

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2009 Data Summary

A Cooperative Study by the Washington State Departments of Ecology and Agriculture





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Cover photo: Jenna Durkee, Department of Ecology employee, sampling for pesticides at Mission Creek on April 21, 2009 during orchard spraying (photo by Dan Dugger).

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A Cooperative Study by the Washington State Departments of Ecology and Agriculture

by Debby Sargeant, Dan Dugger, Paul Anderson, and Evan Newell

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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 conducting in six basins:

- Thornton Creek in the Cedar-Sammamish basin and Longfellow Creek in the Green-Duwamish basin, representing urban land use.
- Lower Skagit-Samish basin, representing western Washington agriculture.
- Lower Yakima basin, representing eastern Washington irrigated agriculture.
- Wenatchee and Entiat basins, representing central Washington tree fruit agriculture.

This report summarizes data collected during 2009 from four basins: Cedar-Sammamish, Green-Duwamish, Skagit-Samish, and lower Yakima. The report also provides a more intensive review of data collected during 2007-2009 from two basins: Wenatchee and Entiat.

In 2009, samples were collected for analysis of over 165 pesticides and pesticide degradates, as well as total suspended solids. Field data were collected for streamflow, temperature, pH, conductivity, and dissolved oxygen.

Changes to the monitoring study during 2009 include:

- Discontinuing monitoring at the upstream Thornton Creek site.
- Adding an urban land-use site in the Green-Duwamish basin (Longfellow Creek).
- Adding analysis for 18 pesticides and degradate pesticides.

An intensive review of pesticide results is conducted on a triennial basis. Year 2009 is the first in a three-year study cycle to investigate pesticides in the Green-Duwamish basin, the fourth in a six-year cycle in the Skagit-Samish basin, and the seventh in a nine-year cycle in the Cedar-Sammamish and Lower Yakima basins. Triennial results for the Wenatchee-Entiat basins are included in this report.

During 2007-09 few pesticides were detected at the Wenatchee-Entiat basin sites with the exception of Brender Creek. This is in part due to higher streamflows at some of the sites including Peshastin Creek and the Wenatchee and Entiat Rivers. Brender Creek endosulfan levels exceeded the endangered species level of concern for salmonids and the Washington State chronic water quality standard, indicating potential chronic health effects to aquatic life during mid-March through May. Pesticide concentrations at the Entiat River site met all U.S. Environmental Protection Agency (EPA) Pesticide Registration Toxicity Criteria and EPA National Recommended Water Quality Criteria as well as Washington State Water Quality Standards.

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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 (e.g., March through October).

WSDA, the U.S. Environmental Protection Agency (EPA), the National Atmospheric and Oceanic Administration (NOAA) National Marine Fisheries Service, and the U.S. Fish and Wildlife Service (USFWS) use the data collected from this study 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 the potential effects of pesticides on endangered salmon species while minimizing the economic impacts to agriculture.

The purpose of this data report is to provide results from monitoring conducted in 2009 in six basins and to document any changes that occurred in the program during the year. This report also includes an in-depth analysis of data collected during 2007-09 in the Wenatchee-Entiat basins. This three-year review includes an examination of trends and relationships and determines if water quality concentrations are healthy for aquatic life.

A triennial report for data collected during 2006-08 from Thornton Creek (Cedar-Sammamish basin), the Skagit-Samish basin, and the lower Yakima basin are included in Sargeant et al. (2010). A triennial review of the Wenatchee-Entiat sites was not included in the 2010 report because only two years of data were available at that time.

Study Area

This pesticide monitoring project has been ongoing since 2003. As the project has progressed, additional sampling areas have been added.

Basins Monitored During 2009

The six basins monitored in 2009 are presented in Figure 1: two urban and four agricultural basins. The urban basins were chosen due to land-use characteristics, history of pesticide detections, and habitat use by salmon. The agricultural basins were chosen because they support several salmonid populations, produce a variety of agricultural commodities, and have a high percentage of cultivated areas.

Monitoring areas and timeframes are:

- Thornton Creek, located in the Cedar-Sammamish basin (WRIA¹ 8), represents an urban land-use area. Two to four sites have been sampled on this creek from 2003-08. One site at the mouth of Thornton Creek was sampled in 2009.
- Longfellow Creek, located in the Green-Duwamish basin (WRIA 9), represents an urban land-use area. Sampling started on this creek at one site in 2009.
- Four sub-basins of the lower Skagit-Samish basin (WRIA 3) were selected to represent western Washington agricultural land-use practices. The Samish River, Big Ditch Slough, Browns Slough, and Indian Slough have been sampled since 2006.
- Three sub-basins of the Lower Yakima basin (WRIA 37) were selected to represent eastern Washington irrigated crop-land agricultural practices. Marion Drain, Sulphur Creek Wasteway, and Spring Creek have been sampled since the start of the project in 2003.
- Four sub-basins of the Wenatchee basin (WRIA 45) and Entiat basin (WRIA 46) were selected to represent central Washington agricultural tree fruit practices. Peshastin Creek, Mission Creek, Brender Creek, and the Wenatchee River (WRIA 45) and the Entiat River (WRIA 46) have been sampled since 2007.

Site locations and duration of sampling are described in Appendix A.

A full description of the Wenatchee-Entiat monitoring sites is included below. A detailed description of the Wenatchee-Entiat sites is provided in this report because of the triennial (2007-09) review. Descriptions of sites in the other four basins, including basin description, site map, climate, agricultural land-use, and the salmon fishery, are included in the last triennial report (Sargeant et al., 2010).

¹ Water Resource Inventory Area





Wenatchee-Entiat Basins, 2007-09

The Wenatchee River drains a portion of the east slopes of the Cascade Mountains in northcentral 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. Lake Wenatchee 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 basin are forestry, wilderness, agriculture, range, residential, and recreation.

The federal government is the largest landowner in the Wenatchee basin, with approximately 671,220 acres, 76% of the basin. 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 basin along the Wenatchee River and its major tributaries (Andonaegui, 2001).

The Wenatchee and Entiat watersheds (WRIAs 45 and 46) 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. Sampling of the Wenatchee-Entiat began in 2007 as described in Dugger et al. (2007).

Sampling Sites

Sampling for this project is conducted at five sites in the Wenatchee-Entiat basins:

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

Figure 2 presents the locations of the five sampling sites. Appendix B describes sampling locations and duration of sampling for each site.



Figure 2. Location of sampling sites in the Wenatchee and Entiat basins.

The sampling sites are located to minimize the influence of residential areas. Brender Creek discharges to Mission Creek downstream of the confluence with Yaksum Creek. Peshastin and Mission Creeks discharge to the Wenatchee River, and the Wenatchee and Entiat Rivers discharge to the Columbia River.

Precipitation and Streamflow

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 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 1) (USGS, 2009a).

Table 1. Average, maximum, and minimum streamflows (cfs) for the Wenatchee River at Monitor, 1963-2009 (USGS, 2009a).

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Mean	1061	2194	1976	1839	1940	2375	3916	8032	8815	4301	1424	785
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 river mile 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 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 for the Mission Creek subbasin is 19 inches. Mission Creek contributes only 1% of the average annual flow of the Wenatchee River. Approximately 0.4% 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.

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 2) (USGS, 2009b).

Table 2. Average, maximum, and minimum streamflows (cfs) for the Entiat River near Entiat,
1996-2009 (USGS, 2009b).

	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Mean	147	216	166	182	174	263	559	1426	1600	675	233	135
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.

Table 3 has estimates of crop totals for the Wenatchee and Entiat basins (WSDA, 2009).

Approximately 0.6% of the Peshastin Creek subbasin is in agricultural production, with major crops being pears, apples, and cherries. For Mission Creek, 4% of the subbasin is in agricultural production, with pears as the major product. The Brender Creek subbasin has the greatest area in agricultural production (11%), with major crops being pears, apples, and cherries. Approximately 1% of the Wenatchee basin is in production with pear and apple orchards.

Less than 1% of the Entiat basin is in agricultural production, with the major crops being pears and apples.

Site and Land Use	Area (acres)	Percent of Basin or Subbasin
Peshastin Creek		
Apple	33	0.038%
Cherry	10	0.012%
Fallow	14	0.016%
Pear	488	0.566%
Total Cropped Area	545	0.632%
Subbasin Area	86250	
Mission Creek		
Alfalfa/Grass, Hay	12	0.023%
Cherry	7	0.014%
Christmas Tree	5	0.009%
Pear	177	0.338%
Total Cropped Area	202	0.385%
Subbasin Area	52386	
Brender Creek		
Apple	112	1.640%
Cherry	59	0.865%
Fallow	23	0.335%
Golf Course	36	0.519%
Pear	525	7.640%
Total Cropped Area	755	11.00%
Subbasin Area	6866	
Wenatchee River		
Alfalfa/Grass, Hay	19	0.002%
Apple	1,018	0.120%
Apricot	1	< 0.001%
Cherry	326	0.038%
Christmas Tree	5	0.001%
Developed	284	0.033%
Fallow	166	0.020%
Golf Course	113	0.013%
Grape, Wine	10	0.001%
Grass, Hay	91	0.011%
Nectarine/Peach	10	0.001%
Nursery, Lavender	1	< 0.001%
Pear	6,509	0.766%
Total Cropped Area	8,554	1.010%
Basin Area	849905	
Entiat River		
Alfalfa/Grass, Hay	1	< 0.001%
Apple	170	0.064%
Cherry	31	0.012%
Fallow	66	0.025%
Grass, Hay	6	0.002%
Pasture	2	0.001%
Pear	529	0.199%
Unknown	3	0.001%
Total Cropped Area	808	0.304%
Basin Area	265434	

Table 3. Crop totals for the Wenatchee-Entiat sites (WSDA, 2009).

Salmonid Fishery Use

A summary of salmonid distribution and use is presented in Table 4. 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 stream reach where the sample station is located; higher quality habitat may be available in the upper watershed.

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 4. Salmonid presence and use for the Wenatchee-Entiat sites. (StreamNet, 2009; Burke et al., 2006.)

Tables 5, 6, and 7 present the life phases and periods when salmonid species are present in Peshastin and Mission Creeks and the lower Wenatchee River (EES Consulting Inc. and Thomas R. Payne & Associates, 2005).

Entiat River salmonid life phases and periods of use are presented in Table 8 (Chelan County Conservation District, 2004).

Table 5. Timing of salmonid life phases in the Peshastin Creek subbasin.

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



Table 6. Timing of salmonid life phases in the Mission Creek subbasin.

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. (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 7. Timing of salmonid life phases in the lower Wenatchee River basin.

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

Species	Life Stage	October	November	December	January	Febr	uary	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 8. Timing of salmonid life phases in the Entiat River basin.

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. (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 Colonization												
	0-Age Active Rearing												
	0-Age Migrant												
	Prespawning migrant + Holding												
Spring	Spawning												
Chinook	Incubation												
	Emergence												
	Fry Colonization												
	0-Age Active Rearing												
	0-Age Migrant												
	1-Age Transient Rearing												
	Prespawning migrant + Holding												
Steelhead	Spawning												
	Incubation												
	Emergence												
	Fry Colonization												
	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

Sampling was designed to address pesticide presence in salmonid-bearing streams during a typical pesticide-use period (e.g., March through September). The focus of monitoring is on currently registered pesticides, but laboratory analysis also included some historically used pesticides. Conventional water quality parameters were measured: total suspended solids (TSS), pH, conductivity, temperature, dissolved oxygen, and streamflow. The conventional parameters provide information to help better determine the factors influencing pesticide toxicity, fate and transport, and general water quality.

Detailed information on study design and methods are described in the Quality Assurance (QA) Project Plan (Johnson and Cowles, 2003), subsequent addendums (Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009), and the triennial reports (Burke et al., 2006; Sargeant et al., 2010).

During 2009, samples were collected for analysis of 169 pesticides and degradates: 70 insecticides, 58 herbicides, 28 degradate pesticides, 10 fungicides, two synergistic compounds, and one wood preservative. Due to concerns about false positive results, the following analytes were rejected and not included in the 2009 data set: 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl.

Sampling Sites and Sampling Frequency

Changes to the 2009 sampling program include discontinuing the upstream Thornton Creek (TC-1) sampling site and adding a site on Longfellow Creek (LC-1) in the Green-Duwamish basin. The new site was selected collaboratively with the USFWS and the NOAA National Marine Fisheries Service. Figure 1 shows the location of the Longfellow Creek sampling site. The QA Project Plan Addendum (Anderson and Sargeant, 2009) describes this change.

In 2009, 27 sampling events were conducted. Sampling began the second week in March and continued through the second week in September at all sites except Marion Drain. As in previous years, Marion Drain sampling continued through the end of October (for a total of 34 sampling events) for organophosphate pesticides and TSS. The upstream Spring Creek site in the lower Yakima basin was sampled every other week for a total of 14 sampling events.

Field Procedures and Laboratory Analyses

A full description of field procedures and laboratory analysis is included in Sargeant et al. (2010). Field methods for grab sampling are a direct application or modification of United States Geological Survey (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).

Field meters were calibrated at the beginning of the field day according to manufacturers' specifications, using Ecology standard operating procedures (SOPs) (Swanson, 2007). Meters were post-checked at the end of the field day using known standards. Conventional parameters measured in the field were replicated once per sample day. Dissolved oxygen meter results were compared to grab samples that were analyzed by Winkler Titration for dissolved oxygen following Ecology SOPs (Ward, 2007). Two to three Winkler grab samples were obtained during each sample day. Continuous, 30-minute interval, temperature data were collected year-round in 2009. Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Wagner et al., 2000). Data quality objectives for field meters are described in Anderson and Sargeant (2009).

Discharge for sites other than Sulphur Creek Wasteway, Wenatchee River, and Entiat River were measured using a Marsh-McBirney flow meter and top-setting wading rod, as described in the USGS method (Rantz et al., 1983). Discharge data for Sulphur Creek Wasteway were 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 data were 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.

Ecology's Manchester Environmental Laboratory (MEL) analyzed all pesticide and TSS samples. Laboratory methods are presented in Table 9. A list of target analytes for this study is presented in Appendix C. Laboratory methods are also discussed in the QA Project Plan (Anderson and Sargeant, 2009); previous QA Project Plan (Johnson and Cowles, 2003) and QA Project Plan addendum (Burke and Anderson, 2006); and SOP for the *Pesticides in Salmonid Streams Project* (Anderson and Sargeant, 2010).

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

Table 9. Summary of 2009 laboratory methods.

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.

MS: mass spectrometry.

HPLC: high performance liquid chromatography.

n/a: not applicable.

Data Quality

Laboratory Data Quality

Performance of laboratory analyses is governed by QA and quality control (QC) protocols. The QA/QC protocol employs 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. A summary of laboratory and field data quality are presented below. For a detailed discussion of 2009 data quality, refer to Appendix C. Data quality results for 2007 and 2008 are presented in Sargeant et al. (2010).

Across the six study basins, field blank detections of certain carbamate compounds indicated problems with select carbamate parameters: 1-naphthol, aldicarb sulfone, aldicarb sulfoxide, and oxamyl. During 2009 an anomaly in the analytical method for carbamate pesticides was identified. This analytical anomaly caused false positive identification for 1-naphthol, aldicarb sulfone, and aldicarb sulfoxide in 2006-2009 and for oxamyl in 2009. Data for these parameters are not reported for this 2009 study. Although QA/QC criteria were met for all reported carbamate values, there is a possibility of some false positives.

In the initial phase of this multi-year project, a large portion of the budget was allocated toward QA/QC. Currently, QA/QC is approximately 17% of the budget. The large number of QA/QC samples necessitates the use of a pre-planned schedule. At a minimum, each week there is at least one replicate, one blank, and one MS/MSD covering at least one of the four laboratory analyses (PESTMS, HERBS, CARBAMLL, and TSS). QA/QC samples were concentrated during April, May, and June to cover the intensive application period for most pesticides. Sites were randomly selected for application of QA/QC samples.

Laboratory Blanks

In 2009 no laboratory blank detections occurred for the pesticide analysis, gas chromatography mass spectrometry (GCMS), or herbicide analysis. There were laboratory blank detections for the low level carbamate analysis (Appendix C, Table C-9). Five of the eight blank detections were for aldicarb sulfone, aldicarb sulfoxide, or oxamyl. Data for 2009 are not reported for these parameters due to concerns about false positives.

Field Blanks

Field blank detections indicate the potential for sample contamination in the field and laboratory as well as the potential for false detections due to analytical error. In 2009 there were two detections in field blanks: one of dichlobenil in Longfellow Creek and one of tricyclazole in Brender Creek.

Dichlobenil was not found in the associated sample at Longfellow Creek but was detected at other western Washington sites on the same day. Dichlobenil was detected in all the other 2009 samples for Longfellow Creek. Because the week in which the field blank detection occurred had no corresponding detection in the associated sample, it is likely that the field blank sample and the associated Longfellow Creek sample were unintentionally switched prior to analysis. However, all western Washington dichlobenil detections for this week (first week of sampling) are still qualified because it is impossible to be certain that this error occurred.

Tricyclazole was not detected in any of 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 was 8.7% during 2009, and 2.5% of the pairs had a detection in at least one replicate. For pesticides, 39 pesticides were detected in 113 replicate pairs. Of these, 81% were consistently identified in both samples. The average relative percent difference (RPD) of consistent field replicate pairs was low, 9.6%, and similarly the median pooled relative standard deviation (RSD) was 6.3%. The 2009, replicate variability is lower than 2006-2008 results (8.1% RSD) and the National Water Quality Assessment (NAWQA) median pooled RSD of 15% at concentrations < 0.01 ug/L and 12% at concentration near 0.01 ug/L (Martin, 2002).

TSS was detected in 32 replicate pairs. TSS replicate pairs were consistently identified, and 75% of the replicates were within the 20% RPD criterion. For the 25% of the replicates that did not meet the 20% RPD criterion, TSS concentrations were at or near the reporting limit. When replicates did not fall within the acceptable range, it is likely due to the high variability in detections near the minimum reporting limit (Mathieu, 2006).

Surrogates and Matrix Spikes

Surrogates are used to evaluate recovery for a group of compounds. The majority of surrogate recoveries fell within the control limits established by Manchester Laboratory for all compounds except chlorpyrifos-D10. Chlorpyrifos-D10 was used as a surrogate for organophosphate pesticides in GCMS analysis in late 2009. Recoveries were high. No sample results were qualified because all other GCMS surrogates, including the other organophosphate surrogate, triphenyl phosphate, were acceptably recovered in all samples.

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 88.7%, and the average RPD between MS/MSD pairs was 12.2%. For most compounds, recovery and RPDs of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Results with an average RPD outside of the \pm 40% criteria were qualified as estimates.

Field Data Quality

A detailed discussion of 2009 field data quality is included in Appendix C. In 2009 the field meter for the lower Yakima and Wenatchee-Entiat sites (eastside sites) met QC objectives including post-checks and Winkler comparisons except on March 18, 2009. Dissolved oxygen meter readings were biased high that day: meter and Winkler dissolved oxygen % RSD ranged from 11.1-13.6%. Only Winkler dissolved oxygen results will be reported for this day.

The field meter for the urban and lower Skagit-Samish sites (westside sites) did not meet postcheck QC objectives for conductivity for the following dates: March 16 and 25, April 22 and 27, May 6, 20, and 26, 2009. Conductivity results for these days are rejected and not reported.

Data Analysis Methods

Field and laboratory data were compiled and organized using Excel[®] spreadsheet software and Access[®] database software (Microsoft Corporation, 2007). Water quality results from field and laboratory work were also entered into Ecology's Environmental Information Management (EIM) database (www.ecy.wa.gov/eim).

This report contains only 2009 data for Thornton and Longfellow Creeks, the Skagit-Samish sites, and the lower Yakima sites. For the Wenatchee-Entiat sites, this report contains a more indepth analysis as part of a three-year review (2007-09). Data analysis methods for the three-year review are described below.

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 10. 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.

Qualifier	Definition
No qualifier	The analyte was detected at the reported concentration. Data are not qualified.
Е	Reported result is an estimate because it exceeds the calibration range.
J	The analyte was positively identified; the associated numeric 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 numeric 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 were made using Excel® software. For statistical trend analysis, WQHYDRO software (Aroner, 2007) was used. For correlation analysis, R statistical software was used (R Foundation for Statistical Computing, 2010).

Replicate Values

Field and laboratory replicates were obtained to determine data quality. Field and laboratory replicates were arithmetically averaged for comparisons to *assessment criteria* and *water quality standards*. For data analysis purposes, field and laboratory replicates were arithmetically averaged. If the sample or the replicate was a non-detect value while the other (either sample or replicate) 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 2007-09, the laboratory analyzed samples for over 160 pesticides and degradates. 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.

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. NJ (analyte was tentatively identified) 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 sampling season were tested where appropriate. Some pesticides are only detected during a select period; this minimizes the number of non-detect data in the analysis.

Assessment Criteria and Washington State Water Quality Standards

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

- EPA FIFRA Pesticide Registration Toxicity 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 wide array of families, including at least one fish species from the family *Salmonidae* and a second species in the class *Osteichthys*. The criteria and standards do not account for the effects of multiple chemicals or pesticide mixtures on an organism. Many of the pesticides included in this study do not have EPA or Washington State criteria.

Aquatic life criteria, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix D. Measured concentrations higher than criteria concentrations do not necessarily indicate that the water quality criteria have not been met. Numeric water quality criteria contain concentration values and duration of exposure components; both must be compared to the measured concentrations to assess compliance with the criteria.

In this report, EPA Pesticide Registration Toxicity 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*. For a description of these criteria and standards for pesticides, refer to Appendix D.

EPA 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 11 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 $1/20^{\text{th}}$ of the acute Lethal Concentration 50 (LC₅₀) for aquatic organisms. To assess the potential risk of a pesticide to salmonids, the LC₅₀ for rainbow trout is commonly used as a surrogate species. Thus the endangered species LOC presented in subsequent tables are $1/20^{\text{th}}$ of

the rainbow trout LC_{50} . When available, the endangered species LOC for specific salmonids is also presented.

Test Data	Risk Quotient	Presumption	
	>0.5	Potentially high acute risk.	
Acute LC ₅₀	>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.	

Table 11. Risk quotient criteria for direct and indirect effects of pesticides on aquatic organisms.

(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 (LC₅₀, or Effective Concentration - EC_{50} for immobility). Acute toxicity testing for aquatic plants is conducted over 96 hours; the criterion is based on reduction in aquatic plant growth (EC_{50}).

Chronic fish tests normally use reproductive effects, or effects to offspring, as the measured effect. 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., LC₅₀ freshwater fish acute toxicity tests are run for 96 hours at a constant concentration). When comparing the monitoring data to either 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 met based solely on an individual sample because the sampling frequency is usually weekly. Weekly sampling does not allow for assessment of the temporal component of the criteria.

EPA 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 Act are based on vertebrate and invertebrate acute and chronic toxicological data. 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. These 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, and growth and reproductive effects, to fish and other aquatic life within the specified exposure periods. The chronic criteria for a number of the chlorinated pesticides are based on protection of 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 federal Clean Water Act section 303(d) listing purposes, measurements of instantaneous concentrations are assumed to represent the averaging periods specified in the water quality standards for both acute and chronic criteria, unless additional measurements are available to calculate averages (Ecology, 2006).

Because few water quality criteria for pesticides have been developed, the majority of comparisons to measured pesticide concentrations contained in this report are made using pesticide registration toxicity criteria.

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

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. Sargeant et al. (2010) provides a full description of the water quality standards and also explains why parameters such as temperature, pH, and dissolved oxygen are important for fish health.

Numeric Water Quality Standards

Thornton Creek subbasin

Beneficial uses for Thornton Creek are *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 12.

Table 12. Freshwater water quality standard for temperature, dissolved oxygen, and pH for *Core Summer Salmonid Habitat* use and *Extraordinary Primary Contact Recreation* use.

Parameter	Condition	Value	
Temperature	Highest 7- DADMax	16° C. Thornton Creek also has <i>Supplemental Spawning</i> <i>and Incubation</i> criteria: during September 15 - May 15, highest 7-DADMax should not exceed 13° C.	
Dissolved Oxygen	Lowest 1-day minimum	9.5 mg/L	
рН		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.

Longfellow Creek subbasin

Beneficial uses for Longfellow Creek include Salmonid Spawning, Rearing, and Migration habitat and Primary Contact Recreation. The numeric water quality standards for temperature, dissolved oxygen, and pH in Longfellow Creek are described in Table 13.

Skagit-Samish basin

Beneficial uses for the Samish River, Indian Slough, Big Ditch, and Browns Slough are *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 13. The site on Browns Slough is marine water and must meet the water quality standards described in Table 14.

Lower Yakima basin

Beneficial uses for Marion Drain, Sulphur Creek Wasteway, and Spring Creek are *Salmonid Spawning, Rearing, and Migration Habitat*. The freshwater water quality standard described in Table 13 applies to these sites.

Wenatchee-Entiat basins

Beneficial uses for the Mission Creek, Brender Creek, Wenatchee River, and Entiat River are *Salmonid Spawning, Rearing, and Migration*. The water quality standard described in Table 13 applies to these sites.

Table 13. Freshwater water quality standard for temperature, dissolved oxygen, and pH for *Salmonid Spawning, Rearing, and Migration Habitat* use and *Primary Contact Recreation* use.

Parameter	Condition	Value
Temperature	Highest 7- DADMax	17.5° C. The Wenatchee River site also has <i>Supplemental Spawning and Incubation</i> criteria: during October 1 - May 15, highest 7-DADMax should not exceed 13° C.
Dissolved Oxygen	Lowest 1-day minimum	8 mg/L
pН		Range within $6.5 - 8.5$, with a human-caused variation within the above range of < 0.5 units.

Table 14. Marine water quality standard for temperature, dissolved oxygen, and pH for *Aquatic Life Excellent* use.

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.

Results

This study investigated pesticide occurrence in select salmon bearing surface waters. Results for Thornton Creek in the Cedar-Sammamish basin, Longfellow Creek in the Green-Duwamish basin, the lower Skagit-Samish basin, and the lower Yakima basin are presented as a data summary for 2009. Results for the Wenatchee and Entiat basins include a three-year triennial review (2007-09) with more in-depth data analysis. Monitoring results for all six basins are available through Ecology's EIM system, <u>www.ecy.wa.gov/eim/</u>.

Pesticide calendars are included in Appendix E. The calendars provide a chronological overview of concentrations and detections during 2009. The calendars also compare EPA Pesticide Registration Toxicity Criteria and EPA National Recommended Water Quality Criteria (*assessment criteria*) to numeric Washington State Water Quality Standards (*water quality standards*). Refer to Appendix D, Assessment Criteria and Water Quality Standards, in this report for information on assessment criteria development.

Cedar-Sammamish Basin (WRIA 8): Thornton Creek, 2009

Pesticide Detections and Concentrations

A total of 27 sampling events were conducted on Thornton Creek between March 11 and September 8, 2009. During 2009 there were 58 detections of 19 pesticides and degradates. The 19 pesticides and degradates included: five carbamate insecticides (6 detections), seven herbicides (42 detections), five degradates (6 detections), a wood preservative (3 detections), and a fungicide (1 detection).

The number and types of pesticide detections are presented in Figure 3. The maximum number of pesticides detected during a sampling event was six (Figure 3). The most frequently detected herbicides were dichlobenil and 2,4-D. Most pesticide detections occurred before June 3.



Figure 3. Pesticide detections by week and type in the Thornton Creek subbasin, 2009.

Table 15 presents a pesticide calendar for Thornton Creek. The calendar provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards*. Appendix E, Table E-1 presents the color codes used to compare detected pesticide concentrations to assessment criteria. In 2009 pesticide concentrations in Thornton Creek met (did not exceed) any available *assessment criteria* or *water quality standard* (Appendix D).



Table 15. Thornton Creek pesticide detections, 2009.

C - Carbamate, D - Degradate, H - Herbicide, I - Insecticide, M - Multiple, WP - Wood Preservative

Conventional Parameters

Conventional water quality parameters were measured in Thornton Creek. All summaries are based on point (discrete) measurements obtained during the time of sampling. Table 16 summarizes results for TSS, streamflow, pH, conductivity, temperature, and dissolved oxygen.

pH levels met water quality standards during 2009. Dissolved oxygen dropped below the 9.5 mg/L water quality standard seven times during June through August 2009.

Table 16. Mean, minimum, and maximum for discrete conventional parameter measurements for Thornton Creek, 2009.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	27	6	2	25
Discharge (cfs)	27	6.8	2.6	28.2
pH (s.u.)	26	7.8	7.4	8.7
Conductivity (umhos/cm)	27	220	120	255
Temperature (°C)	27	13.9	5.7	20.2
Dissolved Oxygen (mg/L)	27	10.1	8.7	12.4

In addition to discrete measurements for temperature, continuous (30-minute interval) measurements were collected year-round. A temperature profile based on continuous temperature measurements is presented in Appendix F, Table F-1. During September 15 - May 15, the highest 7-Daily Average Daily Maximum (DADMax) should not exceed 13° C; during the rest of the year, the highest 7-DADMax should not exceed 16°C.

In 2009, temperatures did not meet (exceeded) the standard during the following periods:

- May 12-15, >13°C.
- May 29-June 21, >16°C.
- June 27-September 14, >16°C.
- September 15-30, >13°C.
- October 16-20, >13°C.
Green-Duwamish Basin (WRIA 9): Longfellow Creek, 2009

Pesticide Detections and Concentrations

A total of 27 sampling events were conducted on Longfellow Creek between March 11 and September 8, 2009. During this period, there were 58 detections of nine pesticide compounds. The nine compounds included one carbamate insecticide (2 detections), five herbicides (50 detections), two degradates (2 detections), and a wood preservative (4 detections).

The maximum number of pesticides detected during a sampling event was five, and most of the pesticides detected were herbicide compounds (Figure 4). The most frequently detected herbicides were dichlobenil, triclopyr, and 2,4-D.



Figure 4. Pesticide detections by week and type in the Longfellow Creek subbasin, 2009.

Table 17 presents a pesticide calendar for Longfellow Creek. The calendar provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards*. Appendix E, Table E-1 presents the color codes used to compare detected pesticide concentrations to *assessment criteria* and *water quality standards*. In 2009, pesticide concentrations in Longfellow Creek met (did not exceed) any available *assessment criteria* and *water quality standards* (Appendix D).

Date		3/11	3/16	3/25	3/30	4/8	4/13	4/22	4/27	5/6	5/12	5/20	5/26	6/3	6/8	6/16	6/22	7/1	7/6	7/17	7/22	7/31	8/4	8/10	8/18	8/28	9/1	9/8
Month			Ma	rch			Ap	oril			М	ay			Ju	ine				July				Au	gust		Septe	mber
Chemical	Туре	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
2,4,6-Trichlorophenol	D-M			0.510																								
2,4-D	Н									0.110	0.038	0.085				0.058	0.110							0.042	0.022		0.027	0.035
3,5-Dichlorobenzoic Acid	D-H			0.520																								
Dichlobenil	н		0.046	0.010	0.016	0.013	0.047	0.014	0.014	0.130	0.019	0.025	0.013	0.012	0.011	0.008	0.010	0.009	0.022	0.011	0.011	0.023	0.021	0.021	0.030	0.025	0.030	0.033
MCPA	н											0.025																
MCPP	н									0.051	0.009																	
Methiocarb	I-C	0.117	0.200																									
Pentachlorophenol	WP		0.028							0.037	0.009																	0.020
Triclopyr	Н		0.095							0.110	0.024	0.071				0.014	0.098					0.015		0.047	0.048	0.034	0.052	0.074
Total Suspended Solids		13	20	3	3	2	7	3	3	38	2	5	4	5	16	4	3	6	3	18	2	2	2	1		3	2	1

Table 17. Longfellow Creek pesticide detections, 2009.

C - Carbamate, D - Degradate, H - Herbicide, I - Insecticide, M - Multiple, WP - Wood Preservative

Conventional Parameters

Conventional water quality parameters were measured in Longfellow Creek. Table 18 summarizes results for TSS, streamflow, pH, conductivity, temperature, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling.

On April 29, 2009, a pH value of 8.7 exceeded the water quality standard of 8.5 standard units (s.u). During 2009 dissolved oxygen levels met the 8.0 mg/L minimum water quality standard.

Table 18. Mean, minimum, and maximum for discrete conventional parameter measurements for Longfellow Creek, 2009.

Parameter	Number	Mean	Minimum	Maximum
Total Suspended Solids (mg/L)	26	6	1	38
Discharge (cfs)	27	1.6	0.5	12.5
pH (s.u.)	26	7.9	7.1	8.7
Conductivity (umhos/cm)	27	271	110	318
Temperature (°C)	27	14	5.4	20.3
Dissolved Oxygen (mg/L)	27	10.2	8.8	14.3

In addition to discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. A temperature profile based on continuous temperature measurements is presented in Appendix F, Table F-2. The temperature standard for Longfellow Creek is: the 7-DADMax should not exceed 17.5° C. During 2009 temperature exceeded the standard during the following periods:

- June 1-6, >17.5 °C.
- June 10-13, >17.5 °C.
- July 1-6, >17.5 °C.
- July 13-August 5, >17.5 °C.
- August 17-21, >17.5 °C.

Lower Skagit-Samish Basin (WRIA 3), 2009

Pesticide Detections and Concentrations

The lower Skagit-Samish sites were sampled for 27 consecutive weeks from March 11 to September 8, 2009. The lower Skagit-Samish sites are: upstream and downstream Big Ditch, Indian Slough, Browns Slough, and Samish River. Browns Slough is classified as marine water while the other four sites are classified freshwater.

For the five Skagit-Samish sites combined, there were a total of 33 pesticides including degradates detected: eight insecticides, 20 herbicides, two fungicides, two degradates, and a wood preservative. For the Skagit-Samish sites, Indian Slough and upstream Big Ditch had the greatest number of pesticide detections, with each having 134 detections. The downstream Big Ditch site had 89 detections, Browns Slough had 46 detections, and the Samish River had 20 detections. The downstream Big Ditch site had the greatest number of pesticides detected in one sample: on May 20, 13 pesticides were detected.

Big Ditch

Two sites on Big Ditch were sampled in 2009. Water quality at the upstream site is influenced by industrial land use and stormwater, while the downstream site is influenced by agricultural land use. In 2009, 27 pesticides and degradates were detected in Big Ditch. Eighteen of these were found at the upstream site, and 23 were found at the lower Big Ditch site.

The maximum number of pesticides detected during a sampling event was 10 at the upstream site (Figure 5) and 13 at the downstream site (Figure 6). Most of the pesticides detected were herbicide compounds. At the upstream site, pesticides were detected during every sampling event; at the downstream site, the greatest number of detections occurred from March through May.

The most frequently detected pesticides at the upstream site were:

- Bromacil (herbicide), 25 detections.
- Dichlobenil (herbicide), 24 detections.
- Picloram (herbicide), 16 detections.
- Tebuthiuron (herbicide), 12 detections.
- Imidacloprid (neonicotinoid insecticide), 12 detections.

The most frequently detected pesticides at the downstream site were:

- Metolachlor (herbicide), 14 detections.
- Dichlobenil (herbicide), 13 detections.
- Bromacil (herbicide), 9 detections.
- 2,4-D (herbicide), 8 detections.



Figure 5. Pesticide detections by week and type for the upstream Big Ditch site, 2009.



Figure 6. Pesticide detections by week and type for the downstream Big Ditch site, 2009.

Tables E-4 and E-5 in Appendix E present the 2009 pesticide calendars for the upstream and downstream Big Ditch sites, respectively. The calendars provide a chronological overview of concentrations and detections during 2009 and compare pesticide concentrations to *assessment criteria* and *water quality standards*.

The downstream Big Ditch site did not exceed any available *assessment criteria* and *water quality standards* (Appendix D). At the upstream Big Ditch site on May 20, there was one detection of malathion, an organophosphate insecticide, that exceeded the endangered species level of concern (ESLOC) for freshwater fish and the EPA chronic invertebrate criteria. No other detections exceeded any available *assessment criteria* or *water quality standards*.

Indian Slough

During 2009 there were 134 detections of 21 pesticides and a degradate. These 21 compounds were 13 herbicides, five insecticides, one fungicide, one degradate, and a wood preservative. The number and types of pesticide detections are presented in Figure 7. The maximum number of pesticides detected during a sampling event was 10 (Figure 7). Of the 134 pesticide detections, 122 were herbicides.



Figure 7. Pesticide detections by week and type for Indian Slough, 2009.

The most frequently detected compounds were the following herbicides:

- Tebuthiuron (19 detections).
- Bromacil (19 detections).
- Dichlobenil (17 detections).
- Diphenamid (16 detections).

During the 2006-08 monitoring, the herbicide diphenamid was detected 52 times in Indian Slough. Diphenamid has not been registered for use by EPA since 1991 (EPA, 2002). It is not known why diphenamid is detected so frequently in Indian Slough. Data quality for herbicide parameters is excellent, and detections are not likely due to field or laboratory error.

Appendix E, Table E-6 presents the 2009 pesticide calendar for Indian Slough. The calendar provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

One detection of malathion at Indian Slough exceeded the ESLOC for freshwater fish and the EPA chronic invertebrate criteria in March 2009. No other pesticide concentrations exceeded available *assessment criteria* or *water quality standards*.

Browns Slough

Browns Slough is sampled downstream of a tidegate. Due to higher salinity at this site marine *assessment criteria* and *water quality standards* are used for evaluating water quality. During 2009 there were 46 detections of 12 pesticides. The 12 pesticides were 10 herbicides, one insecticide, and one wood preservative. The number and types of pesticide detections are presented in Figure 8. The maximum number of pesticides detected during a sampling event was six (Figure 8). Most of the pesticides detected were herbicides (44 out of 46). There were only two pesticide detections after mid-June.



Figure 8. Pesticide detections by week and type for Browns Slough, 2009.

The most frequently detected pesticides were the following herbicides:

- DCPA (dacthal) (13 detections).
- Metolachlor (7 detections).
- Simazine (7 detections).

Appendix E, Table E-7 presents the 2009 pesticide calendar for Browns Slough. The calendar provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards*. In 2009 pesticide concentrations in Browns Slough did not exceed any available marine *assessment criteria* or *water quality standards* (Appendix D).

Samish River

A total of 27 sampling events were conducted on the Samish River between March 11 and September 8, 2009. There were very few pesticide detections (20 detections); these were seven herbicides and a wood preservative. The number and types of pesticide detections are presented in Figure 9. The maximum number of pesticides detected during a sampling event was six (Figure 9). The most commonly detected pesticide was the herbicide dichlobenil, with six detections.



Figure 9. Pesticide detections by week and type for the Samish River, 2009.

Appendix E, Table E-8 presents a pesticide calendar for the Samish River. The calendar provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards*. Samish River did not exceed any available *assessment criteria* or *water quality standards* (Appendix D).

Conventional Parameters

Conventional water quality parameters were measured at the Skagit-Samish sites. Table 19 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling. Browns Slough is a marine site and must meet marine water quality standards; all the other Skagit-Samish sites must meet freshwater quality standards.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)
Big Ditch (upstream	ı)				
number	27	25	26	27	27
mean	17	2.6	7.0	315	8.8
minimum	3	0.4	6.7	135	6.1
maximum	118	13	7.5	426	11.6
Big Ditch (downstre	am)				
number	24	27	26	27	27
mean	12	11.8	7.3	344	9.5
minimum	1	1.7	6.7	44	6.3
maximum	38	23.6	9.4	933	14.3
Indian Slough					
number	26	25	26	27	27
mean	8	15.1	7.0	937	7.1
minimum	2	1.3	6.7	261	5.2
maximum	23	31.0	7.7	2296	9.6
Brown Slough					
number	27	16	26	27	27
mean	9	4.3	7.5	13245	10.1
minimum	4	0.5	7.0	918	2.9
maximum	18	6.6	8.7	30450	16.4
Samish River					
number	27	26	26	27	27
mean	13	166.5	7.2	122	10.3
minimum	2	26.5	6.7	53	8.8
maximum	89	699.4	7.6	442	12.8

Table 19. Mean, minimum, and maximum for discrete conventional parameter measurements for the Skagit-Samish sites, 2009.

During 2009 dissolved oxygen levels did not meet the 8.0 mg/L minimum fresh water quality standard in upper Big Ditch (9 times), lower Big Ditch (7 times), and Indian Slough (22 times). The Samish River met dissolved oxygen water quality standards during all sampling events. Browns Slough did not meet the 6.0 mg/L minimum marine water quality standard for two sampling events.

Upper Big Ditch, Indian Slough, and Samish River met pH water quality standards. Both Browns Slough (marine) and lower Big Ditch (freshwater) did not meet the pH standard once during the sample period.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. A temperature profile based on continuous temperature measurements is presented in Appendix F, Figures F-3 – F-7. The temperature standard for the freshwater sites is the 7-DADMax should not exceed 17.5° C; and for the marine water it should not exceed 16.0° C. Table 20 describes the periods that temperature exceeded the standard.

Site	Periods When Temperature Did Not Meet Standards
Big Ditch (upstream) >17.5°C	May 29-June 18, June 20-21, June 24-July 8, July 11-Sept 20.
Big Ditch (downstream) >17.5°C	April 28-May 1, May 18-June 4, June 10-12, June 28-Sept 25.
Indian Slough >17.5°C	May 25-Sept 23.
Browns Slough >16.0°C	April 18-May 3, May 5-Sept 25, Oct 2-3.
Samish River >17.5°C	June 15-20, June 29-July 4, July 13-Aug 6, Aug 28-Sept 2.

Table 20. Periods of water temperature exceedance for the Skagit-Samish basin sites, 2009.

Lower Yakima Basin (WRIA 37), 2009

Pesticide Detections and Concentrations

In the lower Yakima River basin, downstream Spring Creek, Marion Drain, and Sulphur Creek Wasteway were sampled for 27 consecutive weeks from March 11 to September 9, 2009. The upstream Spring Creek site was sampled every other week during the same period for a total of 14 sampling events. In Marion Drain, weekly sampling for organophosphates continued from September 16 through October 26, 2009. Historically, Marion Drain sampling for organophosphates has continued through the end of October.

For the four sites combined, there were a total of 35 types of pesticides and degradates found. These 35 compounds were 11 insecticides, 20 herbicides, three degradates, and one wood preservative. Marion Drain had the greatest number of detections, 150 (and greatest number of sampling events). Sulphur Creek Wasteway had 124 pesticide detections followed by the downstream Spring Creek site (88 detections) then the upstream Spring Creek site had 42 detections (and the least number of sampling events).

Spring Creek

Two sites on Spring Creek were sampled in 2009. The upstream site was sampled every two weeks, and the downstream site weekly. A total of 19 pesticide and degradate types were detected in Spring Creek: 11 herbicides, five insecticides, two degradates, and one wood preservative. Similar pesticides were detected at both sites with 15 of the pesticides found upstream and 18 found at the downstream site. The number and types of pesticide detections are presented in Figure 10 for the upstream site and Figure 11 for the downstream site. The maximum number of pesticides detected during a sampling event at the upstream site was six (Figure 10) and at the downstream site was eight (Figure 11).

The most frequently detected pesticides at the upstream site were the following herbicides:

- 2,4-D (5 detections).
- Atrazine (5 detections).
- Bentazon (5 detections).

The most frequently detected pesticides at the downstream site were the following herbicides:

- 2,4-D (18 detections).
- Bromacil (15 detections).
- Pendimethalin (9 detections).



Figure 10. Pesticide detections by week and type for upstream Spring Creek, 2009.



Figure 11. Pesticide detections by week and type for downstream Spring Creek, 2009.

Appendix E, Tables E-9 and E-10 present the 2009 pesticide calendars for the upstream and downstream Spring Creek sites, respectively. The calendars provide a chronological overview of concentrations and detections during 2009 and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

At the upstream site, one April sample of 4,4'-DDE did not meet (was above) chronic water quality standards.

At the downstream site, three consecutive detections of chlorpyrifos from March to April were above the chronic *water quality standard* and EPA's chronic invertebrate *criteria*. Three consecutive weeks of detections mean that the four-day time component of the *water quality standard* was not met.

Marion Drain

An additional seven weeks of sampling for organophosphates was conducted on Marion Drain after September 9, 2009. No pesticides were detected during the last two sampling events at the end of October. During 2009 there were 150 detections of 19 pesticides and a degradate. These 19 compounds were 14 herbicides, five insecticides, and one insecticide degradate. The number and types of pesticide detections are presented in Figure 12. The maximum number of pesticides detected during a sampling event was nine (Figure 12). A total of 75% of the detections were herbicides; the rest were insecticides or insecticide degradates.



Figure 12. Pesticide detections by week and type for Marion Drain, 2009.

The most frequently detected compounds were herbicides:

- Terbacil (26 detections).
- 2,4-D (19 detections).
- Dicamba I (18 detections).
- Bentazon (15 detections).

The most frequently detected insecticide was chlorpyrifos with 10 detections during the March through October sampling period.

The 2009 pesticide calendar in Appendix E, Table E-11 provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

One detection of chlorpyrifos was found at the EPA chronic invertebrate criteria once in 2009. This single event did not exceed the 21-day time component of the chronic invertebrate criteria.

Sulphur Creek Wasteway

During 2009 there were 124 detections of 21 pesticides and degradates. These 21 compounds were 15 herbicides, five insecticides, and one insecticide degradate. The number and types of pesticide detections are presented in Figure 13. The maximum number of pesticides detected during a sampling event was eight (Figure 13).



Figure 13. Pesticide detections by week and type for Sulphur Creek Wasteway, 2009.

The most frequently detected compounds were the following herbicides:

- 2,4-D (21 detections).
- Bromacil (18 detections).
- Dicamba I (18 detections).
- Dichlobenil (9 detections).

The 2009 pesticide calendar in Appendix E, Table E-12 provides a chronological overview of concentrations and detections during 2009 and compares pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

4,4'-DDE did not meet the chronic *water quality standard* in March and April. The chronic *water quality standard* for DDT and its metabolites were exceeded due to consistent weekly detections.

There were three consecutive detections of chlorpyrifos above the chronic *water quality standard*; one detection was also above the ESLOC for fish. Because chlorpyrifos was detected in three consecutive weeks, the chronic *water quality standard* was not met.

Conventional Parameters

Conventional water quality parameters were measured at the four lower Yakima sites. Table 21 summarizes results for TSS, streamflow, pH, conductivity, and dissolved oxygen. All summaries are based on point (discrete) measurements obtained during the time of sampling. All sites must meet freshwater quality standards.

With the exception of the upstream Spring Creek site, all sites exceeded the pH water quality standard of 8.5 s.u. The downstream Spring Creek site exceeded the standard 11 times, Marion Drain four times, and Sulphur Creek Wasteway seven times. Maximum pH values are described in Table 21.

All sites met the dissolved oxygen standard with the exception of the upstream Spring Creek site. On July 13, a dissolved oxygen value of 7.9 fell below the minimum water quality standard of 8.0 mg/L.

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. A temperature profile based on continuous temperature measurements is presented in Appendix F, Figures F-8 – F-11. The temperature standard for the freshwater sites is that the 7-DADMax should not exceed 17.5°C. None of the sites met temperature standards during all periods. Table 22 describes the periods that temperature did not meet the standard.

Site	Total Suspended Solids (mg/L)	Flow (cfs)	pH (s.u.)	Conductivity (umhos/cm)	Dissolved Oxygen (mg/L)
Spring Creek (upstre	eam)				
number	14	14	14	14	14
mean	22	6.4	8.0	366	9.4
minimum	4	1.9	7.5	266	7.9
maximum	68	11.9	8.5	502	12.1
Spring Creek (downs	stream)				
number	27	27	27	27	27
mean	14	8.7	8.6	338	9.9
minimum	1	1	7.9	180	8.1
maximum	50	17	9.4	478	13.6
Marion Drain					
number	34	32	34	34	34
mean	13	116	8.1	226	12.5
minimum	2	12.7	7.5	138	9.3
maximum	40	265	9.3	341	17.6
Sulphur Creek Wast	eway				
number	27	27	27	27	27
mean	40	260	8.4	264	10.3
minimum	7	49	7.8	164	9.1
maximum	98	641	8.8	535	12.1

Table 21. Mean, minimum, and maximum for discrete conventional parameter measurements for the lower Yakima sites, 2009.

Table 22. Periods of water temperature exceedance for the lower Yakima sites, 2009.

Site	Periods When Temperature Did Not Meet Standards
Spring Creek (upstream) >17.5°C	May 20-Sept 6, Sept 11-17
Spring Creek (downstream) >17.5°C	April 18-23, May 13-Sept 23
Marion Drain >17.5°C	May 25-Aug 13
Sulphur Creek Wasteway >17.5°C	May 17-Sept 26

Wenatchee-Entiat Basin (WRIAs 45 and 46), 2007-09

This report includes the triennial (2007-09) monitoring summary for the Wenatchee and Entiat basins. In the most recent three-year (2006-08) summary for all other project areas (Sargeant et al., 2010), the Wenatchee and Entiat basins were not included due to having only two years of monitoring data for that three-year period. With the additional data obtained in 2009, the Wenatchee-Entiat three-year summary is instead included within this report.

Sampling of the Wenatchee-Entiat basins began in 2007 as described in Dugger et al. (2007). Sampling is conducted at five sites in the Wenatchee-Entiat:

- Peshastin Creek at river mile 0.1.
- Mission Creek at river mile 3.1.
- Brender Creek at river mile 0.7.
- Wenatchee River at river mile 2.8.
- Entiat River at river mile 1.4.

Figure 1 presents the locations of the sampling sites. Appendix B describes sampling locations and duration of sampling for each site.

Peshastin Creek

Pesticide Detections and Concentrations

During 2007-09 very few pesticides were detected: 14 detections of 12 pesticides and degradates (Table 23).

Comparison to Assessment Criteria and Water Quality Standards

Pesticide calendars in Appendix E, Tables E-13-15, provide a chronological overview of concentrations and detections during 2007-09 and compare pesticide concentrations to *assessment criteria* and *water quality standards*.

During 2007-09 there was one detection of endosulfan that did not meet (was above) the ESLOC criteria for fish in 2008 and again in 2009. A single detection of azinphos-methyl was above the chronic NRWQC in 2007.

			2007			2008			2009	
Pesticide Name and Type	ALPQL		n = 31	1		n = 27		n = 27		
		#Det	Freq	Max	#Det	Freq	Max	#Det	Freq	Max
Insecticides										
Azinphos Methyl	0.038	1	3.2%	0.024	ND			ND		
(Organophosphate)	0.058	1	5.2%	0.024	ND			ND		
Carbaryl (Carbamate)	0.019	1	3.2%	0.019	ND			ND		
Endosulfan I (Organochlorine)	0.050	ND			1	3.7%	0.130	2	7.4%	0.040
Endosulfan II (Organochlorine)	0.050	ND			1	3.7%	0.046	ND		
Methomyl (Carbamate)	0.046	1	3.2%	0.023	ND			ND		
Oxamyl (Carbamate)	0.047	1	3.2%	0.026	1	3.7%	0.010	ND		
Degradates										
Fipronil Sulfide (Pyrethroid)	0.100		MEL	added ar	nalysis ir	n 2009		1	3.7%	0.015
Fipronil Sulfone (Pyrethroid)	0.101		MEL	added ar	nalysis ir	n 2009		1	3.7%	0.016
Oxamyl Oxime (Carbamate)	0.019	1	3.2%	0.012	ND			ND		
Herbicides										
Simazine	0.033	ND			ND			1	3.7%	0.014
Simetryn	0.100	ND			ND			1	3.7%	0.055

Table 23. Summary of pesticide detections (ug/L) in Peshastin Creek, 2007-09.

ALPQL: Average lower practical quantitation limit. ND: Not detected.

Pesticide Distribution

As with the majority of the Wenatchee-Entiat sites, insecticides were the most frequently detected pesticide in Peshastin Creek. Figure 14 presents the distribution of detections by pesticide group for 2007-09 detections. Seven types of insecticides were detected. Endosulfan was most frequently observed with three detections during the three-year period.



Figure 14. Pesticide distribution in Peshastin Creek, 2007-09.

During 2007-09 no co-occurrence of insecticides with the same mode of action (acetylcholinesterase inhibition) occurred during a sampling event.

Mission Creek

Pesticide Detections and Concentrations

During 2007-09 very few pesticides were detected: 19 detections of 11 pesticides and degradates (Table 24).

			2007			2008			2009	
Pesticide Name and Type	ALPQL		n =31			n =27			n =27	
		#Det	Freq	Max	#Det	Freq	Max	#Det	Freq	Max
Insecticides										
Carbaryl (Carbamate)	0.019	ND			1	3.7%	0.014	ND		
Chlorpyrifos (Organophosphate)	0.033	1	3.2%	0.024	ND			ND		
Endosulfan I (Organochlorine)	0.050	1	3.2%	0.017	1	3.7%	0.047	1	3.7%	0.024
Endosulfan II (Organochlorine)	0.050	1	3.2%	0.022	ND			ND		
Methiocarb (Carbamate)	0.019	2	6.5%	0.034	ND			ND		
Methomyl (Carbamate)	0.046	1	3.2%	0.019	ND			ND		
Degradates										
3-Hydroxycarbofuran (Carbamate)	0.047	ND			ND			1	3.7%	0.051
Oxamyl Oxime (Carbamate)	0.019	2	6.5%	0.018	ND			ND		
Synergist										
Piperonyl Butoxide	0.100		MEL a	added an	alysis ir	n 2009		1	3.7%	0.095
Herbicides										
Norflurazon	0.033	2	6.5%	0.041	3	11%	0.034	ND		
Simazine	0.033	ND			1	3.7%	0.019	ND		

Table 24.	Summary of pesticide detections (ug/L) in Mission Creek, 2007	7-09.
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ALPQL: Average lower practical quantitation limit. ND: Not detected.

Comparison to Assessment Criteria and Water Quality Standards

Pesticide calendars in Appendix E, Tables E-16-18, provide a chronological overview of concentrations and detections during 2007-09 and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

During 2007-09 there was one detection of endosulfan not meeting (above) the ESLOC criteria for fish in 2008. No other detections were above *assessment criteria* or *water quality standards*.

Pesticide Distribution

As with the majority of the Wenatchee-Entiat sites, *insecticide* was the most frequently detected type of pesticide at Mission Creek. Figure 15 presents the distribution of detections by pesticide group. Six types of insecticides were detected. Endosulfan was detected most frequently with three detections during the three-year period.

During 2007-09 no co-occurrence of insecticides with the same mode of action (acetylcholinesterase inhibition) occurred during a sampling event.



Figure 15. Pesticide distribution in Mission Creek, 2007-09.

Brender Creek

Pesticide Detections and Concentrations

During 2007-09 Brender Creek had the greatest number of pesticide detections of the Wenatchee-Entiat sites. Brender Creek also has the lowest streamflows of any of the sites; this makes detection of pollutants more likely. Table 25 summarizes pesticide detections. During the three years of sampling, there were 401 detections of 28 pesticides, degradates, and a synergistic compound.

Comparison to Assessment Criteria and Water Quality Standards

Pesticide calendars in Appendix E, Tables E-19-21, provide a chronological overview of concentrations and detections during 2007-09 and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

Endosulfan was detected above the ESLOC for rainbow trout between March and May in six samples in 2007, eight samples in 2008, and four samples in 2009. Each year showed consecutive detections in two or more weeks indicating chronic exceedance.

			2007			2008			2009		
Pesticide Name and Type	ALPQL		n = 30			n = 27			n = 27		
		#Det	Freq	Max	#Det	Freq	Max	#Det	Freq	Max	
Insecticides											
2,4'-DDT (Organochlorine)	0.033	7	23%	0.017	2	7.4%	0.053	2	7.4%	0.019	
4,4'-DDT (Organochlorine)	0.033	27	90%	0.050	26	96.3%	0.300	20	74%	0.037	
Azinphos Methyl	0.038	3	10%	0.530	ND			ND			
Carbaryl (Carbamate)	0.019	4	13%	0.040	1	3.7%	0.024	ND			
Chlorpyrifos (Organophosphate)	0.033	9	30%	0.110	5	18.5%	0.028	6	22%	0.083	
Diazinon (Organophosphate)	0.033	1	3.3%	0.021	ND			ND			
Endosulfan I (Organochlorine)	0.050	7	23%	0.100	5	18.5%	0.089	5	19%	0.100	
Endosulfan II (Organochlorine)	0.050	7	23%	0.074	8	29.6%	0.120	6	22%	0.058	
Imidacloprid (Neonicotinoid)	0.020	MEL add	led analy sis	s in 2008	2	7.4%	0.060	1	3.7%	0.022	
Methiocarb (Carbamate)	0.019	ND			ND			1	3.7%	0.033	
Methomyl (Carbamate)	0.046	1	3.3%	0.017	ND			ND			
Oxamyl (Carbamate)	0.047	1	3.3%	0.027	ND			ND			
Degradates											
2,4'-DDD (Organochlorine)	0.033	2	6.7%	0.018	1	3.7%	0.015	ND			
2,4'-DDE (Organochlorine)	0.033	ND			ND			2	7.4%	0.009	
3-Hy droxy carbofuran (Carbamate)	0.047	ND			ND			1	3.7%	0.106	
4,4'-DDD (Organochlorine)	0.033	16	53%	0.025	20	74.1%	0.025	13	48%	0.030	
4,4'-DDE (Organochlorine)	0.033	29	97%	0.071	22	81.5%	0.045	25	93%	0.047	
Endosulfan Sulfate (Organochlorine)	0.033	17	57%	0.100	24	88.9%	0.160	21	78%	0.098	
Oxamyl Oxime (Carbamate)	0.019	ND			1	3.7%	0.140	ND			
Fungicide											
Triadimefon	0.033	1	3.3%	0.015	ND			ND			
Synergist											
Piperonyl Butoxide	0.100		MI	EL added an	alysis in 20	09		1	3.7%	0.070	
Herbicides											
Dicamba I	0.063	ND			ND			1	3.7%	0.012	
Dichlobenil	0.032	ND			1	3.7%	0.008	10	37%	0.030	
Diuron	0.056	1	3.3%	0.120	2	7.4%	0.220	ND			
МСРА	0.063	1	3.3%	0.072	ND			ND			
Norflurazon	0.033	10	33%	0.160	10	37.0%	0.250	7	26%	0.048	
Prometon	0.033	1	3.3%	0.009	ND			ND			
Simazine	0.033	2	6.7%	0.028	1	3.7%	0.012	1	3.7%	0.096	

Table 25. Summary of pesticide detections (ug/L) in Brender Creek, 2007-09.

ALPQL: Average lower practical quantitation limit. ND: Not detected.

Three detections of chlorpyrifos in March and April of 2007 and 2009 did not meet (were above) the chronic *water quality standard*, and in 2009 detections in two consecutive weeks were above the chronic *water quality standard*. Consecutive weekly detections above numeric criteria indicate the four-day exposure criteria for chronic *water quality standard* was exceeded.

DDT and DDT degradates were found consistently throughout all three years, except for one week in April 2008 and two weeks in May and June 2009. All total DDT concentrations were above the chronic *water quality standard*.

Pesticide Distribution

Unlike the majority of the Wenatchee-Entiat sites, insecticide degradates were the most frequently detected compound in Brender Creek. Figure 16 presents the distribution of detections by pesticide type.



Figure 16. Pesticide distribution in Brender Creek, 2007-09.

The most commonly detected insecticide degradates were:

- 4,4'-DDE (76 detections), a degradate of the legacy pesticide DDT.
- Endosulfan sulfate (62 detections), a degradate of endosulfan.
- 4,4'-DDD (49 detections), degradates of the legacy pesticide DDT.

After degradates, insecticides were the most commonly observed pesticide. Six types of insecticides were detected. The most commonly detected insecticides were:

- 4,4'-DDT (73 detections), a legacy pesticide DDT.
- Endosulfan II (21 detections).
- Chlorpyrifos (20 detections).
- Endosulfan I (17 detections).

The most commonly detected herbicides were:

- Norflurazon (27 detections).
- Dichlobenil (11 detections).

Figure 17 presents Brender Creek carbamate and organophosphate insecticide detections for 2007-09. Carbamate and organophosphate insecticides are both acetylcholinesterase-inhibiting insecticides; they have the same mode of action. When these insecticides co-occur, the effect on aquatic life may be additive or in some cases synergistic (Laetz et al., 2009). In Figure 17 when two pesticides co-occur, the cumulative totals are presented.

During 2007-09 co-occurrence of acetylcholinesterase-inhibiting insecticides occurred four times in 2007, but there was no co-occurrence in 2008 and 2009 (Figure 17.). The greatest cumulative sum of co-occurring acetylcholinesterase-inhibiting insecticides was 0.047 ug/L on May 21, 2007 for a carbamate (carbaryl) and an organophosphate (chlorpyrifos).



Figure 17. Cumulative amount for acetylcholinesterase-inhibiting insecticides (same mode of action) in Brender Creek, 2007-09.

Due to the consistent presence of the legacy DDT and degradate compounds, co-occurrence of organochlorine insecticides occurred frequently. Figure 18 presents cumulative concentrations for total DDT and total endosulfan, both organochlorines.



Figure 18. Cumulative amount for organochlorine insecticide detections in Brender Creek, 2007-09.

Wenatchee River

Pesticide Detections and Concentrations

During 2007-09 there were only 13 detections of eight types of pesticides (Table 26).

Comparison to Assessment Criteria and Water Quality Standards

Pesticide calendars in Appendix E, Tables E-22-24, provide a chronological overview of concentrations and detections during 2007-09 and compare pesticide concentrations to *assessment criteria* and *water quality standards* (Appendix D).

During 2007-09 there was one detection of endosulfan that did not meet (was above) the ESLOC criteria for fish once in 2008 and once in 2009. No other detections were above *assessment criteria* or *water quality standards*.

Pesticide Name and Type	ALPQL		2007 n =30			2008 n =27		2009 n =27		
		#Det	Freq	Max	#Det	Freq	Max	#Det	Freq	Max
Insecticides										
Chlorpyrifos (Organophosphate)	0.033	1	3.3%	0.035	ND			1	3.7%	0.038
Endosulfan I (Organochlorine)	0.050	1	3.3%	0.014	2	7.4%	0.079	1	3.7%	0.061
Endosulfan II (Organochlorine)	0.050	ND			2	7.4%	0.076	ND		
Imidacloprid (Neonicotinoid)	0.020	ND			1	3.7%	0.028	ND		
Methomyl (Carbamate)	0.046	1	3.3%	0.016	ND			ND		
Oxamyl (Carbamate)	0.047	1	3.3%	0.016	ND			ND		
Wood Preservative										
Pentachlorophenol	0.063	ND			ND			1	3.7%	0.014
Herbicides										
2,4-D	0.063	ND			ND			1	3.7%	0.018

Table 26. Summary of pesticide detections (ug/L) in the Wenatchee River, 2007-09.

ALPQL: Average lower practical quantitation limit. ND: Not detected.

Pesticide Distribution

As with the majority of the Wenatchee-Entiat sites, insecticides were the most frequently detected type of pesticide in the Wenatchee River. Figure 19 presents the distribution of pesticide types found. Six types of insecticides were detected. Endosulfan I or II were the most frequently observed with six detections during the three-year period.

During 2007-09 no co-occurrence of insecticides with the same mode of action (acetylcholinesterase inhibition) occurred during a sampling event.



Figure 19. Pesticide distribution in the Wenatchee River, 2007-09.

Entiat River

Pesticide Detections and Concentrations

During 2007-09 the Entiat River had the fewest pesticide detections of any of the sites sampled in the Wenatchee-Entiat basin. Table 27 summarizes pesticide detections. During the three years of sampling, there were nine detections of four pesticides, a degradate, and a synergistic compound.

Pesticide Name and Type	ALPQL		2007 n = 30			$2008 \\ n = 27$		2009 n = 27		
		#Det	Freq	Max	#Det	Freq	Max	#Det	Freq	Max
Insecticides										
Carbaryl (Carbamate)	0.019	1	3.3%	0.016	ND			ND		
Chlorpyrifos (Organophosphate)	0.033	1	3.3%	0.034	ND			1	3.7%	0.023
Endosulfan I (Organochlorine)	0.050	ND			ND			1	3.7%	0.024
Degradates										
3-Hydroxycarbofuran (Carbamate)	0.047	ND			1	3.7%	0.014	ND		
Synergist										
Piperonyl Butoxide	0.100		MEL	added ar	nalysis i	n 2009		3	11.1%	0.100
Herbicides										
Dichlobenil	0.032	1	3.3%	0.065	ND			ND		

Table 27. Summary of pesticide detections (ug/L) in the Entiat River for 2007-09.

ALPQL: Average lower practical quantitation limit. ND: Not detected.

Comparison to Assessment Criteria and Water Quality Standards

Pesticide calendars in Appendix E, Tables E-25-27, provide a chronological overview of concentrations and detections during 2007-09 and compare pesticide concentrations to *assessment criteria* and *water quality standards*. Pesticide concentrations met all *criteria* and *standards*.

Pesticide Distribution

As with the majority of the Wenatchee-Entiat sites, insecticides were the most frequently detected type of pesticide in the Entiat River. Figure 20 presents the distribution of detections by pesticide type. Three types of insecticides were detected. Chlorpyrifos was most frequently found with two detections during the three-year period.

During 2007-09 no co-occurrence of insecticides with the same mode of action (acetylcholinesterase inhibition) occurred during a sampling event.



Figure 20. Pesticide distribution in the Entiat River, 2007-09.

Factors Affecting Pesticide Detections

Environmental Factors

Graphs of streamflow, precipitation, and pesticide concentrations of the most commonly detected pesticides are presented in Appendix G.

Of the Wenatchee-Entiat sites, Brender Creek was the only site to have enough pesticide detections for statistical analysis. 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 detected pesticides and environmental factors such as flow and rainfall. Correlation analysis was also used to examine the association between commonly detected pesticides and TSS. A two-tailed, Kendall's tau-b, non-parametric correlation coefficient was used to test for correlation between parameters. NJ qualified data were used in this test. Previous rainfall was calculated based on sample time.

The results of the statistical test showed that on Brender Creek, there was:

- A positive correlation between total DDT and TSS (Figure 21) (Kendall's tau = 0.43, p<0.01).
- A weak positive correlation between total DDT and flow (Kendall's tau = 0.38, p<0.01).
- A very weak positive correlation between endosulfan sulfate and flow (Figure 22) (Kendall's tau = 0.38, p<0.01).



Figure 21. Brender Creek positive correlation between total DDT and total suspended solids, 2007-09.



Figure 22. Brender Creek weak positive correlation between endosulfan sulfate and flow, 2007-09.

Temporal Factors

There was a seasonal pattern in pesticide detections. Figure 23 presents the type of pesticide detections by month for all the Wenatchee-Entiat sites combined. In looking at the cumulative total for all sites, the greatest number of insecticide detections was observed in April (Figure 23). For Brender Creek, the greatest number of insecticide detections occurred in April and May.

For the cumulative total, degradate detections peaked in May and then decreased each month thereafter. This pattern was similar for Brender Creek but degradate detections peaked in May and June. In Brender Creek the greatest number of herbicide detections occurred in May and June, while for the rest of the sites, a greater number of detections occurred in August.



Figure 23. Number of detections by pesticide type for the Wenatchee-Entiat sites, 2007-09.

Conventional Parameters

Conventional water quality parameters were measured at all Wenatchee-Entiat sites. In 2008 and 2009, Winkler dissolved oxygen measurements were also obtained. Continuous, 30-minute interval temperature data were collected; temperature profiles are presented in Appendix F. Table 28 summarizes results for TSS, flow, pH, conductivity, and dissolved oxygen for all sites. All sites must meet freshwater quality standards.

Dissolved oxygen grab samples were collected in 2008 and 2009. All sites met the dissolved oxygen standard of a minimum of 8.0 mg/L per day.

	Total Suspended Solids (mg/L)		Flow (cubic feet per second)		pH (standard units)		Conductivity (µmhos/cm)		Dissolved Oxygen (mg/L)					
	2007	2008	2009	2007	2008	2009	2007	2008	2009	2007	2008	2009	2008	2009
Peshastin Creek														
Mean ₁	13	5	9	272	222	214	8.1	7.9	8.1	91	90	108	11.3	11.1
Minimum	<1	<1	<1	12	10	13	7.7	7.6	7.5	45	53	56	8.6	8.2
Maximum	218	44	67	1340	929	606	8.5	8.3	8.6	133	180	158	13.8	13.5
Number	31	27	27	31	22	27	31	27	27	31	27	27	26	27
Brender Creek														
Mean ₁	45	36	37	3.2	2.2	2.2	8.2	8.1	8.2	218	210	236	10.6	10.5
Minimum	14	6	7	1.1	0.7	0.3	7.8	7.9	7.8	123	125	151	9.0	9.2
Maximum	155	94	116	8.2	4.5	6.8	9.4	8.3	8.5	411	333	354	12.5	12.2
Number	31	27	27	31	27	27	31	27	27	31	27	27	27	27
Mission Creek														
Mean ₁	37	8	20	36	19	29	8.3	8.3	8.3	196	186	194	11.2	11.2
Minimum	<1	1	<1	0.2	0.1	0.1	7.3	7.3	7.9	120	107	110	8.9	9.2
Maximum	685	42	85	223	60	101	9.2	8.6	8.7	294	328	324	14.0	13.2
Number	31	27	27	31	27	27	31	27	27	31	27	27	26	27
Wenatchee River														
Mean ₁	10	7	8	4793	4465	3775	8.2	8.2	8.2	46	45	51	11.7	11.6
Minimum	1	<1	<1	467	669	493	7.4	7.2	7.0	23	20	22	9.2	9.3
Maximum	102	46	46	12900	19100	13400	9.1	9.2	9.1	83	76	87	15.1	14.8
Number	31	27	27	31	27	27	31	27	27	31	27	27	26.0	27.0
Entiat River														
Mean ₁	9	5	6	833	681	607	8.2	8.3	8.1	57	69	61	11.1	10.9
Minimum	1	1	1	123	107	96	7.3	7.5	7.0	24	23	23	9.0	9.1
Maximum	64	24	46	2490	2780	2330	9.7	9.2	9.0	103	409	99	13.1	13.8
Number	31	27	27	31	27	27	31	27	27	31	27	27	27	27

Table 28. Arithmetic mean and range for conventional parameters (grabs) for the Wenatchee-Entiat sites, 2007-09.

Mean¹: Arithmetic mean

Sites which did not meet (exceeded) the pH standard all three years are: Mission Creek, Wenatchee River, and Entiat River. Of the other two sites, Brender Creek exceeded the standard only in 2007 and Peshastin Creek slightly exceeded the standard in 2009.

Temperature

In addition to the discrete temperature measurements, continuous (30-minute interval) measurements were collected year-round. Temperature profiles based on continuous temperature measurements are presented in Appendix F, Figures F-12 to F-26. There are gaps in temperature data due to thermistors being out of the water during low water levels and datalogger battery malfunction. The temperature standard for the freshwater sites is that the 7-DADMax should not exceed 17.5°C. Mission Creek met temperature standards during 2009 but not during 2007-08 (Table 29). The rest of the sites did not meet temperature standards during 2007-09. Table 29 describes periods when temperature standards were not met.

Site	2007	2008	2009	
Peshastin Creek >17.5°C	July 3-Sept 14	July 11-Aug 26, Sept 4-11	July 3-Sept 4, Sept 11-16	
Mission Creek >17.5°C	July 7-17, July 24-Aug 18, Aug 31-Sept 4	July 18-25, Aug 2-19	no exceedances	
Brender Creek >17.5°C	July 11-14, July 25-26	Aug 14-18	July 24-Aug 4	
Wenatchee River >17.5°C	July 11-Sept 17	July 16-Aug 30, Sept 1, Sept 4-18	July 9-Sept 20	
Wenatchee River >13.0°C	no exceedances	Oct 1-5	Oct 2	
Entiat River >17.5°C	July 21-Sept 14	July 15-Aug 29, Sept 5-10	July 11-Sept 4, Sept 10-26	

Table 29. Periods of water temperature exceedance for the Wenatchee and Entiat sites, 2007-09.

Total Suspended Solids

Boxplots of TSS concentrations and loading for the Wenatchee-Entiat sites are presented in Figures 24 and 25 respectively (both figures are in log scale). While Brender Creek had the highest average TSS concentrations, Mission Creek had the greatest range in values and the highest maximum TSS concentrations. The Wenatchee then the Entiat had the highest TSS loading averages for 2007-09. Both of these rivers have much higher flows than the other sites.



Figure 24. Summary statistics for total suspended solids concentrations for the Wenatchee-Entiat sites, 2007-09.



●Minimum X25th percentile -Median X75th Percentile ●Maximum



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, but this is likely due to the small data set.

Comparison to the Lower Mission Creek Basin TMDL

In 2004, a Total Maximum Daily Load (TMDL) was established for DDT in the lower Mission Creek basin (Serdar and Era-Miller, 2004). Target total-DDT loads were recommended for Mission, Brender, and Yaksum Creeks based on waters meeting 1 ng/L total-DDT, the chronic *water quality standard* for protection of aquatic life. 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 2007-09 study are insufficient to adequately evaluate DDT levels recommended in the 2004 TMDL. Due to the cost of analyzing for a broad suite of pesticides, the reporting limit for the 2007-09 study is higher than the recommended 0.5 ng/L. The 2007-09 average reporting limit for DDT and its degradates was 0.033 ug/L (33 ng/L). Although the laboratory will report positively identified detections below this limit, the detections are qualified as estimates.

During 2007-09 there were no DDT or degradate detections reported at the Mission Creek site; however, the detection limit is higher than the recommended 0.5 ng/L. At the Brender Creek site, there were DDT or degradate compound detections for all but one sampling event in 2008 and for all but two sampling events in 2009. During 2007-09 the Brender Creek site did not meet the TMDL TSS recommended concentration of < 1 mg/L during any sampling event, ranging from a minimum of 7 to a maximum of 155 mg/L.

Discussion for the Wenatchee-Entiat Basins

Pesticide Detections

Monitoring sites in the Wenatchee-Entiat basins represent surface water quality in a tree fruit agricultural area. 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 26 presents the types of pesticides detected at the Wenatchee-Entiat sites for three years of monitoring, 2007-09.

Unlike results for the other monitoring sites, the majority of pesticide detections for the Wenatchee-Entiat sites are insecticides and insecticide degradates. The higher proportion of insecticide and degradate detections observed at the Wenatchee-Entiat sites is in part driven by DDT and DDT degradate detections in Brender Creek.

During 2007-09, 214 pesticide detections in Brender Creek were DDT or DDT degradates. DDT is a legacy pesticide that is no longer registered for use in the United States. Detections of DDT and DDT degradate compounds are a result of historic use and do not reflect current pesticide-use patterns.



Figure 26. Distribution of pesticides detected in the Wenatchee-Entiat project area, 2007-09.

Brender Creek had the most pesticide detections and the greatest number of pesticide concentrations that exceeded an *assessment criteria* or *water quality standard*. Of the 424 pesticide detections during 2007-09, 401 were in Brender Creek. During all but three sampling events, Brender Creek did not meet (exceeded) the chronic *water quality standard* for total DDT.

In Brender Creek during each of the three years, there were four or more total endosulfan concentrations that exceeded the ESLOC for fish. The greater number of pesticide detections and concentrations found above *assessment criteria* and *water quality standards* is due in part to the low volume of water in Brender Creek as compared to the other sites.

Table 30 presents a comparison of average streamflow by year for each of the Wenatchee-Entiat sites. Flow in Mission Creek is an order of magnitude greater than in Brender Creek. Peshastin Creek and the Entiat River are two orders of magnitude greater, and the Wenatchee River flow is three orders of magnitude greater, than Brender Creek flows. Higher flows dilute pollutant concentrations.

Site	2007	2008	2009
Peshastin Creek	91	139	214
Mission Creek	36	19	29
Brender Creek	3.2	2.2	2.2
Wenatchee River	4790	4470	3780
Entiat River	833	681	607

Table 30. Average flow (cfs) during the sampling season the Wenatchee-Entiat sites, 2007-09.

Endosulfan

With the exception of the Entiat River, all sites at one time did not meet (exceeded) the total endosulfan ESLOC for fish. When pesticide concentrations are detected at the sites with greater flows, much higher pesticide loading occurs.

Figure 27 presents total endosulfan loading in grams per day for each of the Wenatchee sites. There were no endosulfan detections in the Entiat River. The Brender and Mission Creek loading scale (right side of the graph) is much less than the loading scale for the Wenatchee River and Peshastin Creek (left side of the graph).

Likely there are smaller tributaries upstream, or upstream inputs, along the Wenatchee River that are contributing endosulfan to the downstream Wenatchee River site. For example, on March 31, 2008 Wenatchee River endosulfan loading was over 400 grams per day. This would mean there would be over 400 Brender Creek loading inputs upstream to account for that amount of loading in the Wenatchee River.

In July 2010, EPA signed an agreement with the registrants of endosulfan that will result in voluntary cancellation and phase out of all existing uses in the United States. Under the agreement, all endosulfan uses will be phased out by July 2016. Endosulfan use on stonefruit

such as nectarines, peaches, cherries, and apricots will be prohibited by July 2012, on pears by July 2013, and on apples by July 2015. EPA is terminating uses of endosulfan to address its unacceptable risks to agricultural workers and wildlife (EPA, 2010).



Figure 27. Total endosulfan loading (in grams per day) for the Wenatchee sites, 2007-09.

Comparing Wenatchee-Entiat Sites to Other Pesticide Monitoring Sites

Table 31 presents the ratio of pesticide detections to sampling events for each area. The Wenatchee-Entiat sites have the lowest ratio of detections per sampling event of any of the areas. This may be in part due to the higher flows at some of the Wenatchee-Entiat sites.

Table 31. Ratio of pesticide detections to the number of sampling events for each site for each project area, 2003-09.

Time Period	Thornto	n Creek	Samish-Skagit	Lower	Yakima	Wenatchee- Entiat
	2003-05	2006-08	2006-08	2003-05	2006-08	2007-09
Number of Sampling Events	109	124	406	279	328	424
Number of Detections	317	189	1216	1078	1115	411
Mean Number of Detections per Sampling Event	2.9	1.5	3.0	3.9	3.4	1.0

Water Quality

Conventional Parameters

None of the Wenatchee-Entiat sites consistently met *water quality standards* for temperature during 2007-09. 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 monitor; Ecology receives more temperature data than for any other parameter.

Dissolved oxygen grab sampling was conducted in 2008 and 2009. All Wenatchee-Entiat sites met the dissolved oxygen standard of a minimum of 8.0 mg/L per day.

Sites which did not meet (exceeded) the pH standard all three years were Mission Creek, Wenatchee River, and Entiat River. Of the other two sites, Brender Creek exceeded the standard only in 2007, and Peshastin Creek slightly exceeded the standard in 2009.

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). The effects of TSS on fish and aquatic invertebrates are a function of sediment concentration and duration of exposure.

Table 32 presents the range of median and maximum TSS concentrations for the three years of sampling for all sites. In 2007 maximum TSS concentration for the Wenatchee basin sites were high but this is likely due to a March 13, 2007 sampling 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. High TSS could also be due to snow melt and runoff. The daily maximum air temperatures in Cashmere increased by 10° F on March 11, 2007. Wenatchee River daily flow went from 2600 cfs on March 11, to 11600 cfs on March 13, 2007.

Site	Median	Maximum		
Peshastin Creek	2-4	44-218		
Mission Creek	4-11	42-685		
Brender Creek	27–39	94-155		
Wenatchee River	4-5	46-102		
Entiat River	3-6	24-64		

Table 32. Median and maximum total suspended solids concentrations (mg/L), 2007-09.
In a review of studies on the effects of suspended solids on fish and aquatic life, Bilotta and Brazier (2008) and Newcombe and MacDonald (1991) reported sub-lethal effects such as:

- Gill hyperplasia and poor condition of fry in chinook salmon exposed to 1.5-2.0 mg/L TSS for 1440 hours (60 days).
- Reduction in growth rate of chinook salmon exposed to 6 mg/L TSS for 1440 hours (60 days).
- Reduction in growth rate of chinook salmon and steelhead exposed to 84 mg/L TSS for 336 hours (14 days).
- 100% mortality of incubating rainbow trout eggs exposed to 47 mg/L TSS for 1152 hours (48 days).
- Reduction in growth rate of rainbow trout exposed to 50 mg/L for 1848 hours (77 days).
- 40% reduction in stream invertebrate diversity after exposure to 130 mg/L TSS for 8760 hours (365 days).
- 77% reduction in population size for benthic invertebrates exposed to 62 mg/L TSS for 2400 hours (100 days).

TSS median and maximum concentrations observed at most of the Wenatchee-Entiat sites likely do not meet the time duration required for sub-lethal effects of salmon or aquatic macroinvertebrates. Brender Creek had the highest TSS concentrations, with median concentrations from 27-39 mg/L over the three-year period. If these TSS concentrations meet the time requirements above, sub-lethal effects to Chinook salmon (first two bullets above) could occur.

Recommendations in the *Lower Mission Creek Basin, Chelan County: TMDL* (Serdar and Era-Miller, 2004) include reductions in TSS to < 1 mg/L in order to meet target DDT loads. Reductions in TSS would help reduce DDT concentrations and reduce possible suspended sediment effects on fish.

Pesticides

During 2007-09 total DDT concentrations regularly exceeded the chronic *water quality standard* in Brender Creek. Brender Creek also had three exceedances for chlorpyrifos and one exceedance for azinphos-methyl. Peshastin Creek had one exceedance for azinphos-methyl as well. No detections of azinphos-methyl occurred after 2007 at any of the Wenatchee-Entiat sites. Azinphos-methyl is being phased out with uses (including on pears, cherries, and apples) prohibited after September 30, 2012.

All of the Wenatchee sites had at least one exceedance of the ESLOC for total endosulfan. Brender Creek total endosulfan concentrations exceeded the ESLOC for fish six, eight, and four times in 2007, 2008, and 2009 respectively. All exceedances occurred during late March through May.

No exceedances of any pesticide *assessment criteria* or *water quality standard* occurred for the Entiat River during 2007-09.

Sub-Lethal Effects and Co-Occurrence of Pesticides

The EPA *assessment criteria* and Washington State *water quality standards* used in this study are based on evaluating the effects of a specific chemical on an organism. The criteria and standards do not take into account (1) the additive or possible synergistic effects of pesticide mixtures or (2) the effects of pesticides when fish are stressed due to environmental factors such as high temperatures or low dissolved oxygen levels.

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. 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.

With the exception of Brender Creek, co-occurrence of the same mode-of-action insecticides did not occur at the Wenatchee-Entiat sites. During the 2007-09 Brender Creek sampling, co-occurrence of AChE-inhibiting insecticides occurred four times. The highest cumulative concentration found was 0.047 ug/L on May 21, 2007 for carbaryl (carbamate) and chlorpyrifos (organophosphate).

The Laetz et al. (2009) study found that insecticide combinations produce additive toxicity at low, environmentally-relevant concentrations (0.1 EC_{50} for juvenile coho). For example, in the study, diazinon and chlorpyrifos were synergistic when combined at 7.3 and 0.1 ug/L, respectively.

The monitoring results from this 2007-09 study illustrate the difficulty of assessing the effects of multiple chemicals on aquatic organisms. The pesticide calendars in Appendix E demonstrate that mixtures of pesticides 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 is 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 during the Pesticide-Use Season (March - September)

In the Wenatchee basin, the greatest concern for salmonids is endosulfan detections not meeting (above) the ESLOC for fish:

• For Peshastin Creek, endosulfan was detected twice above the ESLOC for fish in early April, once in 2007 and again in 2008. During this period, steelhead are spawning and incubating, and spring Chinook and bull trout are incubating and rearing. Temperatures exceed criteria in late July and August with the highest 7-DADMax temperatures for 2007-09 ranging from 22.8 – 25.4°C.

- For Mission Creek, endosulfan was detected once above the ESLOC for fish in early April 2008. In April steelhead spawn and incubate, and spring and summer Chinook are rearing (Table 6). While Mission Creek has lower flows than some of the other sites, very few pesticides are detected in the creek and only the one endosulfan detection was above an *assessment criteria* or *water quality standard*. Temperatures exceed criteria in late July and August with the highest 7-DADMax temperatures for 2007-09 ranging from 18.7 21.7°C.
- For Brender Creek, endosulfan levels regularly exceed the ESLOC for fish during late March through mid-May. During this period, there are chronic aquatic health concerns in Brender Creek due to the frequency of endosulfan detections. As a result of these concerns, WSDA initiated outreach activities with growers in 2008. In 2009 the total number of exceedances of the *water quality standard* and the ESLOC for fish; and the number of detections for endosulfan decreased slightly in Brender Creek. In addition, total DDT is present consistently at concentrations above the chronic *water quality standard*. In April 2009, there were two consecutive weeks of chlorpyrifos detections that indicate a potential chronic aquatic health concern during this period. Temperatures rarely exceed criteria in Brender Creek. The highest 7-DADMax temperatures for 2007-09 range from 17.9 18.2°C.
- For the Wenatchee River, endosulfan was detected twice above the ESLOC for fish once in late March 2008, and once in early April 2009. During this period lower Wenatchee River spring and summer Chinook and bull trout are rearing; and spawning and incubating steelhead are present. Temperatures exceed criteria in late July and August with the highest 7-DADMax temperatures for 2007-09 ranging from 22.1 24.9°C.

In the Entiat basin, pesticides are rarely detected and pesticide levels met all pesticide *assessment criteria* and *water quality standards* for protection of aquatic life. Temperature is the biggest concern for fish during July and August when temperatures exceed 17.5° C. Highest 7-DADMax temperatures for 2007-09 ranged from $20.7 - 23.9^{\circ}$ C.

Factors Affecting Pesticide Detections

There is a positive relationship between the legacy pesticide total DDT and TSS concentrations in Brender Creek.

During 2007-09 the greatest number of insecticide detections occurred in April, and the greatest number of pesticide degradates 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 of specific crops or plants. The results of this 2007-09 study show similar findings.

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Conclusions for the Wenatchee-Entiat Basins

Results from the 2007-09 study of pesticide use in the Wenatchee and Entiat River basins support the following conclusions.

- The major factor in pesticide detections for Wenatchee-Entiat sites is likely the season of the year and the timing of pesticide application for specific crops.
- Brender Creek was the only site where many pesticides were detected. Only a few pesticides were found at all the other sites. This is in part due to higher streamflows at some of the other sites (e.g., Peshastin Creek and the Wenatchee and Entiat Rivers).
- Unlike in the other four basins in this study, the majority of pesticides detected in the Wenatchee-Entiat basins were insecticides and insecticide degradates. Very few herbicides were found.
- Co-occurrence of acetylcholinesterase-inhibiting insecticides rarely occurred and cumulative concentrations were low. Co-occurrence of the organochlorine compounds DDT and its degradates and endosulfan occurred on Brender Creek.
- Consistent detections of total DDT indicate chronic health concerns for aquatic life (e.g., fish) in Brender Creek. There is a positive relationship between DDT and total suspended solids (TSS); therefore, reductions in TSS would likely lead to lower DDT concentrations.
- Endosulfan levels in Brender Creek from mid-March through May indicate chronic aquatic health concerns. These levels are above the endangered species level of concern (ESLOC) for fish.
- While infrequent, the periodic detections of endosulfan in Peshastin Creek and the Wenatchee River are of concern due to the substantial endosulfan loading these detections represent (Figure 27). While these endosulfan concentrations may meet (not exceed) an EPA *assessment criteria* or Washington State *water quality standard*, the loading levels represent significant mass. Endosulfan loading sources are unknown but are likely a combination of contribution from upstream tributaries and aerial pesticide spray drift.
- There are very few pesticide detections at the Entiat River site, and all detections meet EPA *assessment criteria* and Washington State *water quality standards*.

Recommendations for the Wenatchee-Entiat Basins

Results from the 2007-09 study of pesticide use in the Wenatchee and Entiat River basins support the following recommendations.

- EPA will begin phasing out endosulfan use in 2013, with all uses prohibited by 2016. The Washington State Department of Agriculture should continue to work with agricultural stakeholders to explore mitigation measures for endosulfan concentrations found in surface water in the Wenatchee basin. Monitoring should continue to assess the effectiveness of mitigation measures.
- Total suspended solids in Brender Creek should be reduced in order to reduce DDT concentrations in the water column as recommended in the 2004 Total Maximum Daily Load (TMDL) study.
- Pesticide monitoring at the Entiat River site should be discontinued. Few pesticide detections are found at this site, and all detections meet *assessment criteria* and *water quality standards*. This station should be replaced with a lower streamflow surface water site in the Wenatchee or Entiat basin.

Summary of Project Changes for 2009

The following changes were made during the 2009 monitoring of the six basins across Washington State.

- Longfellow Creek in the Green Duwamish basin was added to represent urban land use.
- Monitoring at the upstream Thornton Creek site was discontinued.
- Sampling for the following pesticides or degradates was added for all basins:
 - 4,4'-Dichlorobenzophenone (degradate of dichlorobenzophenone)
 - Acetochlor (herbicide)
 - beta-Cypermethrin (pyrethroid insecticide)
 - Bifenthrin (pyrethroid insecticide)
 - Butachlor (herbicide)
 - Chlorpyrifos O.A. (degradate of chlorpyrifos)
 - Diazoxon (degradate of diazinon)
 - Disulfoton Sulfoxide (degradate of disulfoton)
 - Fenamiphos Sulfone (degradate of fenamiphos)
 - Fipronil (pyrethroid insecticide)
 - Fipronil Disulfinyl (degradate of fipronil)
 - Fipronil Sulfide (degradate of fipronil)
 - Fipronil Sulfone (degradate of fipronil)
 - o lambda-Cyhalothrin (pyrethroid insecticide)
 - Phorate O.A. (degradates of phorate)
 - Piperonyl Butoxide (synergist)
 - Prothiofos (organophosphate insecticide)
 - Tricyclazole (fungicide)
- All 2009 results for the following carbamates were rejected due to concerns above false positives:
 - o 1-naphthol
 - o Aldicarb sulfone
 - Aldicarb sulfoxide
 - o Oxamyl

Project Change Planned for 2010

The following change is planned for the 2010 sampling during the multi-year study.

The carbamate analysis method used for this project has been: EPA Method 8321 AM modified using electrospray ionization (ES) and atmospheric pressure chemical ionization (APCI) and selected ion monitoring mass spectrometry (SIM-MS). During 2010 the following will be used instead: EPA Method 8321 AM modified using electrospray ionization with jet stream technology and triple quadrupole mass spectrometry.

This change will increase accuracy of carbamate analyte detections by providing confirmation of detected analytes. In addition, the new instrumentation may allow for lower detections limits for carbamates.

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Appendices

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Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

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

Assessment criteria: Assessment criteria in this report are numeric criteria included in the EPA FIFRA Pesticide Registration Toxicity Criteria and endpoints; and the EPA National Recommended Water Quality Criteria (NRWQC).

Basin: Watershed. A drainage area 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.

Bioaccumulation: Progressive increase in the amount of a substance in an organism or part of an organism which occurs because the rate of intake exceeds the organism's ability to remove the substance from the body.

Boxplot: A graphical depiction of a data set showing the 25th percentile, 50th percentile or median, the 75th 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.

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

Endosulfan: Endosulfan is an organochlorine insecticide that is registered for use on a number of agricultural commodities. In 2010, EPA signed an agreement with the registrants of endosulfan that will result in voluntary cancellation and phase out of all existing endosulfan uses in the United States. Under this agreement, all endosulfan uses will be phased out by July 2016. EPA is terminating uses of endosulfan to address its unacceptable risks to agricultural workers and wildlife (EPA, 2010).

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.

Legacy pesticide: Banned pesticides no longer used but that persist in the environment.

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.

Reach: A specific portion or segment of a stream.

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

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

Suspended sediment: Solid fragmented material (soil and organic matter) in the water column.

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

Water quality standards: Washington State water quality standards.

Watershed: Basin. A drainage area 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 Washington 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			
DDD	Dichloro-diphenyl-dichloroethane			
DDE	Dichloro-diphenyl-dichloroethylene			
DDT	Dichloro-diphenyl-trichloroethane			
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			
ESLOC	Endangered Species Level of Concern (EPA)			
GC	Gas chromatograph			
GCMS	Gas chromatograph coupled with mass spectrometer			
K _{oc}	Sorption coefficient			

LC_{50}	Lethal concentration to cause mortality in 50% of test species			
LCS	Laboratory control sample			
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			
NOAA	National Oceanic and Atmospheric Administration			
QA	Quality assurance			
QC	Quality control			
RM	River mile			
RPD	Relative percent difference			
RSD	Relative standard deviation			
SOP	Standard operation procedures			
TMDL	(See Glossary above)			
TSS	(See Glossary above)			
USFWS	United States Fish and Wildlife Service			
USGS	United States Geological Survey			
WAC	Washington Administrative Code			
WRIA	Water Resource Inventory Area			
WSDA	Washington State Department of Agriculture			

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
ug/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter

Appendix B. Monitoring Sites and Duration of Sampling

Site	Duration	Latitude	Longitude	Location Description		
Cedar-Sammamish Watershed						
TC-3	March - Sept	47.6958	122.2757	Downstream of pedestrian footbridge near Mathews Beach Park.		
Green-Duwamish Watershed						
LC-1	March - Sept	47.5625	122.367	Upstream of the culvert under the 12th Fairway on the West Seattle Golf Course.		
Skagit-Samish Watershed						
BD-1	March - Sept	48.3086	122.3473	Upstream side of bridge at Milltown Road.		
BD-2	March - Sept	48.3887	122.3329	Upstream side of bridge at Lenor Lane.		
BS-1	March - Sept	48.3406	122.4140	Downstream of tidegate on Fir Island Road.		
IS-1	March - Sept	48.4506	122.4651	Inside upstream side of tidegate at Bayview-Edison Road.		
SR-1	March - Sept	48.5209	122.4113	Upstream side of bridge at Thomas Road.		
Lower Yakima Watershed						
MA-2	March - October	46.3306	120.1989	Approximately 15 meters upstream of bridge at Indian Church Road.		
SP-2	March - Sept	46.2583	119.7101	Downstream side of culvert on McCready Road		
SP-3	March - Sept	46.2344	119.6845	Approximately 3 meters downstream of Chandler Canal overpass.		
SU-1	March - Sept	46.2509	120.0202	Downstream side of bridge at Holaday Road.		
Wenatchee Watershed						
WE-1	March - Sept	47.4721	120.3710	Upstream side of Sleepy Hollow bridge.		
MI-1	March - Sept	47.4893	120.4815	Above Woodring Canyon Road and Mission Creek Road.		
PE-1	March - Sept	47.5570	120.5825	Approximately 30 meters downstream of bridge at Saunders Road.		
BR-1	March - Sept	47.5211	120.4862	Upstream side of culvert at Evergreen Drive.		
Entiat Watershed						
EN-1	March - Sept	47.6633	120.2506	Upstream side of bridge at Keystone Road.		

Table B-1. Station locations, duration of monitoring, and site location descriptions for 2009.

Datum in NAD 83.

Appendices C through G are in a separate electronic file.