05). Figure 10 presents flow, precipitation, and select herbicide concentration at the downstream Thornton Creek site for 2007. While higher concentrations of these herbicides are noted with some rain events, this is not always the case (Figure 10). Additional graphs of flow, precipitation, and the most commonly seen pesticide concentrations for each year and site are presented in Appendix I.

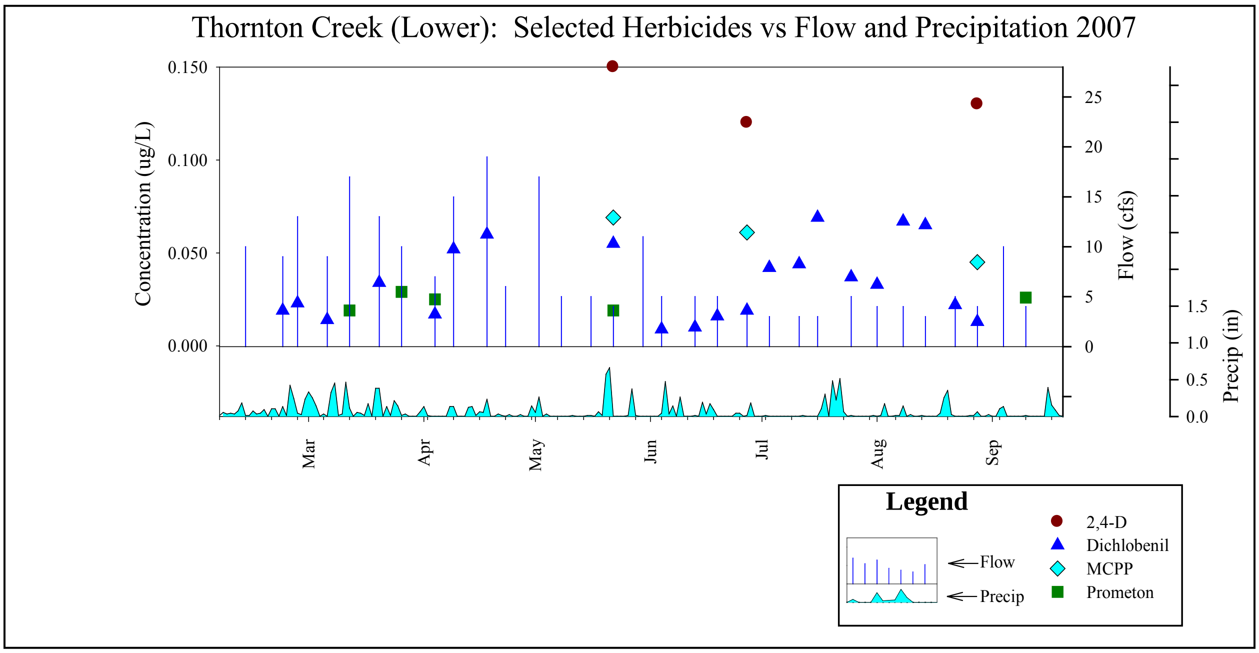


Figure 10. Five of the most commonly detected pesticides, streamflow, and precipitation at the downstream Thornton Creek site, 2007.

Temporal Factors

In the USGS publication, *Surface-Water Quality of the Skokomish, Nooksack, and Green Duwamish rivers and Thornton Creek, Puget Sound Basin, Washington, 1995-98*, Embrey and Frans (2003) looked at correlations between pesticide concentrations and flow. They saw a weak positive correlation between prometon and diazinon concentrations and streamflow, but concluded that season and timing of application appeared to have the greatest influence on pesticide concentrations and detection frequencies in Thornton Creek. Embrey and Frans saw some of the higher concentrations in samples collected in spring or early summer, from about March through May, particularly if during a rain event.

As with the USGS study (Embrey and Frans, 2003), pesticide detections generally increase from March through May, then decrease after May (Figure 11). Figure 11 presents the number of detections by pesticide type and month for the Thornton Creek sites (combined) for the 2006-2008 period. The greatest number of insecticide and degradate compound detections are seen in April. The greatest number of herbicide detections occur in May.

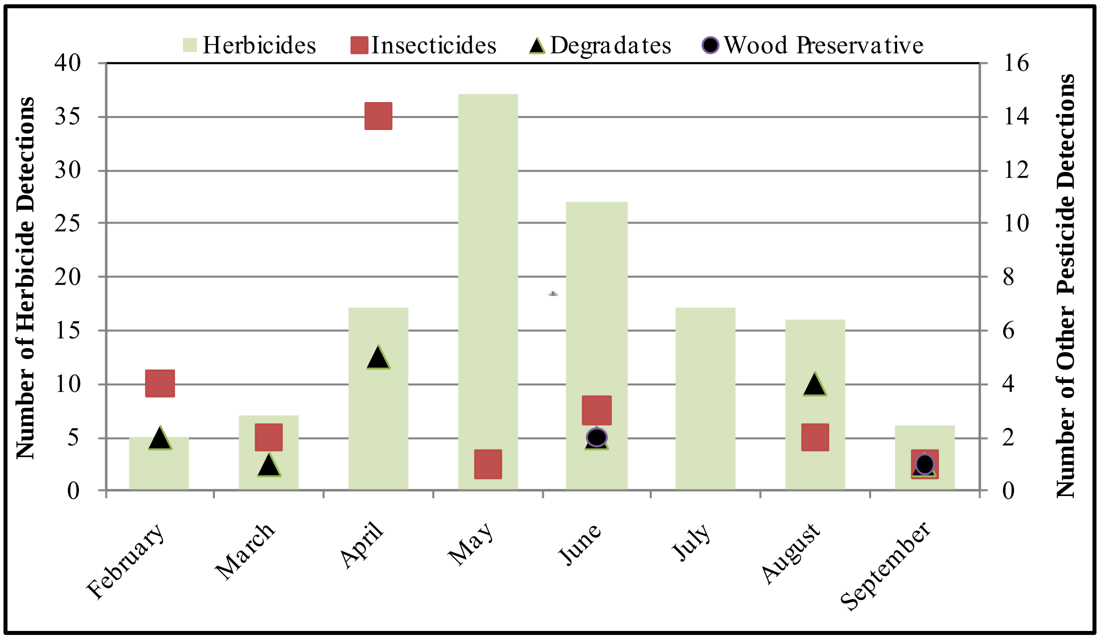


Figure 11. Number of compounds detected per month for upstream and downstream Thornton Creek sites, 2006-2008.

Water Quality Factors

A statistical test for the correlation coefficient (Kendall's tau-b) was used to examine the relationship between selected pesticide concentrations and TSS. Data from all available years were compared. Select periods during the sample season were tested where appropriate.

At the upstream Thornton Creek site, there is a very weak positive correlation (Kendall's tau= 0.30, p=0.07) between TSS and 2,4-D during early April to early June (weeks 15-24). At the downstream site, there is a very weak positive correlation between TSS and 2,4-D (Kendall's tau= 0.22, p<0.01) during early June through late July (weeks 15-30).

There was also a very weak correlation between TSS and flow (Kendall's tau= 0.25, p<0.01).

Conventional Parameters

Conventional water quality parameters were measured at both sites on Thornton Creek. Table 22 summarizes results for TSS, streamflow, pH, conductivity, temperature, and dissolved oxygen.

Table 22. Arithmetic mean and range for conventional parameters (grabs) for upstream and downstream Thornton Creek sites, 2006-2008.

Parameter and Year	Upstream		Downstream	
	Mean[1]	Range	Mean[1]	Range
Total Suspended Solids in mg/L				
2006 n=12 and 24	4.4	3-12	6.3	3 - 49
2007 n=16 and 30	6.5	2-16	12.4	4-77
2008 n=14 and 27	7.6	3-14	8.0	3-41
Flow in cubic feet per second				
2006 n=11 and 24	2	1-4	5	1-14
2007 n=16 and 31	3	0.9-8	8	3-19
2008 n=14 and 27	3.0	0.7-7.3	6.6	2.7-23.8
pH in standard units				
2006 n=11 and 23	7.8	7.0-8.1	7.8	7.1-8.3
2007 n=15 and 31	7.8	7.2-8.0	7.7	7.3-8.3
2008 n=14 and 26	7.8	6.8-8.7	7.7	6.8-8.2
Conductivity in µmhos/cm				
2006 n=12 and 24	186	157-219	201	163-250
2007 n=16 and 31	187	123-244	189	111-247
2008 n=13 and 25	170	122-224	181	116-248
Temperature in °C (grabs)				
2006 n=12 and 24	14.1	8.1-19.9	14.7	8.5-20.9
2007 n=16 and 31	13.1	6.8-18.0	13.7	7.1-19.9
2008 n=14 and 27	12.4	6.4-16.8	12.6	6.4-18.1
Dissolved Oxygen in mg/L (grabs)				
2008 n=11 and 23	10.4	9.3-12.1	10.2	9.0-11.7

Mean[1]: Arithmetic Mean.

Comparison to Water Quality Standards

Grab results for pH and dissolved oxygen and continuous temperature results were compared to water quality standards (Table 18).

The downstream Thornton Creek site met pH standards for all three years. At the upstream site, there was one exceedance of the pH standard at 8.7 standard units (s.u.) in 2008.

Dissolved oxygen was sampled for in 2008. Neither the upstream nor downstream sites met the dissolved oxygen standard. Dissolved oxygen at the upstream site dipped below the 9.5 mg/L standard twice, once in July and once in August. Dissolved oxygen at the downstream site fell below 9.5 mg/L four times.

Continuous, 30-minute interval, temperature data were collected year-round from 2006-2008. Temperature profiles are presented in Appendix J. The temperature standard was exceeded during the periods described in Table 23. During September 15 - May 15, the highest 7-DADMax should not exceed 13° C; during the rest of the year, the highest 7 DADMax should not exceed 16°C.

Table 23. Thornton Creek periods of water temperature exceedance, 2006-2008.

Upstream Site		Downstream Site	
2006			
April 25-27	>13°C	April 22	>13°C
May 13-15	>13°C	April 24 - May 7	>13°C
June 2-5	>16°C	May 12-15	>13°C
June 23 - Sept 6	>16°C	June 2-8	>16°C
Sept 15 - Oct 4	>13°C	June 13-16	>16°C
		June 22 - Sept 9	>16°C
		Sept 15 - Oct 4	>13°C
2007			
May 5-15	>13°C	May 5-15	>13°C
June 1-3	>16°C	May 31 - June 3	>16°C
July 1- Sept 7	>16°C	June 28 - Sept 14	>16°C
Sept 15 - Oct 1	>13°C	Sept 15 - Oct 1	>13°C
2008			
May 14-15	>13°C	May 14-15	>13°C
June 28 - July 16	>16°C	June 26 - Aug 28	>16°C
Aug 4-28	>16°C	Sept 5-14	>16°C
Sept 15 - Oct 1	>13°C	Sept 15 - Oct 7	>13°C

Total Suspended Solids (TSS)

A comparison of 2004-2005 and 2006-2008 results for TSS concentrations and loading are presented in Figures 12 and 13 respectively. Downstream values remain about the same while upstream values increased during 2006-2008. Statistical trends in TSS were examined for both sites using a Seasonal-Kendall trend test. TSS concentrations and loading were compared for the months of March through September for both sites; the median monthly value was chosen for analysis. The upstream site showed increasing concentrations and loading of TSS (concentration slope=+0.87, P value=0.01; loading slope=+10.3, P value=0.04). Both sites generally have low levels of TSS.

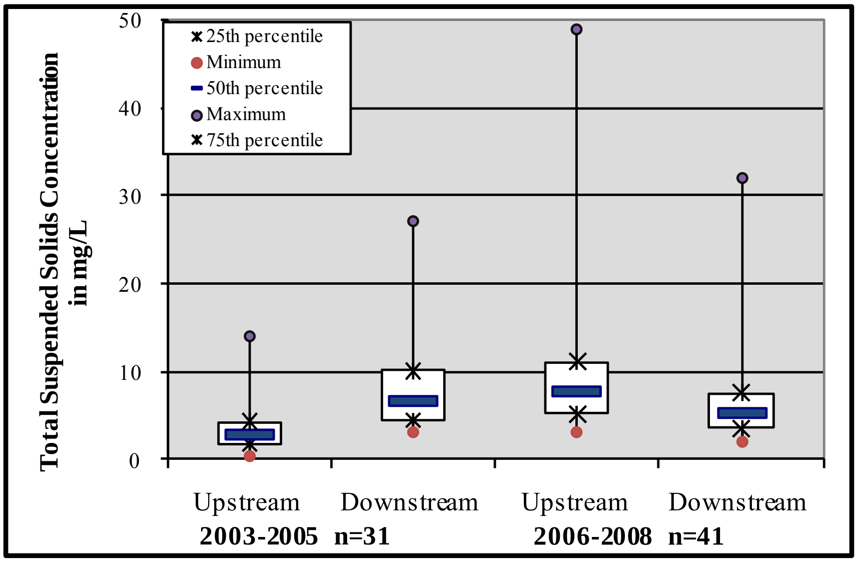


Figure 12. Total suspended solids concentrations at the Thornton Creek sites, 2004-2005 and 2006-2008.

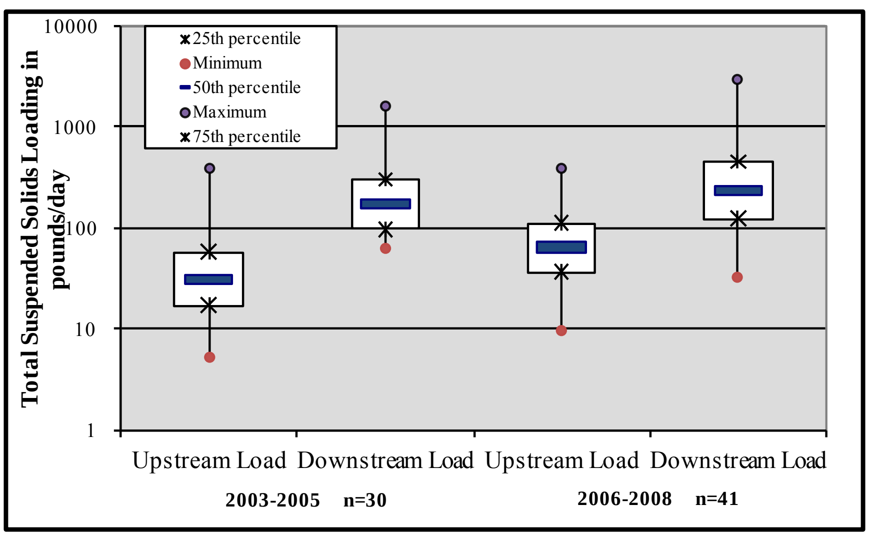


Figure 13. Total suspended solids loading at the Thornton Creek sites, 2004-2005 and 2006-2008.

Lower Skagit-Samish Basin (WRIA 3)

Monitoring in the lower Skagit-Samish basin during 2006-2008 included five sites. In 2007, the upstream Samish River site was dropped and an upstream Big Ditch site was added. The upstream Samish River site was discontinued due to very few pesticide detections at the site.

Sample sites for 2006-2008 are presented in Figure 3. During 2006-2008, 87 sample events occurred for all sites except the upstream Samish River and upstream Big Ditch sites. Fifty-eight sample events occurred at the upstream Big Ditch site (2007-2008), and 29 sample events at the upstream Samish River site (2006). A description of findings for the Samish River site can be found in the 2006 Monitoring Data Summary (Anderson et al., 2007).

Pesticide Detections and Concentrations

Pesticide Detections

A summary of pesticide detections for all Skagit-Samish sites are found in Appendix G. The tables include the average lower practical quantitation limit (ALPQL). The ALPQL is a three-year average of the lowest concentration that can be accurately measured by year. Compounds below this level are qualified as estimates.

Comparison to Assessment Criteria and Water Quality Standards

The 2006-2008 data were compared to assessment criteria and water quality standards. Detailed summaries of the monitoring results can be found in pesticide calendars presented in Appendix H. Highlights of findings are summarized below.

Big Ditch

For both Big ditch sites during the periods sampled, all detected pesticide concentrations met available freshwater assessment criteria or water quality standard. A summary of pesticide detections for both the upstream and downstream Big Ditch sites are presented in Appendix G, Table G-2. Pesticide calendars are presented in Appendix H, Tables H-8 – H-12. In summary, the tables show that in 2006–2008, 28 different pesticides were detected at the upstream Big Ditch site. At the downstream site, 37 pesticides compounds were detected during 2006-2008.

The Big Ditch sites are slightly less than six miles apart. Pesticides found between the two sites differ, likely due to differences in land use and hydrology. Land use at the upstream site is predominantly commercial\industrial. Surface water flows at the downstream site average 88% greater than the upstream site during the sample season (March – September). In June (when rainfall begins to subside), Skagit River water is diverted into the irrigation system and flows into Big Ditch (between the upstream and downstream sites). As the Skagit River drops during the summer, less water is diverted. The diversion gate is closed sometime in late September. When the Skagit River water is diverted, it affects water quality at the downstream Big Ditch site. Noticeable effects include lower water temperatures and conductivity as well as higher flows.

Indian Slough

During 2006-2008, all detected pesticide concentrations met freshwater assessment criteria or water quality standard. A summary of pesticide detections for Indian Slough are presented in Appendix G, Table G-3. Results are presented in the pesticide calendars in Appendix H, Tables H-16 – H-18. In summary, from 2006-2008, 32 different pesticide compounds and degradates were detected in Indian Slough.

Browns Slough

Browns Slough is a marine site and, as such, must meet marine assessment criteria and water quality standards. In summary, 32 pesticides and degradates were detected in Browns Slough from 2006-2008. During the early growing seasons of both 2007 and 2008, chlorpyrifos did not meet (exceeded) the acute and chronic marine water quality standard. In May and June of 2007, two detections of diazinon were found numerically above the NRWQC. A summary of pesticide detections for Browns Slough are presented in Appendix G, Table G-4. Results for 2006-2008 are presented in the pesticide calendars in Appendix H, Tables H-13 – H-15.

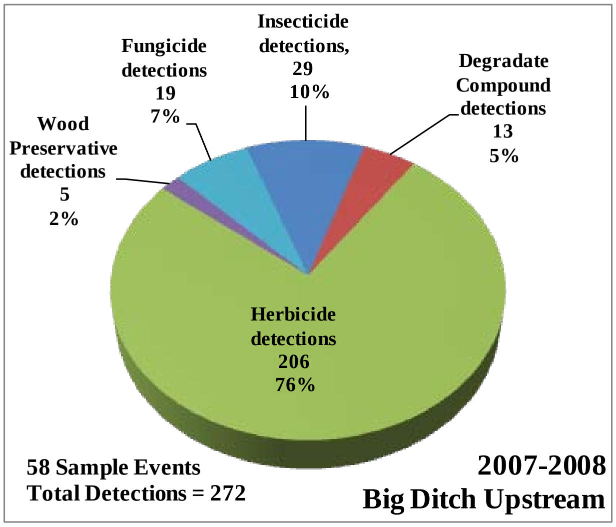
Samish River

All detected concentrations met freshwater assessment criteria or water quality standards for both sites during 2006-2008. The upper site was discontinued after 2006 due to few pesticide detections at the site. A summary of pesticide detections for both the upstream and downstream Samish River sites are presented in Appendix G, Table G-5. Results for 2006-2008 are presented in the pesticide calendars in Appendix H, Tables H-19 - H-22. In summary, 11 pesticides and degradates were detected in the Samish River (upstream and downstream sites) from 2006 to 2008.

Pesticide Distribution

Big Ditch

The distribution of detections by pesticide group at the upstream and downstream sites is similar (Figure 14). The most frequently detected compounds at both sites were herbicides. The percentage of fungicide and insecticide detections found at both sites was also similar. Degradate compounds were more frequently detected at the upstream site. Most of the degradate compound detections are breakdown products of carbamate insecticides.



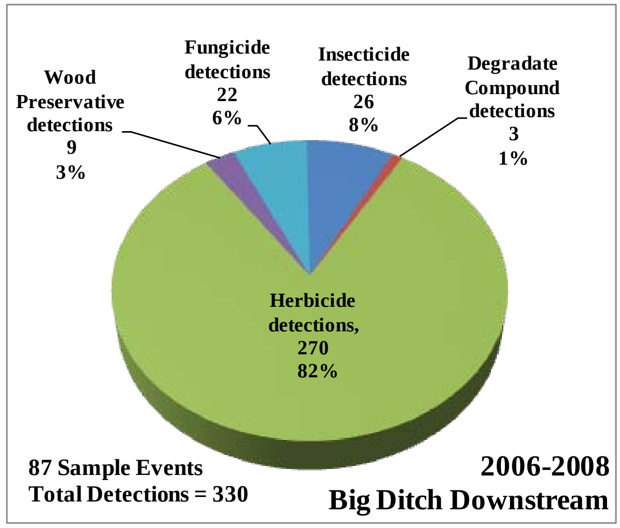


Figure 14. Distribution of types of pesticide in upstream and downstream Big Ditch.

Pesticide compounds detected at each site differ. Table 24 describes the most commonly seen herbicides at the upstream and downstream sites. 2,4-D was the only commonly detected herbicide at both sites.

Table 24. Most frequently seen herbicides at the upstream and downstream Big Ditch sites.

Upstream n=58			Downstream n=87		
Herbicide	Number of detections	Percentage of sample events detected	Herbicide	Number of detections	Percentage of sample events detected
Picloram	37	64%	Metolachlor	32	37%
Tebuthiuron	32	55%	Bentazon	29	33%
Dichlobenil	30	52%	Diuron	28	32%
Bromacil	28	48%	2,4-D	27	31%
2,4-D	17	29%	Eptam	26	30%

Detected insecticides differ between the two sites (Figures 15 and 16). Insecticides with the same mode of action (acetylcholinesterase inhibition) are displayed as stacked bars in the graphs. The predominant insecticide detected at the upstream site is a neonicotinoid insecticide, imidacloprid (Figure 15). Analysis for this compound was added in 2008. During 2008, imidacloprid was detected at the upstream site during 74% of the sample events. Carbamate insecticide detections at both sites are about the same. Organophosphate insecticide detections are infrequent, but tend to be seen at the downstream site (Figure 16). Carbamate degradates are more frequently seen at the upstream site.

Fungicide residues were detected at both the upstream and downstream sites during 30% and 23% of the sample events respectively.

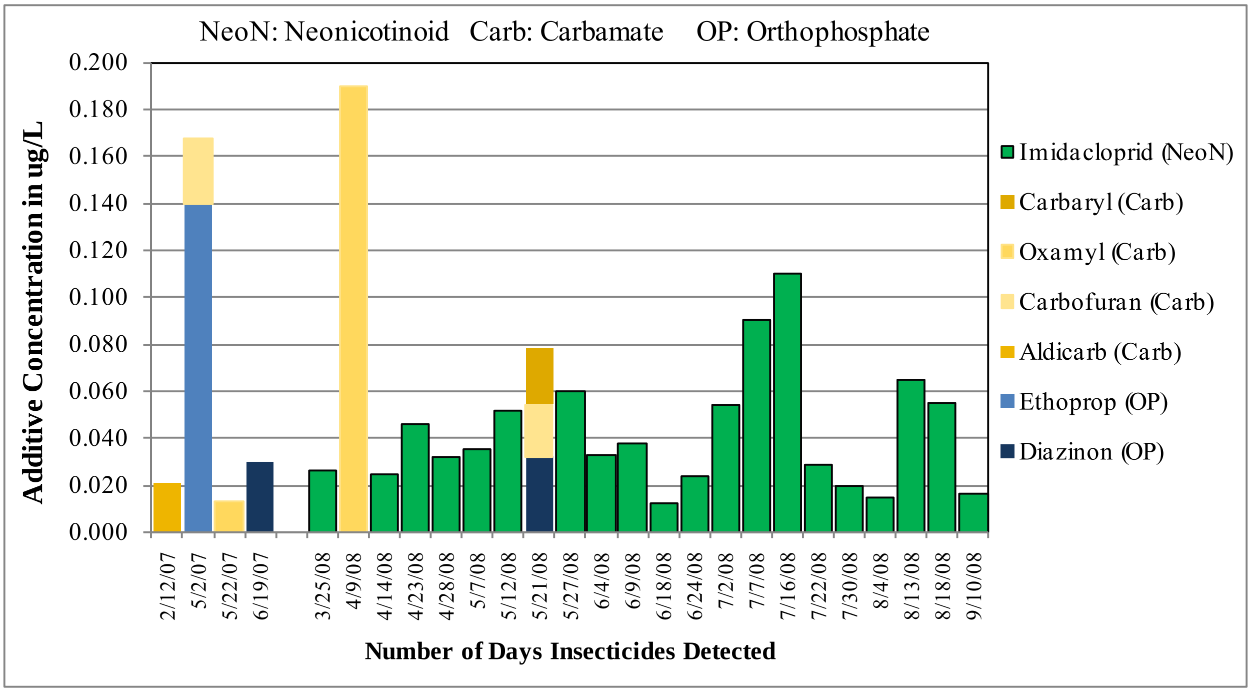


Figure 15. Cumulative total amount for insecticide detections at the upstream Big Ditch site, 2007-2008.

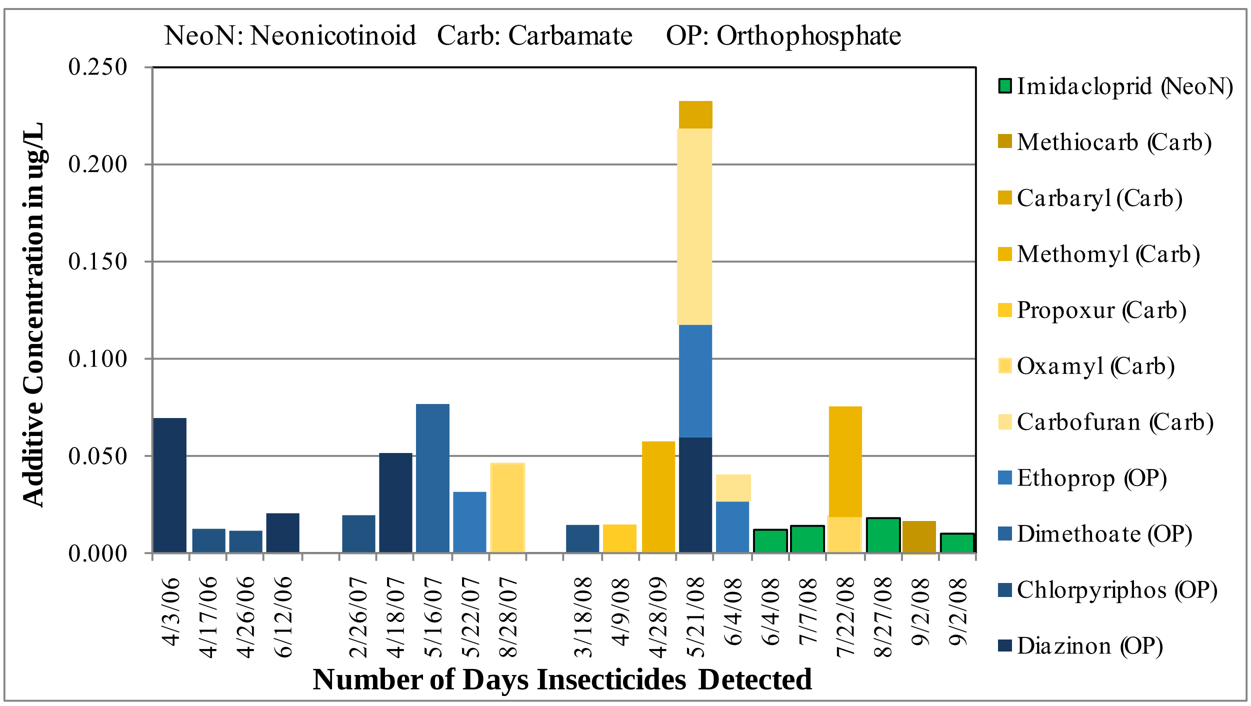


Figure 16. Cumulative total amount for insecticide detections at the downstream Big Ditch site, 2006-2008.

Indian Slough

Distribution of detections by pesticide group for Indian Slough is presented in Figure 17.

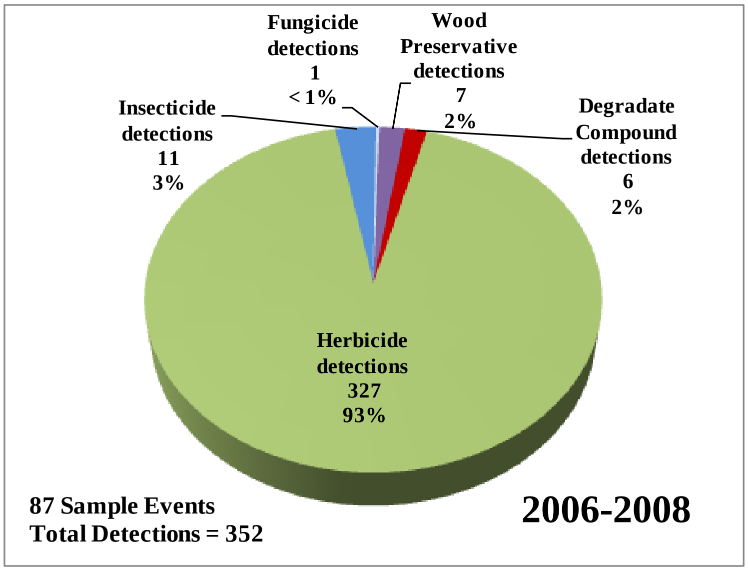


Figure 17. Pesticide distribution by type for Indian Slough, 2006-2008.

Herbicides are the most commonly detected compound found in Indian Slough and occur more frequently here than at other Skagit-Samish sites. The most frequently seen herbicides and the percentage detections are presented in Table 25.

Table 25. Most frequently seen herbicides at the Indian Slough site, 2006-2008.

Herbicide	Number of detections	Percentage of sample events detected
Diphenamid	52	60%
Tebuthiuron	42	48%
2,4-D	36	41%
Dichlobenil	32	37%
Metolachlor	28	32%

Figure 18 presents insecticides detected in Indian Slough during 2006-2008. Insecticides with the same mode of action (acetylcholinesterase inhibition) are displayed as stacked bars in the graphs. Insecticides are rarely detected in Indian Slough. Diazinon, an organophosphate insecticide, has been detected four times during 2006-2008. Carbamate insecticides have been detected five times. Carbamate degradate compounds have been detected five times; all detections occurred in 2008. Fungicides were rarely detected in Indian Slough during 2006-2008.

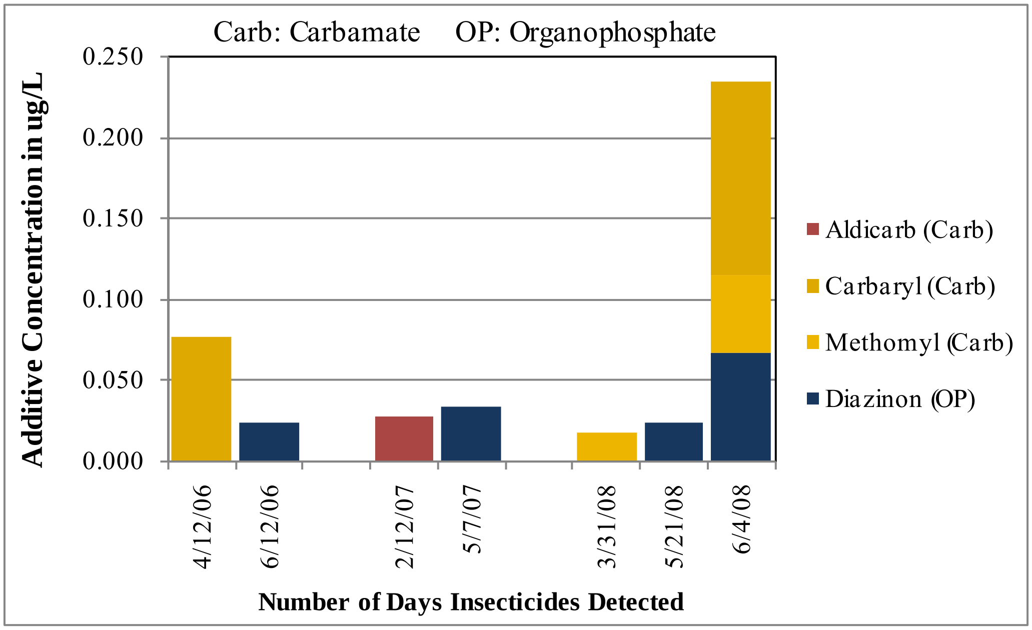


Figure 18. Cumulative total amount for insecticide detections in Indian Slough, 2006-2008.

Browns Slough

The distribution of pesticides by type is presented in Figure 19.

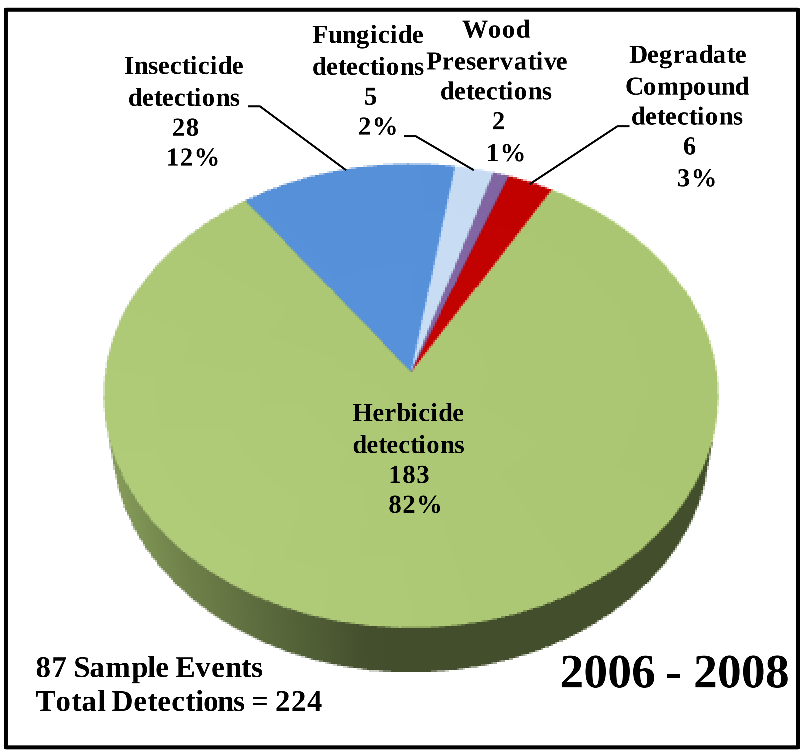


Figure 19. Pesticide distribution by type for Browns Slough, 2006-2008.

Though Browns Slough had the highest number of insecticide detections of the Skagit-Samish sites, herbicides were the most commonly detected compound. The most frequently seen herbicides and percentage of detections are described in Table 26.

Table 26. Most frequently seen herbicides at the Browns Slough site, 2006-2008.

Herbicide	Number of detections	Percentage of sample events detected
Bentazon	27	31%
Simazine	23	26%
Dacthal (DCPA)	20	20%
Diuron	20	20%
Eptam	20	20%

Figure 20 presents Browns Slough insecticide detections during 2006-2008. Insecticides with the same mode of action (acetylcholinesterase inhibition) are displayed as stacked bars in the graphs. No insecticides were detected in Browns Sough in 2006, but in 2007 and 2008, Browns Slough had the greatest variety of compounds, the most detections, and the highest concentration of insecticides seen in the Skagit-Samish project area (Figure 20). Three organophosphate insecticides were detected: diazinon (7 detections), chlorpyrifos (4 detections), and dimethoate (2 detections). Four carbamate insecticides and one neonicotinoid were also detected. Insecticides with similar modes of action (acetylcholinesterase inhibitors) were rarely detected in combination. This occurred only four times in 2006-2008.

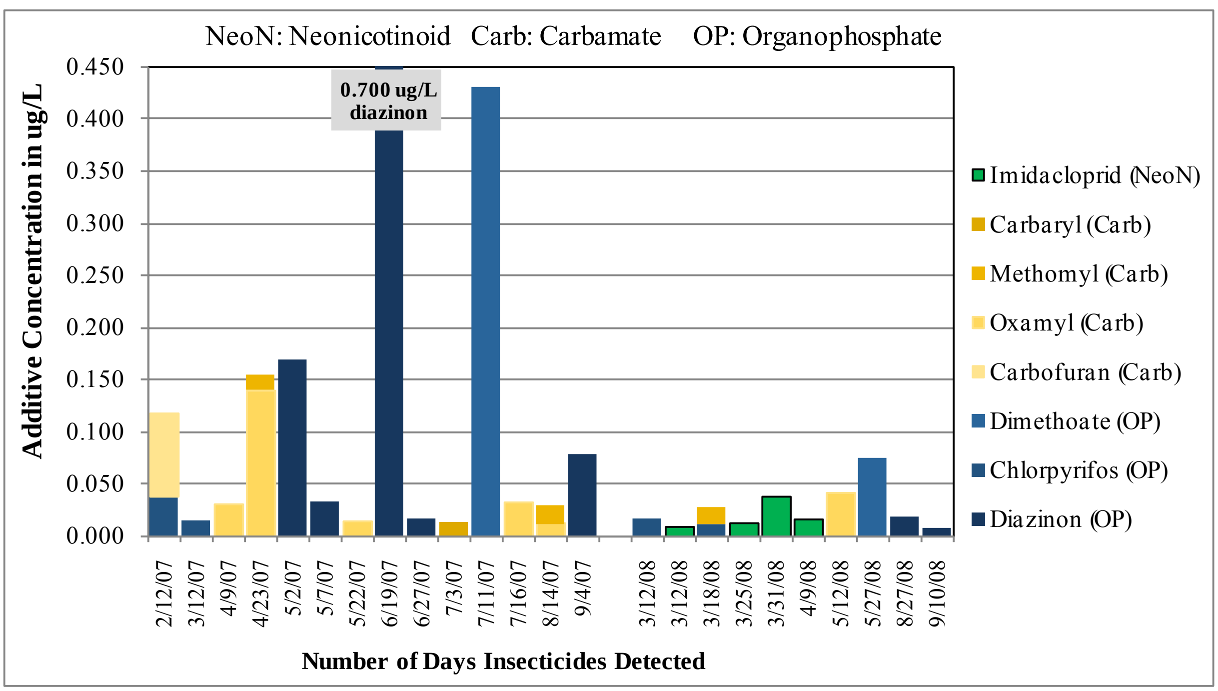


Figure 20. Cumulative total amount for insecticide detections in Browns Slough, 2006-2008.

Degradate compounds detected included carbamate degradates and one endosulfan sulfate detection. Fungicide and wood preservative detections were rare in Browns Slough.

Samish River

The distribution of pesticides for the Samish River downstream site by type is presented in Figure 21. Very few pesticides were detected at the Samish River sites. As with the other sites, herbicides are the most commonly detected compound. The most commonly detected herbicides were bromacil and 2,4-D. Only two insecticide detections occurred during 2006-2008 at the downstream Samish River site. Two detections of carbamate insecticides occurred in 2007 (carbaryl and oxamyl). Concentrations detected were low, < 0.016 ug/L.

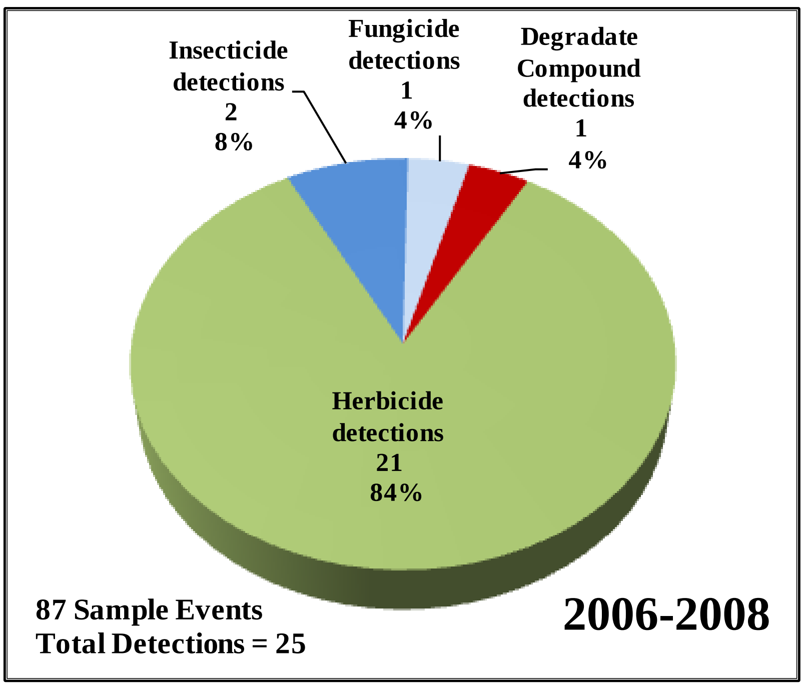


Figure 21. Pesticide distribution by type for the downstream Samish River site.

Comparison of Pesticides at the Upstream and Downstream Big Ditch Sites

A comparison between upstream and downstream detections depends partly on the mobility and persistence of pesticides in the environment. These are determined by the chemical and physical properties of the pesticide. Fate and transport of pesticides varies greatly depending on the compound. Highly soluble compounds, those with high water solubility or low K_{OC} tend to move from the land at relatively high rates. Other factors affecting environmental fate include chemical half life, pattern and extent of chemical use, and physical or hydrologic characteristics of the drainage basin (Carpenter et al., 2008).

The two Big Ditch sites are about six miles apart. Land use affecting water quality at each site differs. Hydrology at each site differs as well, due to the seasonal diversion of Skagit River water between sites. Streamflow increases downstream may dilute pesticide concentrations due to the diversion of Skagit River that influences the downstream Big Ditch site.

During 2007-2008, the upstream and downstream Big Ditch sites were sampled on the same day 58 times. The upstream and downstream presence of a compound did not frequently occur on the same day. Figures 22 and 23 present pesticide loading for the sample days when a specific compound was detected at both sites. Figure 22 presents loading for herbicides, and Figure 23 presents loading for insecticides.

Herbicides most commonly seen at both sites, and their K_{oc} values, are presented in Table 27. Of the four herbicides listed, two (Bromacil and 2,4-D) have low K_{oc} values (higher mobility) compared to the other two (dichlobenil and diuron). Despite differences in mobility (K_{oc}), herbicide detections downstream are more likely due to local herbicide-use patterns rather than transport from the upstream site.

Table 27. Herbicides most frequently detected on the same day at both the upstream and downstream Big Ditch sites and their K_{oc} values.

Herbicide	Detections at both the upstream and downstream sites	K_{oc}
Bromacil	11	32
2,4-D	9	20
Diuron	9	480
Dichlobenil	7	400

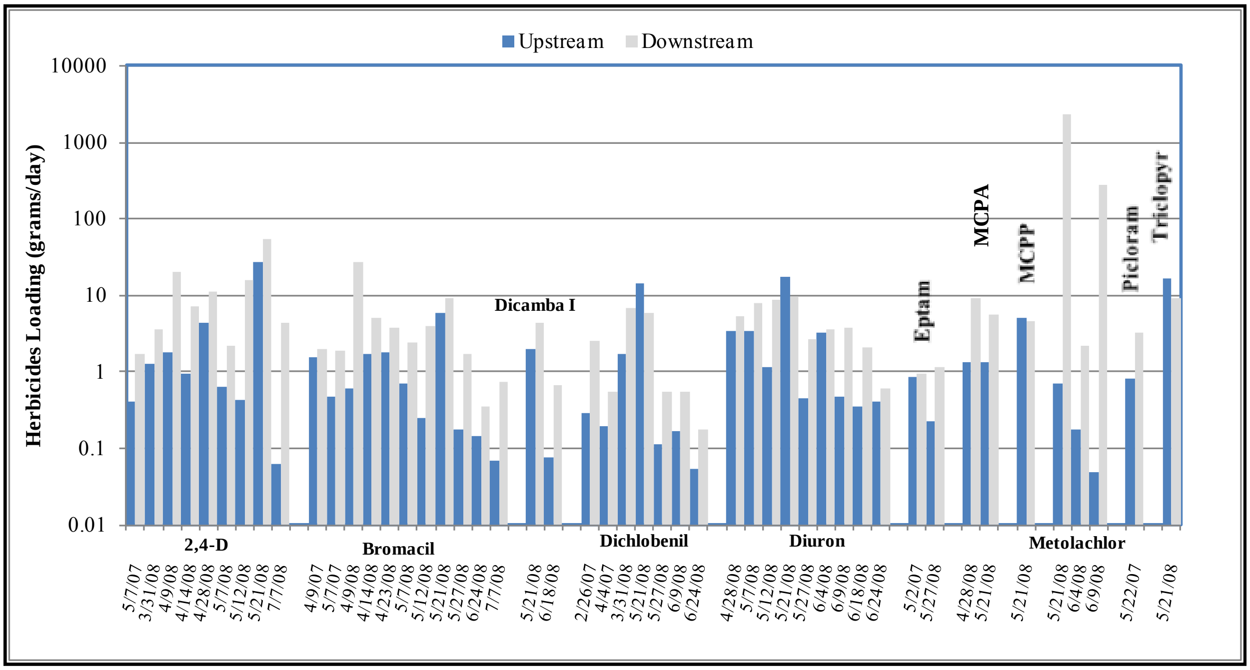


Figure 22. Herbicide loading at the upstream and downstream Big Ditch sites for the days when both sites had detections.

Upstream and downstream insecticide detections on the same day were rarely seen (Figure 23).

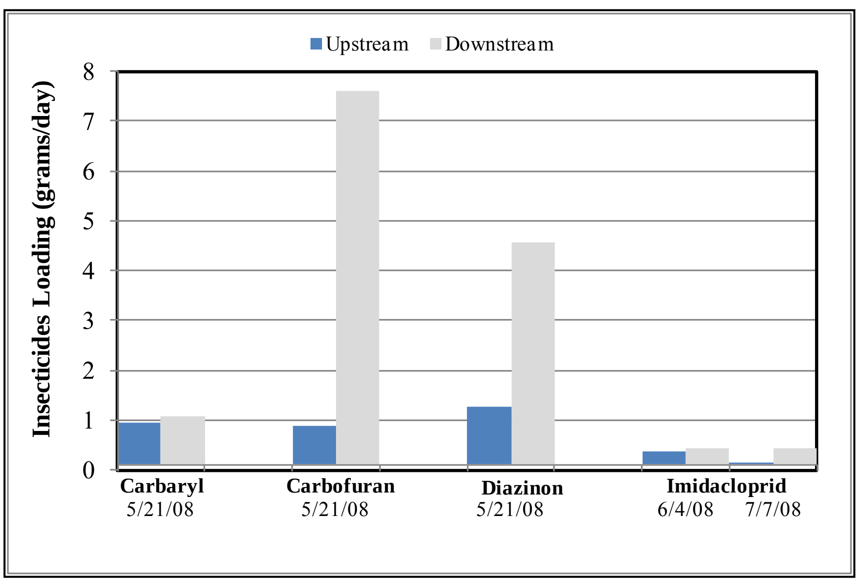


Figure 23. Insecticide loading at the upstream and downstream Big Ditch sites for the days when both sites had detections.

Factors Affecting Pesticide Detections

Environmental Factors

A statistical test for correlation coefficient (Kendall's tau-b) was used to determine if there is a relationship between some of the more commonly seen pesticides (usually herbicides) and environmental factors such as streamflow and rainfall. Data from all available years were compared. Analysis was conducted Big Ditch, Indian Slough, and Browns Slough. The Samish River did not have enough detections to analyze.

At the upstream Big Ditch site, there was a very weak positive relationship between 2,4-D and some of the rainfall comparisons (Kendall's tau= 0.3, $p \leq 0.05$). There was also a very weak negative relationship between picloram and some rainfall comparisons (Kendall's tau= - 0.3, $p \leq 0.05$). Figure 24 presents flow, precipitation, and the most commonly seen herbicide concentrations for 2008. Higher concentrations of 2,4-D occur with some higher rainfall events, and a peak dichlobenil concentration is seen in May with high flow. Graphs of flow, precipitation, and the most commonly seen herbicide and insecticide concentrations for each year and site are presented in Appendix I.

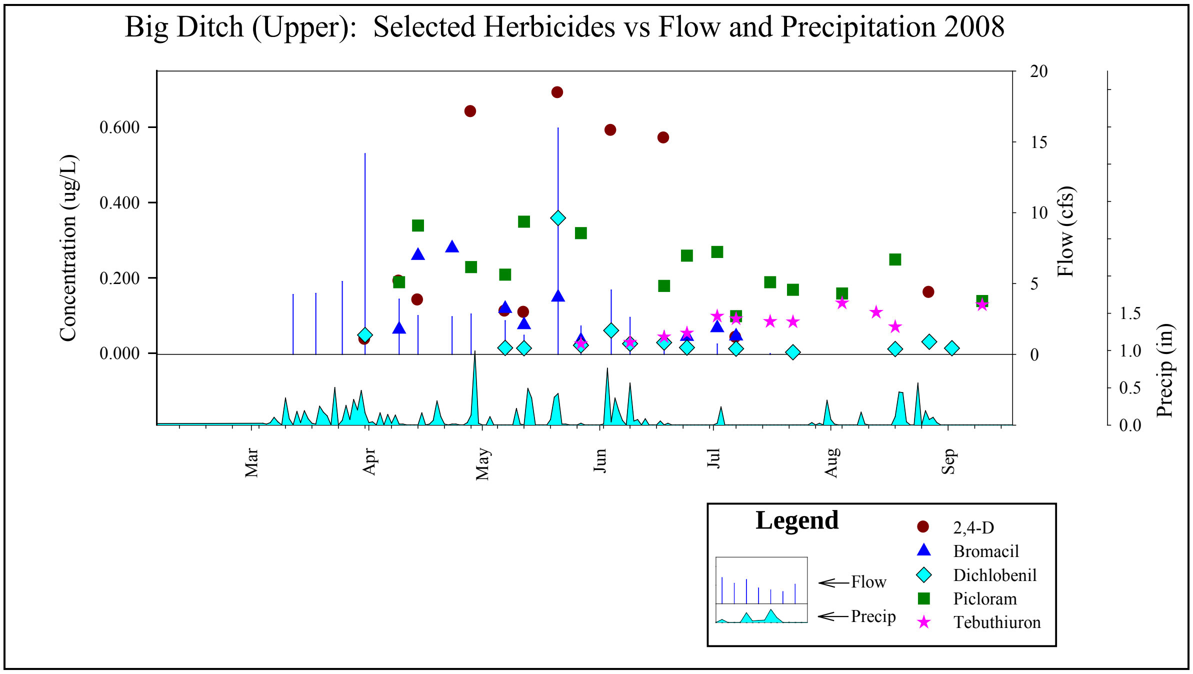


Figure 24. The most commonly seen pesticides (all herbicides) seen at upper Big Ditch in comparison to streamflow and 24-hour precipitation, 2008.

At the downstream Big Ditch site and Browns Slough, there were no statistical correlations between pesticide concentrations tested and flow or rainfall. Graphs of flow, precipitation, and most commonly seen herbicide and insecticide concentrations for each year and site are presented in Appendix I.

At Indian Slough, there were no significant relationships between commonly seen herbicides and rainfall, but there was a weak positive correlation between flow and metolachlor (Kendall's tau= 0.37, p≤ 0.05) and between flow and dichlobenil (Kendall's tau= 0.25 p≤ 0.05). Figure 25 presents the most commonly seen pesticides in comparison to flow and 24-hour precipitation for 2008. Some relationship between flow and metolachlor is evident in Figure 25, with metolachlor detections seen March through early June when flows are higher. Metolachlor detections could be related to higher flows, or application of metolachlor during the March through June period.

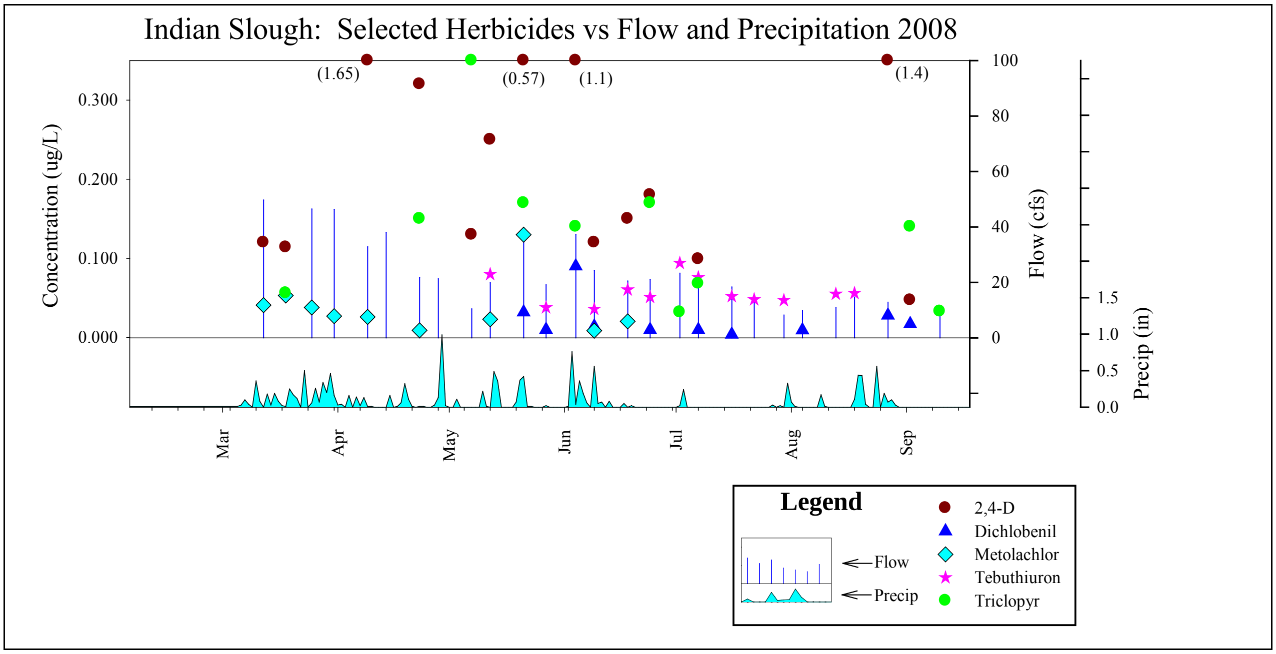


Figure 25. The most commonly seen herbicides in Indian Slough in comparison to flow and 24-hour precipitation, 2008.

Temporal Factors

Figure 26 presents the types of pesticide detections seen by month for the Skagit-Samish sites. Sites show a similar seasonal pattern of pesticide use. Herbicide detections increase from March through April and May, then decrease through September. Insecticide detections peak in May. Degradate compounds, wood preservatives, and fungicides have no clear pattern and were seen throughout the pesticide-use season, March through September.

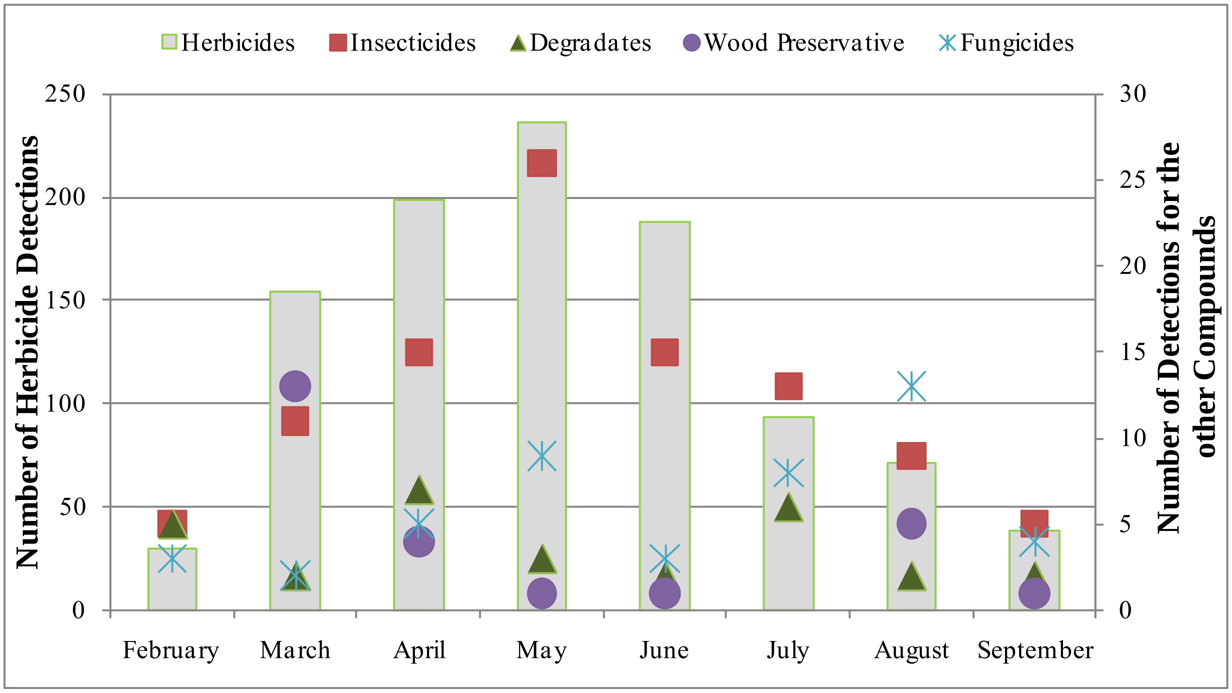


Figure 26. Types of pesticides seen at the Skagit-Samish sites per month, 2006-2008.

Water Quality Factors

A statistical test for correlation coefficient (Kendall's tau-b) was used to determine if there was a relationship between select pesticide concentrations or streamflow and TSS. Data from all years available were compared. Samish River data were only tested for flow and TSS correlation due to low pesticide detections at this site.

No correlation between pesticide concentrations or flow and TSS was seen at the upstream Big Ditch site, although only two years of data were available for analysis. At the downstream site, there was a very weak positive correlation between flow and TSS (Kendall's tau= 0.32, $p < 0.01$).

For Indian Slough, there was a moderate positive correlation between flow and TSS (Kendall's tau= 0.52, $p < 0.01$). There was also a very weak positive correlation between TSS and dichlobenil (Kendall's tau= 0.29, $p < 0.01$).

On Browns Slough, there was a very weak negative correlation between flow and TSS (Kendall's tau= - 0.24, $p = 0.02$). There was also a very weak negative correlation between TSS and bentazon (Kendall's tau= -0.32, $p < 0.01$).

The downstream Samish River site had a strong positive correlation between flow and TSS (Kendall's tau= 0.75, $p < 0.01$). No other TSS and pesticide correlations were seen.

Conventional Parameters

Conventional water quality parameters were measured at all Skagit-Samish sites. In 2008, Winkler dissolved oxygen measurements were also obtained. Continuous, 30-minute interval temperature data were collected (temperature profiles are presented in Appendix J). Table 28 summarizes results for TSS, flow, pH, conductivity, and dissolved oxygen for all of the sites.

Table 28. Arithmetic mean and range for conventional parameters (grabs) for Skagit-Samish basin sites, 2006-2008.

Summary Statistics by Site	Total Suspended Solids (mg/L)			Flow (cubic feet per second)			pH (standard units)			Conductivity (µmhos/cm)			Dissolved Oxygen (mg/L)
	2006	2007	2008	2006	2007	2008	2006	2007	2008	2006	2007	2008	2008
Big Ditch (upstream)													
Mean [1]	--	13.7	9.5	--	2.1	2.7	--	7.0	6.9	--	275	259	7.0
Minimum	--	4	4	--	0.1	0	--	6.6	6.4	--	146	131	2.9
Maximum	--	47	26	--	10.0	16	--	7.7	7.5	--	356	367	10.5
Big Ditch (downstream)													
Mean [1]	10.4	13.8	6.3	12.5	16.7	12.5	7.4	7.7	7.2	365	379	432	9.9
Minimum	2	3	2	0.5	1.8	0.5	5.6	6.3	6.4	37	38	46	5.8
Maximum	57	76	21	59.0	16.7	59.0	8.8	9.5	8.5	954	938	781	17.1
Indian Slough													
Mean [1]	7	7	6	15	22	24	7.3	7.2	7.0	750	1090	760	6.3
Minimum	1	2	2	2	4	8	5.4	6.3	6.6	270	163	206	3.9
Maximum	37	39	15	35	87	50	8.6	8.0	7.3	1940	4410	2100	10.0
Browns Slough													
Mean [1]	8	10	8	7	8	8	7.5	7.6	7.4	14900	11100	8640	10.5
Minimum	4	4	4	0	0	0	6.7	6.7	6.7	7170	2690	795	4.7
Maximum	18	48	14	17	24	17	8.7	8.6	8.4	33700	36400	20500	17.9
Samish River (upstream)													
Mean [1]	4	--	--	108	--	--	7.4	--	--	76	--	--	--
Minimum	1	--	--	26	--	--	5.5	--	--	48	--	--	--
Maximum	20	--	--	289	--	--	8.1	--	--	121	--	--	--
Samish River (downstream)													
Mean [1]	6	14	10	102	223	213	7.4	7.4	7.2	92	93	77	10.7
Minimum	2	2	3	14	22	34	5.5	6.8	6.3	56	45	46	9.5
Maximum	14	115	25	336	1333	511	8.0	7.9	7.9	142	143	136	12.0

Mean[1]: Arithmetic mean.

Comparison to Water Quality Standards

Results for pH, dissolved oxygen (grab samples), and continuous temperature results were compared to water quality standards (Tables 19 and 20).

pH

The upstream Big Ditch site met pH standards the first year sampled (2007), but in 2008, pH fell slightly below the standard in March. During 2006-2008, the downstream site failed pH standards numerous times with pH values both falling below the standard of 6.5 s.u. and exceeding the standard of 8.5 s.u.

Indian Slough pH levels fell slightly below the standard at least once during 2006 and 2007, and exceeded the standard once during 2008.

Browns Slough is a marine site and must meet the marine pH range of 7.0 – 8.5 s.u. During 2006 and 2007, several pH values fell both below and above the marine pH criteria. During 2008, several values fell below the marine standard with a low of 6.7 s.u.

In 2006, two sites on the Samish River were sampled; pH at both sites fell below the standard once during 2006. Only the downstream site was sampled in 2007 and 2008. During 2007-2008, there was one sample event where pH dropped below the standard.

Dissolved Oxygen

Dissolved oxygen grab samples were obtained in 2008. All sites except the Samish River had low dissolved oxygen levels.

For both Big Ditch sites, dissolved oxygen levels fell below the 8.0 mg/L minimum numerous times with a low of 2.9 mg/L at the upstream site and 5.8 mg/L at the downstream site.

Indian Slough dissolved oxygen levels were low, falling below the 8.0 mg/L minimum during most sample events.

Browns Slough is a marine site and as such must meet the marine standard for dissolved oxygen of a minimum of 6.0 mg/L per day. Browns Slough dissolved oxygen levels dropped below the standard four times with a low of 4.7 mg/L in late August.

Samish River dissolved oxygen levels met standards, never dropping below 9.5 mg/L.

Temperature

The temperature standard for the Skagit-Samish sites is: the 7-day average of the daily maximum temperature (DADMax) should not exceed 17.5° C. Continuous, 30-minute interval, temperature data were collected year-round for 2006-2008 at all sites, except the upstream site Big Ditch site (2007-2008) and the upstream Samish River site (2006). Temperature profiles are presented in Appendix J.

None of the sites met temperature standards during various periods. Table 29 presents periods when sites exceeded temperature standards. Browns Slough exceeded the standard on the greatest number of days, but as a marine site, it must meet a more stringent standard (≤ 16.0°C). Big Ditch and Indian Slough also exceeded the standard during long periods during the summer months.

Table 29. Periods of water temperature exceedance for Skagit-Samish basin sites, 2006-2008.

Site	2006	2007	2008
Big Ditch (upstream) >17.5°C	- -	7/13 - 7/21	8/15 - 8/19 8/21 - 8/22
Big Ditch (downstream) >17.5°C	4/26 - 4/27 4/30 - 5/19 5/31 - 9/16 9/24 - 9/30	5/1 5/4 - 5/17 5/21 - 6/3 6/21 - 9/20	5/15 - 5/19 5/25 - 5/29 6/14 - 9/17
Indian Slough >17.5°C	5/15 - 5/20 6/1 - 9/14	5/26 - 6/8 6/17 - 9/18	6/25 - 8/28
Browns Slough >16.0°C	4/20 - 10/7	4/5 - 4/8 4/20 - 4/23 4/26 4/29 - 9/28	4/23 - 4/26 5/3 - 6/3 6/11 - 9/19 9/25 - 10/2
Samish River (upstream) >17.5°C	6/27 - 7/1 7/21 - 7/26	- -	- -
Samish River (downstream) >17.5°C	6/24 - 7/3 7/17 - 7/30 8/2 - 8/10 8/12 8/15 - 8/19	7/2 - 7/18 7/24 - 8/6 8/13 - 8/16	7/12 7/14 8/5 - 8/6 8/12 - 8/17

Table 30 shows the maximum water temperatures seen at each site for each year. Highest water temperatures were seen in 2006. Browns Slough had the highest maximum water temperatures, followed by the downstream Big Ditch site and Indian Slough.

Table 30. Maximum water temperatures at each Skagit-Samish site, 2006-2008.

Site	2006	2007	2008
Big Ditch (upstream)	--	18.4 °C	19.0 °C
Big Ditch (downstream)	28.5 °C	26.4 °C	25.4 °C
Indian Slough	26.6 °C	25.4 °C	23.3 °C
Browns Slough	33.2 °C	28.3 °C	33.0 °C
Samish River (upstream	18.6 °C	--	--
Samish River (downstream)	22.1 °C	21.6 ° C	19.8 ° C

Total Suspended Solids (TSS)

TSS concentration and loading at both the upstream and downstream Big Ditch sites are presented as boxplots in Figures 27 and 28. A paired t-test compared upstream and downstream concentrations and loading (p value ≤ 0.05, two-tailed). There was no statistical difference in concentrations or loading between the sites for 2007-2008. Statistical trends in TSS (concentrations and loading) were examined for both sites using a Seasonal-Kendall trend test (p value ≤ 0.05, two-tailed). No trends were found.

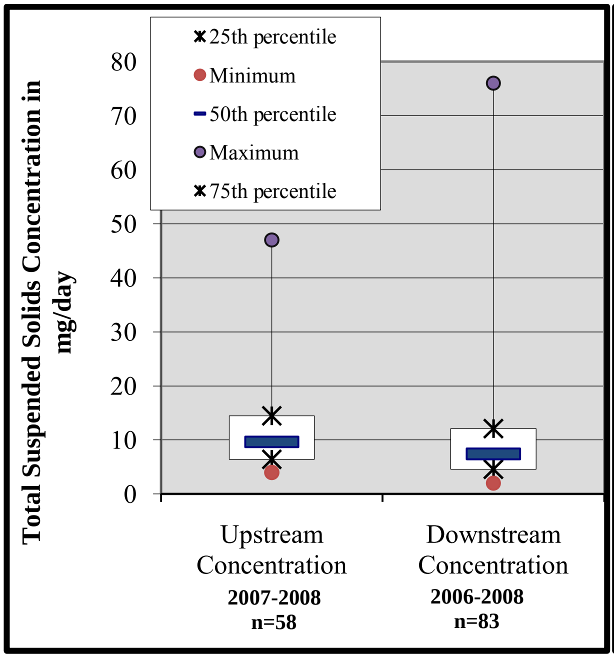


Figure 27. Total suspended solids concentrations for Big Ditch, upstream and downstream.

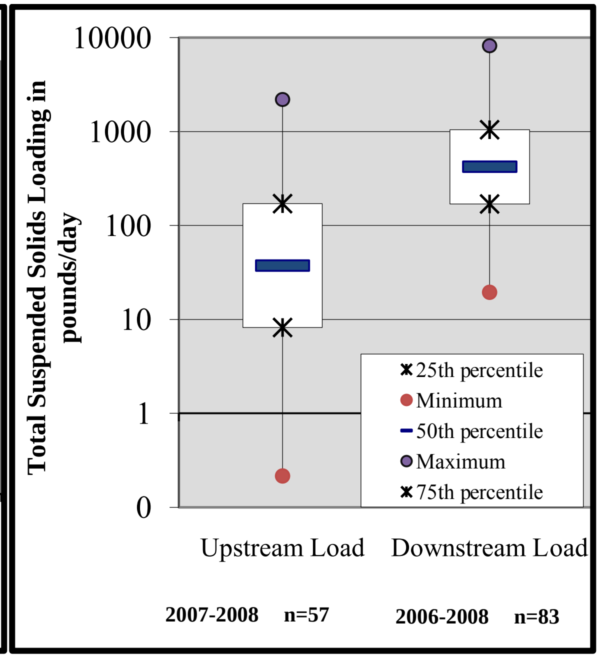


Figure 28. Total suspended solids loading for Big Ditch, upstream and downstream.

Boxplots of TSS concentrations for Indian Slough, Browns Slough, and the Samish River are presented in Figure 29. Statistical trends in TSS (concentrations and loading) were examined for all sites using a Seasonal-Kendall trend test (p value ≤ 0.05, two-tailed). No trends were found.

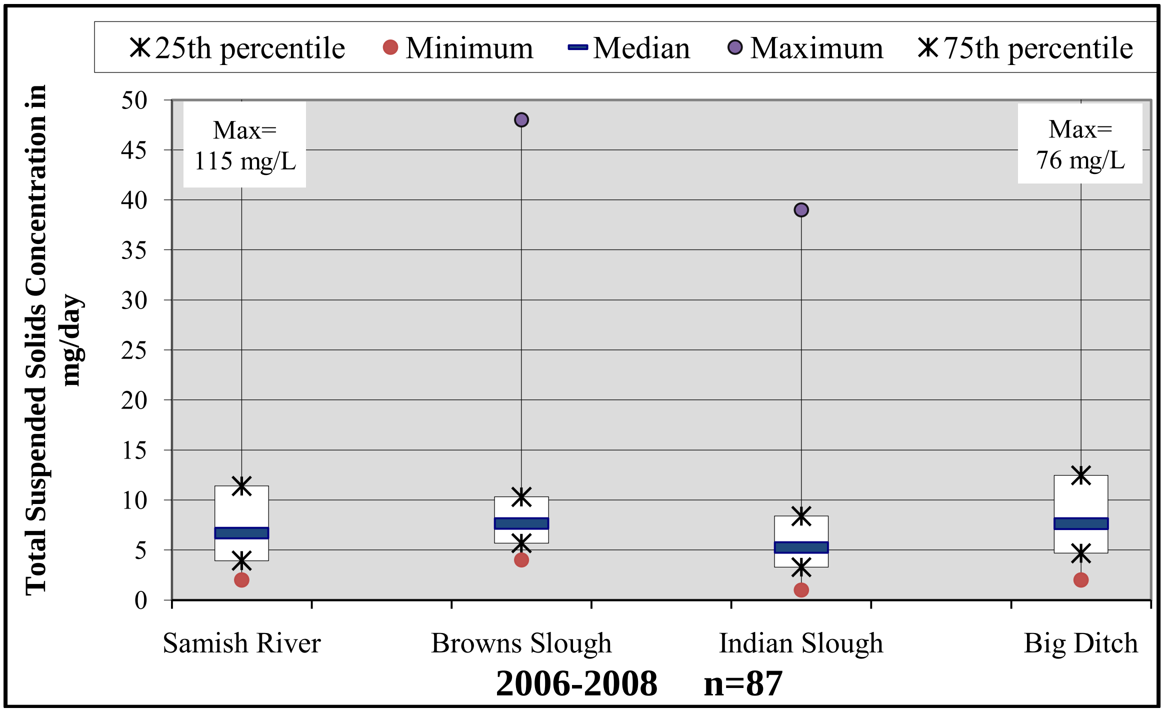


Figure 29. Skagit-Samish site summary statistics for total suspended solids, 2006-2008.

Lower Yakima Basin (WRIA 37)

Six years of monitoring has occurred in the lower Yakima basin. During 2006-2008, four sites were sampled: two on Spring Creek, one on Marion Drain, and one on Sulphur Creek Wasteway (Figure 4). The upstream Spring Creek site was sampled every other week while the other sites are sampled weekly during the monitoring season (March – September or October). During 2006-2008, Spring Creek was sampled 42 times and the other sites 82 times.

Pesticide Detections and Concentrations

Pesticide Detections

A summary of pesticide detections for all four lower Yakima sites are found in Appendix G. The tables include the average lower practical quantitation limit (ALPQL). The ALPQL is a three year average of the lowest concentration that can be accurately measured by year. Compounds below this level are qualified as estimates.

Comparison to Assessment Criteria and Water Quality Standards

The 2006-2008 data were compared to assessment criteria and water quality standards. Detailed summaries of the results can be found in pesticide calendars presented in Appendix H. Highlights of findings are summarized below.

Spring Creek

Two sites on Spring Creek were sampled. The upstream site is sampled every two weeks, and the downstream site was sampled weekly. The two sites are slightly less than three miles apart. Average surface water travel time between the sites is 4.1 hours. The Sunnyside irrigation canal crosses over Spring Creek between the upstream and downstream Spring Creek sites, but occasionally irrigation water is spilled into Spring Creek. During 2003-2006, spill from the Sunnyside irrigation canal discharged to Spring Creek when flows in the canal were too high. During 2007-2008, there was less spillage to Spring Creek due to excess water from the canal being stored in a reservoir (Brouillard, 2010). Flow at the upstream site is slightly lower than the downstream site, averaging 80% less during the sample season.

In 2006-2008, 27 pesticides and degradates were detected in Spring Creek. Nineteen of these were detected at the upstream site, and 26 were detected at the downstream site. A summary of pesticide detections for both Spring Creek sites are presented in Appendix G, Table G-6. Pesticide calendars for 2006-2008 are in Appendix H, Tables H-23 - H-28.

At the upper Spring Creek site, the DDT breakdown product DDE exceeded freshwater chronic water quality standards for total DDT (DDT and breakdown products, DDE and DDD). Concentrations were also numerically above the chronic NRWQC once each in 2006 and 2007. Azinphos-methyl was detected numerically above the chronic NRWQC twice in 2006 and once in 2007. No detections were above assessment criteria or water quality standards at the upper Spring Creek site in 2008.

At the lower Spring Creek site, DDE exceeded the chronic freshwater water quality standard for DDT (and metabolites) in 2007. Azinphos-methyl was numerically above the chronic NRWQC in three consecutive samples in 2006, and in two consecutive samples in 2007. Chlorpyrifos was numerically above the Endangered Species Level of Concern (ESLOC) once in 2007. Chlorpyrifos also exceeded water quality standards and NRWQC, once in 2006 (chronic), twice in 2007 (one acute/chronic and one chronic), and once in 2008 (acute/chronic). Each of these exceedances was also above the EPA chronic invertebrate criteria.

Spring Creek is on Ecology's 303(d) list of impaired waters for chlorpyrifos, DDT, DDE, and DDD.

Marion Drain

In 2006-2008, 28 pesticides and degradates were detected in Marion Drain. Summaries of pesticide detections are presented in Appendix G, Table G-7. Pesticide calendars are presented in Appendix H, Tables H-29 – H-31.

Twice in 2006 and once in 2007, chlorpyrifos levels exceeded acute and chronic water quality standards. In addition, the acute invertebrate criteria were exceeded once each in 2006 and 2007. In fall 2007, four weekly consecutive detections of chlorpyrifos were above chronic water quality standards and the EPA chronic invertebrate criteria. In 2007, a single detection of malathion was numerically above the chronic invertebrate criteria. In 2008, no detections were above water quality standards or assessment criteria.

Sulphur Creek Wasteway

In 2006-2008, 27 pesticides and degradates were detected in Sulphur Creek Wasteway. Summaries of pesticide detections are presented in Appendix G, Table G-8. Pesticide calendars are in Appendix H, Tables H-32 – H-34.

DDE exceeded chronic water quality standards in 2006 and 2007. Azinphos-methyl was detected only in 2006, numerically above the chronic NRWQC. Chlorpyrifos had one detection above the ESLOC for fish in 2007 and was also above the chronic invertebrate criteria once in each of the three years.

Sulphur Creek is on Ecology's 303(d) list of impaired waters for chlorpyrifos, DDT, DDE, and DDD.

Statistical Analysis

To investigate possible long-term changes in pesticide concentrations over time, five of the most commonly detected pesticides were compared using a non-parametric test, Kaplan-Meir. Concentrations found during 2003-2005 were compared to the 2006-2008 concentrations for the downstream Spring Creek site, Marion Drain, and Sulphur Creek (Figure 30). Boxplots for five of the most commonly seen pesticides at the downstream Spring Creek site are shown in Figure 30. Compounds include four herbicides and an insecticide (chlorpyrifos). Concentrations for the herbicides are similar for the two three-year periods (2003-2005 and 2006-2008).

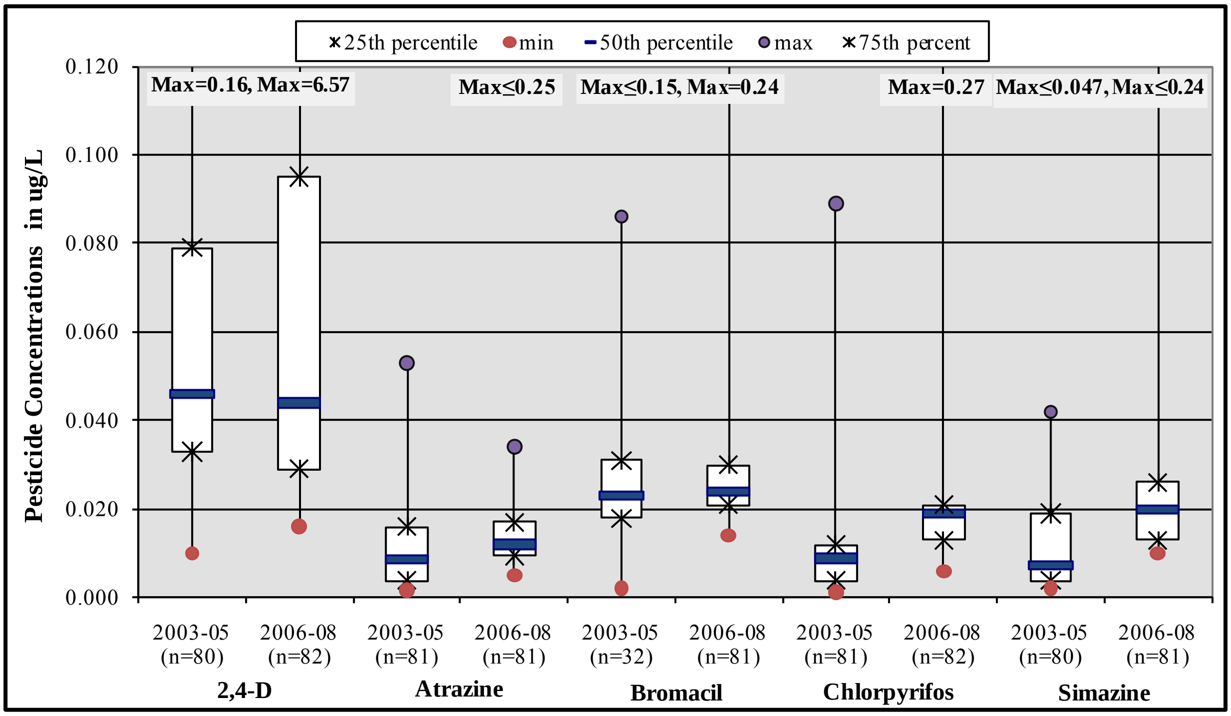


Figure 30. Statistical comparison for five of the most commonly seen pesticides at the downstream Spring Creek site, 2003-2005 and 2006-2008.

In 2006-2008, chlorpyrifos concentrations increased but the increase was not statistically significant and was likely due to a change in reporting limits. During 2003-2005, the average LPQL for chlorpyrifos was 0.026 µg/L; during 2006-2008, it was 0.033 µg/L. This change affects calculated Kaplan-Meir summary statistics.

Boxplots for five of the most commonly seen pesticides in Marion Drain are shown in Figure 31. Compounds include four herbicides and an insecticide. The herbicides 2,4-D, atrazine, pendimethalin, and terbacil were compared as well as the insecticide chlorpyrifos. Comparing concentrations for 2003-2005 and 2006-2008 showed no statistically significant differences between the two three-year periods.

The most commonly seen pesticides in Sulphur Creek Wasteway included 2,4-D, atrazine, bromacil, terbacil, and the insecticide chlorpyrifos. A comparison of concentrations of these pesticides showed no differences between the two periods.

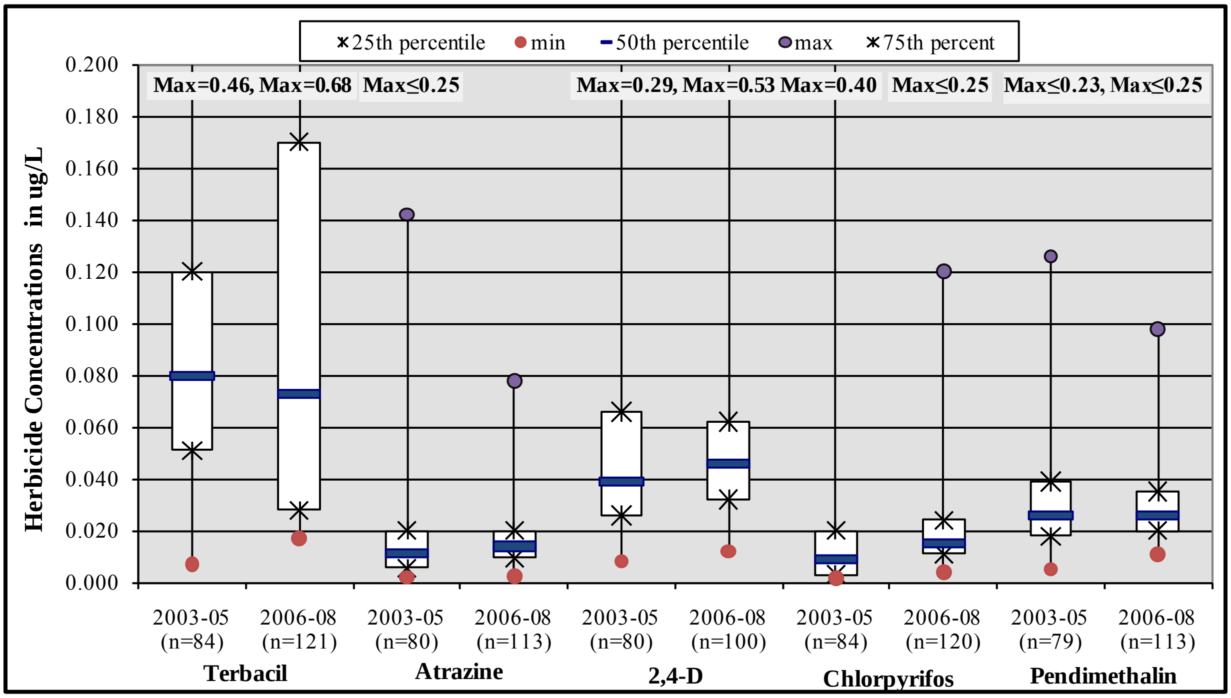


Figure 31. Statistical comparison for five of the most commonly seen pesticides in Marion Drain, 2003-2005 and 2006-2008.

Pesticide Distribution

Spring Creek

Distribution of detections by pesticide group for both the Spring Creek sites in 2006-2008 are presented in Figure 32. Pesticide distribution at the upstream and downstream sites was similar. The most frequently detected compounds were herbicides, followed by insecticides (Figure 32). The percentage of insecticide and degradate compounds found at each site were similar.

Likewise the distribution of pesticides was similar at the Spring Creek sites for the 2003-2005 (Figure 33).

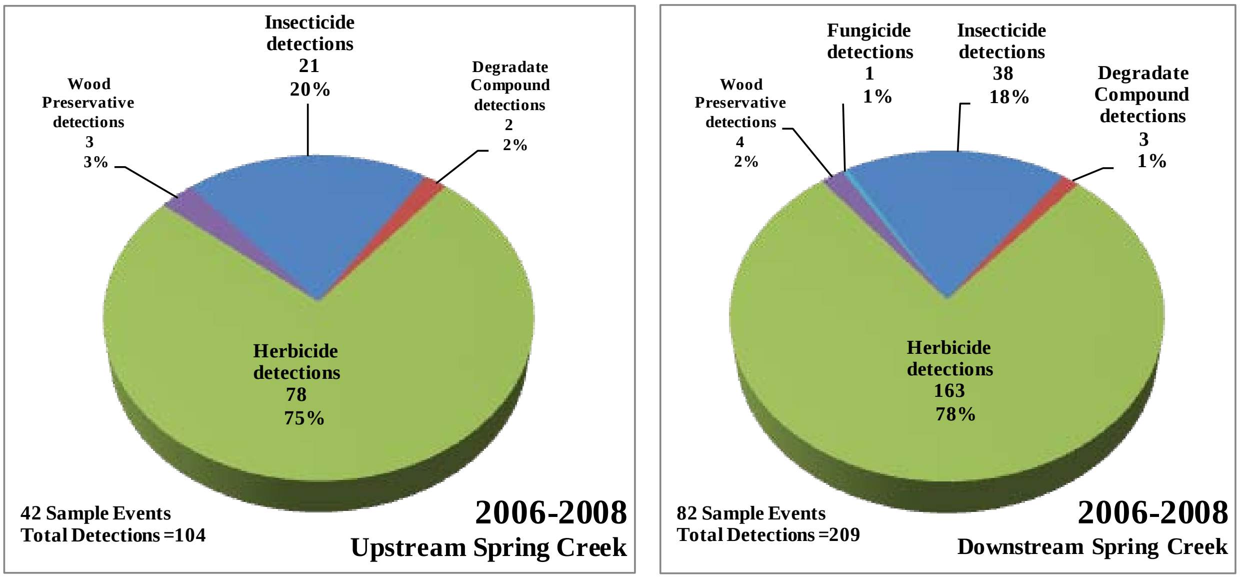


Figure 32. Distribution of types of pesticide seen at upstream and downstream Spring Creek, 2006-2008.

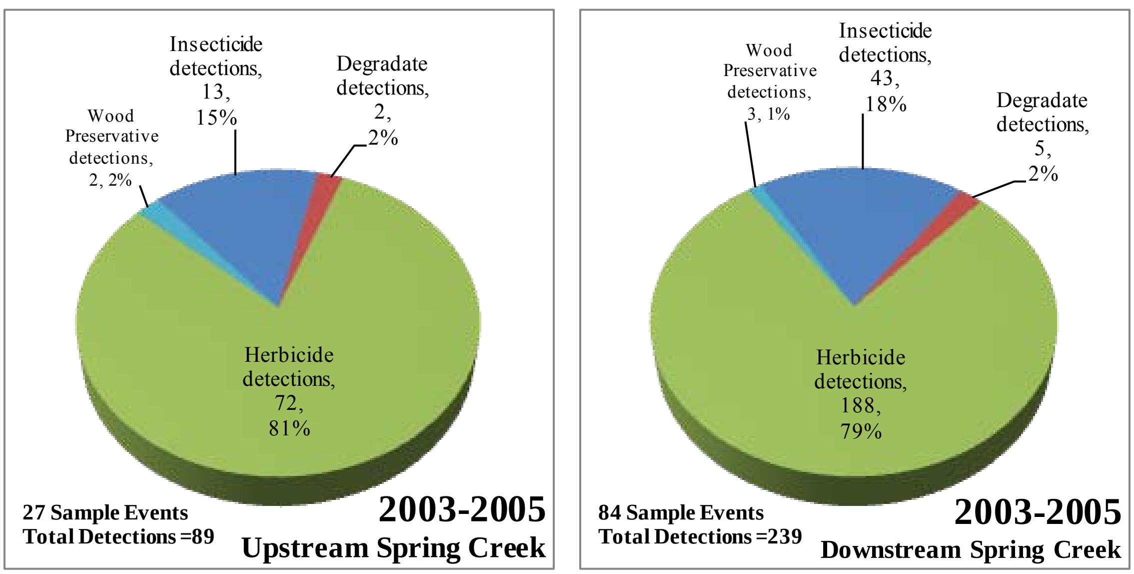


Figure 33. Distribution of types of pesticides seen at upstream and downstream Spring Creek, 2003-2005.

Table 31 presents the most commonly seen herbicides for the upstream and downstream Spring Creek sites. Similar herbicide compounds are seen at both sites; the most commonly detected herbicides are atrazine and 2,4-D. A variety of insecticides were detected at both sites, but the most commonly detected insecticide was chlorpyrifos (Figures 34 and 35). Insecticides were rarely seen in combination at either of the Spring Creek sites (Figures 34 and 35).

Table 31. Most frequently seen herbicides at the upstream and downstream Spring Creek sites, 2006-2008.

Upstream n=42			Downstream n=82		
Herbicide	Number of detections	Percentage of sample events detected	Herbicide	Number of detections	Percentage of sample events detected
Atrazine	25	60%	Atrazine	45	50%
2,4-D	14	33%	2,4-D	34	41%
Bentazon	12	29%	Bromacil	26	32%
Simazine	10	24%	Simazine	24	29%
Norflurazon	8	19%	Norflurazon	10	12%

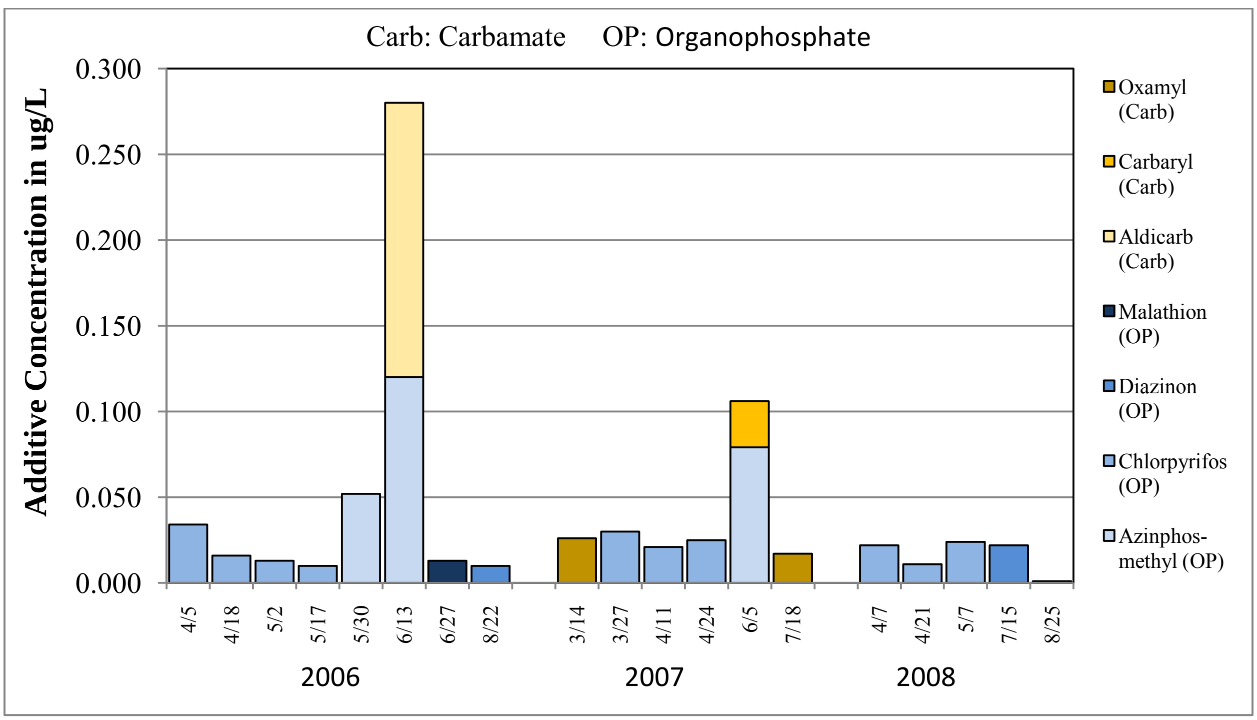


Figure 34. Cumulative total for insecticide detections at the upstream Spring Creek site, 2006-2008.

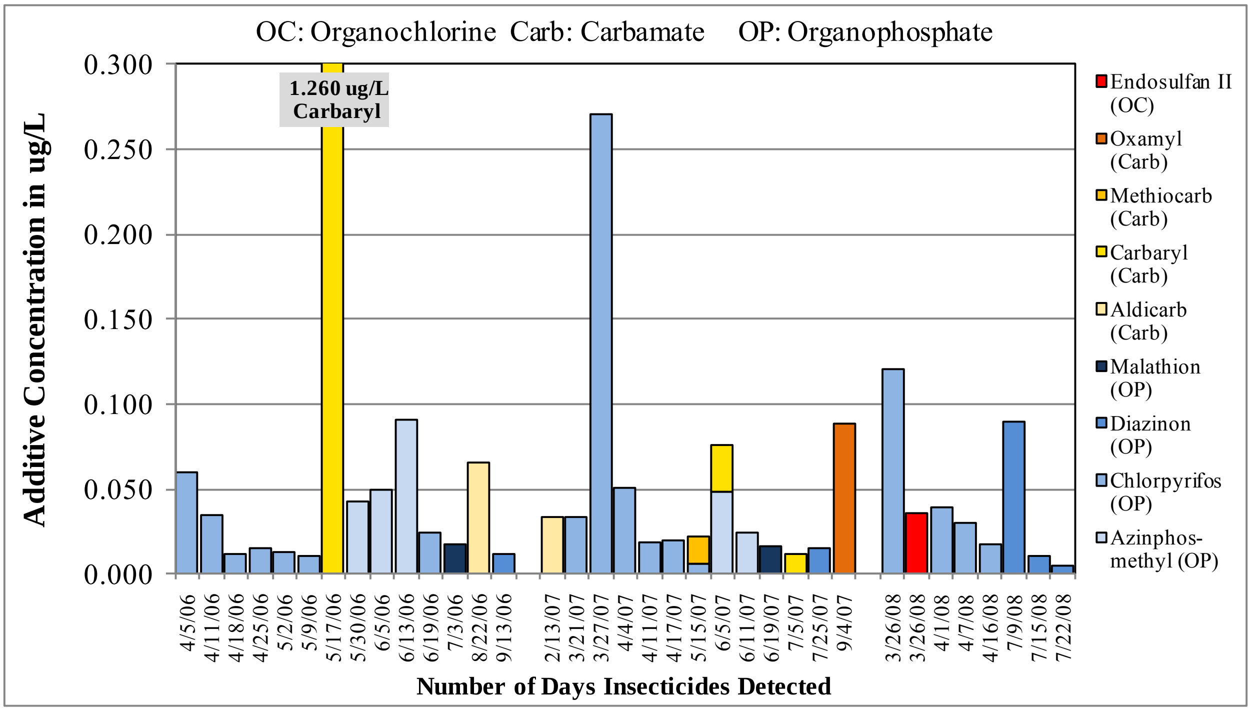


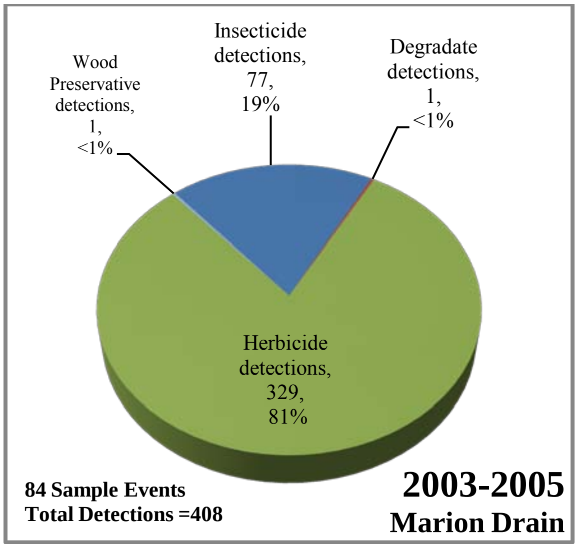
Figure 35. Cumulative total amount for insecticide detections at the downstream Spring Creek site, 2006-2008.

The number of pesticide detections seen during both sample periods was similar (Figures 32 and 33). A statistical test of proportions was used to compare the ratio of detections and no-detection of the three pesticide groups: herbicide, insecticide, and degradate compounds. The results of the test showed no statistical difference between 2003-2005 and 2006-2008 in the number of herbicide, insecticide, or degradate compound detections.

Marion Drain

Distribution of detections by pesticide group for the Marion Drain site during 2003-2005 and 2006-2008 are presented in Figure 36. Organophosphate sampling at this site extended an extra month (through the end of October) due to historic detections of chlorpyrifos through mid-October.

The number of pesticide detections during both sample periods was similar. A statistical test of proportions was used to compare the ratio of detections and no-detection of the three pesticide groups: herbicide, insecticide, and degradate compounds. The results of the test showed no statistical difference between 2003-2005 and 2006-2008 in the number of herbicide, insecticide, or degradate compound detections. Figure 36 presents types of pesticide detections for the two periods.



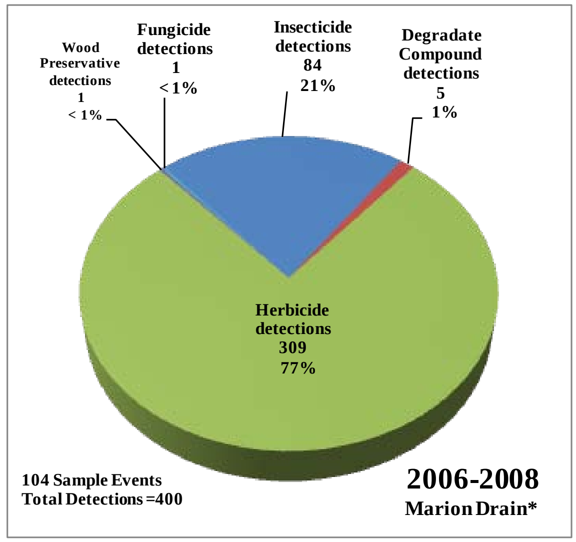


Figure 36. Distribution of types of pesticides seen in Marion Drain, 2003-2005 and 2006-2008.
**2008 intensive sampling results not included.*

Herbicides were the most commonly detected pesticide in Marion Drain, followed by insecticides. Marion Drain had the most herbicides detections of any of the lower Yakima sites. The most commonly seen herbicide was terbacil, detected during 77% of the sample events (Table 32).

Table 32. Most frequently detected herbicides in Marion Drain, 2006-2008.

Herbicide	Number of detections	Percentage of sample events detected
Terbacil	93	77%
Atrazine	50	41%
Pendimethalin	43	36%
Bentazon	39	32%
Trifluralin	38	31%

Marion Drain also has the most insecticide detections of any of the lower Yakima sites. There were 61 detections of chlorpyrifos, the most commonly detected insecticide. Malathion, the second most commonly seen insecticide, was detected 12 times. Figure 37 presents the sum of insecticide detections per sample day for each insecticide.

In 2006, there were five sample events with multiple insecticide detections; these detections were usually confined to two insecticides. In 2007, there were 10 sample events where two insecticides were detected, and on May 29, 2007 four insecticides were detected. In 2008, no multiple insecticide detections occurred, and in general insecticide detections were lower.

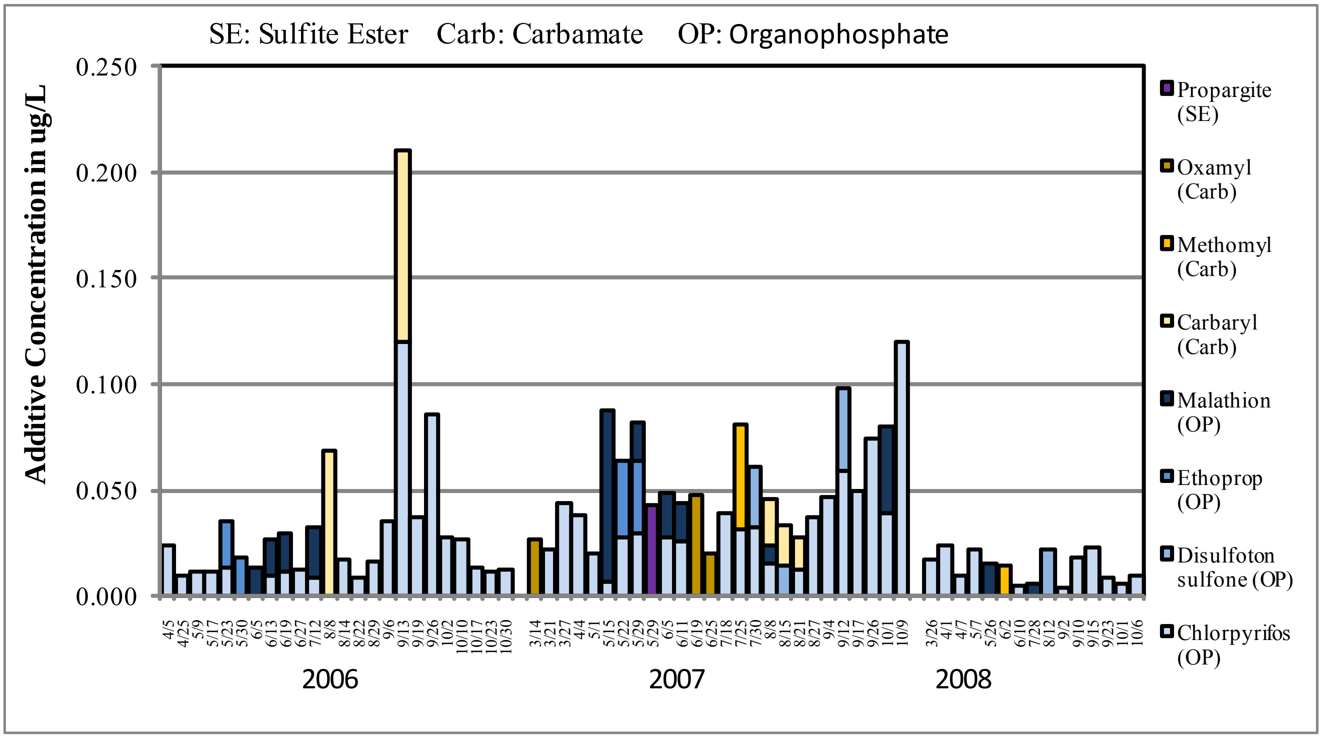


Figure 37. Cumulative amount for insecticide detections at the Marion Drain site, 2006-2008.

2007 Intensive Monitoring In Marion Drain

As a part of this project, Ecology conducted an additional monitoring study in spring 2007. Staff conducted an intensive 22-day pesticide sampling effort in Marion Drain to compare daily and weekly sampling frequencies using conventional grab samples (Dugger et al., 2008). In addition, two types of passive samplers, Semi-Permeable Membrane Devices (SPMD) and Polar Organic Chemical Integrative Samplers (POCIS), were deployed for the 22-day period.

A total of 21 pesticide compounds were detected during the study. Daily grab sampling detected one more pesticide compound than did the weekly sampling. Daily grabs detected six pesticide compounds not found in the SPMD analysis. The SPMDs detected five compounds that were not found in the daily grab sampling. Results from the POCISs were compromised by positive detections in the sample blank and by inconsistent detections between sample replicates.

Conclusions of the study were that SPMDs complemented grab sampling activities by increasing the detection rate for hydrophobic pesticides. Daily grab sampling detected more variations in pesticide concentrations that were missed in the weekly sampling, including maximum concentrations. No differences were seen in determining exceedances of water quality standards or assessment criteria between the daily and weekly sampling During the daily sampling, only one assessment criteria (for malathion) was exceeded, this was also found in the weekly sampling. Differences in the number of detections were minimal. The full report for this 2007 monitoring project can be found at: www.ecy.wa.gov/biblio/0803020.html.

Sulfur Creek Wasteway

Distribution of detections by pesticide group for the Sulphur Creek Wasteway site during 2003-2005 and 2006-2008 are presented in Figure 38. A test of proportions shows no statistical difference between the two periods in the number of herbicide, insecticide, or degradate compounds detections.

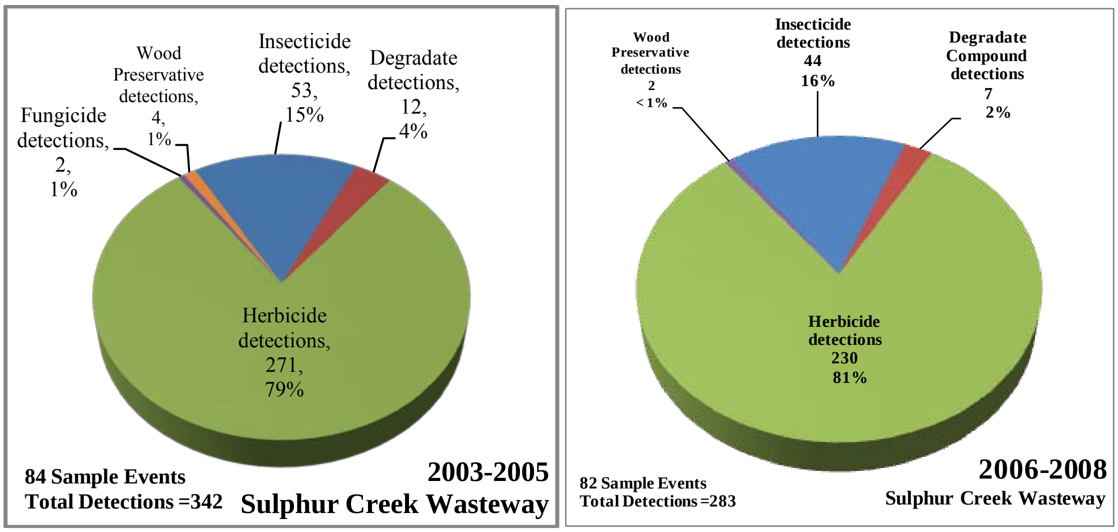


Figure 38. Distribution of types of pesticides detected in Sulphur Creek Wasteway, 2003-2005 and 2006-2008.

Herbicides were the most commonly detected pesticides in Sulphur Creek Wasteway, followed by insecticides. The most commonly detected herbicide was 2,4-D, seen during 60% of the sample events, followed by atrazine, bromacil, DCPA, and dicamba I (Table 33).

Table 33. Most frequently detected herbicides in Sulphur Creek Wasteway, 2006-2008.

Herbicide	Number of detections	Percentage of sample events detected
2,4-D	49	60%
Atrazine	29	35%
Bromacil	29	35%
DCPA	20	24%
Dicamba I	20	24%

The most commonly seen insecticide was carbaryl, followed by chlorpyrifos. Figure 39 presents the sum of insecticide concentrations seen in Sulphur Creek. At most, two insecticides were detected during one sample event. The greatest sum of insecticides was seen on June 5, 2006, with detections of two organophosphates, azinphos-methyl (0.033 µg/L), and dimethoate (0.45 µg/L).

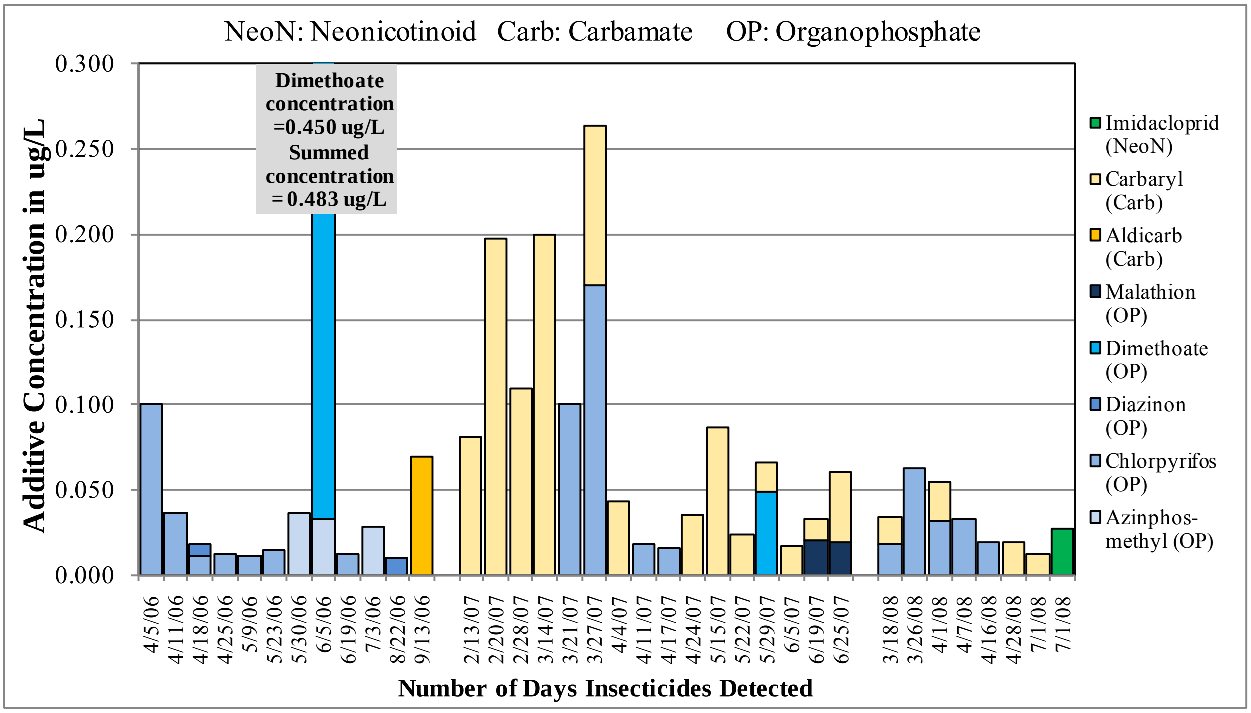


Figure 39. Cumulative amount for insecticide detections at the Sulphur Creek Wasteway site, 2006-2008.

Comparison of Pesticides Detections at the Upstream and Downstream Spring Creek Sites

A comparison between upstream and downstream Spring Creek detections depends partly on the mobility and persistence of pesticides in the environment. These are determined by the chemical and physical properties of the pesticide. Fate and transport of pesticides vary greatly depending on the compound. Highly soluble compounds, those with high water solubility or low K_{OC} tend to move from the land at relatively high rates. Other factors affecting environmental fate include chemical half life, pattern and extent of chemical use, and physical or hydrologic characteristics of the drainage basin (Carpenter et al., 2008).

During 2006-2008, both Spring Creek sites were sampled on the same day 42 times. The sites are 2.9 miles apart; average water travel time between the two sites (March through September) is approximately 4.1 hours. The upstream site averages 80% of the flow of the downstream site. The Sunnyside irrigation canal crosses Spring Creek, and occasionally irrigation water is spilled into Spring Creek between the two sites. Thus pesticides present in irrigation water could be detected at the downstream Spring Creek site during spillage.

An upstream and downstream presence of a compound did not frequently occur on the same day. Figures 40 and 41 present the sample days when a specific compound was detected at both sites. Figure 40 presents loading for herbicides, and Figure 41 presents loading for insecticides. Atrazine and 2,4-D were the most frequently detected herbicides at both sites.

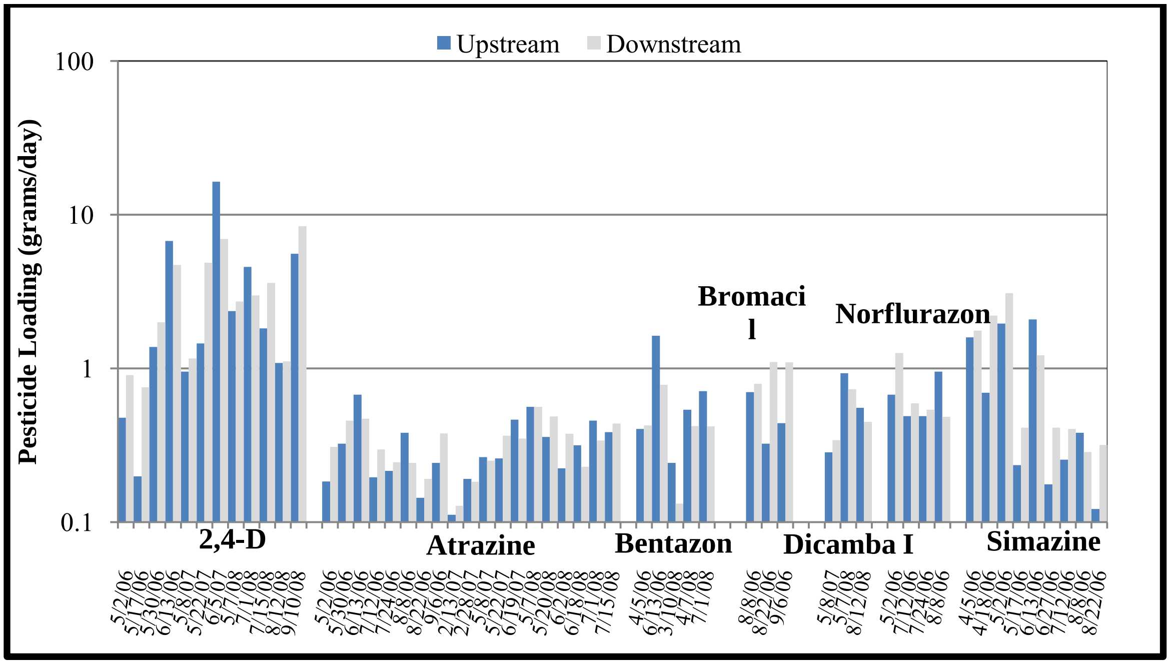


Figure 40. Herbicide loading at the upstream and downstream Spring Creek sites for the days when both sites had detections, 2006-2008.

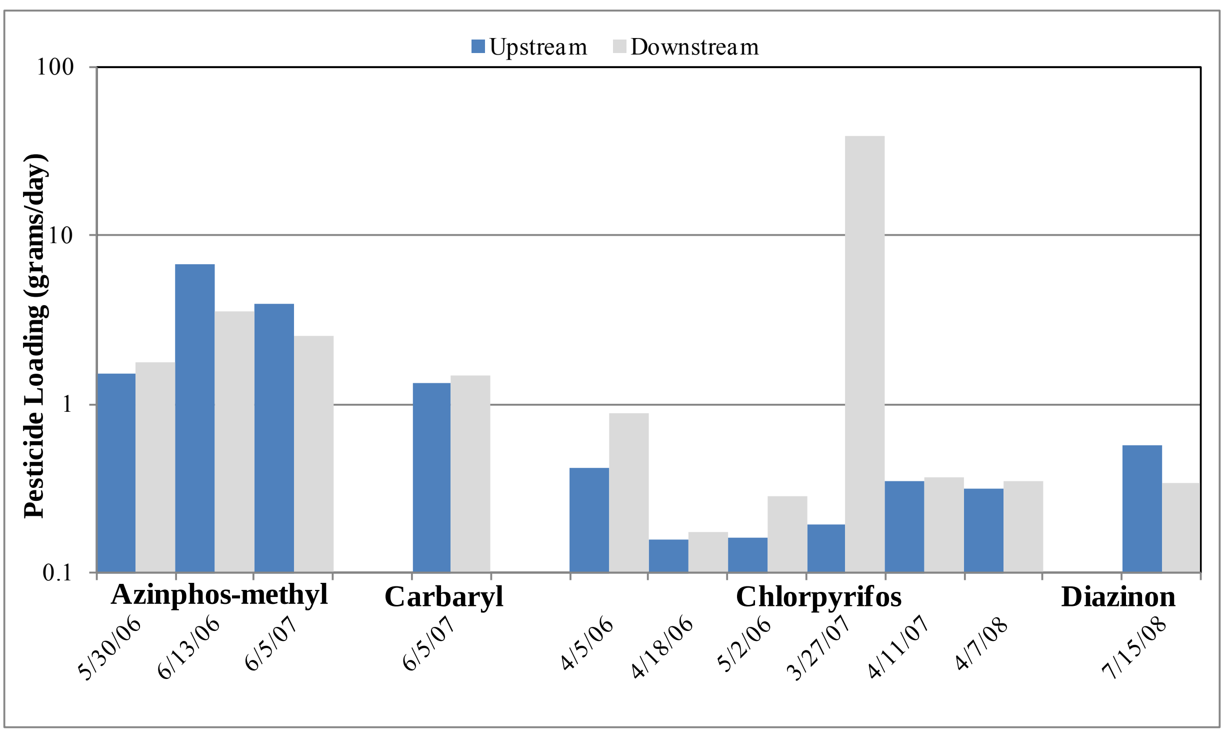


Figure 41. Insecticide loading at the upstream and downstream Spring Creek sites for the days when both sites had detections, 2006-2008.

Out of 41 sample events, atrazine was seen 19 times and 2,4-D was seen 12 times. Simazine was detected at both the upstream and downstream sites nine times. All three of these herbicides have a low K_{oc} and thus less tendency to bind to soils.

For insecticides, upstream and downstream detections were rarely seen (Figure 41). The most commonly seen insecticide at both sites was chlorpyrifos which has the highest K_{oc} of any of the insecticides detected. Likely chlorpyrifos is seen most frequently due to more use in the subbasin.

Factors Affecting Pesticide Detections

Environmental Factors

A statistical test for correlation coefficient (Kendall's tau-b) was used to determine if there was a relationship between some of the more commonly seen pesticides at a site and environmental factors such as flow and rainfall. Data from all available years were compared.

At the upstream Spring Creek site, there was:

- A very weak positive correlation between 2,4-D and previous 24-hour rainfall. (Kendall's tau= 0.24, $p \leq 0.05$).
- A very weak positive correlation between chlorpyrifos and previous 24-hour rainfall. (Kendall's tau= 0.26, $p \leq 0.05$).
- A stronger positive correlation between 2,4-D and flow. (Kendall's tau= 0.46, $p < 0.01$).
- A negative correlation between flow and both atrazine and bentazon. (Kendall's tau= -0.39, $p < 0.01$ and Kendall's tau= -0.52, $p < 0.01$ respectively).

At the downstream Spring Creek site, there was a very weak negative correlation between two herbicides, atrazine and bentazon, and flow (Kendall's tau= - 0.31, $p < 0.01$; Kendall's tau= -0.24, $p < 0.01$ respectively).

In Marion Drain and Sulphur Creek Wasteway, there was a weak negative correlation between bentazon and flow (Kendall's tau = - 0.42, $p<0.01$ and Kendall's tau= -0.28, $p<0.01$, respectively). Graphs of flow, precipitation, and most commonly seen herbicide and insecticide concentrations for each year and site are presented in Appendix I.

Temporal Factors

There was a seasonal pattern in pesticide detections. The Spring Creek sites and Sulphur Creek Wasteway showed a similar pattern (Figure 42). Herbicide detections were highest May through June, and the greatest number of insecticide detections occurred in April. Chlorpyrifos was the most commonly detected insecticide at all lower Yakima sites. Figure 43 presents flow, 24-hour precipitation, and most commonly detected insecticides for upper Spring Creek. The majority of chlorpyrifos detections were seen during April through May. Azinphos-methyl detections occurred in June in both 2006 and 2007; detections coincide with increased flow and precipitation.

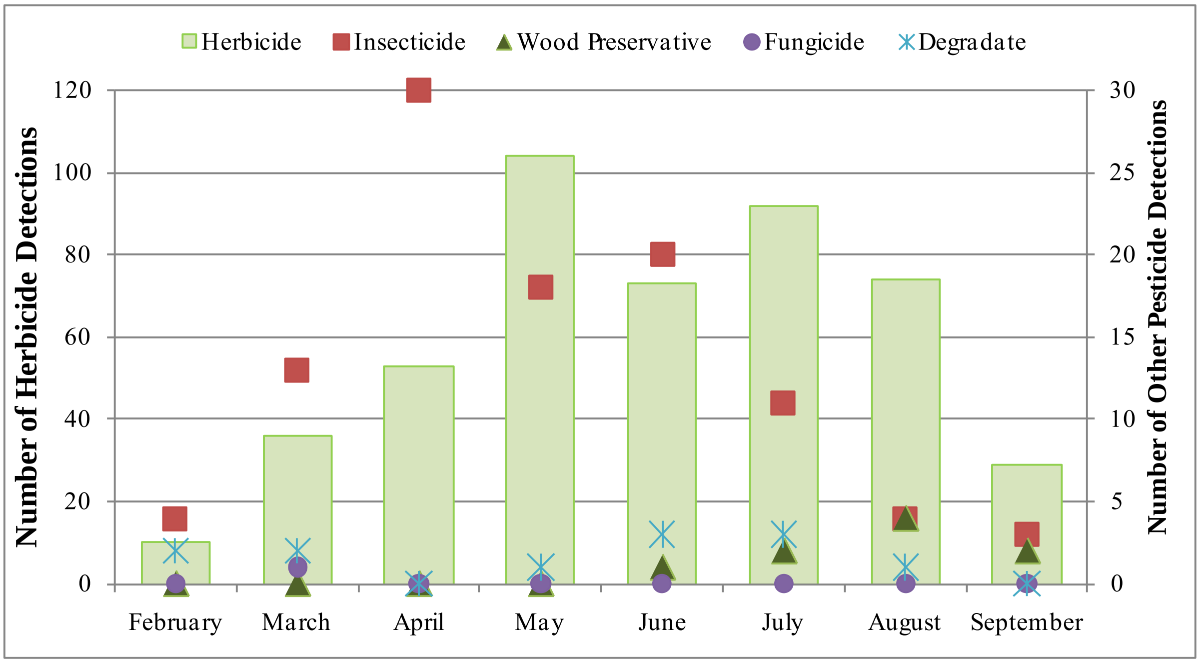


Figure 42. Number of compounds detected by pesticide type for the upstream and downstream Spring Creek sites and Sulphur Creek Wasteway, 2006-2008.

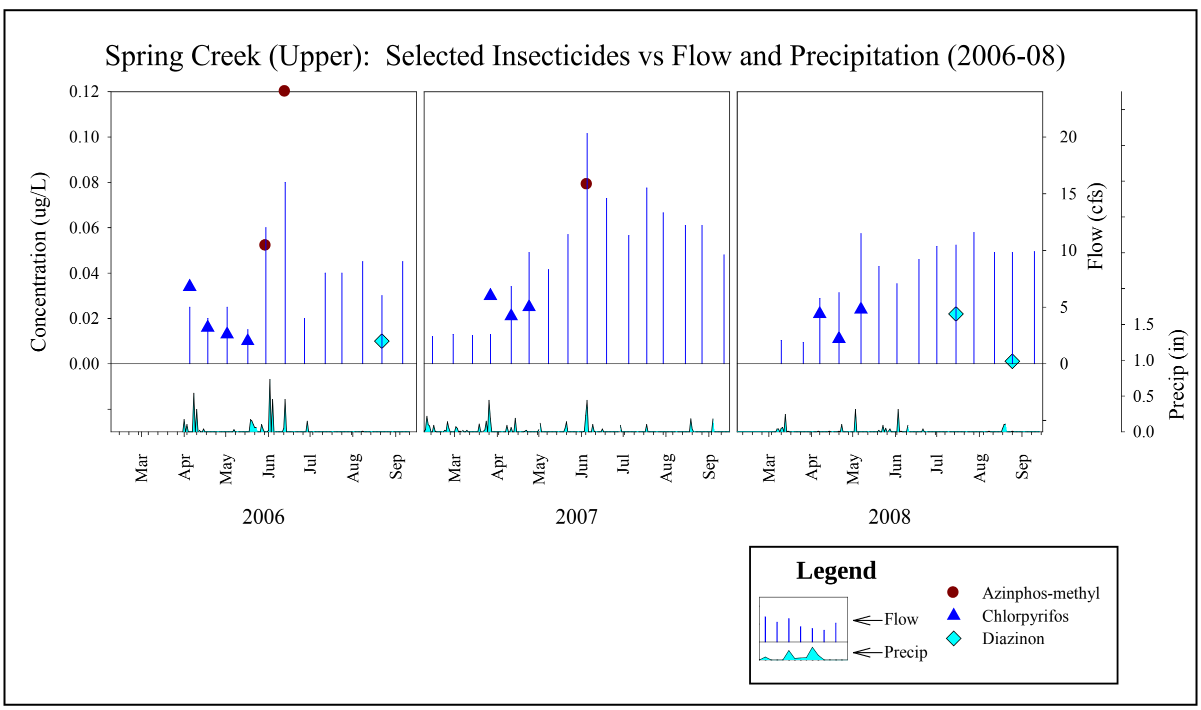


Figure 43. Streamflow, 24-hour precipitation, and the most commonly detected insecticides at the upstream Spring Creek site, 2006-2008.

Figure 44 presents the number of detections by type of pesticide for the Marion Drain site. In Marion Drain the greatest number herbicide detections occurred in May. The greatest number of insecticide detections occurred May-June and again in September. Chlorpyrifos insecticide detections increased in May-June, decreased in July, and increased again in late August and September (Appendix I, Figure I-19).

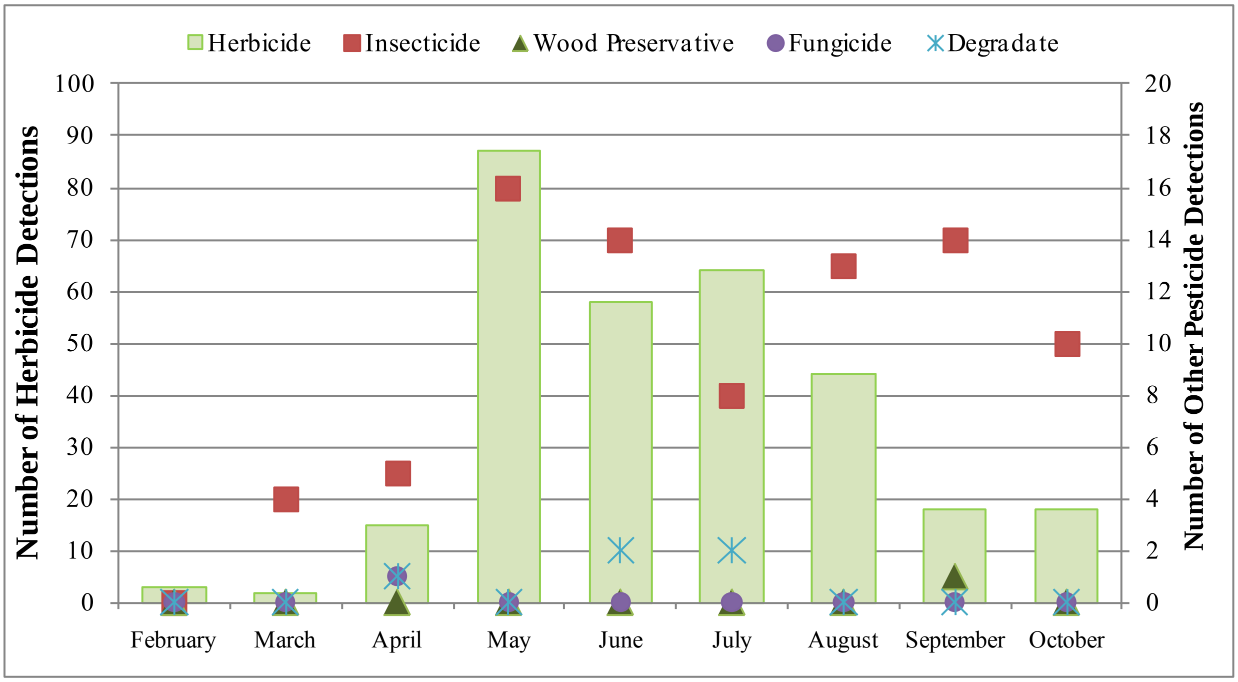


Figure 44. Number of compounds detected by pesticide type for Marion Drain, 2006-2008. *Marion Drain Intensive Monitoring Study data not included.*

Water Quality Factors

A statistical test for correlation coefficient (Kendall's tau-b) was used to determine if there was a relationship between TSS and flow, and select pesticide concentrations. Data from all years were compared.

At the upstream Spring Creek site there was:

- A positive correlation between TSS and flow (Kendall's tau= 0.45, p< 0.01).
- A weak positive correlation between TSS and 2,4-D (Kendall's tau= 0.37, p<0.01)
- A weak positive correlation between TSS and chlorpyrifos (Kendall's tau= 0.33, p<0.01).
- A weak negative correlation between TSS and bentazon (Kendall's tau= - 0.32, p<0.01).

The downstream Spring Creek site showed the same pattern:

- A positive correlation between TSS and flow (Kendall's tau= 0.54, p< 0.01).
- A weak negative correlation between TSS and the atrazine (Kendall's tau= - 0.24, p<0.01).
- A weak negative correlation between TSS and bentazon (Kendall's tau= - 0.26, p<0.01).

In Marion Drain there was:

- A positive correlation between TSS and flow (Kendall's tau= 0.51, p< 0.01).
- A weak negative correlation between TSS and bentazon (Kendall's tau= - 0.35, p<0.01).

Sulphur Creek Wasteway showed the same pattern as the other sites:

- A weak positive correlation between TSS and flow (Kendall's tau= 0.0.31, p< 0.01).
- A weak negative correlation between TSS and bentazon (Kendall's tau= - 0.25, p<0.01).

Conventional Parameters

Conventional water quality parameters were measured at all the lower Yakima basin sites. In 2008, Winkler dissolved oxygen measurements were also obtained. Continuous, 30-minute interval temperature data were collected; temperature profiles are presented in Appendix J. Table 34 summarizes results for TSS, flow, pH, conductivity, and dissolved oxygen for all sites.

Table 34. Arithmetic mean and range for conventional parameters (grabs) for the lower Yakima basin sites, 2006-2008.

	Total Suspended Solids (mg/L)			Flow (cubic feet per second)			pH (standard units)			Conductivity (µmhos/cm)			Dissolved Oxygen (mg/L)
	2006	2007	2008	2006	2007	2008	2006	2007	2008	2006	2007	2008	2008
Spring Creek (upstream)													
Mean[1]	17	21	24	7	10	8	8.1	8.0	8.0	352	339	313	9.3
Minimum	7	4	3	3	2	2	7.8	7.8	7.8	258	218	233	7.8
Maximum	54	53	72	16	20	12	8.4	8.6	8.4	499	561	538	11.6
Spring Creek (downstream)													
Mean[1]	20	15	20	14	13	12	8.8	8.8	8.6	318	328	301	10.2
Minimum	3	3	2	6	2	1	8.4	8.3	8.0	189	111	145	8.7
Maximum	86	42	90	62	58	33	9.7	9.8	9.4	434	578	505	12.7
Marion Drain													
Mean[1]	15	12	15	120	123	147	8.1	8.1	8.0	218	210	198	11.9
Minimum	1	2	2	10	17	21	7.3	7.6	7.4	138	134	139	8.6
Maximum	51	31	46	296	286	345	9.2	9.0	9.1	461	299	259	17.3
Sulphur Creek Wasteway													
Mean[1]	38	45	37	209	290	213	8.4	8.4	8.2	281	308	252	10.3
Minimum	12	8	4	89	48	60	7.8	7.8	7.8	149	165	150	8.1
Maximum	116	409	115	546	922	752	8.8	9.0	8.6	668	658	610	12.6

Mean[1]: Arithmetic Mean.

Comparison to Water Quality Standards

Grab results for pH, dissolved oxygen, and continuous temperature were compared to water quality standards (Table 19). Measurements made during site visits were designated as "grab" to distinguish them from continuously recorded data.

pH

All of the sites except the upstream Spring Creek sites did not meet (exceeded) pH standards all three years sampled. The upstream Spring Creek site had one exceedance at 8.6 s.u. of the pH standard in 2007.

Dissolved Oxygen

Dissolved oxygen grab samples were obtained in 2008. All sites met the dissolved oxygen standard of a minimum of 8.0 mg/L per day.

Temperature

The temperature standard for the lower Yakima sites is the 7-day average of the daily maximum temperature (DADMax) which should not exceed 17.5° C. Continuous, 30-minute interval, temperature data were collected year-round from 2006-2008 at all sites. There are gaps in temperature data due to thermistors being out of the water during low water levels. None of the sites met the temperature standards during all of 2006-2008. Table 35 describes periods when temperature standards were not met.

Table 35. Water temperature exceedances for lower Yakima basin sites, 2006-2008.

Site	2006	2007	2008
Spring Creek (upstream) >17.5°C	May 14-22 May 30 - Aug 30 Sept 6-7	June 18 - Sept 8 Sept 14	May 14-22 May 26 - June 2 June 12 - Aug 31 Sept 7-10
Spring Creek (downstream) >17.5°C	April 19 - Sept 11	May 5-19 May 24 Sept 17	May 2 - Sept 17
Marion Drain >17.5°C	May 15-20 June 4 - Sept 13	May 27 - Sept 16	May 16-19 June 13 - Aug 16
Sulphur Creek Wasteway >17.5°C	May 13 - May 21 May 31 - Sept 13	May 7 - May 17 May 25 - June 5 June 13 - Sept 18	May 13-19 May 29 - June 2 June 11 - Sept 20

Total Suspended Solids (TSS)

A comparison of TSS concentration and loading for both the upstream and downstream Spring Creek sites is presented in Figures 45 and 46. TSS values appear to be decreasing at the downstream site (2003-2008) while increasing at the upstream site (2005-2008). While flows were greater at the downstream site, loading at both the upstream and downstream sites were similar in 2007-2008 (Figure 46).

Statistical trends in TSS (concentrations and loading) were examined for both sites using a Seasonal-Kendall trend test (p value ≤ 0.05, two-tailed) for the March through September sampling period. The downstream site had six years of data (2003-2008), and the upstream sites had four years of data (2005-2008). The upstream site showed a trend toward increasing TSS concentrations and loading (Figure 47). The downstream site showed a trend toward decreasing TSS concentrations and loading (Figure 48).

Boxplots of TSS concentrations in Marion Drain and Sulphur Creek for 2003-2005 and 2006-2008 are presented in Figure 49. Marion Drain tended to have lower TSS concentrations that the other lower Yakima sites. Sulphur Creek Wasteway has some of the highest TSS concentrations of the lower Yakima sites. Statistical trends in TSS (concentrations and loading) were examined for both sites using a Seasonal-Kendall trend test ($p \leq 0.05$, two-tailed). No trends were found.

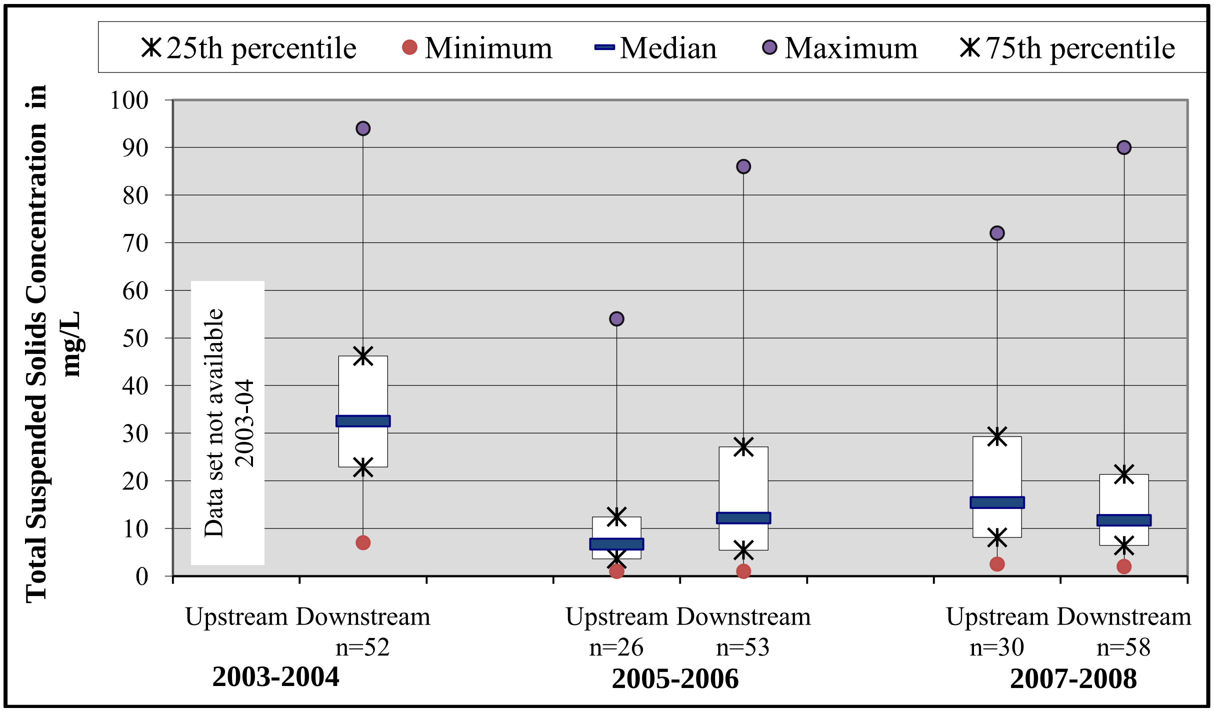


Figure 45. Summary statistics for total suspended solids concentrations at the upstream and downstream Spring Creek sites, 2003-2008.

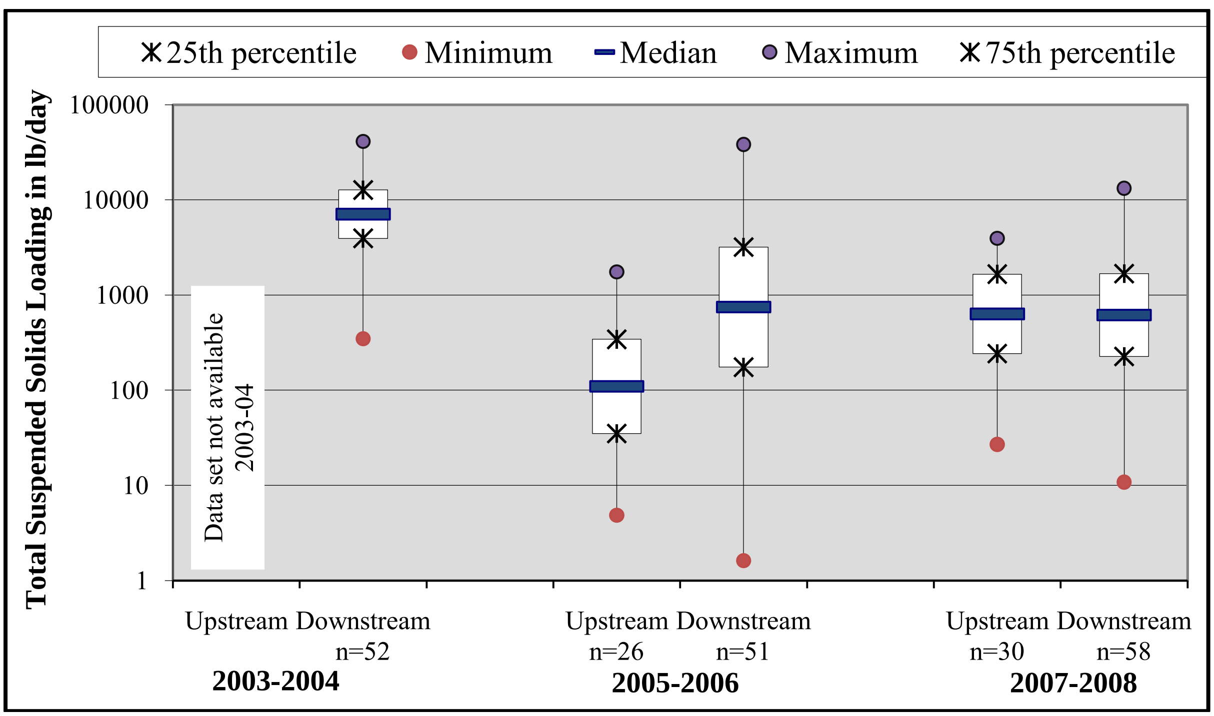


Figure 46. Summary statistics for total suspended solids loading at the upstream and downstream Spring Creek sites, 2003-2008.

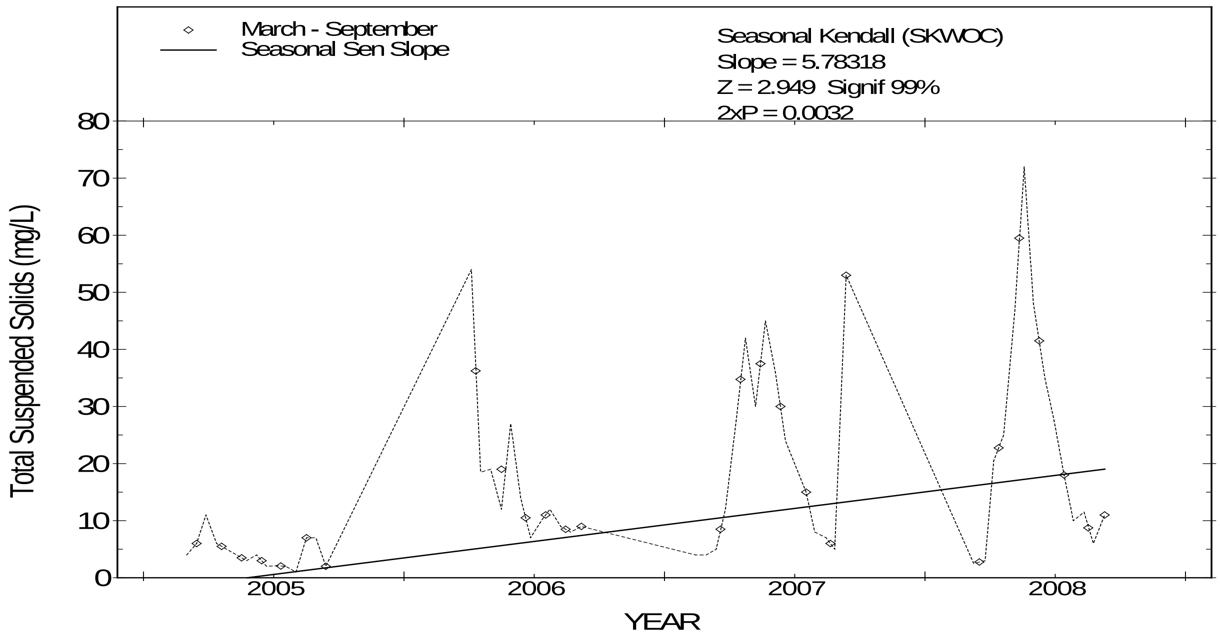


Figure 47. The upstream Spring Creek site showing increasing trends in total suspended solids concentrations, 2005-2008.

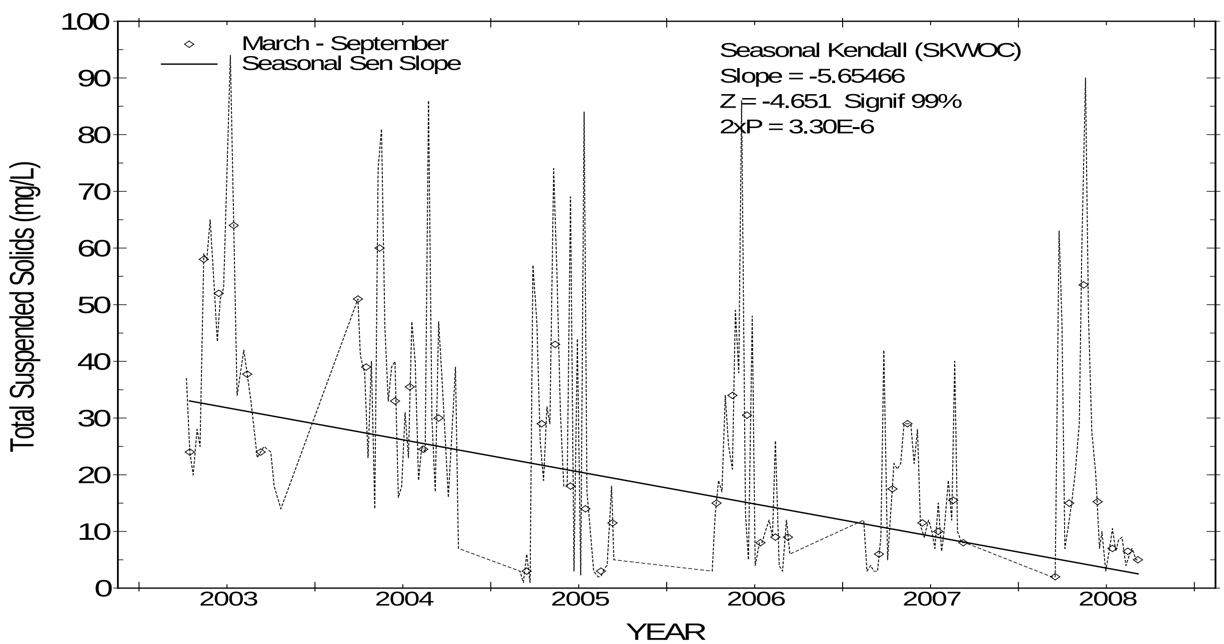


Figure 48. The downstream Spring Creek site showing decreasing trends in total suspended solids concentrations, 2003-2008.

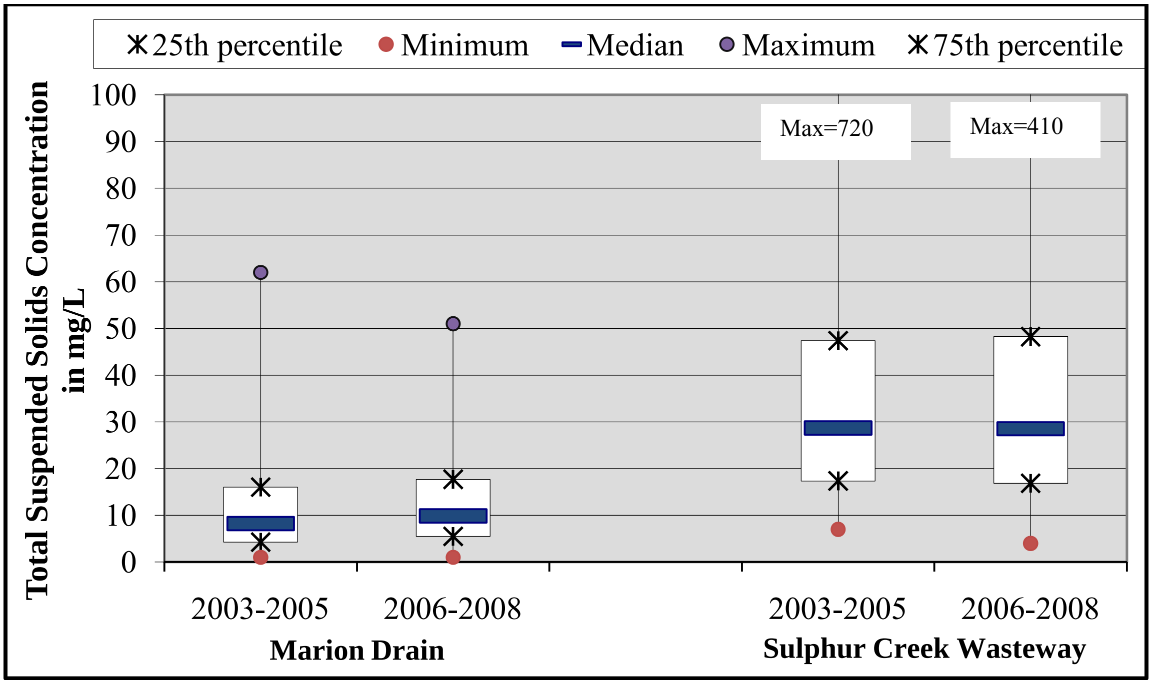


Figure 49. Summary statistics for total suspended solids concentrations at Marion Drain and Sulphur Creek Wasteway, 2003-2005 and 2006-2008.

Comparison to Lower Yakima Suspended Sediment and DDT TMDL

The *Lower Yakima River Suspended Sediment and DDT TMDL* was established in 1998 (Joy and Patterson, 1997). The Total Maximum Daily Load (TMDL) set numeric water quality targets to be achieved for DDT compounds, dieldrin, suspended sediment, and turbidity, as well as schedules for meeting the targets. The premise behind the TMDL is that DDT and other pesticides attached to farm soils are being washed into the river at levels that adversely affect aquatic life and cause an increased health risk to people consuming fish. Because of the correlation between TSS and total DDT, long-term TSS reduction goals were set to achieve the t-DDT water quality criterion for protection of aquatic life from chronic toxicity. Ecology is currently in the process of assessing targets to meet human health criteria in the lower Yakima River basin.

The Lower Yakima River TMDL report included pollutant targets and a schedule for pollutant reduction. In accordance with the TMDL, by 2002 the mouths of all tributaries and drains were to meet a 90th percentile turbidity target of 25 NTUs or 56 mg/L TSS. By 2007 all points within tributaries and drains were to meet this criterion. This TSS and turbidity target was set to provide a moderate level of protection from suspended sediment for the fisheries resource, particularly threatened and endangered salmonids. In addition, meeting the target would significantly reduce t-DDT loads to protect aquatic communities. Based on the TMDL correlation equation, tributary TSS concentrations needed to be further reduced to 7 mg/L to meet the 1 ng/L DDT chronic toxicity criterion for protection of aquatic life. A current Ecology assessment will determine if this tributary target is appropriate (Johnson et al., 2009).

Table 36 presents estimated 90th percentile for TSS and turbidity as well as the number of sample events for the lower Yakima sites in this study. Turbidity is estimated based on the turbidity-TSS correlation from *Yakima River Pesticides and PCBs Total Maximum Daily Load, Volume 1 Water Quality Study* (Johnson et al., 2009). The turbidity and TSS relationship has changed since the original TMDL study was done (Joy and Patterson, 1997). Based on the current correlation, a TSS of 56 mg/L is equivalent to 20 NTU (Table 36). In the original TMDL, 56 mg/L TSS was equivalent to 25 NTU.

Table 36. Estimated yearly 90th percentile values for turbidity and TSS, lower Yakima sites, 2003-2008.

Turbidity estimated based on correlation equation Turbidity=0.8375(TSS)$^{0.7933}$(Johnson et al., 2009).

Site	2003		2004		2005		2006		2007		2008	
	Tur-bidity (NTU)	TSS (mg/L)	Tur-bidity (NTU)	TSS (mg/L)	Tur-bidity NTU)	TSS (mg/L)	Tur-bidity (NTU)	TSS (mg/L)	Tur-bidity (NTU)	TSS (mg/L)	Tur-bidity (NTU)	TSS (mg/L)
Upstream Spring Creek												
90th percentile	n/a		n/a		5	8	12	29	19	53	21	59
Sample events (n)	n/a		n/a		13		12		13		13	
Downstream Spring Creek												
90th percentile	23	66	22	60	26	75	17	43	13	31	17	45
Sample events (n)	21		30		26		24		26		25	
Marion Drain												
90th percentile	18	48	10	24	9	19	15	37	10	22	14	36
Sample events (n)	21		29		30		30		32		31	
Sulphur Creek Wasteway												
90th percentile	19	51	24	70	25	73	25	72	30	92	26	77
Sample events (n)	21		30		26		24		26		25	

The original TMDL targets were based on the March 20 - October 20 irrigation period. The sample period for this March-September study varied slightly, and with the exception of Marion Drain sampling did not usually include the entire irrigation period.

During 2005 through 2008, sampling ended in mid to late September in Spring Creek and Sulphur Creek Wasteway. Generally the highest TSS and turbidity levels were seen in the early irrigation period, then tapered off toward the end of the irrigation period. This means that the estimated 90th percentile values for TSS and turbidity values in Spring Creek and Sulphur Creek Wasteway may have been biased high during 2005 through 2008 because lower values for the end of the irrigation season were not captured.

Consistent with Figures 47 and 48, TSS values have increased over time at the upstream Spring Creek site and decreased at the downstream site. For meeting the 90th percentile TSS target of ≤ 56 mg/L:

- Marion Drain met the target during all years, 2003-2008.
- Downstream Spring Creek met the target during 2006-2008.
- Upstream Spring Creek did not meet the target in 2008 but did during 2005-2007.
- Sulphur Creek Wasteway did not meet the target during 2004- 2008.

In general, reporting limits for this study are inadequate to evaluate the 2012 TMDL target goal of 1 ng/L for DDT, the chronic toxicity criterion for protection of aquatic life. During 2006-2008, the average reporting limit for the DDT and degradate compounds was 0.033 µg/L, or 33 ng/L. DDT and degradate detections below the reporting limit are reported by MEL if the analyte (such as DDT or degradates) are positively identified. The numeric value is qualified as an estimate in this case.

During the 2006-2008, there were no detections of DDT or degradate compounds in Marion Drain. The upstream Spring Creek sites had three detections of DDE, with a maximum detection of 10 ng/L, in 2007. The downstream Spring Creek sites had one detection of DDE, at 10 ng/L, in 2007. Sulphur Creek Wasteway had five detections of DDE, with a maximum detection of 10 ng/L, in 2006-2007. No DDT or DDT degradate compounds were detected at any of the lower Yakima sites in 2008.

Wenatchee-Entiat Basin (WRIAs 45 and 46)

The Wenatchee and Entiat sites have been sampled for two years (2007-2008) and are briefly discussed here. A comprehensive review of these sites will be included in next year's report when three years of data will be available.

Except for the Entiat River, there was at least one detection of endosulfan above the ESLOC for rainbow trout at each site in 2007-2008. Brender Creek had multiple detections above the ESLOC for rainbow trout during both years. The Washington State Department of Agriculture and the Wenatchee-Entiat stakeholder group are currently working with growers to reduce endosulfan levels. Future monitoring will show if these efforts are successful.

There were consistent detections of DDT and its degradates, DDD and DDE, in Brender Creek. DDT is a legacy pesticide and is no longer registered for use.

The following is a data summary of 2007-2008 results for the Wenatchee-Entiat sites. Sample sites are presented in Figure 5.

Pesticide Detections and Concentrations

Pesticide Detections

A summary of 2007-2008 pesticide detections for the Wenatchee-Entiat sites is presented in Appendix G. The tables include the average lower practical quantitation limit (ALPQL). For the Wenatchee-Entiat sites, the ALPQL is a two-year average of the lowest concentration that can be accurately measured by year in 2007 and 2008. Compounds below this level are qualified as estimates.

Comparison to Assessment Criteria and Water Quality Standards

The 2007-2008 pesticide data were compared to assessment criteria and water quality standards. Detailed summaries of the monitoring results can be found in pesticide calendars presented in Appendix H. Highlights of findings are summarized below.

Peshastin Creek

Very few pesticides were detected in Peshastin Creek. A summary of pesticide detections for 2007-2008 are presented in Appendix G, Table G-9. Pesticide calendars presented in Appendix H, Tables H-35 and H-36, show that seven pesticides and degradates were detected in Peshastin Creek from 2007 to 2008. In 2008, a detection of endosulfan was above the ESLOC criteria for fish. A single detection of azinphos-methyl was numerically above the chronic NRWQC.

Mission Creek

Very few pesticides were detected in Mission Creek. A summary of pesticide detections for 2007-2008 are presented in Appendix G, Table G-10. Nine pesticides and degradates were detected in Mission Creek; results are presented in Appendix H, Tables H-37 and H-38. One detected concentration of endosulfan was numerically above the ESLOC criteria for fish in 2008.

Lower Mission Creek is on Ecology's 303(d) list of impaired waters for DDT and its degradates, DDD and DDE. No detections of DDT or DDT constituents occurred during 2007- 2008.

Brender Creek

Twenty-three pesticides and degradates were detected in Brender Creek from 2007 to 2008. A summary of pesticide detections are presented in Appendix G, Table G-11. Pesticide calendars are presented in Appendix H, Tables H-39 and H-40.

Endosulfan was detected above the ESLOC for rainbow trout in 14 samples between March and May in 2007 and 2008. A single detection of chlorpyrifos in 2007 was numerically above the chronic assessment criteria for invertebrates.

All reported DDT detections did not meet the chronic water quality standard or the chronic NRWQC for salmonids. The chronic water quality standard is based on a 24-hour average concentration. DDT or DDT degradates were detected in every sample from Brender Creek for both years, except for the first week of April 2008.

Wenatchee River

Very few pesticides were detected in the Wenatchee River. A summary of pesticide detections for 2007-2008 are presented in Appendix G, Table G-12. Six pesticides were detected in the Wenatchee River. Pesticide calendars are presented in Appendix H, Tables H-41 and H-42. Endosulfan I was numerically above the ESLOC for rainbow trout in both years. Endosulfan I and II was numerically above the ESLOC for rainbow trout in multiple samples in 2008.

The lower Wenatchee River is on Ecology's 303(d) list of impaired waters for DDE. No detections of DDE occurred during the 2007-2008 sampling.

Entiat River

Very few pesticides were detected in the Entiat River. A summary of pesticide detections for 2007-2008 are presented in Appendix G, Table G-13. Four pesticides and degradates were detected in the Entiat River in both 2007 and 2008. No detected concentrations were above any regulatory criteria. Pesticide calendars are presented in Appendix H, Tables H-43 and H-44.

Conventional Parameters

Conventional water quality parameters were measured at all five Wenatchee-Entiat sites. In 2008, Winkler dissolved oxygen measurements were also obtained. Continuous, 30-minute interval, temperature data were collected; temperature profiles are presented in Appendix J. Table 37 summarizes results for TSS, flow, pH, conductivity, and dissolved oxygen for all of the sites.

Table 37. Arithmetic mean and range for conventional parameters (grabs) for Wenatchee-Entiat basin sites, 2007-2008.

Site and Statistic	Total Suspended Solids (mg/L)		Flow (cubic feet per second)		pH (standard units)		Conductivity (µmhos/cm)		Dissolved Oxygen (mg/L)
	2007	2008	2007	2008	2007	2008	2007	2008	2008
Peshastin Creek									
Mean [1]	13	5	272	139	8.1	7.9	91	90	11.3
Minimum	1	< 1	12	10	7.7	7.6	45	53	8.6
Maximum	218	44	1340	> 350	8.5	8.3	133	180	13.8
Mission Creek									
Mean [1]	35	8	36	19	8.3	8.3	196	186	11.2
Minimum	1	1	< 1	< 1	7.6	7.3	120	107	8.9
Maximum	685	42	223	60	9.2	8.6	294	328	14.0
Brender Creek									
Mean [1]	48	36	3	2	8.2	8.1	218	210	10.5
Minimum	13	7	1	1	7.8	7.9	123	125	9.1
Maximum	156	94	8	4	9.4	8.3	411	333	12.5
Wenatchee River									
Mean [1]	10	7	4790	4470	8.2	8.2	46	45	11.7
Minimum	1	< 1	467	669	7.4	7.2	23	20	9.2
Maximum	102	46	12900	19100	9.1	9.2	83	76	15.1
Entiat River									
Mean [1]	9	5	833	681	8.3	8.3	57	69	11.1
Minimum	2	1	123	107	7.3	7.5	24	23	9.0
Maximum	64	24	2490	2780	9.7	9.2	100	410	13.1

Mean[1]: Arithmetic Mean.

Comparison to Water Quality Standards

Grab results for pH, dissolved oxygen, and continuous temperature were compared to water quality standards (Table 19).

pH

Mission Creek and Wenatchee River pH levels did not meet (exceeded) the 8.5 s.u. criteria several times during 2007 and 2008. Brender Creek exceeded the pH standard twice in 2007, but met standards in 2008.

Dissolved Oxygen

Dissolved oxygen grab samples were obtained in 2008. All sites met dissolved oxygen criteria, with levels > 8.5 mg/L.

Temperature

The temperature standard for the Wenatchee-Entiat sites is the 7-day average of the daily maximum temperature (DADMax) which should not exceed 17.5° C. In addition, the Wenatchee River has a supplemental spawning and incubation criteria for the October 1 – May 15 period: the highest 7-DADMax should not exceed 13°C. Continuous, 30-minute interval, temperature data were collected year-round from 2007-2008. Graphs of these data are available in Appendix J. None of the sites met temperature criteria. Table 38 describes periods when violations occur.

Table 38. Periods of water temperature exceedance for the Wenatchee-Entiat basin sites, 2007-2008.

Site	2007	2008
Peshastin Creek >17.5°C	July 3 - Sep 14	July 11 - Aug 26 Sept 4-11
Mission Creek >17.5°C	July 7-17 July 24 - Aug 18 Aug 31 - Sept 4	July 18-25 Aug 2-19
Brender Creek >17.5°C	July 11-14 July 25-26	Aug 14-18
Wenatchee River >17.5 °C	July 11 - Sept 17	July 16 - Aug 30 Sept 1 Sept -18
Wenatchee River >13.0 °C	Oct 1 - May 15	Oct 1-5

Comparison to the Lower Mission Creek Basin, Chelan County TMDL

In 2004, a TMDL was established for DDT in the lower Mission Creek basin (Serdar and Era-Miller, 2004). Target t-DDT loads were recommended for Mission, Brender, and Yaksum Creeks based on waters meeting 1 ng/L t-DDT. Recommendations also included reductions in TSS to < 1 mg/L in order to meet target DDT loads. Phase one of the TMDL compliance schedule included interim monitoring of TSS and DDT at select locations in Yaksum and Brender Creeks. The TMDL recommended the reporting limit for DDT and its degradates, DDD and DDE, in water samples be no higher than 0.5 ng/L.

The reporting limits for this study are insufficient to adequately evaluate DDT levels recommended in the 2004 TMDL. Due to the cost of analyzing for a broad sweep of pesticides, the reporting limit for our study is higher than the 0.5 ng/L. The 2007- 2008 average reporting limit for DDT and its degradates was 0.033 µg/L (33 ng/L). Although the laboratory will report positively identified detections below this limit, they are qualified as estimates.

During 2007-2008, there were no DDT or degradate detections reported at the Mission Creek site. At the Brender Creek site, there were DDT or degradate compound detections for all but one sample event. TSS trends will be evaluated for Mission Creek and Brender Creek sites after three years of data have been collected.

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Discussion

Pesticide Results by Basin

Thornton Creek and the lower Yakima basin sites have been monitored for six years, and the Skagit-Samish and the Wenatchee-Entiat sites for three and two years respectively. Each of these project areas represents a different land use. Pesticide distribution differs among project areas, as do the pesticides most frequently detected.

Thornton Creek

Thornton Creek sites are in a heavily urbanized area. Approximately 50% of the basin is covered in impervious surface. Figure 50 presents the distribution of pesticides detected in Thornton Creek for all sample events (2003-2008).

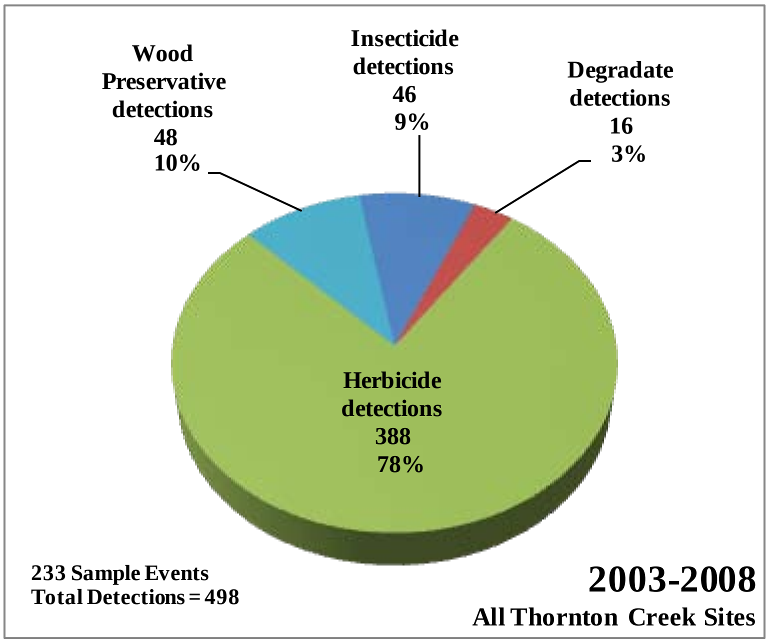

Figure 50. Distribution of pesticides for all Thornton Creek sites for all sample events, 2003-2008.

Figure 51 presents the most commonly detected pesticides for the Thornton Creek sites during the 2003-2005 and 2006-2008 project periods. While the frequency of herbicide detections has decreased, the herbicide compounds seen remain similar between the two periods. For insecticides, there were fewer diazinon detections during 2006-2008.

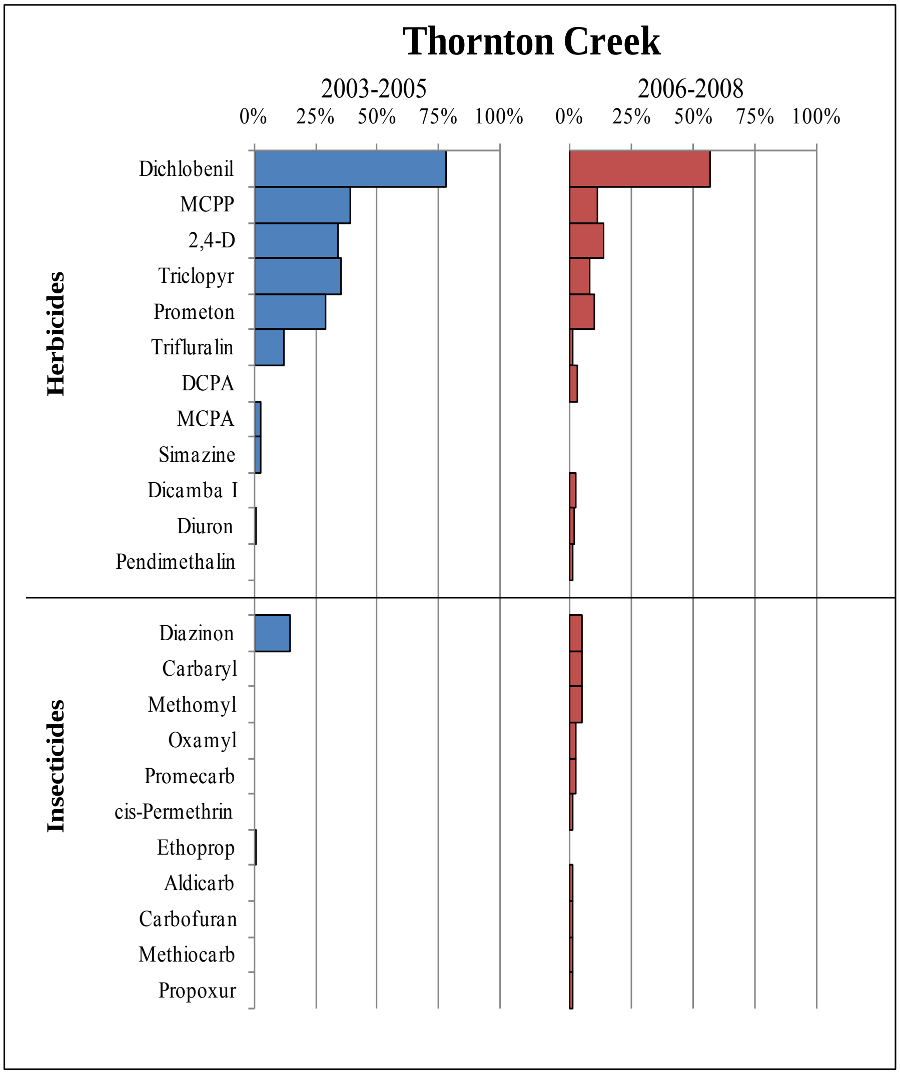

Figure 51. Percentage of pesticide detections per sample event for the Thornton Creek sites, 2003-2005 and 2006-2008.

Skagit-Samish Basin

The Skagit-Samish basin represents a western Washington agricultural area. A large variety of vegetable crops are grown in the Skagit-Samish delta. Much of the world's seed production for spinach, beets, brussel sprouts, and radishes are grown in this area. Major crops include potatoes, corn, peas, berries, wheat, and numerous vegetable crops. One site (upstream Big Ditch) largely represents commercial/industrial land use.

Figure 52 presents the distribution of pesticides detected at the Skagit-Samish sites during 2006-2008. A higher percentage of herbicides and fungicides, and lower percentage of insecticides, occur in the Skagit-Samish in comparison to the other agricultural areas in this study.

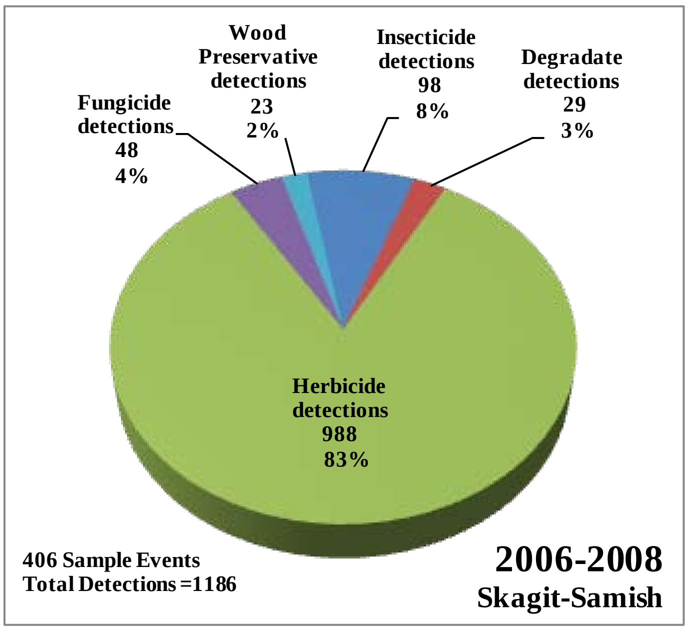

Figure 52. Distribution of pesticides detected in the Skagit-Samish sites, 2006-2008.

Figure 53 presents the most commonly detected pesticides in the Skagit-Samish basin. The widest variety of herbicides was seen in the Skagit-Samish and the lower Yakima areas. The high percentage of imidacloprid detection was driven by frequent detections of imidacloprid at the upstream Big Ditch site in 2008. For the other Skagit-Samish sites, insecticides were rarely seen.

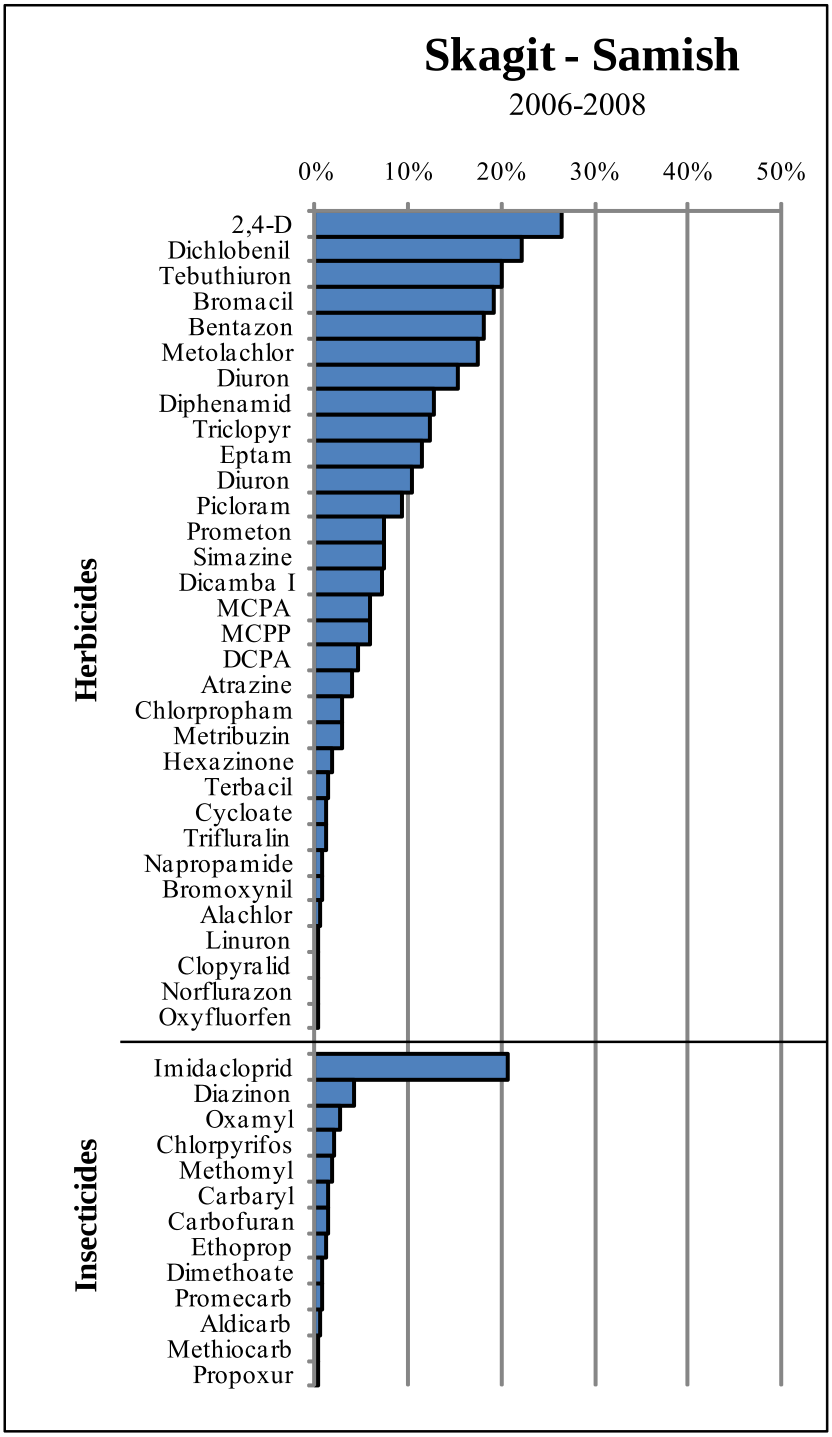

Figure 53. Percentage of pesticide detections per sample event for the Skagit-Samish sites, 2006-2008.

Lower Yakima Basin

The lower Yakima basin is a large agricultural area that is irrigated by a series of canals and waterways. The lower Yakima sites represent irrigated agricultural land use. The irrigation period varies slightly from year to year, but it generally begins in early April and ends in mid-October. A large percentage of the basin is in agricultural production; a wide variety of crops are grown in this region. Major crops include grapes, corn, apples, hops, wheat, mint, and a variety of vegetable crops. Figure 54 presents the distribution of pesticides seen at the lower Yakima sites during 2003-2008.

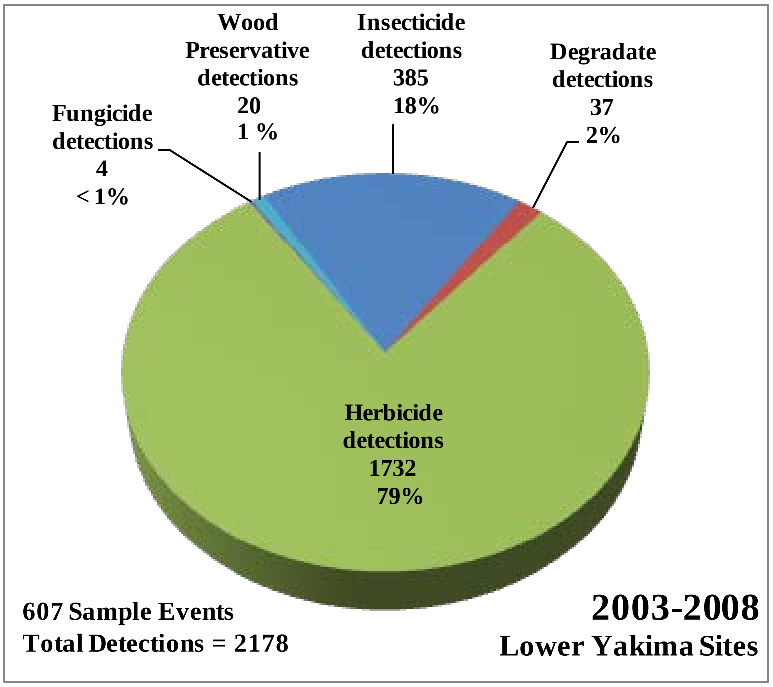

Figure 54. Distribution of pesticides detected at the lower Yakima sites, 2003-2008.

The distribution of pesticide type is similar between the 2003-2005 and 2006-2008 monitoring periods. Of all the project areas, the lower Yakima has the most pesticide detections, including the greatest number of herbicide and insecticide detections.

Figure 55 presents the most commonly detected pesticides in the lower Yakima area for 2003-2005 and 2006-2008.

The widest variety of herbicides was seen in the lower Yakima and the Skagit-Samish areas. The widest variety of insecticides was seen in the lower Yakima area.

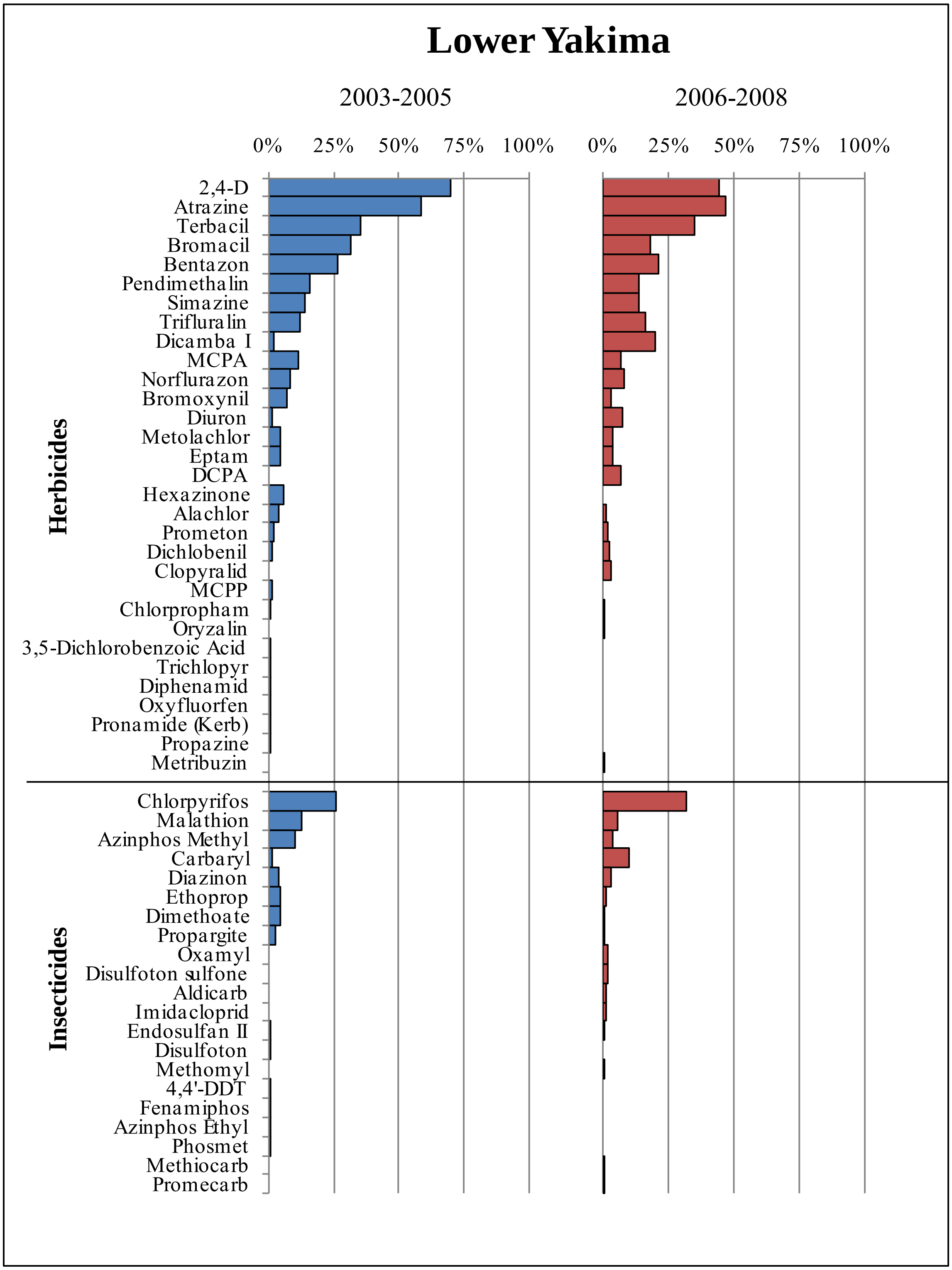

Figure 55. Percentage of pesticide detections per sample event for the lower Yakima sites, 2003-2005 and 2006-2008.

Wenatchee and Entiat Basins

The Wenatchee-Entiat basins represent tree fruit agriculture. A large portion of acreage in the uplands is in forest land, and much of the lowland area is in agricultural production. Major crops include pears, apples, and cherries. Figure 56 presents the types of pesticides seen at the Wenatchee-Entiat sites for two years of monitoring, 2007-2008.

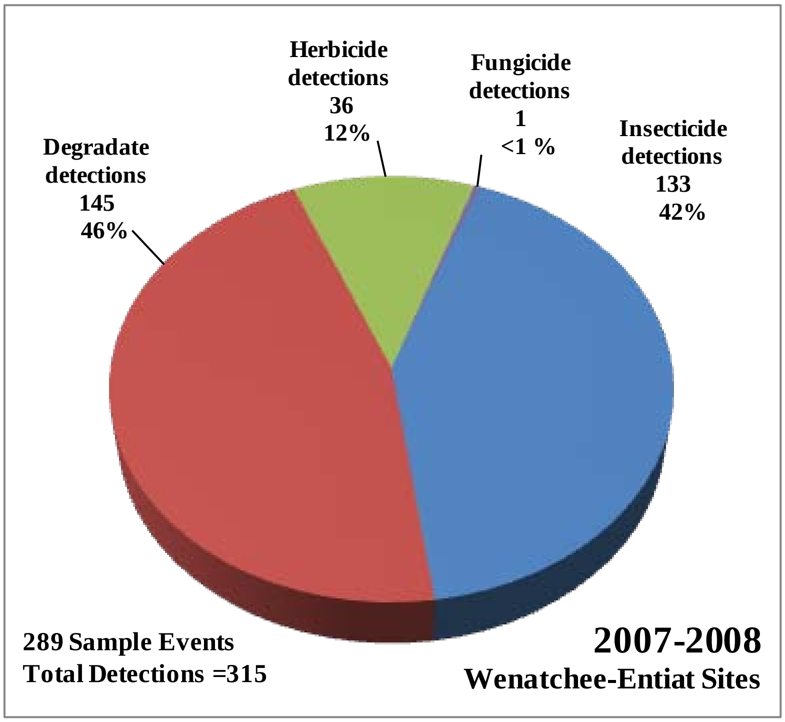

Figure 56. Distribution of pesticides detected in the Wenatchee-Entiat sites, 2007-2008.

The majority of pesticide detections were insecticides and degradate compounds. Most degradate compounds are products of insecticides. The higher proportion of insecticides seen in the Wenatchee-Entiat basins is in part driven by DDT and endosulfan detections in Brender Creek. DDT is a legacy pesticide that is no longer registered for use in the United States. Detections of DDT and its degradates are a result of historic use and do not reflect current pesticide-use patterns. A majority of the Wenatchee-Entiat sites have higher streamflows which tend to dilute pesticide concentrations, while Brender Creek has very little flow. Compared to the other project areas, the Wenatchee-Entiat area has the lowest percentage of herbicide detections as compared to other pesticide detections.

Figure 57 presents the most commonly detected pesticides in the Wenatchee-Entiat basin for 2007-2008.

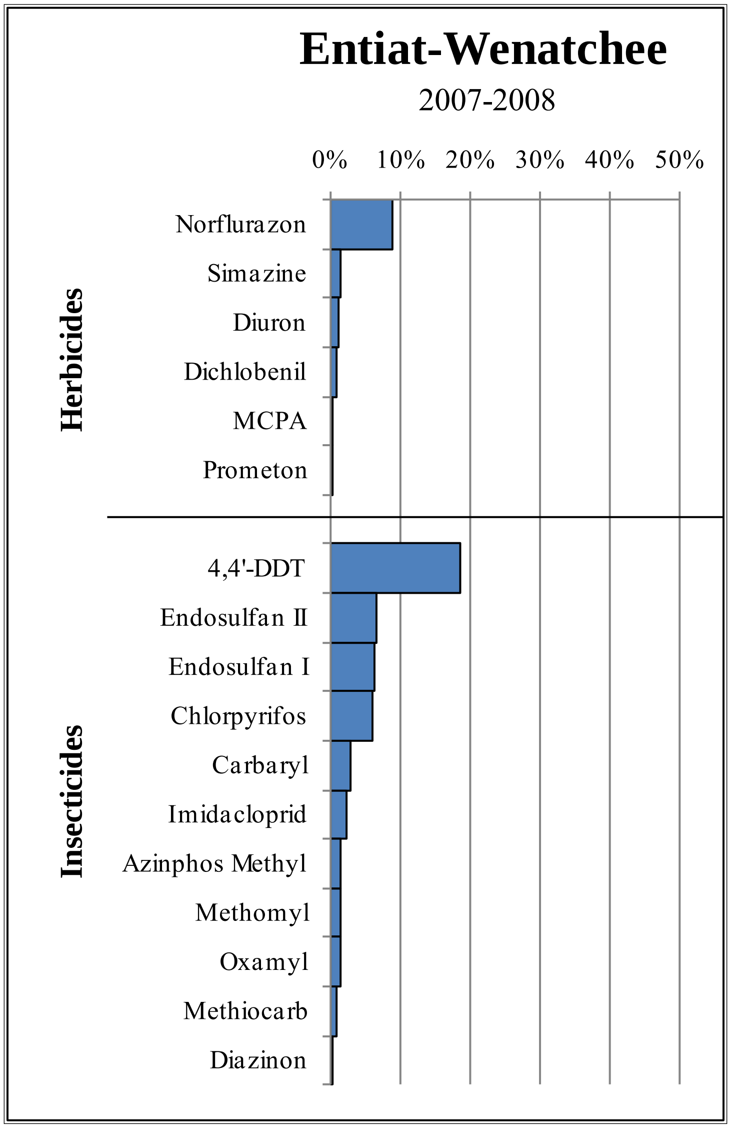

Figure 57. Percentage of pesticide detections per sample event for the Wenatchee-Entiat basin, 2007-2008.

Comparing the Monitoring Areas

Comparison among the project areas is complicated by differences in the number of sample events, sites, and monitoring periods. Table 39 presents the ratio of pesticide detections to sample events for each area.

Table 39. Ratio of pesticide detections to the number of sample events for each site within each project area.

Time Period	Thornton Creek		Samish-Skagit	Lower Yakima		Wenatchee-Entiat
	2003-2005	2006-2008	2006-2008	2003-2005	2006-2008	2007-2008
Number of Sample Events	109	124	406	279	328	289
Number of Detections	317	181	1186	1078	1100	315
Ratio of Detections to One Sample Event	2.9:1	1.5:1	2.9:1	3.9:1	3.4:1	1.1:1

The lower Yakima area had the highest number of pesticide detections per sample event, with more detections per event seen during 2003-2005.

The lowest number of detections per event was seen for the Wenatchee-Entiat sites, though this area has been sampled for only two years. In addition, some of the Wenatchee-Entiat sites had the highest flows of any of the project areas; this would provide dilution and lower pesticide concentrations, as noted previously.

Other than the Wenatchee-Entiat area, Thornton Creek had the fewest pesticide detections during 2006-2008. In 2006-2008, pesticide detections for Thornton Creek decreased due to fewer herbicide detections.

Six years of monitoring data are available for the lower Yakima area (irrigated agriculture) and Thornton Creek (urban). For the lower Yakima, the distribution of pesticides remained similar during both 2003-2005 and 2006-2008. The types of pesticides detected most frequently were also similar for the two periods. For Thornton Creek, fewer pesticide detections occurred during 2006-2008, due to decreased detections of herbicides. In Thornton Creek, the pesticides detected remained the same with the exception of select insecticides. Diazinon detections decreased during 2006-2008, and carbamate detections increased. Changes in insecticide distribution in Thornton Creek are likely due to increased laboratory testing for carbamate insecticides as well as the removal of "homeowner use" from diazinon registration in 2004.

Water Quality and Salmonid Presence

Conventional Parameters

None of the project area sites consistently met temperature standards during the 2006-2008 monitoring period. Currently 29% of Ecology's 303(d) listings of impaired waters (Category 5) are for temperature. In part, this is because temperature is the easiest and least costly parameter to study, and Ecology receives more temperature data than data for any other parameter.

The only areas to meet the dissolved oxygen standard in 2008 were the lower Yakima and Wenatchee-Entiat sites. In Thornton Creek, dissolved oxygen levels fell slightly below standards at both sites (9.3 mg/L upstream and 9.0 mg/L downstream). The Samish River met dissolved oxygen standards, but none of the other Skagit-Samish sites did. Browns Slough, Indian Slough, and Big Ditch had low dissolved oxygen levels, coupled with higher water temperatures.

It is likely that actual instream minimum dissolved oxygen levels are lower than values obtained during this study. This is because dissolved oxygen grab samples were obtained during morning or afternoon hours. Both dissolved oxygen and temperature fluctuate during a 24-hour period. The lowest dissolved oxygen levels are found in the early morning hours before plant photosynthesis begins. Oxygen levels affect the growth rates of salmonids as well as their swimming ability, susceptibility to disease, and their relative ability to endure other environmental stressors and pollutants (Ecology 2000 and 2002; Carter, 2008).

During 2006-2008, most sites fell below or exceeded (did not meet) the pH standard. The sites east of the Cascade Mountains tended toward exceedances of the pH standard, while the sites west of the mountains tended to fall below the standard.

Turbidity and TSS are common measures to determine the effect of suspended sediment on salmonids. There are water quality standards for turbidity but not for TSS. TSS is a direct measure of suspended sediment while turbidity is only an indicator. Thus TSS more accurately reflects possible effects on salmonids (Bolton et al., 2001). High sediment levels can have a range of effects from fatal to sub-lethal effects such as reduction of foraging capability, reduced growth, increased stress, and interference with cues necessary for orientation in homing and migration (Bolton et al., 2001).

TSS levels for the westside sites were generally lower than the eastside. The lower Yakima sites had higher TSS concentrations than at other sites. Sulphur Creek had the highest TSS concentrations, averaging 40 mg/L over the 2006-2008 sample period.

Average TSS for the Wenatchee basin sites were also high, but this is likely due to a March 13, 2007 sample event where TSS values were in the hundreds (mg/L) range at all sites. Higher TSS concentration on this day could have been due to the first flush of water from the irrigation system and/or to snowmelt and runoff. The daily maximum air temperatures in Cashmere increased by 10° F on March 11, 2007. Wenatchee River daily flow went from 2,600 cfs on March 11, to 11,600 cfs on March 13.

Pesticides

During 2006-2008, few pesticide detections did not meet (exceeded) a water quality criterion or assessment criteria. During this period, 64 current-use pesticides and seven legacy pesticides and degradate compounds were detected:

- 34 herbicides
- 23 insecticides
- 8 degradates
- 5 fungicides
- 1 wood preservative

Of the 71 pesticides or degradates, six currently registered pesticides exceeded water quality standards or assessment criteria: permethrin, chlorpyrifos, diazinon, azinphos-methyl, malathion, and endosulfan. Also DDT and its degradates (DDD and DDE) exceeded water quality standards. DDT has not been registered for use in the United States since 1972 (EPA, 1972).

The pesticides that exceeded assessment criteria or water quality standard are:

- Permethrin exceeded the EPA Endangered Species Level of Concern (ESLOC) in Thornton Creek once (Cedar-Sammamish basin).

- Chlorpyrifos exceeded the marine acute and chronic water quality standard twice in both 2007 and 2008 in Browns Slough (lower Skagit-Samish basin). Chlorpyrifos exceeded the freshwater water quality standard (acute and chronic) in Sulphur Creek Wasteway (four times), Marion Drain (eight times), and lower Spring Creek (four times) as well as the ESLOC for fish once in Spring Creek and Sulphur Creek Wasteway (lower Yakima basin).

- Diazinon exceeded the marine acute and chronic NRWQC for invertebrates twice in Browns Slough in 2007 (lower Skagit-Samish basin).

- Azinphos-methyl exceeded the chronic NRWQC eight times in Spring Creek, as well as three times in Sulphur Creek Wasteway in 2006 (lower Yakima basin).

- Malathion exceeded chronic NRWQC in Marion Drain once in 2007 (lower Yakima basin).

- DDT and its metabolites exceeded the chronic water quality standard in (1) Spring Creek three times and Sulphur Creek Wasteway 5 times (lower Yakima basin); and (2) Brender Creek during all sample events but one (Wenatchee basin).

- Endosulfan exceeded the chronic water quality standard and the ESLOC for fish 14 times in Brender Creek as well as once in Peshastin and Mission Creeks and the Wenatchee River (Wenatchee basin).

Sub-Lethal Effects and Co-Occurrence of Pesticides

Background

The EPA and Washington State assessment criteria used in this report are based on evaluating the effects of a specific chemical on an organism. The criteria do not take into account the additive or possible synergistic effects of pesticide mixtures, or the effects of pesticides when fish are stressed due to environmental factors such as high temperatures or low dissolved oxygen levels.

Organophosphate and carbamate insecticides inhibit the activity of acetylcholinesterase (AChE). Environmental mixtures of these insecticides have the potential to exert toxic effects on exposed organisms at concentrations lower than expected from the effects predicted from single chemical toxicity studies. Recent work by Laetz et al. (2009) found additive and synergistic toxicity to juvenile coho salmon for the binary combinations of several organophosphate and carbamate insecticides.

One finding illustrative of synergism reported by Laetz et al. was juvenile coho exposed to a combination of malathion and diazinon. At one-tenth the median effective concentration (EC_{50}) for the individual compounds, coho exhibited nearly 100% suppression of AChE activity when compared to controls after 96 hours of exposure. The 0.1 EC_{50} for juvenile coho determined by Laetz et al. was 7.5 and 14.5 µg/L for malathion and diazinon, respectively. The maximum environmental concentration found for malathion and diazinon during this current project (2003-2008) was 3.1 µg/L in Marion Drain on July 21, 2004 and 0.7 µg/L in Browns Slough on June 19, 2007, respectively.

Currently EPA and National Marine Fisheries Service (NMFS) are completing consultation under the Endangered Species Act on the effects of chlorpyrifos, diazinon, and malathion on EPA-listed salmon in the Pacific Northwest. On September 10, 2009, EPA notified NMFS of their plan to implement the mitigation measures specified in the November 18, 2008 Biological Opinion (BiOp) (EPA, 2009). The BiOp raised specific concerns about the co-occurrence and potential synergistic or additive effects of chlorpyrifos, diazinon, and malathion to listed salmonids and their prey base. EPA has determined that a cumulative concentration of chlorpyrifos, diazinon, and malathion below 1.122 µg/L should not result in jeopardy to listed salmon. *Jeopardy* refers to whether or not a listed species is put at risk for extinction.

This 2006-2008 Study

For illustrative purposes, we have summed the concentration of organophosphate and carbamate insecticides (AChE inhibitors) found in several of the basins monitored from 2006-2008 (Figures 9, 15, 16, 18, 20, 34, 35, 37, and 39). Note we have included compounds that are not part of the BiOp or assessed by Laetz et al. to show the maximum summed concentration of AChE-inhibiting compounds detected.

For Thornton Creek, the highest additive concentration of AChE inhibitors occurred on April 28, 2008. The sum concentration of diazinon, methomyl, and oxamyl was 0.395 µg/L. This additive value is well below either compound's acute LC_{50} and below the chronic criteria for fish.

In the Skagit delta, multiple detections of AChE inhibitors rarely occurred. The highest additive concentrations of AChE-inhibiting insecticides were found at Browns Slough on April 23, 2007. The sum concentration of the carbamate insecticides, oxamyl and methomyl, was 0.155 µg/L. This additive value is well below either compound's LC_{50} and below the chronic criteria for fish.

In the lower Yakima basin, multiple detections of AChE insecticides rarely occurred in Spring Creek or Sulphur Creek Wasteway. The highest additive concentration of these insecticides in Spring Creek was found upstream on June 13, 2006; the sum concentration of azinphos-methyl (0.12 µg/L) and aldicarb (0.16 µg/L) was 0.280 µg/L. The azinphos-methyl concentration exceeds the chronic NRWQC, and the sum total of both compounds exceeds the azinphos-methyl chronic criteria for fish and the ESLOC for coho salmon.

For Sulphur Creek Wasteway, the highest summed concentration of AChE-inhibitor compounds involved two organophosphates, azinphos-methyl and dimethoate. On June 5, 2006, azinphos-methyl (0.033 µg/L) and dimethoate (0.45 µg/L) were detected for a sum total of 0.483 µg/L. While the individual concentrations do not exceed any assessment criteria or water quality standard, the summed total exceeds the azinphos-methyl chronic NRWQC.

In Marion Drain, on September 9, 2006 the highest summed AChE concentration was chlorpyrifos (0.12 µg/L) and carbaryl (0.09 µg/L) for a sum total of 0.21 µg/L. Both of these compounds were tested by Laetz et al. (2009) who determined the 0.1 EC_{50} for chlorpyrifos to be 0.2 µg/L. The monitored concentration for carbaryl is below the lowest concentration used to determine the EC_{50} reported by Laetz et al.

The monitoring results from this 2006-2008 study illustrate the difficulty of assessing the effects of multiple chemicals on aquatic organisms. The pesticide occurrence calendars in Appendix H demonstrate that mixtures of pesticide are common. However, concentrations are typically below the effects threshold for single chemical toxicity testing, and when mixtures occur, the various pesticides detected have different modes of action (e.g., not all pesticides inhibit AChE). Even when mixtures of AChE-inhibiting compounds occur, there are limited toxicity data available to assess the potential effects of the mixture. Further confounding the assessment are the effects of environmental factors such as temperature, dissolved oxygen, or pH that can further stress aquatic organisms.

Salmonid Presence by Basin, 2006-2008

Thornton Creek

In Thornton Creek, the greatest number of herbicide detections occurred in May, and the highest number of insecticide detections were found in April. Chinook fry emerge during March through April when the greatest number of insecticides is detected. Coho fry may reside over a year instream. While the greatest number of pesticide detections was found when salmon fry were present, pesticide concentrations at both sites on Thornton Creek were low. With the exception of one permethrin detection in April 2007 that exceeded the ESLOC for fish, all pesticide detections were below assessment criteria and water quality standards.

Dissolved oxygen and temperature standards for Thornton Creek are more stringent than the other study sites. The highest water temperatures occurred in August but rarely exceeded 19°C. The lowest dissolved oxygen level of 9.0 mg/L occurred at the downstream site in August.

Skagit-Samish basin

In the Skagit-Samish basin, several species of salmonids are present. Intergravel development and emergence for salmon species can occur from fall through late spring depending on the species. The greatest number of herbicide and insecticide detections occurred in April through June, peaking in May.

With the exception of six organophosphate pesticide detections observed in Browns Slough in 2007-2008 (which exceeded the chronic exposure criteria for aquatic invertebrates toxicity), pesticide detections were below water quality standards and assessment criteria. Browns Slough is classified as marine water which has lower assessment criteria than freshwater. The four (two in 2007 and 2008) exceedances of the marine aquatic invertebrate criteria for chlorpyrifos were observed in February and March. Two exceedances for diazinon were seen in May and June of 2007. None of the measured concentrations for chlorpyrifos and diazinon exceeded the no- jeopardy concentration (1.122 µg/L) established by EPA for implementation of the NMFS biological opinion.

Browns Slough, Indian Slough, and Big Ditch had high water temperatures coupled with low dissolved oxygen levels. Temperatures were highest during June through August; dissolved oxygen levels were lowest in August. Browns Slough had the highest temperatures, reaching maximums greater than 25°C during late June through August during both years. High water temperatures in Browns Slough could be due to (1) an influx of warm flood waters from the shallow Skagit tidal flats or (2) warm upstream water. Temperature and dissolved oxygen levels in Browns Slough, Big Ditch, and Indian Slough are highly stressful to fish and reduce the ability of salmonids to endure environmental stressors and pollutants such as pesticides (Ecology, 2000 and 2002; Carter, 2008). Generally, higher temperatures and lower dissolved oxygen levels occur during June through early September.

Lower Yakima basin

In the lower Yakima tributaries, steelhead fry emerge from June through August (Haring, 2001; modification Kohr, 2009). The greatest number of herbicide detections occurred in May, and the greatest number of insecticide detections occurred in April or May depending on the site.

Of current-use pesticides, chlorpyrifos, malathion, and azinphos-methyl did not meet (exceeded) assessment criteria. The lower Yakima sites had the greatest number of pesticide detections that exceeded water quality standards and NRWQC. The exceedances of standards indicate the most concern for chronic to acute risk for aquatic invertebrates. The azinphos-methyl detections occurred in May and June, when salmon fry emerge. Chlorpyrifos exceedances occurred in March and April; Marion Drain had another peak in September. Both Spring Creek and Sulphur Creek Wasteway exceeded the ESLOC for fish once in late March 2007. None of the chlorpyrifos concentrations exceeded the no-jeopardy concentration of 1.122 µg/L established by EPA for implementation of the NMFS biological opinion for the registration of chlorpyrifos, diazinon, and malathion.

Water temperatures exceeded temperature criteria during June and July at all lower Yakima sites with the maximum temperatures greater than 20°C. The presence of mid-Columbia summer steelhead in the Yakima River basin is influenced by water temperature and other habitat conditions of the agricultural drainages. Midsummer (late June through August) temperatures may present a thermal blockage to steelhead migration (Burke et al., 2006). High TSS levels were seen during March through June at the lower Yakima sites.

Wenatchee-Entiat basins

In the Wenatchee basin, endosulfan was above the ESLOC assessment criterion from mid-March through late April. In Brender Creek, exceedances were seen from mid-March through mid-May. Endosulfan levels exceeded water quality standards and (1) the chronic NRWQC in Peshastin and Brender Creeks and the Wenatchee River, and (2) the ESLOC for fish in Brender, Mission, and Peshastin Creeks and the Wenatchee River. Salmonid incubation can occur from February through July depending on the species.

Highest water temperatures were seen in August. The smaller tributaries, Brender and Mission Creeks, generally had cooler summer temperatures than the larger waterbodies. Maximum temperatures for the Wenatchee and Entiat Rivers and Peshastin Creek were greater than 20°C.

Trends

No trends toward increasing or decreasing pesticide concentrations were noted for the sites with six years of monitoring data in Thornton Creek and the lower Yakima basin.

At the downstream Thornton Creek site, a significant reduction in the number of herbicide detections occurred during 2006-2008 as compared to 2003-2005. No trend in the number of detections was noted for the lower Yakima sites. No trends were noted for other types of compounds (insecticides, degradates, fungicides, or wood preservatives).

From 2005 through 2008, the upstream Spring Creek site (lower Yakima basin) showed a significant trend toward increasing TSS concentrations and loading. The downstream Spring Creek site showed a trend toward decreasing TSS concentrations and loading from 2003-2008.

Factors Affecting Pesticide Detections

For the western Washington sites, rain events and streamflow at the agricultural sites may play a minor role in detections of some herbicides. For the lower Yakima basin sites, flow may play a minor role in detection of pesticides. For Thornton Creek, the Skagit-Samish basin, and the lower Yakima basin, the greatest number of herbicide detections occurred in May. In Thornton Creek and Marion Drain (lower Yakima), the greatest number of insecticide detections occurred in April; for the rest of the 2006-2008 study sites, the most insecticide detections occurred in May.

USGS (Embrey and Frans, 2003) found the greatest influence on pesticide concentrations and detections appeared to be the season and timing of pesticide application to specific crops or plants. The results of this 2006-2008 study show similar findings, with the season and timing of application for specific crops being the major determining factor in pesticide detections.

Detections of Pesticides Not Registered for Use

There were consistent detections of DDT and its degradates (DDD and DDE) in Brender Creek and a few detections of DDT degradates in Spring Creek and Sulphur Creek Wasteway. DDT is a legacy pesticide and is no longer registered for use. Detections of DDT and its degradates are a results of historic use and do not reflect current pesticide-use patterns.

During 2006-2008, the herbicide, diphenamid, was detected 52 times in Indian Slough. Diphenamid has not been registered by EPA since 1991 (EPA, 2002). It is not known why diphenamid was detected so frequently in Indian Slough. The detections are not likely due to field or laboratory errors.

The carbamate insecticide, promecarb, was detected twice during 2007, once in Thornton Creek and once in Spring Creek. There were also promecarb detections in the field blank samples during the first three weeks of July 2008. Promecarb was also detected in laboratory blank samples. Promecarb detections in field samples could be an artifact of laboratory analysis. Promecarb has never been registered for use in the United States; it is not known why these detections occurred.

Conclusions

As a result of this 2006-2008 study, the following conclusions are made:

- Data analysis showed the major factors in pesticide detections are season and timing of pesticide application for specific crops.
- The majority of detected pesticides met (did not exceed) water quality criteria.
- For all sites, co-occurrence of acetylcholinesterase-inhibiting insecticides rarely occurred.
- Thornton Creek in the Cedar-Sammamish basin had one exceedance of an assessment criterion for permethrin, an insecticide.
- In Thornton Creek, there has been a statistically significant decrease in herbicide detections during 2003-2008.
- In the Skagit-Samish basin, with the exception of a few exceedances in Browns Slough, pesticide concentrations met water quality standards or assessment criteria.
- In the Skagit-Samish basin, high water temperatures and low dissolved oxygen levels are of concern for the fisheries resource in Indian Slough, Browns Slough, and Big Ditch.
- The lower Yakima basin sites had the greatest number of pesticide detections that did not meet water quality standards or assessment criteria. The greatest concern is for chronic and acute risk for aquatic invertebrates which are part of the prey base for salmonids.
- In the lower Yakima basin, elevated water temperatures from late June through August may present a thermal blockage to steelhead migration and make fish more susceptible to pesticide toxicity (Mayer and Ellersick, 1986 as referenced in Burke et al., 2006).
- In the lower Yakima basin, an increase in total suspended solids was observed at the upstream Spring Creek site, while the downstream site showed a decreasing trend in total suspended solids.
- In the Wenatchee basin, endosulfan levels from mid-March through May indicate chronic aquatic health concerns. These endosulfan levels are periodically above the Endangered Species Level of Concern (ESLOC) for fish.

Recommendations

As a result of this 2006-2008 study, the following recommendations are made:

- Conduct intensive weekly sampling during periods when the greatest number of detections occurs for organophosphate insecticides.
- Install an additional continuous temperature monitoring device in Browns Slough to determine if the influx of warmer water is from upstream or downstream sources.
- Explore opportunities to evaluate the effects of pesticide concentrations and mixtures on aquatic invertebrates and salmonids. Include the effects of other environmental stressors such as temperature and dissolved oxygen in laboratory toxicity testing.
- WSDA continue to work with agricultural stakeholders to explore mitigation measures for endosulfan concentrations found in surface water in the Wenatchee basin. Continue to monitor the effectiveness of mitigation measures.
- Continue efforts to resolve the issue of blank detections in the carbamate analysis.
- Evaluate the need for adding new pesticides to the monitoring program.

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Appendices

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Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Additive: An additive effect occurs when the combined effect of two chemicals is equal to the sum of the effects of each chemical.

Boxplot: A graphical depiction of a data set showing the 25^{th} percentile, 50^{th} percentile or median, the 75^{th} percentile, range of data, and outliers.

Carbamate insecticide: N-methyl carbamate insecticides are similar to organophosphate insecticides in that they are nerve agents that inhibit cholinesterase enzymes. However they differ in action from the organophosphate compounds in that the inhibitory effect on cholinesterase is brief.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Degradate: Pesticide breakdown product.

Diel: Of, or pertaining to, a 24-hour period.

Dissolved oxygen (DO): A measure of the amount of oxygen dissolved in water.

Exceeded criteria: Did not meet criteria.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Herbicide: A substance used to kill plants or inhibit their growth.

K_{oc} (sorption coefficient): The tendency of a pesticide to bind to soil particles. Sorption retards movement, and may also increase persistence because the pesticide is protected from degradation. The higher the K_{oc}, the greater the sorption potential. K_{oc} is derived from laboratory data. Many soil and pesticide factors may influence the actual sorption of a pesticide to soil.

Loading: The input of pollutants into a waterbody.

Organochlorine insecticide: Organochlorine insecticides are neurotoxins that are highly lipophilic, very hydrophobic, and chemically stable. As a result, organochlorine insecticides are persistent in the environment and have a long half-life. The lethal mechanism of action is a persistent opening of the sodium channels in neurons, resulting in repetitive firing of action potentials.

Organochlorine pesticide: Organochlorine pesticides are hydrocarbons that contain chlorine (e.g., DDT, endrin and endosulfan).

Organophosphate pesticide: Organophosphate pesticides are derived from phosphoric acid and are highly neurotoxic typically inhibiting cholinesterase

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Pesticide: A pesticide is any substance or mixture of substances intended for killing, repelling or mitigating any pest. Pests include nuisance microbes, plants, fungus, and animals.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Sources of pollution that discharge at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Pollution: Such contamination, or other alteration of the physical, chemical, or biological properties, of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Salmonid: Any fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and watercourses within the jurisdiction of Washington State.

Synergistic: A synergistic effect occurs when the combined effects of two chemicals are greater than the predicted sum each chemicals effects.

Total Maximum Daily Load (TMDL): Water cleanup plan. A distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): The suspended particulate matter in a water sample as retained by a filter.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State periodically to prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

7-DADMax or 7-day average of the daily maximum temperatures: The arithmetic average of seven consecutive measures of daily maximum temperatures. The 7-DADMax for any individual day is calculated by averaging that day's daily maximum temperature with the daily maximum temperatures of the three days prior and the three days after that date.

Acronyms and Abbreviations

7-DADMax	7-day Average of the Daily Maximum Temperatures
AChE	Acetylcholinesterase enzyme
ALPQL	Average practical quantitation limit
CFS	Cubic feet per second
DDD	Dichloro-diphenyl-dichloroethane
DDE	Dichloro-diphenyl-dichloroethylene
DDT	Dichloro-diphenyl-trichloroethane
DO	Dissolved Oxygen
DPS	Distinct Population Segment
EC_{50}	Effective concentration to cause immobility in 50% of an invertebrate species, or a reduction in growth of 50% of an aquatic plant species.
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management (Ecology)
EPA	United States Environmental Protection Agency
ESA	Endangered Species Act
ESLOC	Endangered Species Level of Concern (EPA)
ESU	Evolutionary Significant Unit
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
FR	Federal Register
GC	Gas chromatograph
GCMS	Gas chromatograph coupled with mass spectrometer
HPLC	High performance liquid chromatography
K_{oc}	Sorption coefficient
LC50	Lethal concentration to cause mortality in 50% of test species
LCMS	Liquid chromatograph coupled with mass spectrometer
LCMS-SIM	Liquid chromatograph coupled with mass spectrometer, selected ion monitoring
LOC	Level of concern
LPQL	Lower practical quantitation limit
MEL	Manchester Environmental Laboratory
MS	Mass spectrometer
MS/MSD	Matrix spike/matrix spike duplicate
n	Number
NAD	North American Datum
NRWQC	National Recommended Water Quality Criteria (EPA)
NIST	National Institute of Standards and Technology
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOEC	No observable effect concentration
NAWQA	National Water Quality Assessment Program (USGS)
QA	Quality assurance

QC	Quality control
POCIS	Polar Organic Chemical Integrative Sampler
RM	River mile
RQ	Risk quotient
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SPMD	Semi-Permeable Membrane Devices
t-DDT	Total DDT
TMDL	Total Maximum Daily Load
TSS	Total suspended solids (see Glossary above)
TSU	Toxics Studies Unit
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area
WSDA	Washington State Department of Agriculture
WSPMP	Washington State Pesticide Monitoring Program

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
cms	cubic meters per second, a unit of flow
ft	feet
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
m	meter
mg	milligrams
mg/d	milligrams per day
mg/L	milligrams per liter (parts per million)
mL	milliliters
mm	millimeters
ng/g	nanograms per gram (parts per billion)
NTU	nephelometric turbidity units
psu	practical salinity units
s.u.	standard units
µg/g	micrograms per gram (parts per million)
µg/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter
µS/cm	microsiemens per centimeter, a unit of conductivity

Appendices B through J are in a separate electronic file.