Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2007 Data Summary

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

April 2008

Publication No. 08-03-009

Publication Information

This report is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0803009.html and the Department of Agriculture's website at http://agr.wa.gov/PestFert/NatResources/SWM/default.htm

Data for this project are available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, CBUR0004.

Ecology's Project Tracker Code for this project is 03-501-05.

For more information contact:

Publications Coordinator
Environmental Assessment Program
Washington State Department of Ecology
P.O. Box 47600
Olympia, WA 98504-7600

E-mail: jlet461@ecy.wa.gov
Phone: 360-407-6764

Washington State Department of Ecology - www.ecy.wa.gov/

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

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

by

Paul D. Anderson
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

and

Dan Dugger
Central Regional Office
Environmental Assessment Program
Washington State Department of Ecology
Yakima, Washington 98902-3452

Waterbody Numbers:

WA-03-2010, WA-03-3100, WA-03-4000,
WA-08-1020,
WA-37-1014, WA-37-1025, WA-37-1030,
WA-45-1010, WA-45-1011, WA-45-1013, WA-45-1100,
WA-46-1010

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Abstract

From February through October 2007, the Washington State Department of Ecology and the Washington State Department of Agriculture conducted pesticide sampling in the Cedar-Sammamish, Lower Skagit-Samish, Lower Yakima, Wenatchee, and Entiat watersheds.

The sampling was part of the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams.*

The purpose of this data summary is to (1) provide results of the 2007 sampling program, and (2) propose changes for the 2008 program. For the 2007 results, the report summarizes water quality results and discusses quality of the data.

Year 2007 is the first in a three-year study cycle to investigate pesticides in the Wenatchee and Entiat watersheds, the second in a three-year cycle in the Skagit-Samish watershed, and the fifth in a six-year cycle in the Cedar-Sammamish and Lower Yakima watersheds.

Laboratory analyses were conducted for 152 pesticides and degradates, as well as total suspended solids. Field data were collected for discharge, temperature, pH, conductivity, and dissolved oxygen.

Acknowledgements

The authors of this report would like to thank the following people for their contribution to this study:

- Moses Squeochs, James Thomas, and Joanne Cornwall (Yakama Nation) for permission to sample the Marion Drain, technical expertise, outreach coordination, historical and operational knowledge, and ecological insight.
- Joseph Gilbert, Richard Wagner, and Sandra Embrey (USGS) for data coordination and agency assistance.
- Staff with the Washington State Department of Agriculture (project sponsor):
  - Jim Cowles for project support and report review.
  - Deborah Bahs for crop and pesticide use information.
- Staff with the Washington State Department of Ecology:
  - Dale Norton for review of project plans and reports.
  - Field assistance: Chad Althause, Dan Baker, Katie Curl, Casey Deligeannis, Kelly Donegan, Brandee Era-Miller, Chad Furl, Nicholas Grant, Jean Hays, Sean Hopkins, Brandi Lubliner, Patti Sandvik, Trevor Swanson, Rebecca Wood, and Maiko Yasu.
  - Analysis of samples and reviewing results: Bob Carrell, Dickey Huntamer, Jeff Westerlund, Kamilee Ginder, Dean Momohara, Stuart Magoon, Pam Covey, Karin Feddersen, Dan Baker, Kelly Donegan, Cherlyn Milne, Rebecca Woods, Myrna Mandjikov, John Weakland, and other Manchester Environmental Laboratory staff.
  - Joan LeTourneau and Cindy Cook for editing and formatting of final report.

Introduction

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) are conducting a long-term monitoring study to characterize pesticide concentrations in surface water during the typical pesticide-use season (Johnson and Cowles, 2003).

The purpose of this data report is to provide results from monitoring conducted in 2007 and to document any changes that occurred in the program during the year. An in-depth analysis of data collected between 2003 and 2005 in the Cedar-Sammamish and Lower Yakima watersheds was reported in 2006 (Burke et al., 2006). A second tri-annual report evaluating data collected from 2006-2008 will be published in 2009.

Five watersheds are being monitored for this study because they support several salmonid populations, produce a variety of agricultural commodities, and have a high percentage of cultivated land area (Johnson and Cowles, 2003; Burke and Anderson, 2006; Dugger et al., 2007):

1. Thornton Creek, located in the Cedar-Sammamish Water Resource Inventory Area (WRIA) 8, was selected as the urban watershed due to listed fish species, prior salmonid habitat enhancement efforts, and the occurrence of pre-spawning mortality in coho salmon (Anchor Environmental, 2004; NOAA Fisheries, 2005).

2. Four sub-basins of the Lower Skagit-Samish WRIA 3 were selected to represent western Washington agricultural land-use practices: Samish River, Big Ditch Slough, Browns Slough, and Indian Slough.

3. Three sub-basins of the Lower Yakima WRIA 37 were selected to represent eastern Washington irrigated agriculture land-use practices: Marion Drain, Sulphur Creek Wasteway, and Spring Creek.

4. Four sub-basins of the Wenatchee WRIA 45 were selected to represent central Washington agricultural (tree fruit) land-use practices: Wenatchee River, Mission Creek, Peshastin Creek, and Brender Creek.

5. One sub-basin of the Entiat WRIA 46 was selected to represent central Washington agricultural (tree fruit) land-use practices: Entiat River.

Year 2007 was the first year of monitoring in the Wenatchee and Entiat watersheds.

Figure 1 shows the locations of the five watersheds.

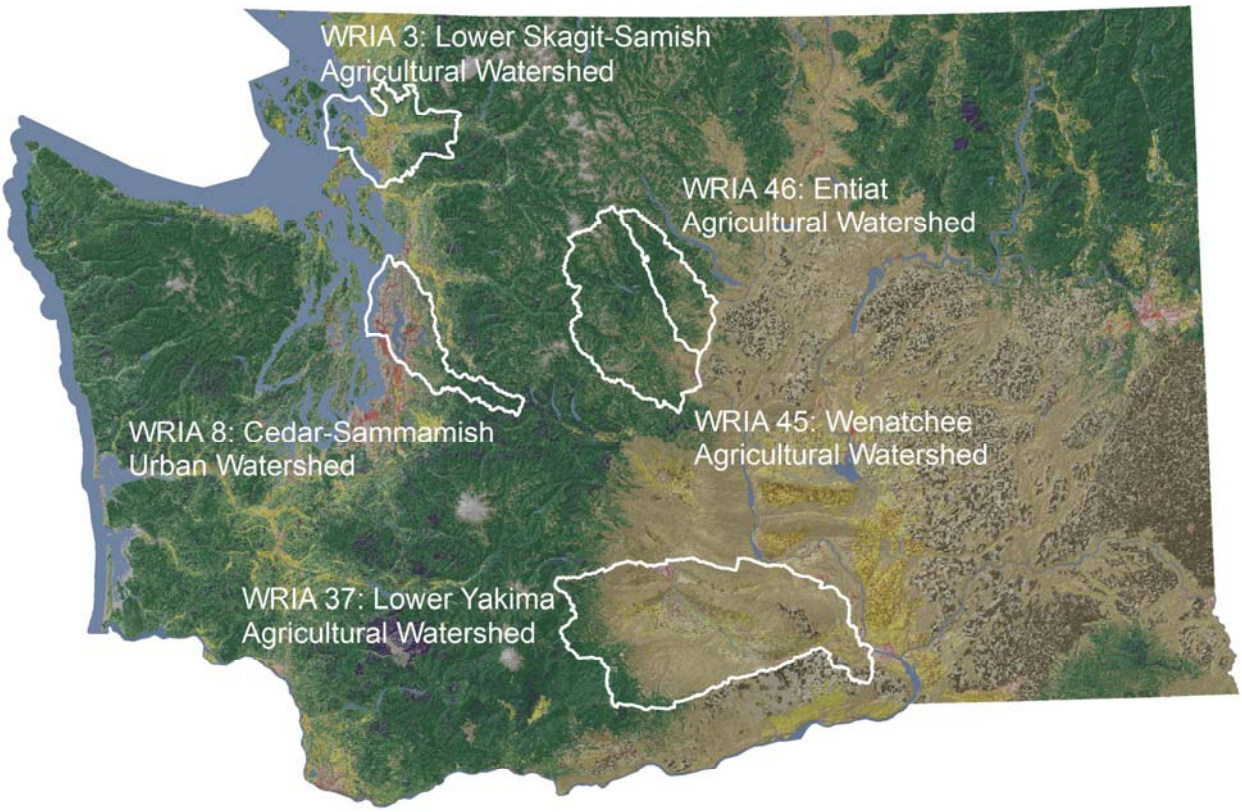

Figure 1. State map showing locations of urban and agricultural watersheds in this 2007 study.

Methods

Sampling was designed to address pesticide presence in salmonid-bearing streams during typical pesticide application periods. Registered and historical-use pesticides were analyzed, including organochlorine, organophosphorus, and carbamate pesticides. Conventional water quality parameters – total suspended solids, pH, conductivity, temperature, dissolved oxygen, and flow – were measured to better understand factors influencing pesticide toxicity, fate and transport, and general water quality.

Sampling frequency, field procedures, and laboratory procedures are described in previous reports and quality assurance (QA) project plans (Johnson and Cowles, 2003; Anderson et al., 2004; Burke et al., 2005, 2006; Burke and Anderson, 2006; Dugger et al., 2007). All laboratory evaluations were conducted by Manchester Environmental Laboratory (MEL). Sample locations and duration of sampling are described in Appendix A.

Changes to Sampling Procedures

For the 2007 study year, four sampling sites were added in the Wenatchee watershed (Wenatchee River, Mission Creek, Peshastin Creek, and Brender Creek), and an additional site was added in the Entiat watershed (Entiat River). Any changes to sampling procedures are described in Dugger et al. (2007) and are summarized below. Figure 2 shows the locations of the sampling sites within the Wenatchee and Entiat watersheds.

Sites within these basins have physical characteristics (example: stream depth and velocity) that require similar sampling procedures as described in the 2006 data summary (Anderson et al., 2007). A Marsh-McBirney Flo-Mate Model 2000 portable discharge meter was used to measure flow. When depth and velocity were too great for safe instream sampling, samples were taken with bridge sampling equipment. Discharge at the time of sampling was collected from the closest available Ecology, United States Bureau of Reclamation, or United States Geological Survey (USGS) discharge stations. Bridge samples were collected using rope and a USGS D-95 depth integrating sampler. Sampling and cleaning were conducted according to USGS procedures (USGS, 2007).

For 2007, sampling began in February approximately one month earlier than in past years. This shift was implemented to capture any pesticide residues that may have occurred as a result of early applications. Early March sampling in previous years showed detections of compounds that appear to have been the result of early season use of pesticides.

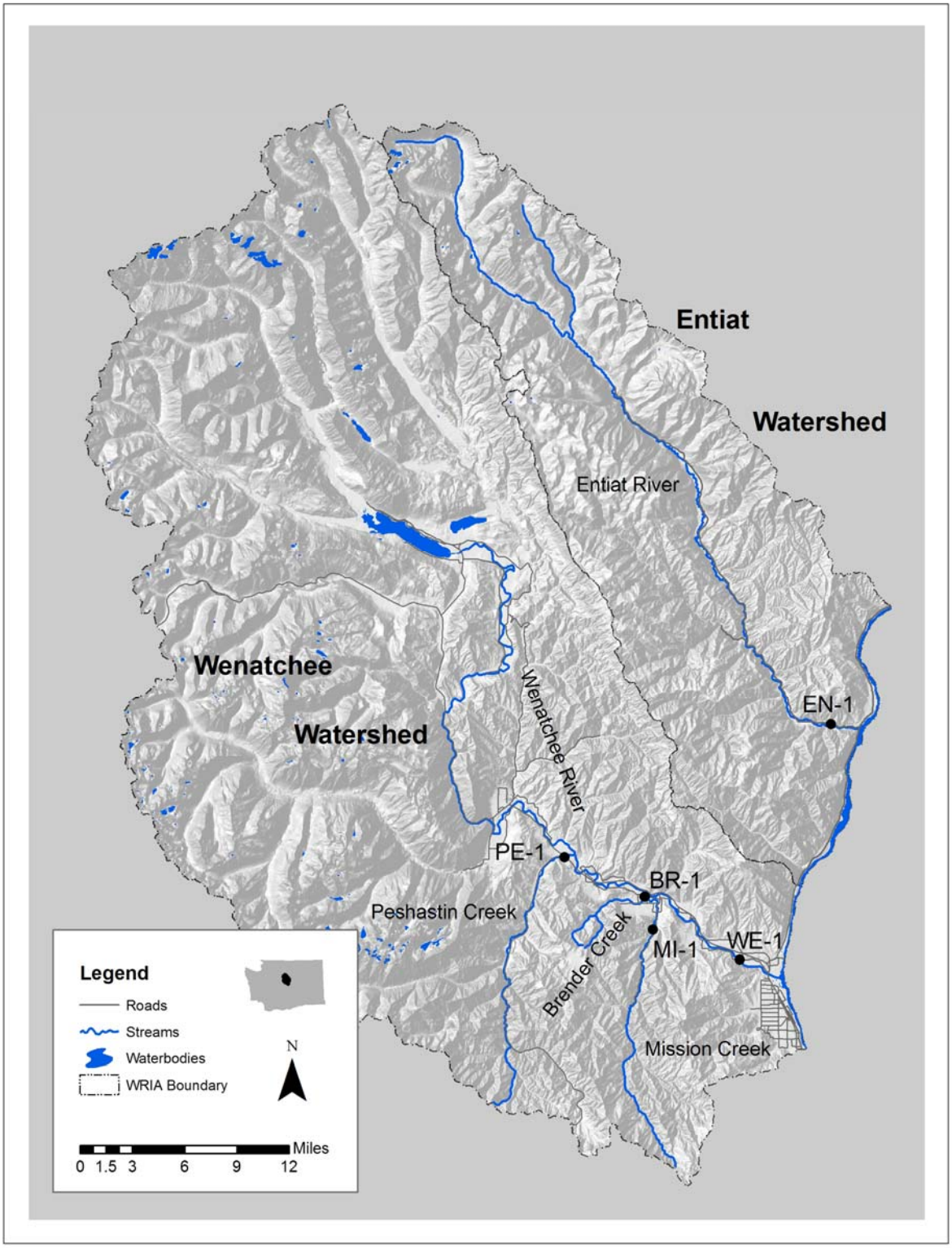

Figure 2. Sampling locations in the Wenatchee and Entiat watersheds.

Changes at Manchester Environmental Laboratory

During 2007, Manchester Environmental Laboratory (MEL) changed the reporting limits for carbamate analysis. MEL determined that reporting limits for carbamates were too low, which increased the chances of false positives. The change in reporting limits was documented in the MEL Week 18 (April 30-May 4, 2007) report detailing laboratory results and quality assurance. Reporting limits for the final MEL reports for weeks 7-17 were not changed. Table 1 outlines the reporting limits for carbamates for the weeks 7-17 and weeks 18-38.

Table 1. MEL changes in reporting limits for carbamates during 2007 weeks 7-17 and 18-38.

Carbamate Compound	Reporting Limit	
	Weeks 7-17	Weeks 18-38
Methomyl oxime	0.010	0.020
Oxamyl oxime	0.010	0.020
Aldicarb sulfoxide	0.010	0.020
Aldicarb sulfone	0.020	0.050
Oxamyl (Vydate)	0.020	0.050
Methomyl	0.010	0.050
3-Hydroxycarbofuran	0.020	0.050
Aldicarb	0.020	0.100
Baygon (Propoxur)	0.020	0.050
Carbofuran	0.010	0.020
Carbaryl	0.010	0.020
1-Naphthol	0.050	0.050
Methiocarb	0.010	0.020
Promecarb	0.050	0.020

Data Quality

Ecology calibrated all field monitoring equipment according to the manufacturers' specifications, using Ecology Standard Operating Procedures (Ecology, 2007) where available and established methods. All methods may be directly referenced to the USGS, American Public Health Association (Standard Methods), or American Society for Testing Materials (USGS, 2007; APHA, 2005; ASTM, 2005-2007).

Extractions for all analyses were carried out using solid phase extraction procedures: U.S. Environmental Protection Agency (EPA) Method (modified) SW 846 – 3535M (MEL, 2007b, c, and d). This procedure deviates from previous extractions conducted by liquid-liquid methods. The change in method was instituted to reduce the volume of organic solvents used and reduce the volume of water collected in the field.

Use of Liquid Chromatography coupled with Mass Spectrometry (LCMS) and large volume injection in Gas Chromatography coupled with Mass Spectrometry (GCMS) procedures has allowed MEL to (1) analyze additional (currently registered) pesticides and breakdown products, and (2) lower reporting limits of most target compounds (Appendix B, Table B-2).

The monitoring program used field/laboratory blanks, replicates, matrix spike/matrix spike duplicates, and laboratory control standards and surrogates to ensure quality assurance and control (QA/QC). Fifteen to 25% of the total laboratory budget was assigned to QA/QC in each watershed, ensuring all QA/QC parameters were evaluated at a rate greater than 1 test per 20 samples, or 1 test per batch (when < 20 samples) as defined in the EPA Superfund Methods for Organic Data Review (EPA, 2005). QA/QC results are presented in Appendix B.

Field and Laboratory Blanks

A single positive detection of Total Suspended Solids (TSS) at 3 mg/L was found in a field blank at the upper Spring Creek 2 site. All other field blanks had no detections, indicating both field and laboratory methods were free from contamination.

Throughout the 2007 sampling year there was consistent detection of an interfering analyte with a similar retention time as aldicarb sulfone, a breakdown product of aldicarb, in laboratory blanks. In early 2007 MEL upgraded their LCMS hardware to achieve lower reporting limits for carbamate analysis. With the increased sensitivity, MEL saw interference in the aldicarb sulfone method blanks. The interfering peak had a similar mass to aldicarb sulfone and was initially reported as a detected analyte. MEL has been working on eliminating this background interference in the method blank.

A full description of this issue and efforts to eliminate background interference are described in Appendix C. Since the background interference inhibits MEL's ability to accurately quantify Aldicarb sulfone at low levels, reporting limits were raised from 0.020 to 0.050 µg/L, and all detections were flagged as estimated concentrations for the 2007 data set (qualifications presented in Appendix B, Table B-1).

Field Replicates

The median relative percent difference (RPD) of consistently identified replicate results was 9.9%. Consistent identification refers to compounds which had a positive identification in both the original sample and field replicate. Inconsistently identified replicate pairs are those in which the compound was identified in one sample but not the other.

Inconsistently detected replicates pairs show a lower degree of reproducibility with pesticide monitoring results of the USGS-NAWQA (Martin, 2002) and Ecology. The rate in replicate inconsistency is similar among entities, 10-20% at concentrations below 0.1 µg/L.

Laboratory Quality Assurance

Surrogate analyses evaluate accuracy of recovery for a group of compounds, and are analyzed in each sample set. For instance, triphenyl phosphate (TPP) is a surrogate for organophosphorus insecticides (Appendix B, Figure B-1). The median recovery of TPP standards is 67%, while one standard deviation (σ) of values falls within 50-91%, and 2σ of values fall within 29-112%.

Laboratory control samples (LCS) evaluate accuracy of pesticide residue recovery for a specific pesticide and are applied on a rotating basis. The majority of LCS in Appendix B, Figure B-2 fall within an 80-120% recovery range. Fifteen to 80 LCS tests were applied for each of 152 separate pesticide residues. Residues with less than 30 tests must be evaluated as estimates because they do not meet requirements of the central limit theorem. Two such residues include the herbicide diuron and the insecticide azinphos methyl.

The median recoveries of these products are 109% and 82%, respectively, yet large outliers skew the standard deviation of both products to show low 2σ (2.5% of lower values) evaluations. In the case of outlier recoveries, representative detected compounds are qualified as estimates or rejected, depending on the degree of recovery.

Matrix Spikes

Results of matrix spike/matrix spike duplicates (MS/MSD) reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. This measure is the best overall indicator of accuracy, precision, and reproducibility of the entire sampling process. The average RPD between MS/MSD pairs is 16%, and the average recovery of reviewed compounds is 77%. The RPD and recovery of MS/MSD pairs shows good performance, and are within the limits of the QA project plans (Johnson and Cowles, 2003; Burke and Anderson, 2006; Dugger et al., 2007).

Accuracy, precision, and reproducibility are the most important components to verify a sampling and analysis program. Other key aspects of environmental investigations include the ability to detect compounds at relevant concentrations, and to analyze for emerging products. The *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams* consistently

strives to lower pesticide detection limits and increase the breadth of analysis for currently registered products, while retaining acceptable performance measures of accuracy, precision, and reproducibility.

With the exception of the TSS blank detection and detections of aldicarb sulfone in laboratory blanks, all data meet quality objectives as described in Johnson and Cowles (2003).

Results

This study investigated pesticide occurrence in selected salmonid-bearing surface waters. Watersheds and monitoring locations were chosen that had a likely combination of off-site pesticide transport and use by salmonids. All results are presented as a sum of stations within the watershed, throughout the 2007 sampling season.

At the Marion Drain sampling site, a study designed to compare daily sampling, weekly sampling, and passive sampling was conducted. Sampling took place over a 22-day period from April 24 to May 15, 2007. The results of this comparison will be published later in 2008.

Conventional Water Quality Parameters

Conventional water quality parameters were measured at all sites. Results for the physical parameters of discharge, temperature, and TSS are presented in Table 2. Results for chemical parameters of conductivity, pH, and dissolved oxygen are in Table 3. All summaries are based on point (discrete) measurements obtained during the time of sampling, over the entire 2007 sampling period.

Table 2. Conventional physical parameter results, February to October 2007.

Site	Discharge (cfs)				Temperature (°C)				Total Suspended Solids (mg/L)			
	n	min	med	max	n	min	med	max	n	min	med	max
Thornton Creek	47	1	5	19	47	6.8	13.7	19.9	47	2	8	55
Big Ditch	59	0	3	59	62	6.8	15.1	25.2	62	3	10	76
Browns Slough	27	0	5	24	31	7.6	17.8	25.7	31	4	7	48
Indian Slough	27	4	17	87	31	7.1	16.5	22.5	31	2	5	39
Samish River	30	22	78	1333	30	5.6	13.1	19.4	31	2	5	115
Marion Drain	35	17	113	286	38	8.4	14.9	22.5	38	2	11	31
Sulphur CW	30	48	272	542	31	8.2	15.6	21.2	31	8	25	409
Spring Creek	47	2	11	58	47	8.3	18.2	31.0	47	3	12	53
Wenatchee River	31	467	4500	12900	31	3.3	10.9	20.3	29	1	4	102
Brender Creek	31	1	3	8	31	3.7	11.3	15.5	30	13	34	156
Mission Creek	30	1	25	223	31	2.7	9.2	17.4	29	1	5	685
Peshastin Creek	31	12	216	1340	30	2.4	8.1	16.7	29	1	3	218
Entiat River	31	123	809	2490	31	3.7	9.4	20.4	30	2	5	64

Table 3. Conventional chemical parameter results, February to October 2007.

Site	Conductivity (µmhos/cm)				pH				Dissolved Oxygen (mg/L)			
	n	min	med	max	n	min	med	max	n	min	med	max
Thornton Creek	47	111	201	247	47	6.1	7.8	8.3	47	8.8	10.2	12.8
Big Ditch	62	38	297	938	62	6.3	7.1	9.5	62	2.9	8.4	18.0
Browns Slough	31	2686	9204	36436	31	6.7	7.6	8.7	31	3.4	10.6	18.2
Indian Slough	31	163	906	4410	30	6.3	7.2	8.0	31	4.6	8.0	11.1
Samish River	30	45	100	143	30	6.8	7.4	7.9	30	8.9	11.0	12.8
Marion Drain	38	134	207	299	37	7.6	8.1	9.0	37	8.9	11.8	16.0
Sulphur CW	31	165	251	658	30	7.8	8.4	9.0	31	8.9	11.0	14.9
Spring Creek	47	111	291	578	45	7.8	8.5	9.8	47	7.8	9.9	14.5
Wenatchee River	31	23	43	83	30	7.5	8.1	9.1	30	9.4	12.4	18.7
Brender Creek	31	123	227	411	31	7.8	8.2	9.4	31	9.8	11.6	13.5
Mission Creek	31	120	183	294	31	7.3	8.4	9.2	31	9.9	12.3	14.5
Peshastin Creek	31	45	92	133	31	7.7	8.2	8.5	31	10.0	12.4	14.4
Entiat River	31	24	54	103	31	7.3	8.4	9.7	31	8.7	12.3	14.8

Continuous, 30-minute interval, temperature data were collected January to December 2007. The sites in the Wenatchee and Entiat watersheds have data collected from February through December. A new site on upper Big Ditch (Big Ditch 2) has data collected from March through December. Temperature profiles for all sites are shown in Appendix D.

Pesticide Detections by Basin

1. Cedar-Sammamish Watershed – Thornton Creek

A total of 46 sampling events were conducted within Thornton Creek (15 upstream and 31 downstream) between February 12 and September 10, 2007. A total of 16 compounds were detected. Six of these compounds were detected in greater than 10% of samples. Thornton Creek pesticide results are summarized in Table 4. Figure 3 shows number of pesticide detections by week. Thornton Creek was sampled every other week upstream and weekly downstream.

Table 4. Summary of pesticide detections in Thornton Creek, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Dichlobenil	Casoron	H	0.033	29	63%	0.02	0.069
Prometon	Pramitol	H	0.033	7	15%	0.025	0.031
Carbaryl	Sevin	I-C	0.017	6	13%	0.02	0.048
2,4-D	(weed & feeds)	H	0.062	5	11%	0.13	0.22
MCPP	(weed & feeds)	H	0.062	5	11%	0.068	0.076
Oxamyl oxime		D	0.017	5	11%	0.02	0.12
4-Nitrophenol		D	0.062	3	7%	0.12	0.78
1-Naphthol		D	0.051	2	4%	0.357	0.641
Propoxur	(ant & roach baits)	I-C	0.040	1	2%	0.03	0.03
Carbofuran	Furadan	I-C	0.017	1	2%	0.16	0.16
cis-Permethrin		I-P	0.05	1	2%	0.11	0.11
Diuron	Diuron	H	0.056	1	2%	0.032	0.032
Methomyl	Lannate	I-C	0.037	1	2%	0.17	0.17
Oxamyl	Vydate	H	0.042	1	2%	0.011	0.011
Promecarb		L	0.032	1	2%	0.063	0.063
Trifluralin	(weed & feeds)	H	0.033	1	2%	0.016	0.016

Sample Events – 46.
D – Degradate.
H – Herbicide.
L – Legacy pesticide.
I-C – Insecticide/Carbamate.
I-P – Insecticide/Pyrethroid.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

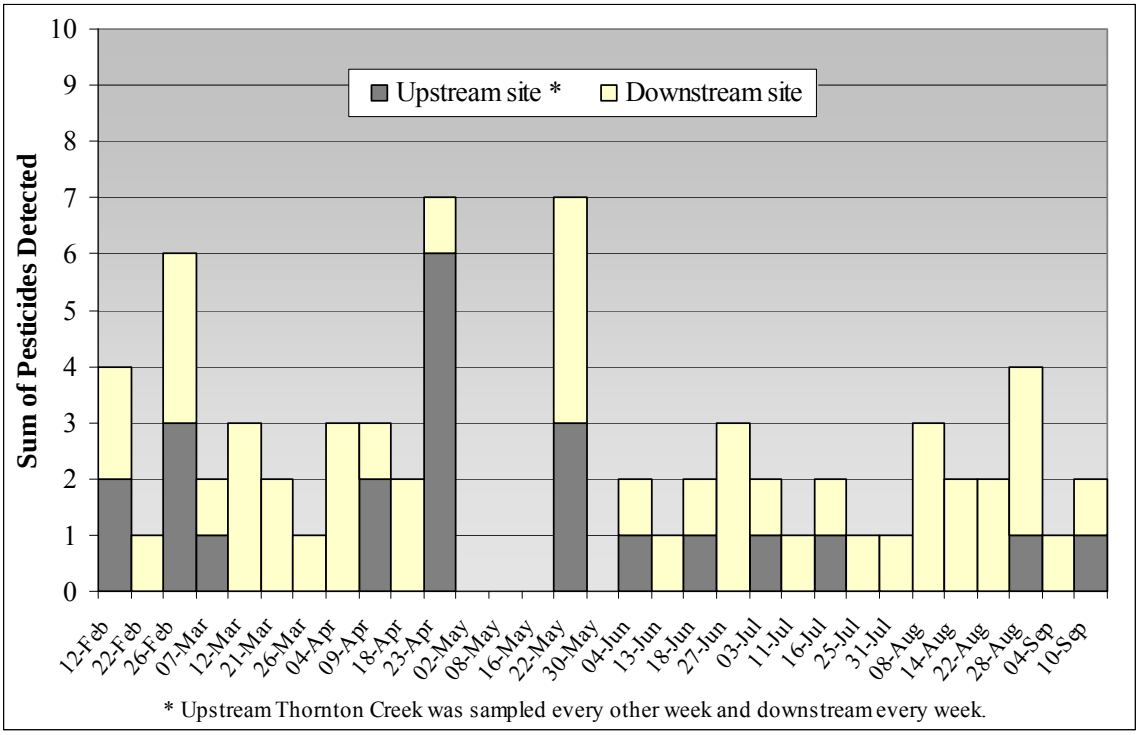

Figure 3. Sum of 2007 pesticide detections by week in the Thornton Creek watershed.

2. Lower Skagit-Samish Watershed – Big Ditch Slough, Browns Slough, Indian Slough, and the Samish River

All lower Skagit-Samish sites were sampled for 31 consecutive weeks from February 12 to September 10, 2007. Figure 4 shows the sum of detections for the Skagit-Samish watershed by week (graph includes data from both Big Ditch Slough sites).

Results are presented in Tables 5 through 8. Big Ditch Slough, Table 5, is a combination of upstream and downstream monitoring sites.

The combination of the upper and lower monitoring sites in Big Ditch had a total of 31 detected compounds with nine found in greater than 10% of samples. Browns Slough had 25 compounds detected with 10 found in greater than 10% of samples. Fifteen compounds were detected in Indian Slough with seven found in greater than 10% of samples. The Samish River site had four compounds detected with one found in greater than 10% of samples.

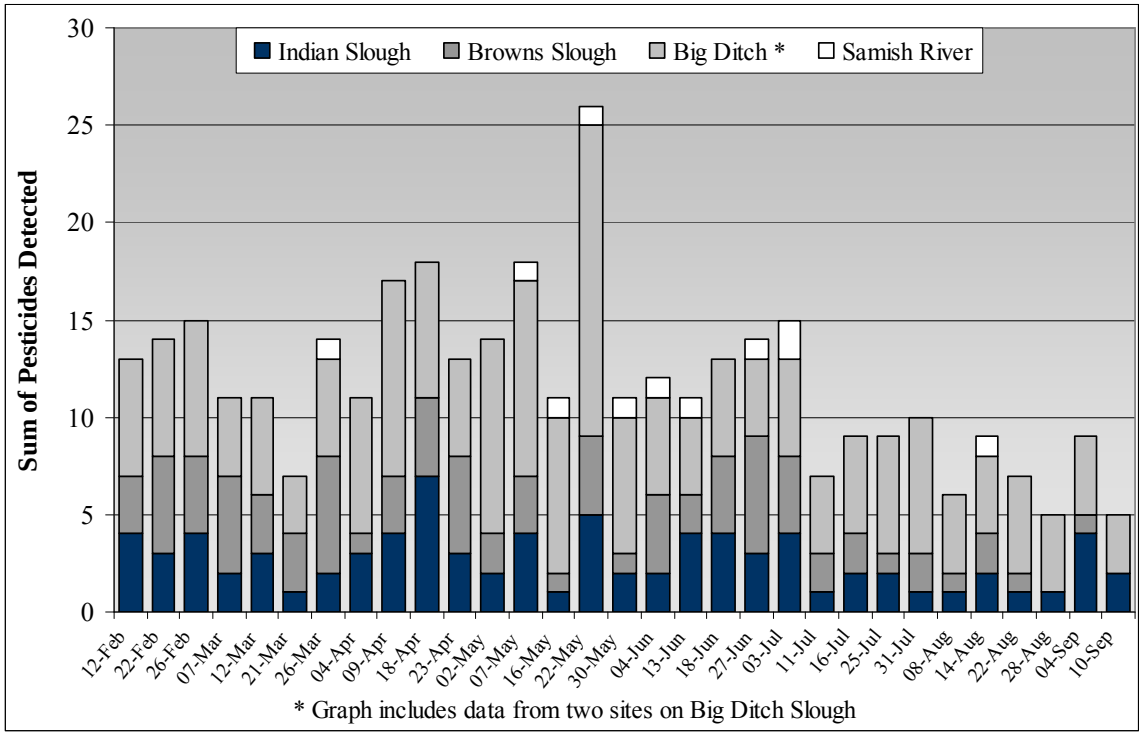

Figure 4. Sum of 2007 pesticide detections by week in the Skagit-Samish watershed.

Table 5. Summary of pesticide detections in Big Ditch Slough, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Picloram	Tordon	H	0.062	23	37%	0.31	0.58
Bromacil	Hyvar	H	0.034	20	32%	0.06	0.13
Dichlobenil	Casoron	H	0.033	20	32%	0.02	0.059
Tebuthiuron	Spike	H	0.033	19	31%	0.13	0.22
Metalaxyl	Ridomil Gold	F	0.033	15	24%	0.12	0.51
Prometon	Pramitol	H	0.033	14	23%	0.03	0.12
Diuron	Direx, Karmex	H	0.056	11	18%	0.07	0.16
2,4-D	(several)	H	0.062	9	15%	0.17	0.74
EPTC	Eptam	H	0.033	8	13%	0.07	0.25
Metolachlor	Dual Magnum	H	0.033	5	8%	0.019	0.048
Oxamyl oxime		D	0.017	5	8%	0.021	0.068
Bentazon	Basagran	H	0.062	4	6%	0.057	0.087
4-Nitrophenol		D	0.062	3	5%	0.05	0.56
Atrazine	(several)	H	0.033	3	5%	0.036	0.084
3-Hydroxycarbofuran		D	0.404	2	3%	0.12	0.15
Aldicarb Sulfone		D	0.062	2	3%	0.36	0.51
Diazinon	(several)	I-OP	0.033	2	3%	0.04	0.052
Dicamba I	(several)	H	0.062	2	3%	0.04	0.04
Ethoprop	Mocap	I-OP	0.033	2	3%	0.09	0.14
MCPP	(several)	H	0.062	2	3%	0.1	0.1
Metribuzin	Sencor	H	0.033	2	3%	0.02	0.024
Oxamyl	Vydate	I-C	0.042	2	3%	0.03	0.046
1-Naphthol		D	0.051	1	2%	0.22	0.22
Alachlor	Intrro, Lariat	H	0.033	1	2%	0.15	0.15
Aldicarb	Temik	I-C	0.073	1	2%	0.021	0.021
Carbofuran	Furadan	I-C	0.017	1	2%	0.028	0.028
Chlorpyrifos	Lorsban	I-OP	0.033	1	2%	0.02	0.02
Dimethoate	(several)	I-OP	0.033	1	2%	0.077	0.077
Linuron	Linex, Lorox	H	0.064	1	2%	0.054	0.054
MCPA	(several)	H	0.062	1	2%	0.3	0.3
Methomyl oxime		D	0.017	1	2%	0.039	0.039
Triadimefon	Bayleton	F	0.033	1	2%	0.019	0.019

Sample Events – 62.
D – Degradate.
F – Fungicide.
H – Herbicide.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 6. Summary of pesticide detections in Browns Slough, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Diuron	Direx, Karmex	H	0.056	14	45%	0.12	4.1
Bentazon	Basagran	H	0.062	8	26%	0.09	0.14
Simazine	(several)	H	0.033	7	23%	0.07	0.19
EPTC	Eptam	H	0.033	6	19%	0.02	0.24
DCPA	Dacthal	H	0.062	5	16%	0.09	0.22
Diazinon	(several)	I-OP	0.033	5	16%	0.1	0.7
Oxamyl	Vydate	H	0.042	5	16%	0.03	0.14
2,4-D	(several)	H	0.062	4	13%	0.08	0.19
4-Nitrophenol		D	0.062	4	13%	0.09	0.11
Dicamba I	(several)	H	0.062	4	13%	0.04	0.086
Atrazine	(several)	H	0.033	3	10%	0.06	0.11
Dichlobenil	Casoron	H	0.033	3	10%	0.014	0.034
Chlorpyrifos	Lorsban	I-OP	0.033	2	6%	0.027	0.038
MCPA	(several)	H	0.062	2	6%	0.44	0.48
Methomyl	Lannate	I-C	0.037	2	6%	0.017	0.018
Trifluralin	Treflan	H	0.033	2	6%	0.023	0.031
Aldicarb Sulfoxide		D	0.017	1	3%	0.03	0.03
Bromoxynil	Buctril	H	0.062	1	3%	0.64	0.64
Carbaryl	Sevin	I-C	0.017	1	3%	0.013	0.013
Carbofuran	Furadan	I-C	0.017	1	3%	0.08	0.08
Dimethoate	(several)	I-OP	0.033	1	3%	0.43	0.43
Endosulfan Sulfate		D	0.033	1	3%	0.025	0.025
Metribuzin	Sencor	H	0.033	1	3%	0.058	0.058
Norflurazon	Solicam	H	0.033	1	3%	0.04	0.04
Tebuthiuron	Spike	H	0.033	1	3%	0.069	0.069

Sample Events – 31.
D – Degradate.
H – Herbicide.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 7. Summary of pesticide detections in Indian Slough, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Tebuthiuron	Spike	H	0.033	21	68%	0.1	0.15
Diphenamid		L	0.033	19	61%	0.02	0.033
Metolachlor	Dual Magnum	H	0.033	12	39%	0.03	0.052
Dichlobenil	Casoron	H	0.033	8	26%	0.02	0.037
2,4-D	(several)	H	0.062	6	19%	0.09	0.26
Bentazon	Basagran	H	0.062	5	16%	0.025	0.038
Diuron	Direx, Karmex	H	0.056	4	13%	0.04	0.06
Bromacil	Hyvar	H	0.034	2	6%	0.07	0.11
4-Nitrophenol		D	0.062	1	3%	0.061	0.061
Alachlor	Intrro, Lariat	H	0.033	1	3%	0.022	0.022
Aldicarb	Temik	I-C	0.073	1	3%	0.027	0.027
Diazinon	(several)	I-OP	0.033	1	3%	0.034	0.034
Oxyfluorfen	Goal	H	0.033	1	3%	0.034	0.034
Simazine	(several)	H	0.033	1	3%	0.0084	0.0084
Trifluralin	Treflan	H	0.033	1	3%	0.017	0.017

Sample Events – 31.
H – Herbicide.
I-C - Insecticide/carbamate.
I-OP - Insecticide/organophosphate.
L – Legacy pesticide.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 8. Summary of pesticide detections in the Samish River, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Bromacil	Hyvar	H	0.034	8	26%	0.02	0.15
Carbaryl	Sevin	I-C	0.017	1	3%	0.011	0.011
Diuron	Direx, Karmex	H	0.056	1	3%	0.061	0.061
Oxamyl	Vydate	H	0.042	1	3%	0.015	0.015

Sample Events – 31.
H – Herbicide.
I-C – Insecticide/Carbamate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

3. Lower Yakima Watershed – Marion Drain, Sulphur Creek Wasteway, and Spring Creek.

The Lower Yakima sites were sampled for 31 consecutive weeks from February 13 to September 12, 2007. Figure 5 shows the sum of pesticide detections for the Lower Yakima watershed by week (graph includes data from the upper and lower Spring Creek sites). The results are presented in Tables 9 through 11. Spring Creek, Table 11, is a combination of upstream and downstream monitoring sites. The upstream site was sampled every other week during the monitoring period. Marion Drain sampling was extended through October 29, 2007.

A total of 22 pesticides were detected in Marion Drain with 12 of these found in greater than 10% of samples. Sulphur Creek Wasteway had 21 pesticides detected with 11 found in greater than 10% of samples. In Spring Creek the combined sites had a total of 23 detected pesticides with five of these found in greater than 10% of samples.

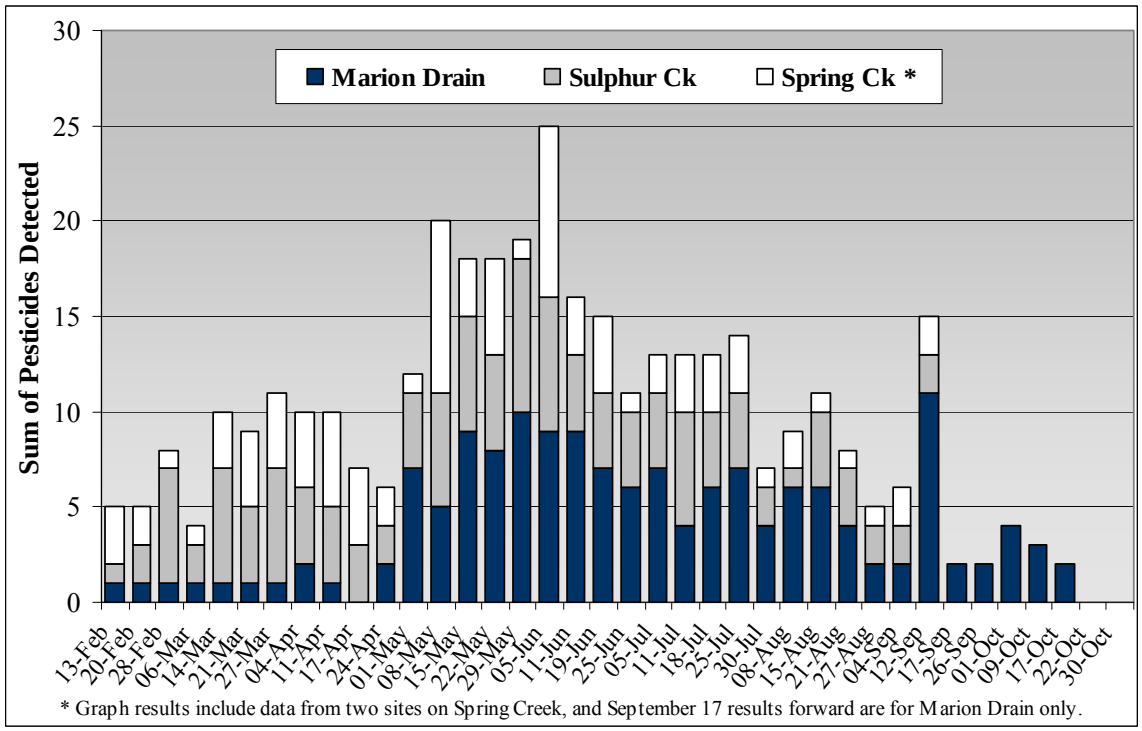

Figure 5. Sum of 2007 pesticide detections by week in the Lower Yakima watershed.

Table 9. Summary of pesticide detections in Marion Drain, February to October 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Terbacil	Sinbar	H	0.033	25	66%	0.1	0.38
Chlorpyrifos	Lorsban	I-OP	0.033	21	55%	0.03	0.12
Atrazine	(several)	H	0.033	18	47%	0.02	0.028
Bentazon	Basagran	H	0.062	11	29%	0.05	0.17
Pendimethalin	Prowl	H	0.033	10	26%	0.04	0.074
Trifluralin	Treflan	H	0.033	8	21%	0.03	0.047
Dicamba I	(several)	H	0.062	6	16%	0.016	0.017
Malathion	(several)	I-OP	0.294	6	16%	0.020	0.082
2,4-D	(several)	H	0.062	5	13%	0.06	0.12
Clopyralid	Stinger	H	0.062	5	13%	0.037	0.065
Metolachlor	Dual Magnum	H	0.033	4	11%	0.02	0.21
Oxamyl oxime		D	0.017	4	11%	0.021	0.033
Carbaryl	Sevin	I-C	0.017	3	8%	0.019	0.022
Disulfoton sulfone		D	0.099	3	8%	0.029	0.039
Diuron	Direx, Karmex	H	0.056	3	8%	0.028	0.028
MCPA	(several)	H	0.062	3	8%	0.04	0.043
Oxamyl	Vydate	I-C	0.042	3	8%	0.03	0.048
Simazine	(several)	H	0.033	3	8%	0.011	0.019
Ethoprop	Mocap	I-OP	0.033	2	5%	0.035	0.036
EPTC	Eptam	H	0.033	1	3%	0.024	0.024
Methomyl	Lannate	I-C	0.037	1	3%	0.05	0.05
Propargite	Comite, Omite	I-SE	0.033	1	3%	0.043	0.043

Sample Events – 38.
D – Degradate.
H – Herbicide.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
I-SE – Insecticide/Sulfite Ester.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 10. Summary of pesticide detections in Sulphur Creek Wasteway, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Bromacil	Hyvar	H	0.034	20	65%	0.03	0.16
Carbaryl	Sevin	I-C	0.017	13	42%	0.04	0.2
Diuron	Direx, Karmex	H	0.056	13	42%	0.1	0.27
2,4-D	(several)	H	0.062	12	39%	0.08	0.22
DCPA	Dacthal	H	0.062	11	35%	0.03	0.079
Atrazine	(several)	H	0.033	10	32%	0.02	0.05
Terbacil	Sinbar	H	0.033	6	19%	0.023	0.064
Dicamba I	(several)	H	0.062	5	16%	0.012	0.035
Trifluralin	Treflan	H	0.033	5	16%	0.02	0.028
Chlorpyrifos	Lorsban	I-OP	0.033	4	13%	0.1	0.17
Dichlobenil	Casoron	I-OP	0.033	4	13%	0.023	0.034
4,4'-DDE		D	0.033	3	10%	0.0089	0.0096
Norflurazon	Solicam	H	0.033	3	10%	0.032	0.083
Simazine	(several)	H	0.033	3	10%	0.022	0.045
Malathion	(several)	I-OP	0.294	2	6%	0.02	0.021
MCPA	(several)	H	0.062	2	6%	0.037	0.038
Oxamyl oxime		D	0.017	2	6%	0.020	0.022
1-Naphthol		D	0.051	1	3%	0.013	0.013
Dimethoate	(several)	I-OP	0.033	1	3%	0.049	0.049
Pendimethalin	Prowl	H	0.033	1	3%	0.046	0.046
Prometon	Pramitol	H	0.033	1	3%	0.061	0.061

Sample Events – 31.
D – Degradate.
H – Herbicide.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 11. Summary of pesticide detections in Spring Creek, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Atrazine	(several)	H	0.033	21	45%	0.015	0.034
2,4-D	(several)	H	0.062	11	23%	0.10	6.57
Bromacil	Hyvar	H	0.034	10	21%	0.04	0.069
Chlorpyrifos	Lorsban	I-OP	0.033	9	19%	0.03	0.27
Bentazon	Basagran	H	0.062	5	11%	0.05	0.06
Azinphos Methyl	Guthion	I-OP	0.033	3	6%	0.048	0.079
Carbaryl	Sevin	I-C	0.017	3	6%	0.027	0.028
Dicamba I	(several)	H	0.062	3	6%	0.014	0.015
Diuron	Direx, Karmex	H	0.056	3	6%	0.042	0.081
Oxamyl	Vydate	I-C	0.042	3	6%	0.026	0.089
4,4'-DDE		D	0.033	2	4%	0.01	0.01
MCPA	(several)	H	0.062	2	4%	0.09	0.14
Prometon	Pramitol	H	0.033	2	4%	0.041	0.055
Simazine	(several)	H	0.033	2	4%	0.029	0.031
Norflurazon	Solicam	H	0.033	1	2%	0.024	0.024
Aldicarb	Temik	I-C	0.073	1	2%	0.034	0.034
Diazinon	(several)	I-OP	0.033	1	2%	0.015	0.015
Endosulfan Sulfate		D	0.033	1	2%	0.033	0.033
Malathion	(several)	I-OP	0.294	1	2%	0.016	0.016
Oryzalin	Surflan	H	0.098	1	2%	0.44	0.44
Oxamyl Oxime		D	0.017	1	2%	0.013	0.013
Promecarb		L	0.032	1	2%	0.015	0.015
Terbacil	Sinbar	H	0.033	1	2%	0.032	0.032

Sample Events – 31.
D – Degradate.
H – Herbicide.
L – Legacy pesticide.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

4. Wenatchee Watershed – Wenatchee River, Mission Creek, Peshastin Creek, and Brender Creek

All Wenatchee and Entiat sites were sampled for 31 consecutive weeks from February 14 to September 10, 2007. Figure 6 shows the sum of pesticide detections by week for the Wenatchee watershed. The majority of the detections shown in Figure 6 occur in Brender Creek. The results are presented in Tables 12 through 15.

The Wenatchee River, Mission Creek, and Peshastin Creek monitoring sites had few detections over the sampling period. None of the pesticides detected were found in greater than 6% of samples with the majority found in 3% of the samples. Brender Creek had a total of 21 detected pesticides with 10 found in greater than 10% of samples.

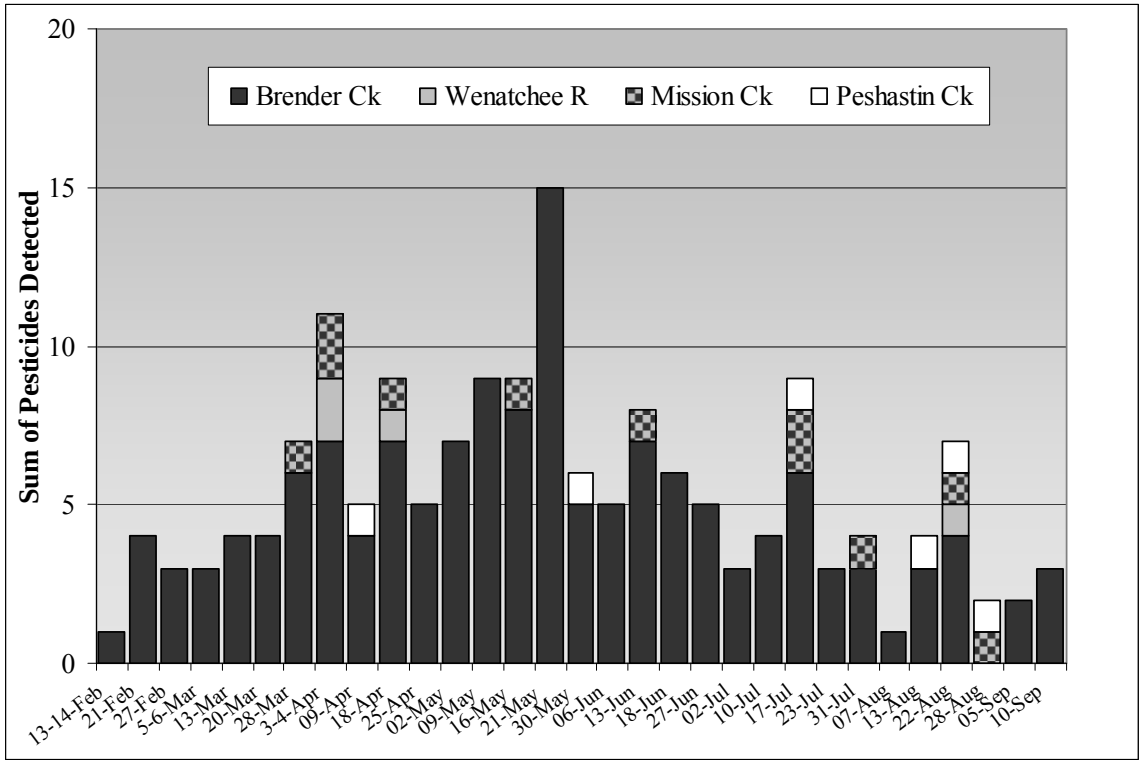

Figure 6. Sum of 2007 pesticide detections by week in the Wenatchee watershed.

Table 12. Summary of pesticide detections in the Wenatchee River, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Chlorpyrifos	Lorsban	I-OP	0.033	1	3%	0.035	0.035
Endosulfan I	Thionex	I-OC	0.05	1	3%	0.035	0.035
Methomyl	Lannate	I-C	0.037	1	3%	0.016	0.016
Oxamyl	Vydate	I-C	0.042	1	3%	0.016	0.016

Sample Events – 31.
I-C - Insecticide/Carbamate; I-OP - Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 13. Summary of pesticide detections in Mission Creek, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Norflurazon	Solicam	H	0.033	2	6%	0.034	0.041
Methiocarb	Mesurol	I-C	0.017	2	6%	0.025	0.034
Chlorpyrifos	Lorsban	I-OP	0.033	1	3%	0.024	0.024
Endosulfan II	Thionex	I-OC	0.05	1	3%	0.022	0.022
Methomyl	Lannate	I-C	0.037	1	3%	0.019	0.019
Oxamyl Oxime		D	0.017	1	3%	0.017	0.017
Endosulfan I	Thionex	I-OC	0.05	1	3%	0.017	0.017

Sample Events – 31.
D – Degradate.
H – Herbicide.
I-C - Insecticide/Carbamate; I-OP - Insecticide/Organophosphate; I-OC – Insecticide/Organochlorine.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 14. Summary of pesticide detections in Peshastin Creek, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
1-Naphthol		D	0.051	1	3%	0.01	0.01
Azinphos Methyl	Guthion	I-OP	0.033	1	3%	0.024	0.024
Carbaryl	Sevin	I-C	0.017	1	3%	0.019	0.019
Methomyl	Lannate	I-C	0.037	1	3%	0.023	0.023
Oxamyl	Vydate	I-C	0.042	1	3%	0.026	0.026
Oxamyl oxime		D	0.017	1	3%	0.026	0.026

Sample Events – 31.
D – Degradate.
I-C - Insecticide/Carbamate; I-OP - Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Table 15. Summary of pesticide detections in Brender Creek, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
4,4'-DDE		D	0.033	29	94%	0.03	0.071
4,4'-DDT		D	0.033	27	87%	0.02	0.05
Endosulfan Sulfate		D	0.033	17	55%	0.03	0.1
4,4'-DDD		D	0.033	16	52%	0.01	0.025
Chlorpyrifos	Lorsban	I-OP	0.033	9	29%	0.03	0.11
Norflurazon	Solicam	H	0.033	9	29%	0.03	0.16
2,4'-DDT		D	0.033	7	23%	0.011	0.017
Endosulfan I	Thionex	I-OC	0.05	7	23%	0.03	0.1
Endosulfan II	Thionex	I-OC	0.05	7	23%	0.04	0.071
Carbaryl	Sevin	I-C	0.017	4	13%	0.02	0.04
Azinphos Methyl	Guthion	I-OP	0.033	3	10%	0.03	0.53
2,4'-DDD		D	0.033	2	6%	0.013	0.018
Simazine	(several)	H	0.033	2	6%	0.025	0.028
1-Naphthol		D	0.051	1	3%	0.011	0.011
Diazinon	(several)	I-OP	0.033	1	3%	0.021	0.021
Diuron	Direx, Karmex	H	0.056	1	3%	0.12	0.12
MCPA	(several)	H	0.062	1	3%	0.072	0.072
Methomyl	Lannate	I-C	0.037	1	3%	0.017	0.017
Oxamyl	Vydate	I-C	0.042	1	3%	0.027	0.027
Prometon	Pramitol	H	0.033	1	3%	0.0094	0.0094
Triadimefon	Bayleton	F	0.033	1	3%	0.015	0.015

Sample Events – 31.
D – Degradate.
F – Fungicide.
H – Herbicide.
I-C – Insecticide/Carbamate.
I-OC – Insecticide/Organochlorine.
I-OP – Insecticide/Organophosphate.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events

5. Entiat Watershed – Entiat River

The Entiat River sampling site was sampled for 31 consecutive weeks from February 14 to September 10, 2007. Over the sampling period, three pesticides were detected and all were found in 3% of samples. The results are presented in Table 16.

Table 16. Summary of pesticide detections in the Entiat River, February to September 2007.

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Carbaryl	Sevin	I-C	0.017	1	3%	0.016	0.016
Chlorpyrifos	Lorsban	I-OP	0.033	1	3%	0.034	0.034
Dichlobenil	Casoron	H	0.033	1	3%	0.065	0.065

Sample Events – 31.
I-C – Insecticide/Carbamate.
I-OP – Insecticide/Organophosphate.
H – Herbicide.
[1]ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix B.
[2]Detection frequency is calculated as detections divided by total number of sample events.

Detailed results for all five watersheds are presented in the following appendices:

- Appendix A. Monitoring Location and Duration of Sampling.
- Appendix B. Quality Assurance/Quality Control.
- Appendix D. Continuous Temperature Profiles.

Summary of Project Changes

During 2007, the following changes were made to the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams*:

- Four basins were added in the Wenatchee watershed: Wenatchee River, Mission Creek, Peshastin Creek, and Brender Creek.
- One basin was added in the Entiat watershed: Entiat River.
- The sampling season was extended into early February at all sites to determine if early season detections were being missed.
- One sampling site in the Skagit-Samish watershed was moved: The upper Samish River site (SR-2) was dropped, and an upstream site on Big Ditch Slough was added.
- Eighteen new pesticide residues and degradate products were added for analysis through review of laboratory protocols (GCMS/LCMS), change to solid phase extraction, and development of laboratory methods.
- The laboratory extraction method changed from liquid-liquid to solid phase for all analyses.
- On September 5 and 10, 2007, the Mission Creek sample site had no surface water. Therefore, for these dates, samples were collected at an upstream location (47.4803° N, 120.4882° W).

Proposed Changes for 2008

As a result of this 2007 study, the following changes are recommended for 2008:

- Continue to work with the Manchester Environmental Laboratory on resolving the issue of blank detections in the carbamate analysis.

- Add more pesticides to the suite of chemicals analyzed, if there is no additional cost to the monitoring program.

- Based on data from the 2007 extended sampling season, the monitoring program should continue early February sampling in both the Skagit-Samish watershed and Brender Creek in the Wenatchee watershed, unless budget constraints do not allow for this.

References

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Appendices

Appendix A. Monitoring Sites and Duration of Sampling

Table A-1. Station locations, duration of monitoring, and descriptions for 2007.

Site	Duration	Latitude	Longitude	Location Description
Cedar-Sammamish Watershed				
Thornton 1	Feb. - Sept.	47.7082	122.2897	NE 110th Street upstream of pedestrian footbridge.
Thornton 3	Feb. - Sept.	47.6958	122.2757	Downstream of pedestrian footbridge near Mathews Beach Park.
Skagit/Samish Watershed				
BD-1	Feb. - Sept.	48.3086	122.3473	Upstream side of bridge at Milltown Road.
BD-2	Feb. - Sept.	48.3887	122.3329	Upstream side of bridge at Eleanor Lane.
BS-1	Feb. - Sept.	48.3406	122.4140	Downstream of tidegate on Fir Island Road.
IS-1	Feb. - Sept.	48.4506	122.4651	Upstream side of tidegate at Bayview-Edison Road.
SR-1	Feb. - Sept.	48.5209	122.4113	Upstream side of bridge at Thomas Road.
Lower Yakima Watershed				
Marion 2	Feb. - Oct.	46.3306	120.1989	~15 meters upstream of bridge at Indian Church Road.
Spring 2	Feb. - Sept.	46.2583	119.7101	Downstream side of culvert on McCready Road.
Spring 3	Feb. - Sept.	46.2344	119.6845	~3 meters downstream of Chandler Canal overpass.
Sulphur 1	Feb. - Sept.	46.2509	120.0202	Downstream side of bridge at Holaday Road.
Wenatchee Watershed				
WE-1	Feb. - Sept.	47.4721	120.3710	Upstream side of Sleepy Hollow bridge.
MI-1	Feb. - Sept.	47.4893	120.4815	Above Woodring Canyon Road and Mission Creek Road.
PE-1	Feb. - Sept.	47.5570	120.5825	~30 meters downstream of bridge at Saunders Road.
BR-1	Feb. - Sept.	47.5211	120.4862	Upstream side of culvert at Evergreen Drive.
Entiat Watershed				
EN-1	Feb. - Sept.	47.6633	120.2506	Upstream side of bridge at Keystone Road.

Appendix B. Quality Assurance and Quality Control

Data may be qualified if one or more analytical factors affect confidence in the prescribed data value. Manchester Environmental Laboratory qualifies data according to the National Functional Guidelines for Organic Data Review (EPA, 2005). Data qualification is presented in Table B-1.

Table B-1. Data qualification.

Qualifier	Definition
U	The analyte was not detected at or above the reported sample quantitation limit.
J	The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample (either certain quality control criteria were not met or the concentration of the analyte was below the 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 be imprecise.
REJ	The sample results are unusable due to the quality of the data generated because certain criteria were not met. The analyte may or may not be present in the sample.
NAF	Not analyzed for
NJ	The analysis indicates the presence of an analyte that has been tentatively identified and the associated numerical value is the approximate concentration.
NC	Not calculated

MEL, 2000, 2007a; EPA, 2005.

Lower performance practical quantitation limits (LPQL) were calculated for each study year of the project. The LPQL is determined by averaging the lower reporting values, per analyte, for all batches over each study year. The LPQL is the limit at which laboratories may report data without classifying the concentration as an estimate below the lowest calibration standard. LPQL data and updates to the analytical schedule are presented in Table B-2.

Table B-2. Mean Performance Lower Practical Quantitation Limits (µg/L).

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3] 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL	2007 LPQL
1-Naphthol	Degradate/C	Carbaryl	LCMS	0.19	0.13		0.065	0.051
3-Hydroxycarbofuran	Degradate/C	Carbofuran	LCMS	0.19	0.13	0.11	0.063	0.040
Aldicarb	Insecticide/C		LCMS	0.19	0.13	0.1	0.063	0.073
Aldicarb sulfone	Degradate/C	Aldicarb	LCMS			0.1	0.095	0.062
Aldicarb sulfoxide	Degradate/C	Aldicarb	LCMS			0.11	0.069	0.017
Aldicarb sulfoxide+s	Degradate/C	Aldicarb	LCMS	0.19	0.13	0.16		
Bendiocarb	Insecticide/C		LCMS	0.19	0.13	0.131		
Carbaryl	Insecticide/C		LCMS	0.19	0.13	0.11	0.054	0.017
Carbofuran	Insecticide/C		LCMS	0.19	0.13	0.104	0.063	0.017
Dioxacarb	Insecticide/C		LCMS	0.19	0.13			
Diuron	Herbicide		LCMS				0.055	
Linuron	Herbicide		LCMS				0.064	
Methiocarb	Insecticide/C		LCMS	0.19	0.13	0.11	0.1	0.017
Methomyl	Insecticide/C		LCMS	0.19	0.13	0.12	0.055	0.037
Methomyl oxime	Degradate/C	Methomyl	LCMS				0.07	0.017
Oxamyl	Insecticide/C		LCMS	0.19	0.13	0.11	0.071	0.042
Oxamyl oxime	Degradate/C	Oxamyl	LCMS				0.092	0.017
Promecarb	Insecticide/C		LCMS	0.19	0.13	0.093	0.101	0.032
Propoxur	Insecticide/C		LCMS	0.19	0.13	0.11	0.054	0.040
2,3,4,5-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079	0.062
2,3,4,6-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079	0.062
2,4,5-T	Herbicide		GCMS-H	0.125	0.079	0.081	0.079	0.062
2,4,5-TP	Herbicide		GCMS-H	0.125	0.079	0.081	0.079	0.062
2,4,5-Trichlorophenol	Fungicide		GCMS-H	0.5	0.079	0.081	0.079	0.062
2,4,6-Trichlorophenol	Fungicide		GCMS-H	0.495	0.079	0.081	0.079	0.062
2,4-D	Herbicide		GCMS-H	0.16	0.079	0.081	0.078	0.062
2,4-DB	Herbicide		GCMS-H	0.19	0.079	0.081	0.079	0.062
3,5-Dichlorobenzoic Acid	Herbicide		GCMS-H	0.16	0.079	0.084	0.079	0.062
4-Nitrophenol	Degradate/H-OP	multiple	GCMS-H	0.29	0.079	0.238	0.079	0.062
Acifluorfen	Herbicide		GCMS-H	0.64	0.079	0.085	0.079	0.062
Bentazon	Herbicide		GCMS-H	0.235	0.079	0.082	0.078	0.062
Bromoxynil	Herbicide		GCMS-H	0.16	0.079	0.093	0.079	0.062
Clopyralid	Herbicide		GCMS-H					0.062
Dacthal	Herbicide		GCMS-H	0.125	0.079	0.081	0.079	0.062
Dicamba I	Herbicide		GCMS-H	0.16	0.079	0.081	0.078	0.062
Dichlorprop	Herbicide		GCMS-H	0.17	0.079	0.081	0.079	0.062
Diclofop-Methyl	Herbicide		GCMS-H	0.24	0.079	0.081	0.079	0.062
Dinoseb	Herbicide		GCMS-H	0.24	0.079	0.083	0.079	0.062
Ioxynil	Herbicide		GCMS-H	0.16	0.079	0.103	0.079	0.062
MCPA	Herbicide		GCMS-H	0.315	0.079	0.081	0.079	0.062
MCPP	Herbicide		GCMS-H	0.315	0.079	0.077	0.079	0.062

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3] 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL	2007 LPQL
Pentachlorophenol	WP		GCMS-H	0.08	0.079	0.08	0.079	0.062
Picloram	Herbicide		GCMS-H	0.16	0.079	0.081	0.079	0.062
Triclopyr	Herbicide		GCMS	0.13	0.079	0.079	0.079	0.062
2,4'-DDD	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032	0.033
2,4'-DDE	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032	0.033
2,4'-DDT	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032	0.033
4,4'-DDD	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032	0.033
4,4'-DDE	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032	0.033
4,4'-DDT	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032	0.033
Acephate	Insecticide/OP		GCMS		1.594	1.5	0.032	
Alachlor	Herbicide		GCMS	0.335	0.112	0.12	0.032	0.033
Aldrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032	0.033
Alpha-BHC	Insecticide/OC		GCMS	0.018	0.079	0.077	0.032	0.033
Ametryn	Herbicide		GCMS	0.033	0.031	0.035		
Atraton	Herbicide		GCMS	0.052	0.047	0.048		
Atrazine	Herbicide		GCMS	0.039	0.032	0.037	0.032	0.033
Azinphos Ethyl	Insecticide/OP		GCMS	0.053	0.05	0.06	0.032	0.033
Azinphos methyl	Insecticide/OP		GCMS	0.053	0.05	0.052	0.032	0.033
Benefin	Herbicide		GCMS	0.05	0.047	0.208	0.032	0.033
Bensulide	Herbicide/OP		GCMS		14.187	1.5	0.032	0.033
Benthiocarb	Herbicide		GCMS					0.099
Benzamide, 2,6-dichloro-	Degradate/H-OP	Dichlobenil	GCMS	0.22				
Beta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.076	0.032	0.033
Bolstar	Insecticide/OP		GCMS	0.023	0.022	0.034		
Bromacil	Herbicide		GCMS	0.135	0.126	0.126	0.032	0.034
Butachlor	Herbicide		GCMS	0.199	0.189	0.185		
Butylate	Herbicide		GCMS	0.066	0.063	0.08	0.032	0.033
Captafol	Fungicide		GCMS	0.063	0.394	0.41		
Captan	Fungicide		GCMS	0.089	0.213	0.21	0.032	0.033
Carbophenothion	Insecticide/OP		GCMS	0.033	0.031	0.049		
Carboxin	Fungicide		GCMS	0.199	0.189	0.186	0.032	0.033
Chlorothalonil	Herbicide		GCMS	0.079	0.075	0.084	0.032	0.033
Chlorpropham	Herbicide		GCMS	0.132	0.127	0.121	0.032	0.033
Chlorpyrifos	Insecticide/OP		GCMS	0.026	0.025	0.029	0.032	0.033
Cis-Chlordane	Insecticide/OC		GCMS	0.017	0.079	0.083	0.032	0.033
Cis-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.258	0.032	0.033
cis-Permethrin	Insecticide/Py		GCMS					0.05
Coumaphos	Insecticide/OP		GCMS		1.504	1.497	0.032	0.033
Cyanazine	Herbicide		GCMS	0.05	0.047	0.051	0.032	0.033
Cycloate	Herbicide		GCMS	0.066	0.063	0.067	0.032	0.033
Delta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.078	0.032	0.033
Deltamethrin	Insecticide/Py		GCMS					0.098
Demeton (O+S)	Insecticide/OP		GCMS			0.023		
Demeton-O	Insecticide/OP		GCMS	0.033	0.022	0.022		

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3] 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL	2007 LPQL
Demeton-S	Insecticide/OP		GCMS	0.033	0.022	0.093		
Di-allate	Herbicide		GCMS	0.345	0.221	0.211	0.032	0.033
Diazinon	Insecticide		GCMS	0.027	0.026	0.032	0.032	0.033
Dichlobenil	Herbicide		GCMS	0.065	0.063	0.068	0.032	0.033
Dichlorvos	Insecticide/OP							0.055
Dicofol	Insecticide/OC		GCMS	0.051	0.315	0.274	0.319	
Dieldrin	Insecticide/OC		GCMS	0.018	0.079	0.076	0.08	0.05
Dimethoate	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032	0.033
Diphenamid	Herbicide		GCMS	0.099	0.094	0.091	0.032	0.033
Disulfoton	Insecticide/OP		GCMS	0.02	0.019	0.035	0.032	0.033
Disulfoton sulfone	Degradate/I-OP	Disulfoton	GCMS					0.099
Diuron	Herbicide		GCMS	0.195	0.189	0.19	0.033	0.056
Endosulfan I	Insecticide/OC		GCMS	0.018	0.079	0.083	0.08	0.05
Endosulfan II	Insecticide/OC		GCMS	0.018	0.079	0.083	0.08	0.05
Endosulfan Sulfate	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032	0.033
Endrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.08	0.05
Endrin Aldehyde	Degradate/OC	Endrin	GCMS	0.018	0.079	0.083	0.08	0.05
Endrin Ketone	Degradate/OC	Endrin	GCMS	0.018	0.079	0.077	0.032	0.033
EPN	Insecticide/OP		GCMS	0.033	0.031	0.036	0.032	0.033
Eptam	Herbicide		GCMS	0.066	0.063	0.064	0.032	0.033
Ethalfluralin	Herbicide		GCMS	0.05	0.047	0.047	0.032	0.033
Ethion	Insecticide/OP		GCMS	0.023	0.022	0.023	0.032	0.033
Ethoprop	Insecticide/OP		GCMS	0.027	0.025	0.029	0.032	0.033
Fenamiphos	Insecticide/OP		GCMS	0.05	0.047	0.054	0.032	0.033
Fenarimol	Fungicide		GCMS	0.099	0.094	0.091	0.032	0.033
Fenitrothion	Insecticide/OP		GCMS	0.023	0.022	0.024		
Fensulfothion	Insecticide/OP		GCMS	0.033	0.031	0.032		
Fenthion	Insecticide/OP		GCMS	0.023	0.022	0.026		
Fenvalerate (2 isomers)	Insecticide/Py		GCMS			0.083	0.032	0.033
Fluridone	Herbicide		GCMS	0.199	0.189	0.18	0.064	0.099
Fonofos	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032	0.033
Gamma-BHC	Insecticide/OC		GCMS	0.018	0.079	0.082	0.032	0.033
Heptachlor	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032	0.033
Heptachlor Epoxide	Degradate/OC	Heptachlor	GCMS	0.018	0.079	0.083	0.032	0.033
Hexachlorobenzene	Fungicide		GCMS	0.018	0.079	0.079	0.032	0.033
Hexazinone	Herbicide		GCMS	0.05	0.047	0.048	0.08	0.05
Imidan	Insecticide/OP		GCMS	0.036	0.035	0.041	0.032	0.033
Malathion	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032	0.294
Merphos (1 & 2)	Herbicide/OP		GCMS	0.04	0.038	0.055		0.055
Metalaxyl	Fungicide		GCMS	0.199	0.189	0.34	0.032	0.033
Methamidophos	Insecticide/OP		GCMS		1.594	1.7	0.032	0.033
Methidathion	Insecticide/OP		GCMS		1.594	1.47	0.319	0.294
Methoxychlor	Insecticide/OC		GCMS	0.088	0.079	0.076	0.032	0.033
Methyl Chlorpyrifos	Insecticide/OP		GCMS	0.027	0.025	0.026	0.032	0.033

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3] 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL	2007 LPQL
Methyl Paraoxon	Degradate/I-OP	Methyl Parathion	GCMS					0.099
Methyl Parathion	Insecticide/OP		GCMS	0.023	0.022	0.034	0.032	0.033
Metolachlor	Herbicide		GCMS	0.133	0.127	0.121	0.032	0.033
Metribuzin	Herbicide		GCMS	0.033	0.031	0.056	0.032	0.033
Mevinphos	Insecticide-OP		GCMS					0.05
MGK264	Synergist/I		GCMS	0.263	0.252	0.26	0.032	0.033
Mirex	Insecticide/OC		GCMS	0.018	0.079	0.081	0.032	0.033
Molinate	Herbicide		GCMS	0.066	0.063	0.223		
Monocrotophos	Insecticide/OP		GCMS					0.05
Naled	Insecticide/OP		GCMS		1.594	1.502	0.032	0.039
Napropamide	Herbicide		GCMS	0.099	0.094	0.096	0.08	0.05
Norflurazon	Herbicide		GCMS	0.066	0.063	0.071	0.032	0.033
Oryzalin	Herbicide		GCMS					0.098
Oxychlordane	Degradate/OC	Chlordane	GCMS	0.018	0.079	0.088	0.032	0.033
Oxyfluorfen	Herbicide		GCMS	0.134	0.127	0.121	0.032	0.033
Parathion	Insecticide/OP		GCMS	0.027	0.025	0.03	0.032	0.033
Pebulate	Herbicide		GCMS	0.066	0.063	0.064	0.032	0.033
Pendimethalin	Herbicide		GCMS	0.05	0.046	0.051	0.032	0.033
Pentachloroanisole	Degradate/WP	PCP	GCMS	0.018	0.079	0.08		
Pentachlorophenol (PCP)	WP		GCMS	0.08	0.079	0.08	0.08	
Phenothrin	Insecticide/Py		GCMS			0.061	0.032	0.033
Phorate	Insecticide/OP		GCMS	0.023	0.022	0.029	0.319	0.295
Profluralin	Herbicide		GCMS	0.079	0.075	0.081		
Prometon	Herbicide		GCMS	0.032	0.031	0.033	0.032	0.033
Prometryn	Herbicide		GCMS	0.033	0.031	0.043	0.032	0.033
Pronamide	Herbicide		GCMS	0.169	0.127	0.127	0.032	0.033
Propachlor	Herbicide		GCMS	0.079	0.075	0.078	0.032	0.033
Propargite	Insecticide/SE		GCMS	0.066	0.063	0.063	0.032	0.033
Propazine	Herbicide		GCMS	0.033	0.031	0.035	0.032	0.033
Resmethrin	Insecticide/SE		GCMS			0.061	0.064	0.05
Ronnel	Insecticide/OP		GCMS	0.023	0.022	0.024		
Simazine	Herbicide		GCMS	0.033	0.031	0.031	0.032	0.033
Simetryn	Herbicide		GCMS					0.099
Sulfotepp	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032	0.033
Tebuthiuron	Herbicide		GCMS	0.05	0.047	0.054	0.037	0.033
Terbacil	Herbicide		GCMS	0.099	0.093	0.09	0.032	0.033
Terbutryn	Herbicide		GCMS	0.033	0.031	0.035		
Tetrachlorvinphos	Insecticide/OP		GCMS					0.05
Tokuthion	Insecticide/OP		GCMS					0.05
Tralomethrin	Insecticide/Py		GCMS					0.098
Trans-Chlordane	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032	0.033
Trans-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.08	0.032	0.033
Triadimefon	Fungicide		GCMS	0.086	0.082	0.087	0.032	0.033

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3] 2003 LPQL	2004 LPQL	2005 LPQL	2006 LPQL	2007 LPQL
Triallate	Herbicide		GCMS	0.099	0.094	0.098	0.032	0.033
Trifluralin	Herbicide		GCMS	0.05	0.047	0.054	0.032	0.033
Trichloronat	Insecticide/OP		GCMS					0.05
Vernolate	Herbicide		GCMS	0.066	0.063	0.066		

[1] C = carbamate, H = herbicide, I = insecticide, OC = organochlorine, OP = organophosphorus, Py = pyrethroid, SE = sulfite ester, WP = wood preservative.

[2] LCMS = High performance liquid chromatography/mass spectroscopy. Carbamate analyses run by HPLC in 2003. 2003 results run by PSC/Maxxum analytical laboratory in Vancouver, BC.
GCMS = Gas chromatography/mass spectroscopy. 2003 results run by GCMS and Atomic Emission Detection (AED).
GCMS-H = Herbicide GCMS method SW 846 8270M has been used throughout this project.

[3] Washington State Department of Agriculture. Average of lower performance (reporting) values, per analyte for all batches over each study year (14-31 batches per year).
LPQL: Lower performance practical quantitation limit.

Results for pesticide replicate samples are presented in Tables B-3 and B-4.

Table B-3 presents the data value, data qualification (if assigned), and relative percent difference (RPD) between the quantitated values for pesticides which were consistently identified in both the sample and replicate. Consistent identification refers to pesticides which had a positive identification and includes all flag codes except U and UJ. Inconsistently identified replicate pairs are those in which the compound was identified in one sample but not the other.

Inconsistently identified replicate pairs are presented in Table B-4.

Table B-3. Consistently identified, field replicate results (µg/L).

Chemical	Sample		Replicate		RPD
2,4-D	0.16	NJ	0.16	NJ	0.00
2,4-D	0.023	NJ	0.023	NJ	0.00
2,4-D	0.075		0.068		9.79
2,4-D	0.11	NJ	0.11	NJ	0.00
2,4-D	0.13		0.15		14.29
				Mean =	4.82
4,4'-DDD	0.015	J	0.016	J	6.45
4,4'-DDE	0.012	J	0.016	J	28.57
4,4'-DDE	0.0099	J	0.014	J	34.31
				Mean =	23.11
4,4'-DDT	0.023	J	0.024	J	4.26
4,4'-DDT	0.025	J	0.025	J	0.00
				Mean =	2.13
Atrazine	0.034		0.034		0.00
Atrazine	0.021	J	0.021	J	0.00
Atrazine	0.0087	J	0.0087	J	0.00
Atrazine	0.0075	J	0.0082	J	8.92
Atrazine	0.014	J	0.013	J	7.41
				Mean =	3.26
Azinphos methyl	0.53	J	0.52	J	1.90
Bentazon	0.091	NJ	0.086	NJ	5.65
Bentazon	0.048	J	0.044	J	8.70
				Mean =	7.17
Bromacil	0.072	J	0.062	J	14.93
Bromoxynil	0.019	NJ	0.016	NJ	17.14
Carbaryl	0.188	J	0.208	J	10.10
Chlorpyrifos	0.029	J	0.03	J	3.39
Chlorpyrifos	0.0061	J	0.0064	J	4.80
Chlorpyrifos	0.074		0.075		1.34
				Mean =	3.18
Dacthal (DCPA)	0.075		0.072		4.08
Dacthal (DCPA)	0.02	J	0.027	J	29.79
				Mean =	16.93

Chemical	Sample		Replicate		RPD
Dicamba I	0.0034	J	0.0044	J	25.64
Dicamba I	0.017	J	0.02	J	16.22
Dicamba I	0.035	J	0.039	J	10.81
				Mean =	17.56
Dichlobenil	0.019	J	0.018	J	5.41
Dichlobenil	0.037	NJ	0.035	NJ	5.56
Dichlobenil	0.037	NJ	0.036	NJ	2.74
Dichlobenil	0.022	J	0.021	J	4.65
				Mean =	4.59
Disulfoton sulfone	0.056	NJ	0.049	NJ	13.33
Diuron	0.079		0.063		22.54
Endosulfan I	0.1		0.092		8.33
Endosulfan II	0.067		0.074		9.93
Endosulfan sulfate	0.029	NJ	0.03	NJ	3.39
Endosulfan sulfate	0.072		0.074		2.74
				Mean =	3.06
Eptam	0.024	J	0.023	J	4.26
Malathion	0.082		0.081		1.23
Malathion	0.02	J	0.02	J	0.00
				Mean =	0.61
MCPP (Mecoprop)	0.065	NJ	0.076	NJ	15.60
MCPP (Mecoprop)	0.028	NJ	0.021	NJ	28.57
				Mean =	22.09
Norflurazon	0.053	NJ	0.05	NJ	5.83
Pendimethalin	0.035		0.034		2.90
Pendimethalin	0.05		0.049		2.02
				Mean =	2.46
Pentachlorophenol	0.029	NJ	0.02	NJ	36.73
Picloram	0.14	NJ	0.11	NJ	24.00
Simazine	0.027	NJ	0.027	NJ	0.00
Simazine	0.048	NJ	0.031	NJ	43.04
				Mean =	21.52
Tebuthiuron	0.18	J	0.15	J	18.18
Terbacil	0.11		0.084		26.80
Terbacil	0.12		0.12		0.00
Terbacil	0.31		0.3		3.28
				Mean =	10.03
Treflan (Trifluralin)	0.021	J	0.022	J	4.65
Treflan (Trifluralin)	0.025	J	0.025	J	0.00
				Mean =	2.33

Table B-4. Inconsistently identified, field replicate results (µg/L).

Chemical	Sample		Replicate		RPD
1-Naphthol	0.011	J	0.05	U	127.87
2,4-D	0.26		0.061	U	123.99
2,4-D	0.023	NJ	0.06	U	89.16
4-Nitrophenol	0.11	NJ	0.062	U	55.81
4-Nitrophenol	0.077		0.063	U	20.00
4-Nitrophenol	0.11	NJ	0.081	J	30.37
Atrazine	0.013	NJ	0.014	J	7.41
Atrazine	0.0063	NJ	0.032	U	134.20
Bentazon	0.056	J	0.064		13.33
Bentazon	0.047	NJ	0.05	J	6.19
Bentazon	0.063	U	0.034	NJ	59.79
Bentazon	0.11		0.11	NJ	0.00
Bromacil	0.019	J	0.019	NJ	0.00
Bromacil	0.038	NJ	0.038		0.00
Chlorpyrifos	0.02	J	0.02	NJ	0.00
Clopyralid	0.046	NJ	0.04	J	13.95
Dacthal (DCPA)	0.074	NJ	0.074		0.00
MCPA	0.025	NJ	0.061	U	83.72
MCPA	0.061	U	0.015	NJ	121.05
Methiocarb	0.016	J	0.02	U	22.22
Norflurazon	0.032	U	0.027	J	16.95
Oxamyl oxime	0.02	U	0.018	J	10.53
Promecarb	0.015	J	0.02	U	28.57
Prometon (Pramitol 5p)	0.033	U	0.017	NJ	64.00
Simazine	0.0067	J	0.031	U	128.91
Simazine	0.019	J	0.033	U	53.85
Simazine	0.033	U	0.021	NJ	44.44
Terbacil	0.025	J	0.024	NJ	4.08
Terbacil	0.032	U	0.015	NJ	72.34
Treflan (Trifluralin)	0.014	J	0.033	U	80.85
					Mean = 47.12

Surrogate analyses evaluate accuracy of recovery for a group of pesticides, and are analyzed in each sample set. For instance, triphenyl phosphate (TPP) is a surrogate for organophosphorus insecticides (Table B-5).

Table B-5. Surrogate pesticides.

Surrogate Compound	Surrogate
1,3-Dimethyl-2-nitrobenzene	N-Pesticide
2,4,6-Tribromophenol	Herbicide
2,4-Dichlorophenylacetic acid	Herbicide
4,4'-DDE-d8	Cl-Pesticide
Carbaryl C13	Carbamate
Decachlorobiphenyl (DCB)	Cl-Pesticide
gamma-BHC-d6	Cl-Pesticide
Triphenyl Phosphate	OP-Pesticide

N = nitrogen containing.
Cl = chlorinated.
OP = organophosphate.

The median recovery of TPP standards is 67%, while one standard deviation (σ – edges of box) of values fall within 50% to 91%, and 2 σ (whiskers) of values fall within 29 to 112% (Figure B-1).

Laboratory control samples (LCS) evaluate accuracy of pesticide residue recovery for a specific pesticide and are applied on a rotating basis. The majority of LCS in Figure B-2 fall within 80-120% recovery, well within the acceptable range of 40-150% (EPA, 2005; Burke et al., 2005, 2006; Burke and Anderson, 2006).

A range of 15-80 LCS tests were applied for each of 150 separate pesticide residues. Residues with less than 30 tests must be evaluated as estimates because they do not meet requirements of the central limit theorem. Two such residues include the herbicide diuron and the insecticide azinphos methyl. The median recoveries of the products are 109 and 82%, respectively, yet large outliers skew the standard deviation of both products to show low 2σ (2.5% of lower values) evaluations. In the case of outlier recoveries, representative detected pesticides are qualified as estimates or rejected, depending on the degree of recovery.

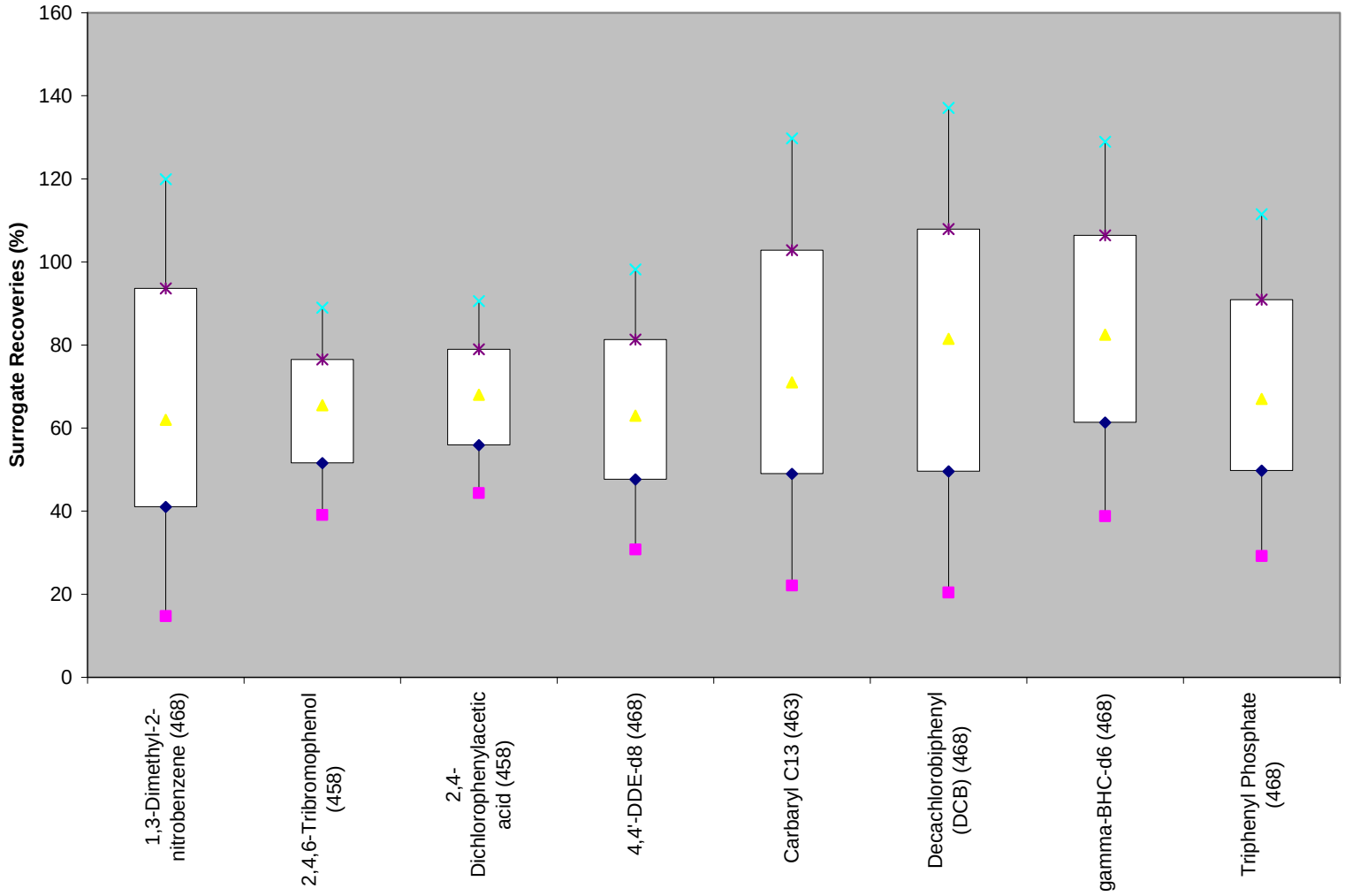

Figure B-1. Selected 2007 surrogate recovery data. Triangle represents the median; box defines one standard deviation; and whiskers are two standard deviations.

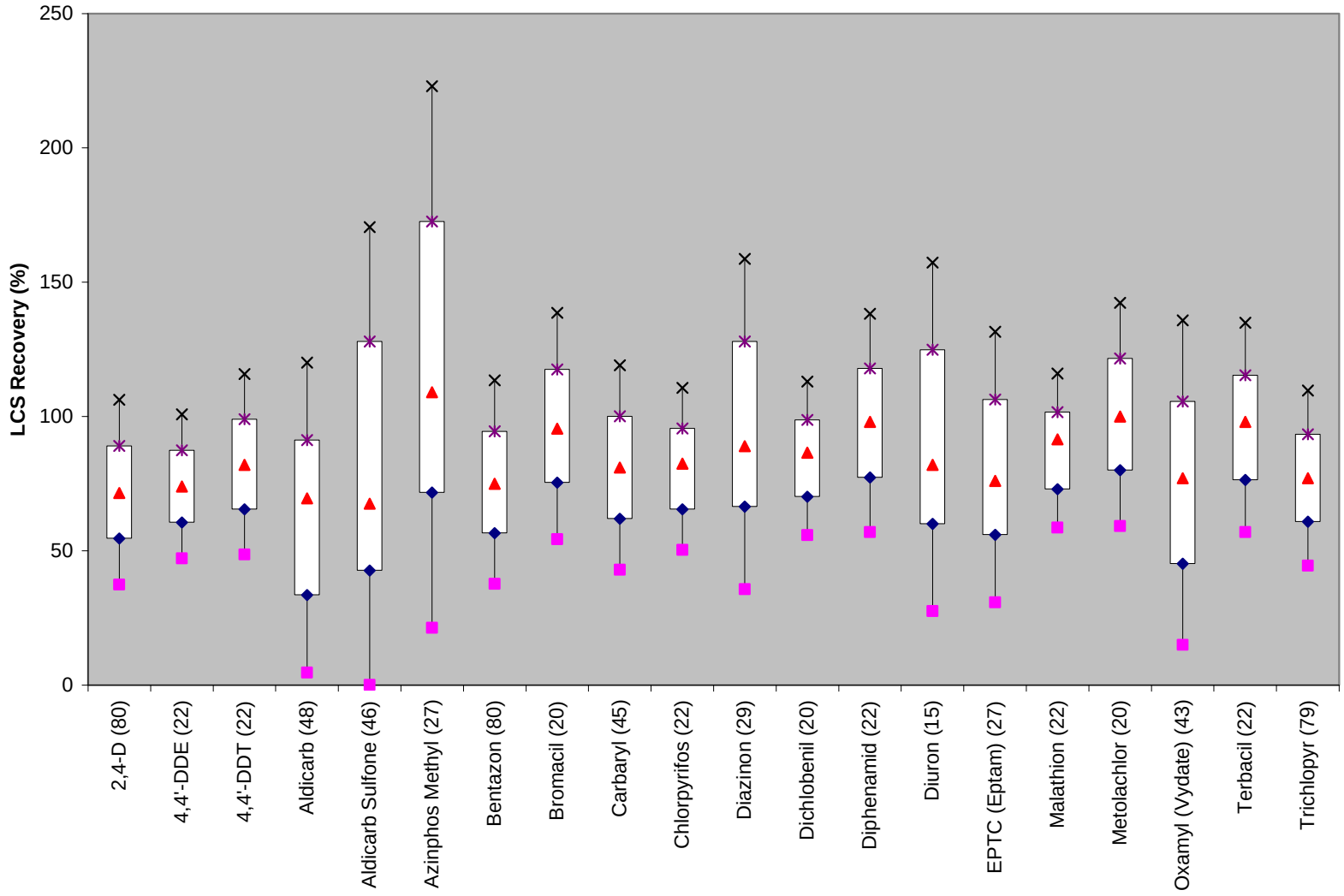

Figure B-2. Selected 2007 laboratory control sample (LCS) recovery data. Triangle is the median; box defines one standard deviation; and whiskers are two standard deviations.

Results of matrix spike/matrix spike duplicates (MS/MSDs) reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. This measure is the best overall indicator of accuracy, precision, and reproducibility of the entire sampling process. MS/MSD results and relative percent difference (RPD) for pairs of pesticides are presented in Table B-6.

Table B-6. Matrix spike/matrix spike duplicate results for selected pesticides (%).

Chemical	MS	MSD	RPD
2,4-D	70	73	4
	50	50	0
	57	57	0
	70	65	7
	72	84	15
	76	70	8
	50	47	6
	68	64	6
	54	72	29
	53	57	7
	47	44	7
	55	58	5
	59	61	3
	72	54	29
	7	89	171
	73	75	3
	66	69	4
	83	78	6
	60	68	13
	72	71	1
		Mean =	16
4,4'-DDT	78	83	6
	64	62	3
	39	31	23
	70	90	25
	43	53	21
	43	36	18
	59	49	19
	66	80	19
	50	67	29
	60	48	22
	93	73	24
	92	84	9
	45	54	18
		Mean =	18

Chemical	MS	MSD	RPD
Atrazine	91	80	13
	93	104	11
	95	94	1
	93	89	4
	107	104	3
	64	66	3
	77	63	20
	88	83	6
	85	71	18
	94	83	12
	115	109	5
	113	118	4
	59	88	39
		Mean =	11
Bentazon	58	61	5
	56	74	28
	73	69	6
	74	75	1
	58	57	2
	68	65	5
	73	65	12
	74	86	15
	77	73	5
	60	56	7
	47	44	7
	63	64	2
	60	65	8
	73	55	28
	5	80	176
	75	80	6
	70	74	6
	79	75	5
	70	77	10
	81	80	1
		Mean =	17
Bromacil	102	91	11
	102	111	8
	98	101	3
	103	123	18
	65	62	5
	76	76	0
	86	83	4
	99	93	6
	121	132	9
	99	97	2
	127	122	4
	63	90	35
		Mean =	9

Chemical	MS	MSD	RPD
Carbaryl	80	81	1
	125	94	28
	82	74	10
	45	43	5
	77	76	1
	59	77	26
	52	40	26
	60	59	2
	81	77	5
	72	72	0
	71	66	7
	63	56	12
	102	86	17
	67	57	16
	78	80	3
	74	62	18
	83	65	24
	79	79	0
	89	82	8
	91	102	11
	80	70	13
	104	91	13
	84	91	8
		Mean =	11
Chlorpyrifos	85	79	7
	74	80	8
	74	68	8
	86	75	14
	51	65	24
	58	54	7
	70	65	7
	54	67	21
	68	58	16
	68	60	13
	121	102	17
	93	89	4
	42	69	49
		Mean =	15
Dichlobenil	80	72	11
	88	112	24
	61	62	2
	53	66	22
	105	102	3
	73	58	23
	83	76	9
	88	90	2
	102	107	5
	77	49	44
	76	79	4

Chemical	MS	MSD	RPD
	75	73	3
	95	96	1
	53	72	30
		Mean =	13
Diphenamid	93	80	15
	86	91	6
	74	96	26
	80	85	6
	56	59	5
	72	74	3
	80	76	5
	97	92	5
	108	115	6
	120	110	9
	98	88	11
	118	115	3
	137	135	1
	70	98	33
		Mean =	10
Diuron	81	77	5
	89	88	1
	72	66	9
	74	74	0
	60	44	31
	89	90	1
	71	73	3
	253	245	3
		Mean =	7
Endosulfan I	90	76	17
	80	68	16
	48	74	43
	55	62	12
	67	67	0
	57	54	5
	91	76	18
	93	79	16
	54	73	30
	70	73	4
	84	66	24
	115	99	15
	128	132	3
	75	87	15
		Mean =	16
Methomyl	104	110	6
	102	144	34
	59	52	13
	43	39	10
	35	41	16
	17	5	109

Chemical	MS	MSD	RPD
	8	0	200
	51	51	0
	36	27	29
	46	33	33
	47	40	16
	31	46	39
	45	53	16
	48	46	4
	48	43	11
	33	44	29
	67	46	37
	111	89	22
	44	78	56
	77	72	7
	56	51	9
		Mean =	33
Oxamyl (Vydate)	225	217	4
	103	75	31
	127	130	2
	116	120	3
	109	117	7
	71	12	142
	70	92	27
	36	29	22
	96	77	22
	46	45	2
	94	134	35
	77	77	0
	12	24	67
	106	98	8
	84	131	44
	117	80	38
	45	45	0
	18	63	111
	51	33	43
	93	71	27
	63	67	6
	117	128	9
	42	55	27
		Mean =	29
Picloram	59	61	3
	48	46	4
	53	50	6
	53	47	12
	54	65	18
	52	55	6
	47	39	19
	65	63	3

Chemical	MS	MSD	RPD
	49	66	30
	43	43	0
	39	36	8
	41	45	9
	50	55	10
	55	39	34
	5	55	167
	58	59	2
	73	77	5
	76	78	3
	50	59	17
	76	76	0
		Mean =	18
Tebuthiuron	103	105	2
	138	135	2
	109	106	3
	130	120	8
	140	150	7
	148	163	10
	150	140	7
	140	129	8
	156	150	4
	124	126	2
	26	48	59
		Mean =	10
Terbacil	108	94	14
	108	116	7
	76	79	4
	82	89	8
	73	73	0
	83	79	5
	89	86	3
	100	95	5
	110	115	4
	120	98	20
	98	89	10
	126	122	3
	110	108	2
	55	84	42
		Mean =	9

Appendix C. Aldicarb Sulfone Memorandum from Manchester Environmental Laboratory

March 18, 2008

TO: Jim Cowles, Ph.D
Washington State Department of Agriculture

Deborah Sargeant
Washington State Department of Ecology

THROUGH: Stuart Magoon
Washington State Department of Ecology

FROM: John Weakland
Washington State Department of Ecology

SUBJECT: **Presence of Aldicarb sulfone in method blanks for CY 2007**

This memorandum describes the presence of Aldicarb sulfone in method blanks. It discusses the history of the interference, what we have and are doing to reduce it, and the impact on sample results.

History of aldicarb sulfone in method blanks. Historically we saw an intermittent peak in the area of the Aldicarb sulfone below our reporting limit. The peak was too low and did not affect results. Prior to calendar year (CY) 2007 however, we installed the LCMS hardware upgrade to achieve lower reporting limits and noticed problems with the peak.

The upgrade increased our sensitivity and reduced our reporting limits in half from 0.10µg/L to 0.050µg/L. With the increased sensitivity, we saw Aldicarb sulfone in some of our samples and method blanks. The interfering peak ionizes and has a similar mass to Aldicarb sulfone and therefore reported as a detected analyte.

The amount found in method blanks for CY 2007 year varied from "not detected" at 0.020µg/L to as high as 0.10µg/L. We reported detections of Aldicarb sulfone in 29 of the 74 reported method blanks for the CY 2007.

What we have done and are doing to eliminate method blank background. We evaluated all of the materials and solvents used in our analytical process and could not locate the source. The amount of interference fluctuates and is inconsistent from sample to sample. Analysis of lab control sample and matrix spikes show the peak as a distinct shoulder on the Aldicarb sulfone peak.

With certain notable exceptions, the interference appeared to be higher in the spring and early summer than later in the fall. It could be at a fairly consistent level then spike up to almost two fold then drop back down.

Chromatographically we tried to alter the retention times so the interference would separate from the Aldicarb sulfone. Because it is very water soluble, we could not alter the retention times without adding length to our analytical column. Lengthening the column significantly increases the analytical run time.

We wanted to evaluate the interference peak using EPA's LC MS/MS but could not schedule a good time. We will work with EPA to analyze some of our samples and method blanks. We hope using the LC MS/MS will verify the peak is not Aldicarb sulfone and point to a potential source of the interference.

For unrelated reasons, we are switching from electro spray to APCI during CY 2008 for some our selective ion monitoring (SIM) windows. We hope the switch will stabilize our more difficult compounds. Because Aldicarb sulfone is in one of these SIM windows, we will evaluate if changing the ionization decreases our interference.

Impact on sample results. The interference inhibits our ability to accurately quantify Aldicarb sulfone at low levels. We compare the detections of Aldicarb sulfone in samples with the associated method blank to minimize reporting false positives. For CY 2007, we raised the reporting limits for 292 out of 541 total samples.

We use the "five times rule" when comparing sample results with the associated method blank:

- If the amount in the sample is *less* than 5 times the associated method blank, the reporting limit is raised to the level detected and reported UJ, not detected at the estimated reporting limit.
- If the amount in the sample is *greater* than 5 times the associated method blank, the sample result is reported detected at the amount found. In these instances, the amount of the suspected contamination is considered insignificant relative to the amount native to the sample.

We reported two samples with detections for Aldicarb sulfone in CY 2007. Both of the samples contained Aldicarb sulfone at more than five times the amount detected in their associated method blanks. This indicates Aldicarb sulfone is native to the samples and laboratory contamination is less significant.

Appendix D. Continuous Temperature Profiles

Temperature measurements were made at 30-minute intervals for the duration of the 2007 analysis.

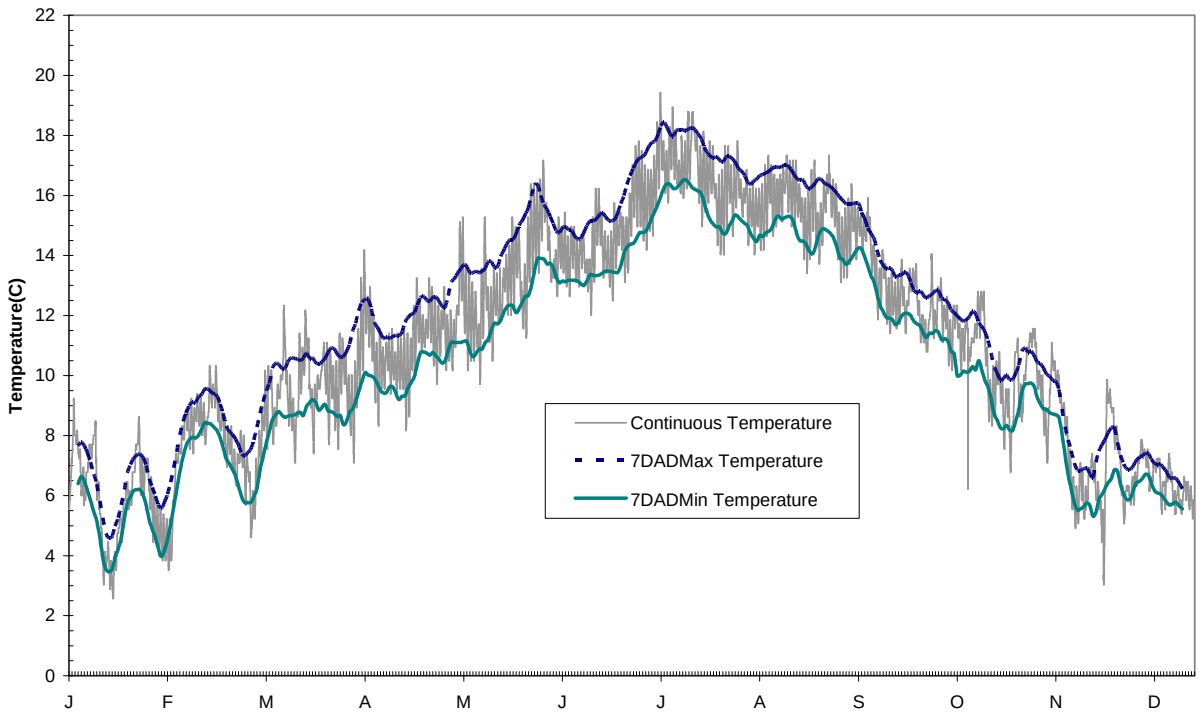

Figure D-1. 2007 continuous temperature profile for the North Fork of Thornton Creek.

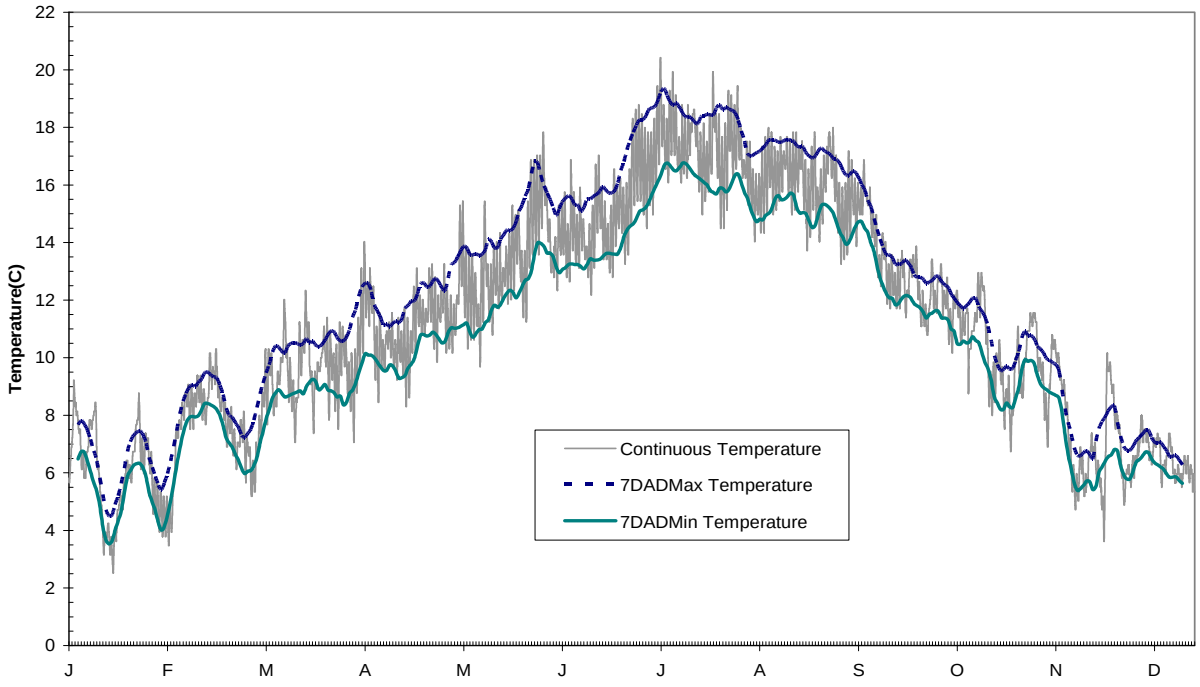

Figure D-2. 2007 continuous temperature profile for the mainstem of Thornton Creek.

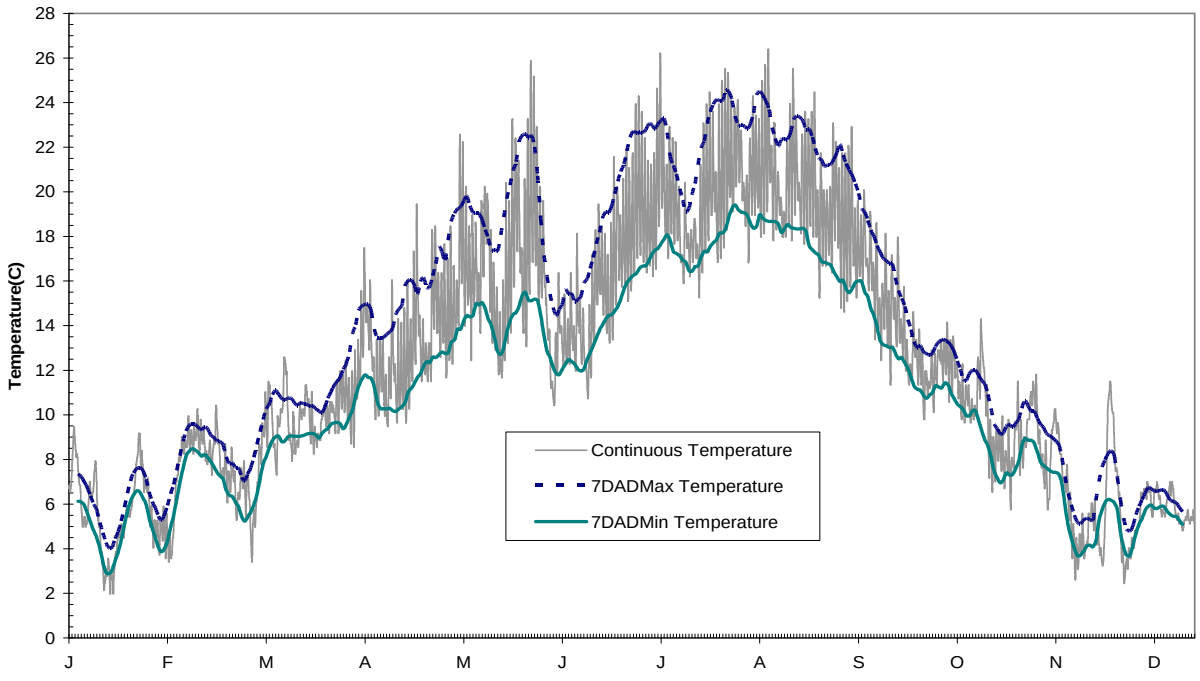

Figure D-3. 2007 continuous temperature profile for lower Big Ditch Slough.

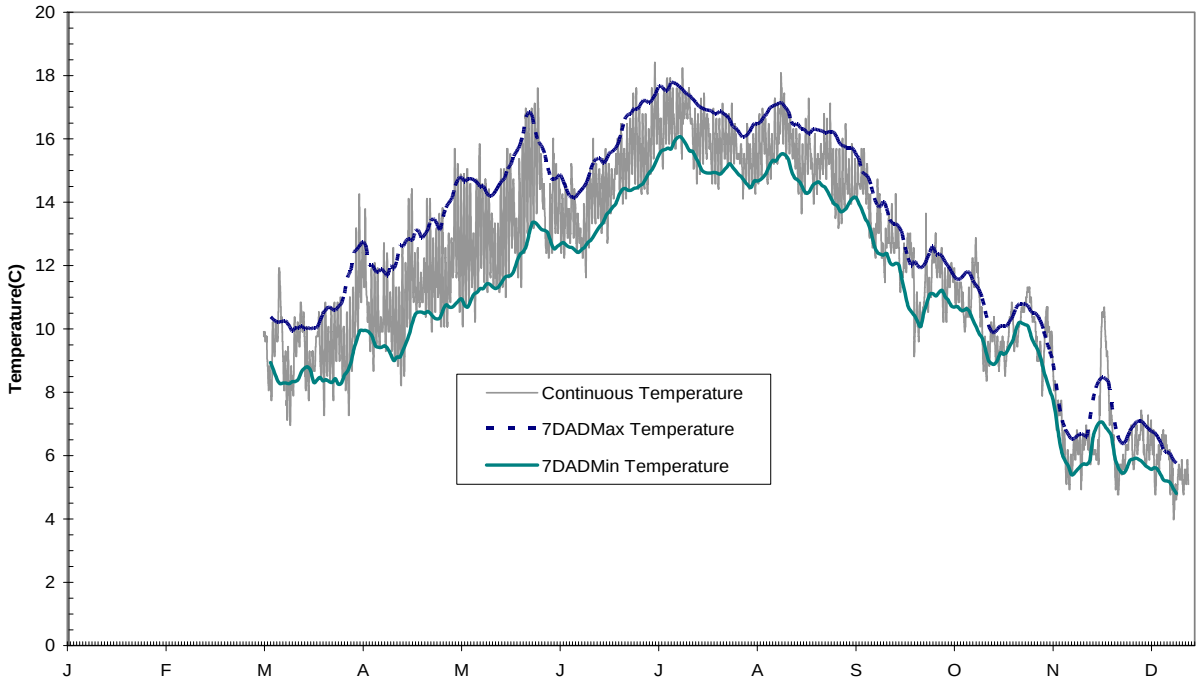

Figure D-4. 2007 continuous temperature profile for upper Big Ditch Slough.

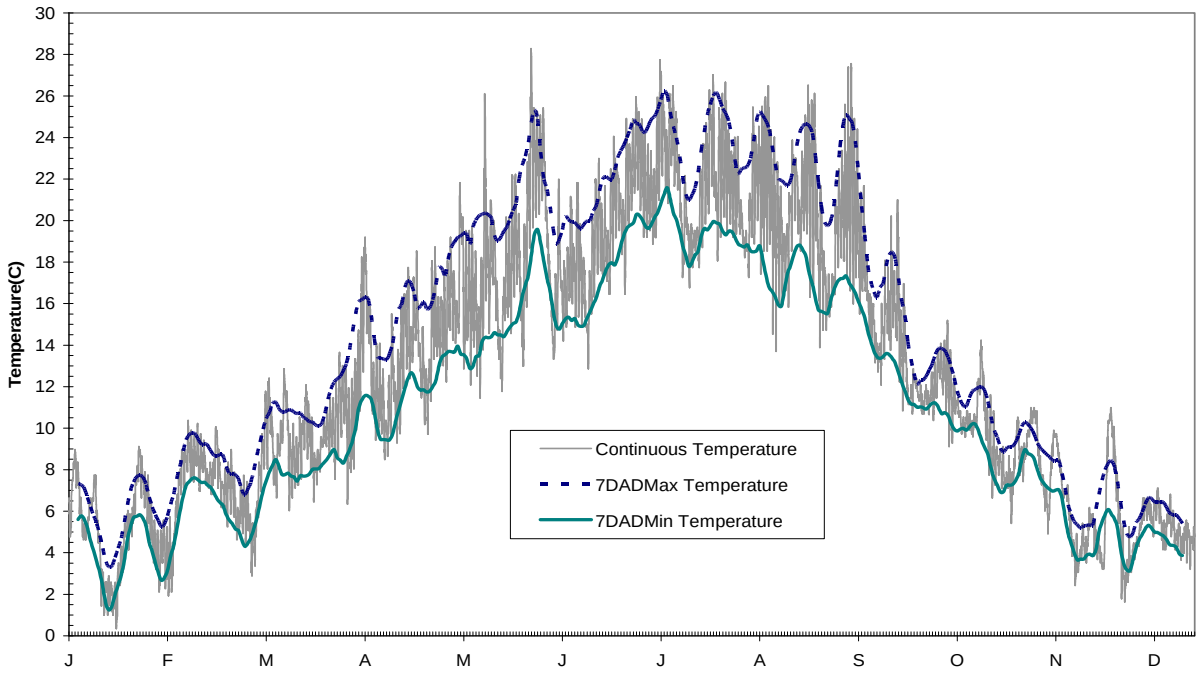

Figure D-5. 2007 continuous temperature profile for Browns Slough.

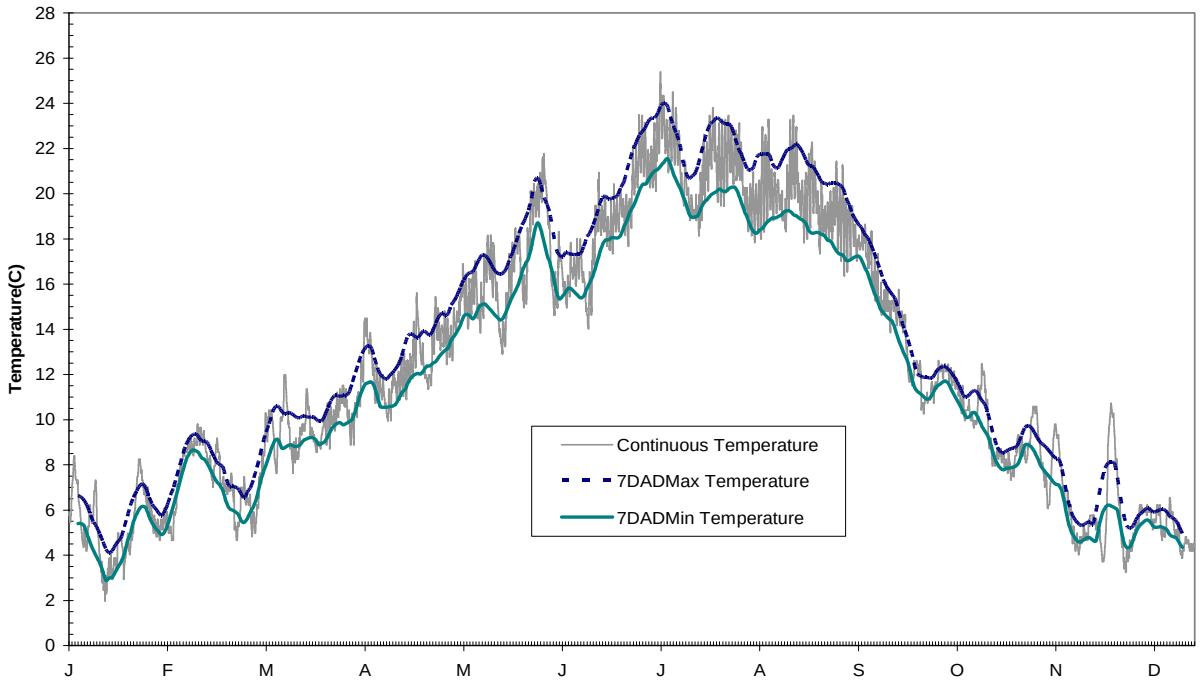

Figure D-6. 2007 continuous temperature profile for Indian Slough.

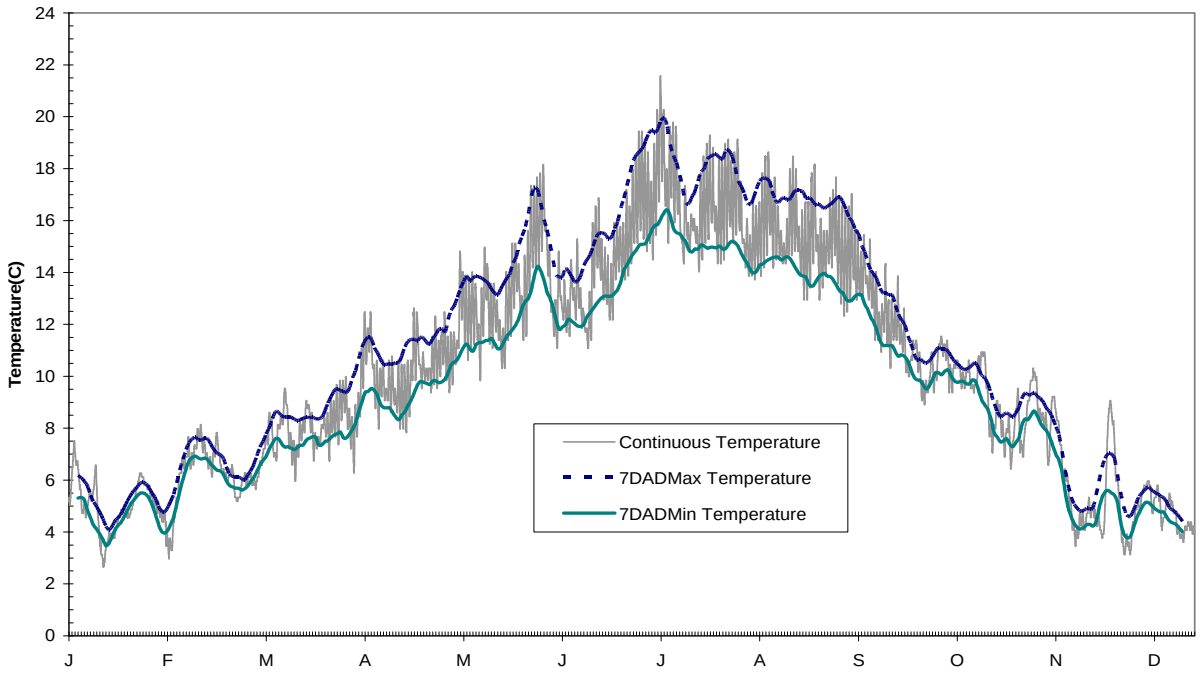

Figure D-7. 2007 continuous temperature profile for the Samish River.

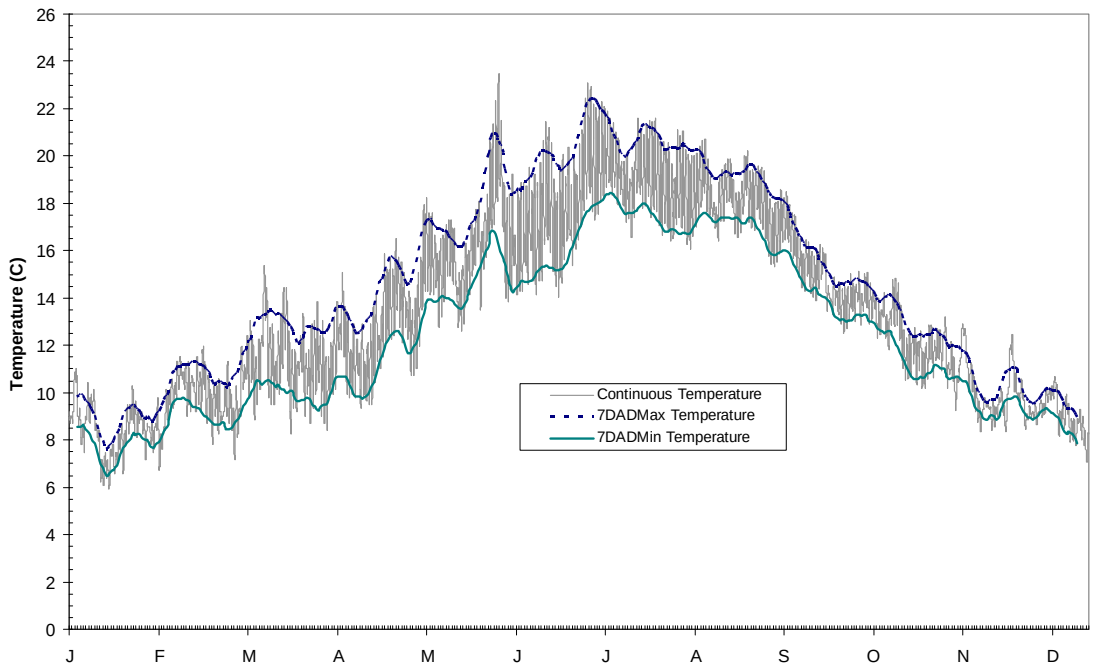

Figure D-8. 2007 continuous temperature profile for the Marion Drain.

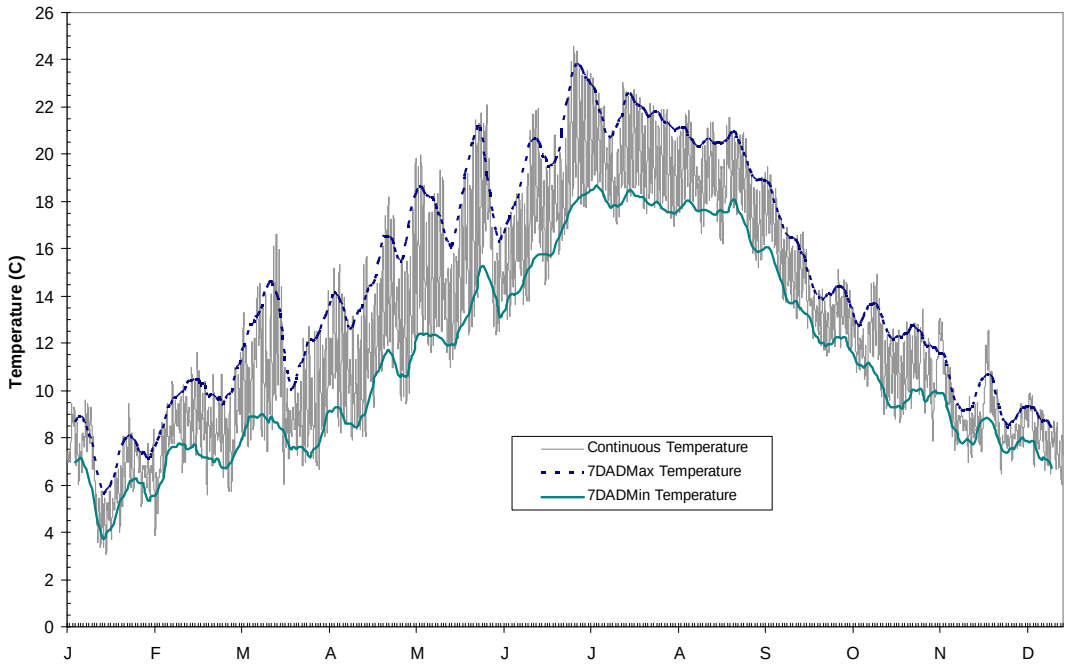

Figure D-9. 2007 continuous temperature profile for the Sulphur Creek Wasteway.

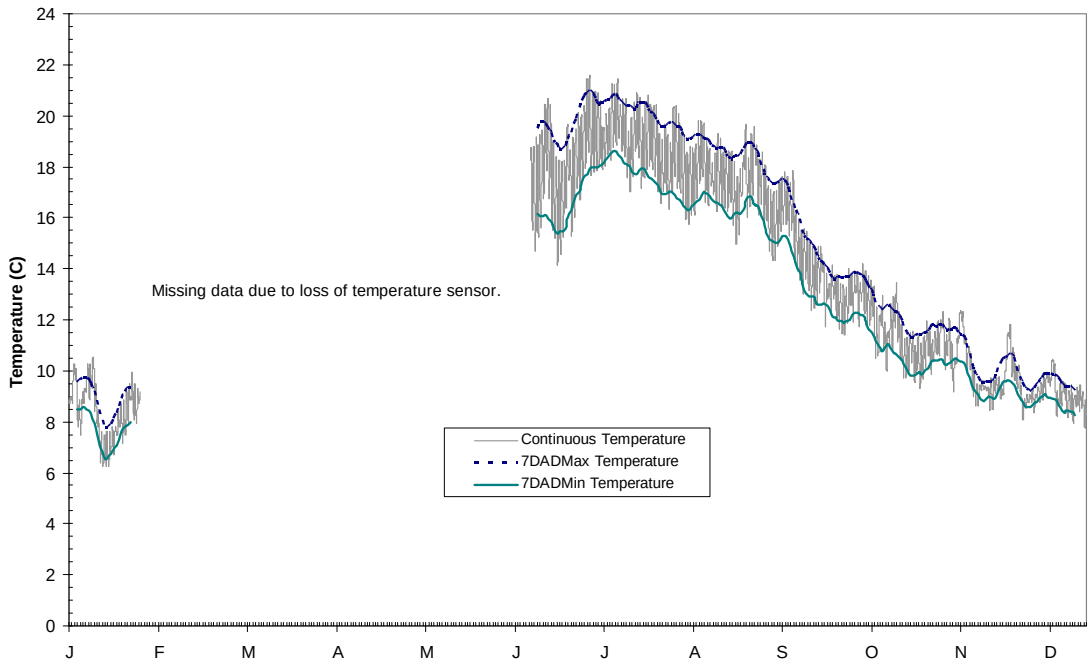

Figure D-10. 2007 continuous temperature profile for upper Spring Creek.

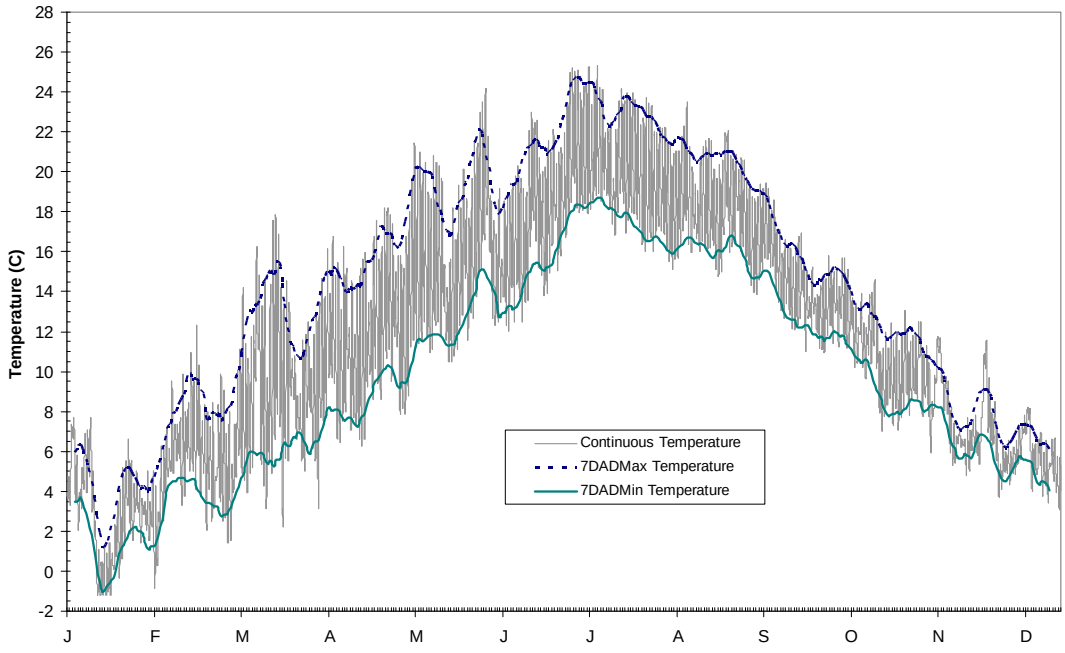

Figure D-11. 2007 continuous temperature profile for lower Spring Creek.

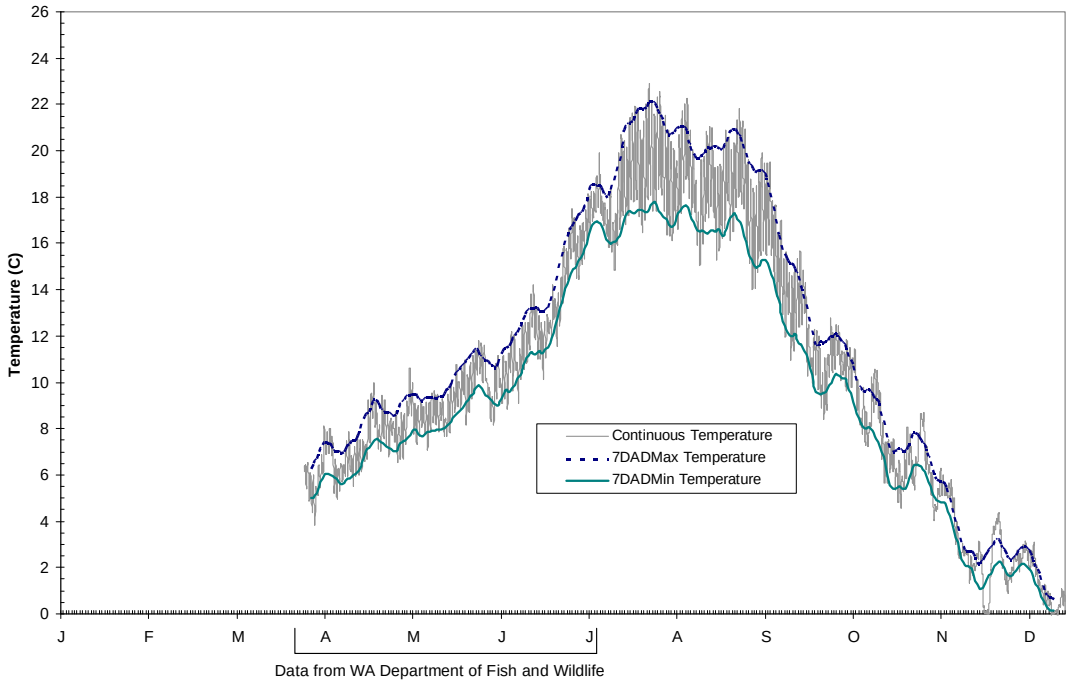

Figure D-12. 2007 continuous temperature profile for the Wenatchee River.

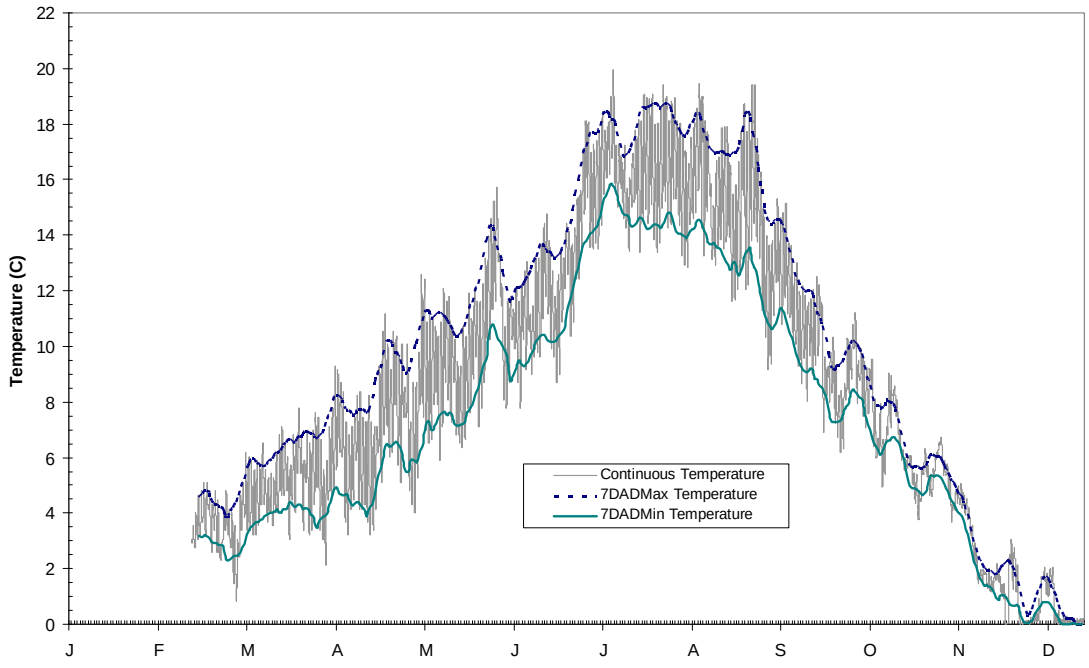

Figure D-13. 2007 continuous temperature profile for Mission Creek.

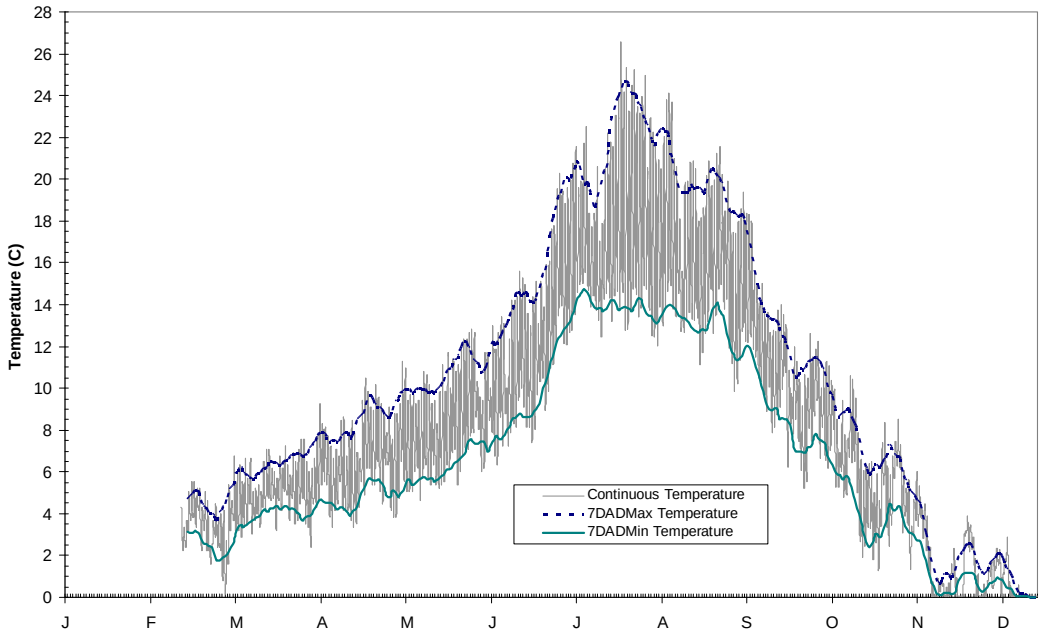

Figure D-14. 2007 continuous temperature profile for Peshastin Creek.

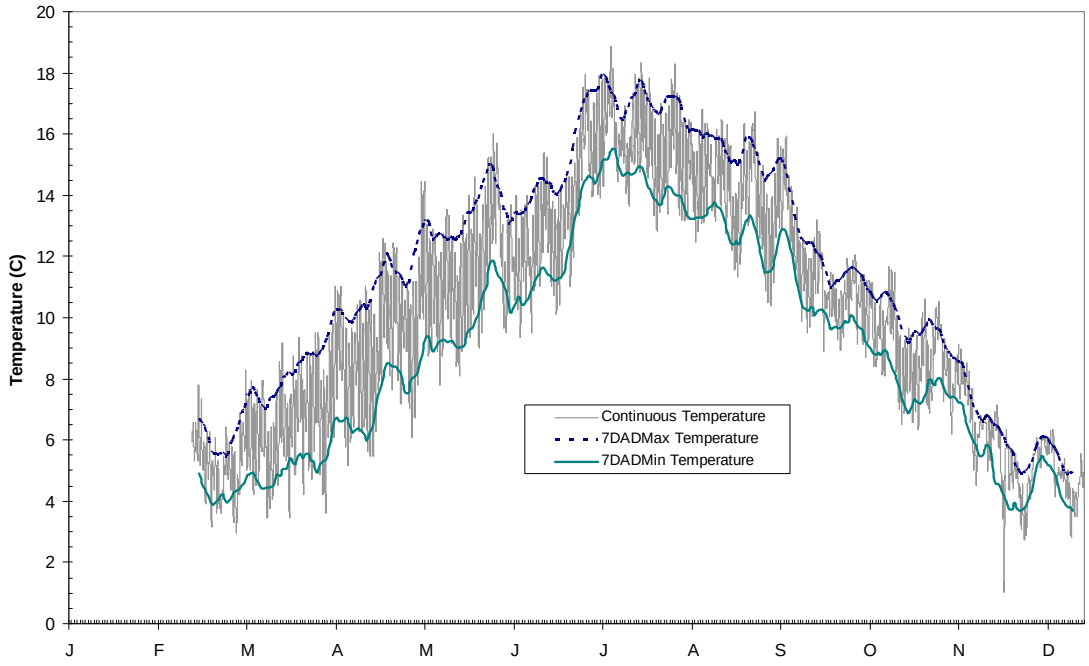

Figure D-15. 2007 continuous temperature profile for Brender Creek.

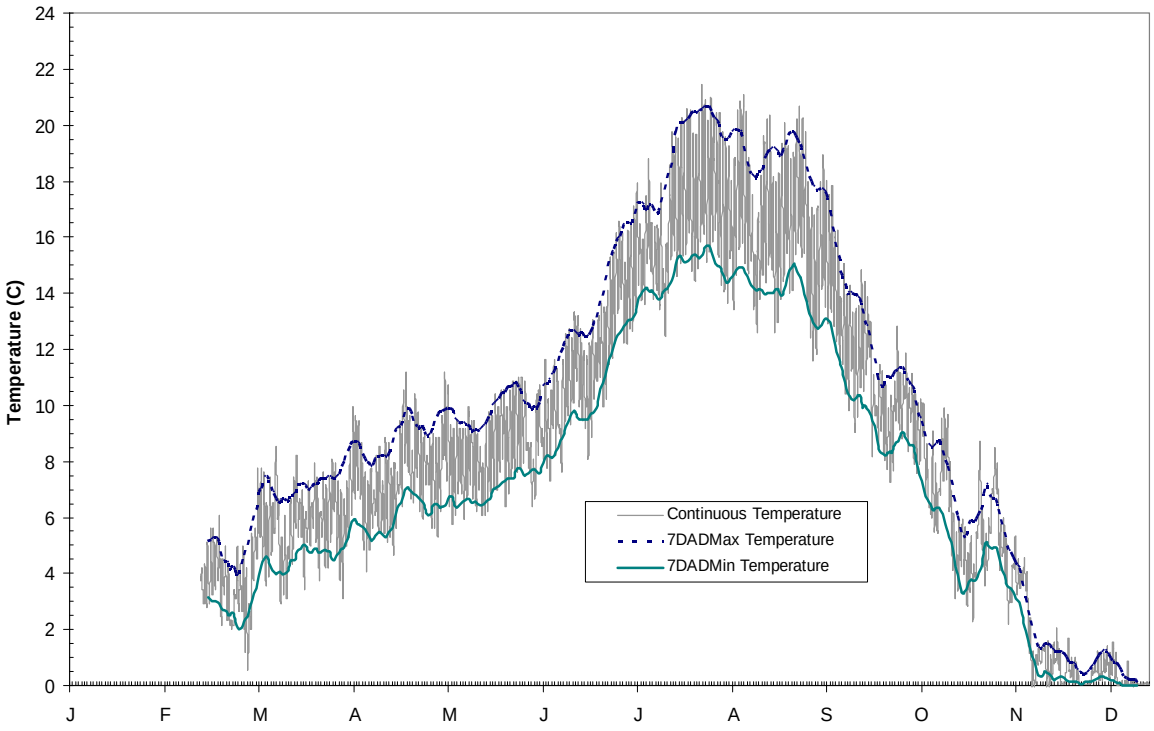

Figure D-16. 2007 continuous temperature profile for the Entiat River.