WASHINGTON STATE DEPARTMENT OF ECOLOGY

Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2006 Monitoring Data Summary

Abstract

From March through October 2006, pesticide sampling was conducted in the Cedar-Sammamish, Lower Skagit-Samish, and Lower Yakima watersheds as part of the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams.* This report summarizes data and briefly analyzes quality assurance/control performance for data verification.

Year 2006 is the first of a three-year study cycle to investigate pesticide occurrence in the Skagit-Samish watershed, and the fourth in a six-year cycle to study pesticides in the Cedar-Sammamish and Lower Yakima watersheds. The purpose of this data summary is to provide results and document changes to the sampling program that occurred in 2006.

Laboratory analyses were conducted for total suspended solids and 165 pesticide, herbicide, and degradate compounds. Field data were collected for discharge, temperature, pH, conductivity and dissolved oxygen.

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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 second three-year study cycle started in 2006.

The purpose of this data report is to provide results from monitoring in 2006 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.)

Three sub-basins were selected 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):

1. Thornton Creek, located in the Cedar-Sammamish Water Resource Inventory Area (WRIA) 8, was selected as the urban watershed due to listed 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 (Samish River, Big Ditch Slough, Browns Slough, and Indian Slough) were selected to represent western Washington agricultural land-use practices. 2006 was the first year of monitoring in the Lower Skagit-Samish watershed.

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

Figure 1 shows the locations of the three watersheds:

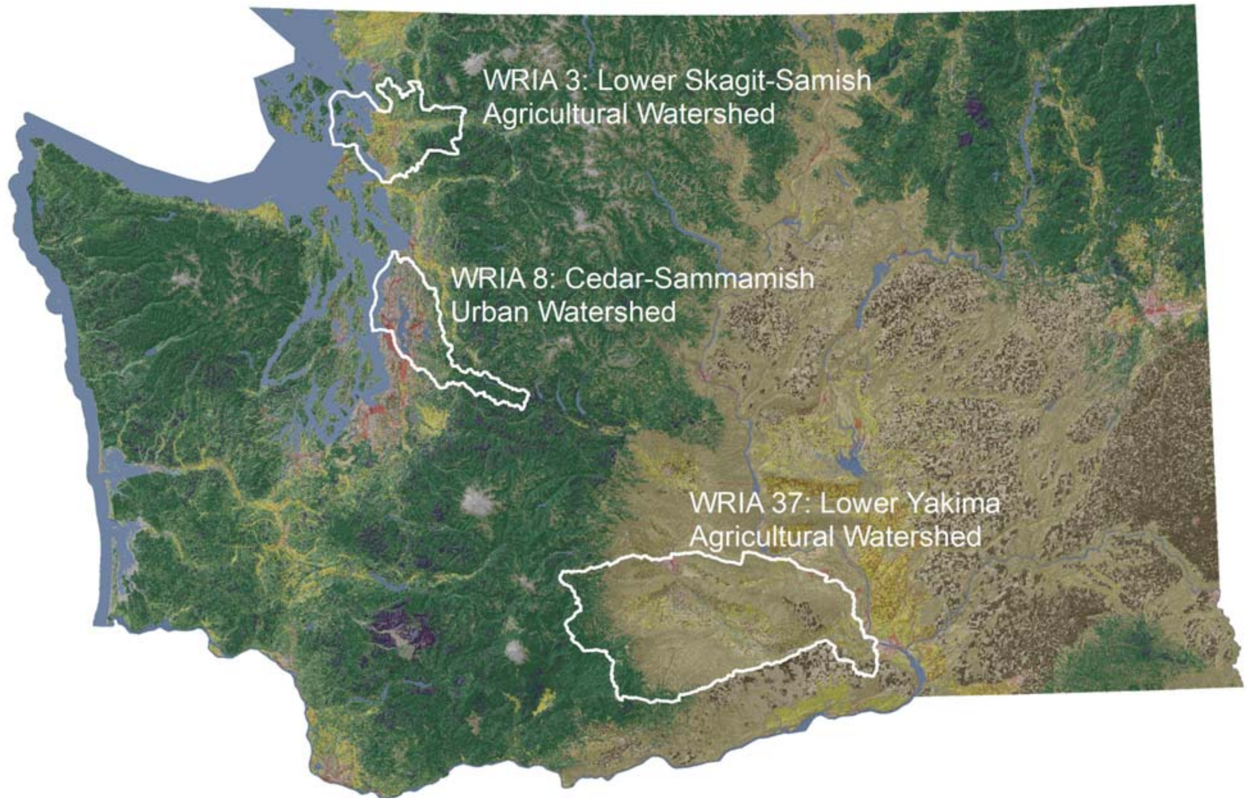

Figure 1. State map showing locations of urban and agricultural watersheds in this 2006 study.

Methods

Sampling was designed to address pesticide presence salmonid-bearing streams during typical pesticide-use periods. Registered and historical-use pesticides were analyzed, including organochlorine, organophosphorus, and carbamate functional groups. Conventional water quality parameters – total suspended solids, pH, conductivity, temperature, 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 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. Sample locations and duration of sampling are described in Appendix A.

Changes to Sampling Procedures

For the 2006 study year, the Lower Skagit-Samish watershed was added (Figure 2). Several of the five sites within this sub-basin have physical characteristics (example: stream depth and velocity) that required new sampling procedures. To ensure the collection of representative samples, integrated sampling procedures were used at those sites where stream depth, velocity, or both, were an issue.

When depth and velocity were too great for Ecology staff to wade the stream to measure discharge and collect samples, bridge measurement equipment was used. Equipment for measuring discharge consisted of a United States Geological Survey (USGS) A-55 sounding reel, bridge board, sounding weights, and a Marsh-McBirney Flo-Mate Model 2000 portable discharge meter (adapted for use with A-55 sounding reel). Sample collection equipment was made up of a USGS DH-76 depth integrating sampler. Sampling and cleaning were conducted according to USGS procedures (USGS, 2007).

Tidal Influence on the Lower Skagit – Samish Sampling Sites

Several downstream sites in the Lower Skagit-Samish watershed are influenced by tides. A tide gate stops saltwater from entering Browns Slough at Fir Island Road. Indian Slough has a set of tide gates that stop saltwater from intruding beyond Bayview-Edison Road. Big Ditch also has a set of tide gates that stop saltwater at a wildlife refuge at the Big Ditch discharge to Skagit Bay. An effort was made to sample at times when the tide was low. Sampling at low tide allowed for collection of water as it was discharging to Skagit or Padilla bays. When sampling at low tide was not possible, and water was very shallow and not flowing out, samples were collected from a bridge using the DH-76 or pole grab. Samples were not collected by wading in order to minimize contamination from disturbed bottom sediment.

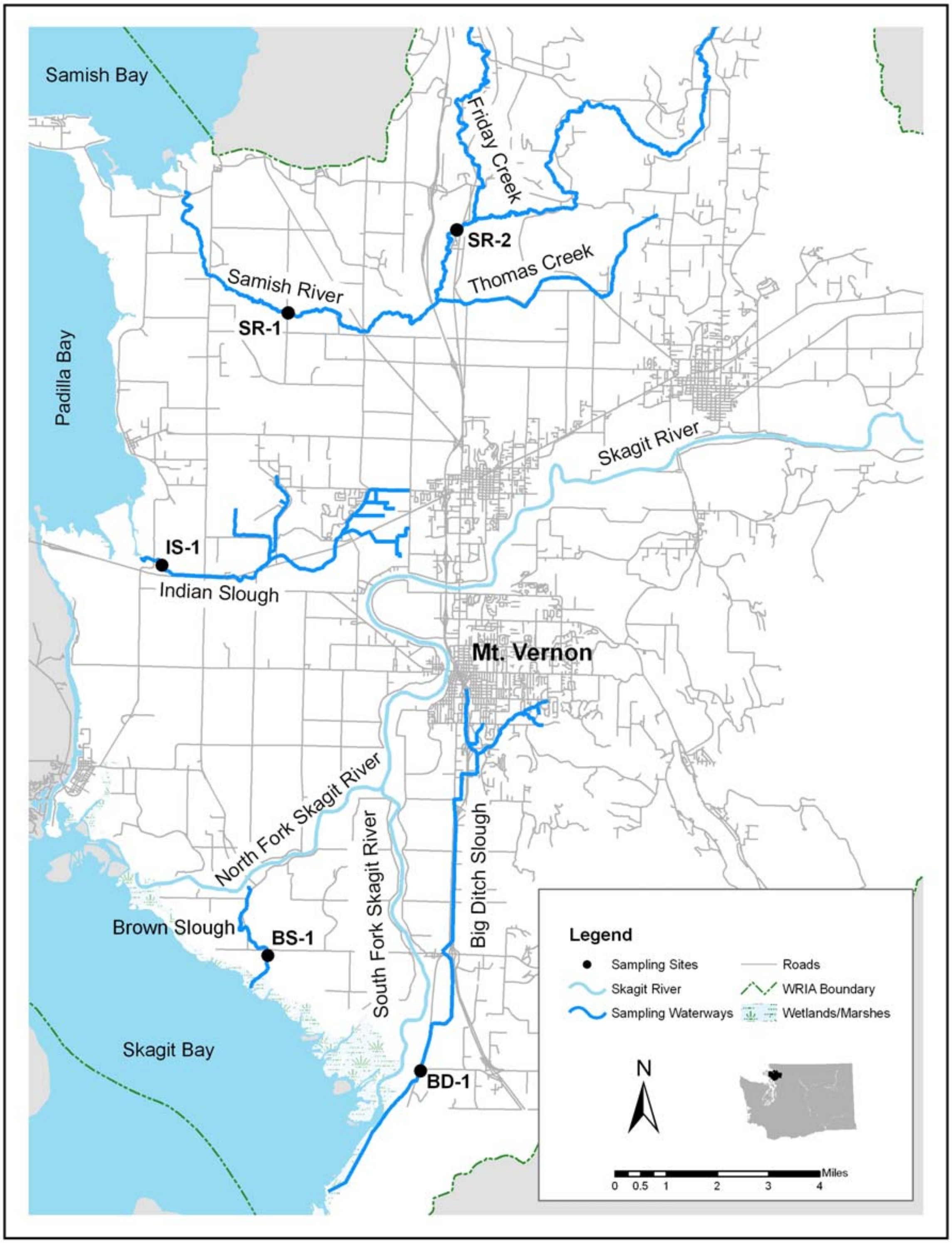

Figure 2. Sampling locations in the Lower Skagit-Samish watershed.

Data Quality

Ecology calibrated all field monitoring equipment according to the manufacturers' specifications, using Ecology Standard Operating Procedures where available (Ecology 2007) 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).

Carbamate analyses, and confirmation for the herbicides diuron and linuron, were carried out using Liquid Chromatography coupled with Mass Spectrometry (LCMS) - EPA Method (modified) SW 846 - 3535M/8321AM. This procedure deviates from previous analyses conducted by High Performance Liquid Chromatography (HPLC - 8318/531.1M) or Gas Chromatography coupled with Mass Spectrometry (GCMS - 3510/8270M). In prior years the analysis was restricted to identification of a breakdown product of diuron and linuron. As such, all detections were qualified as an estimate of identification, and not used in risk assessment (qualification presented in Appendix B-1). Additionally, use of LCMS and large volume injection in GCMS procedures has allowed this monitoring program to analyze additional (currently registered) pesticides and to lower reporting limits of most target compounds (Appendix 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.

One positive detection of pentachlorophenol was found in a blank collected at the upper Samish River 2 site. The detection was NJ qualified which means pentachlorophenol was identified at an approximate concentration, yet identification was not secondarily confirmed, and both the identification and concentration are qualified as estimates. All other blanks had no detections, indicating both field and laboratory methods were free from contamination.

The median percent relative standard deviation (RSD) of consistently identified replicate results is 6.3%. 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. Similar to USGS-National Water Quality Assessment analyses (Martin 2002), the median percent RSD is higher for compounds near the analytical detection limit;

- 10.7% RSD for detections below 0.025 µg/L
- 5.6% RSD for detections between 0.025 µg/L and 0.1 µg/L
- 2.6% RSD for detections above 0.1 µg/L

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.

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-1). The median recovery of TPP standards is 107%, while one standard deviation (σ) of values falls within 93-123% and 2σ of values fall within 78-138%.

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 Figure B-2 fall within 80-120% recovery. A range of 11-32 LCS tests was applied for each of 150 separate pesticide residues, and 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 insecticide aldicarb and one breakdown product, aldicarb sulfone. The median recoveries of both products are 70%, yet two large outliers skew the standard deviation of both products to show very 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.

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 RSD between MS/MSD pairs is 9.8%, and the average recovery of reviewed compounds is 98.5%. The RSD and recovery of MS/MSD pairs shows excellent performance, and is within the limits of the project QA Project Plans (Johnson and Cowles, 2003; Burke and Anderson, 2006).

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. Results of 97% of all analyses were within quality control limits recommended by the Superfund Methods for Organic Data Review (EPA, 2005).

Results

This study investigated pesticide occurrence in selected salmonid-bearing surface waters. Watersheds and monitoring locations were chosen that had a likely combination of (1) off-site pesticide transport and (2) use by salmonids. All results are presented as a sum of stations within the watershed, throughout the 2006 sampling season.

Conventional Water Quality Parameters

Conventional water quality parameters were measured at all sites. Results for the physical parameters of discharge, temperature, and total suspended solids (TSS) are presented in Table 1. Results for chemical parameters of conductivity, pH, and dissolved oxygen are presented in Table 2. All summaries are based on point (discrete) measurements obtained during the time of sampling, over the entire 2006 sampling period.

Table 1. Conventional physical parameter results in 2006.

Site	Discharge (cfs)				Temperature (°C)				Total Suspended Solids (mg/L)			
	n	Min	Med	Max	n	Min	Med	Max	n	Min	Med	Max
Thornton Creek	36	1	4	14	36	8.1	15.4	20.9	36	3	5	49
Big Ditch	29	0	10	46	29	7.9	17.0	24.8	29	2	7	57
Brown Slough	29	0	3	17	29	7.3	18.8	28.1	29	4	7	18
Indian Slough	29	0	6	35	29	7.5	17.7	24.2	29	1	5	37
Samish River	57	14	106	336	58	6.8	13.2	21.7	58	1	4	20
Marion Drain	28	10	87	296	31	10.5	14.8	23.6	31	1	9	51
Sulphur CW	24	89	192	546	24	8.8	17.5	22.8	24	12	31	116
Spring Creek	36	3	10	62	36	12.1	19.3	27.2	36	3	12	86

Table 2. Conventional chemical parameter results in 2006.

Site	Conductivity (µmhos/cm)				pH				Dissolved Oxygen mg/L			
	n	Min	Med	Max	n	Min	Med	Max	n	Min	Med	Max
Thornton Creek	36	157	197	250	35	7	7.8	8.3	36	7.7	9.6	12.3
Big Ditch	29	37	350	954	28	5.6	7.2	8.8	29	4.2	8.9	15.4
Brown Slough	29	7166	11561	33667	26	6.7	7.4	8.7	28	2.3	8.5	16.3
Indian Slough	29	270	690	1941	27	5.4	7.2	8.6	29	4.2	7.1	11.1
Samish River	57	48	76	142	54	5.5	7.5	8.1	57	8.5	10.6	12.3
Marion Drain	31	138	212	461	31	7.3	8.1	9.2	30	8.0	11.6	16.8
Sulphur CW	24	149	269	668	24	7.8	8.3	8.8	24	8.1	10.2	12.7
Spring Creek	36	189	329	499	35	7.8	8.6	9.7	36	7.3	8.9	12.3

Continuous, 30-minute interval, temperature data were collected at all sites for 2006. The sites in the Lower Skagit-Samish watershed have data collected from only March through December. Due to the inaccessibility of the temperature collection device at the Upper Samish River site, the temperature graph shows data from only March through late July. Temperature profiles for all sites are shown in Appendix C.

Pesticide Detections by Basin

1. Cedar-Sammamish Watershed – Thornton Creek

A total of 36 sampling events were conducted within Thornton Creek (12 upstream and 24 downstream) between March 2 and September 11, 2006. Thornton Creek pesticide results are summarized in Table 3.

Table 3. Summary of pesticide detections in Thornton Creek in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Dichlobenil	Casoron	H	0.032	21	58%	0.0089	0.031
2,4-D	(several)	H	0.078	8	22%	0.026	0.12
Triclopyr	(several)	H	0.078	8	22%	0.034	0.097
MCPP	Mecoprop	H	0.078	4	11%	0.027	0.049
Diazinon	(several)	I-OP	0.032	2	6%	0.047	0.076
Pentachlorophenol	Penta	WP	0.078	2	6%	0.0073	0.0077
Prometon	Pramitol 5PS	H	0.032	2	6%	0.0285	0.039
Aldicarb	Temik	I-C	0.060	1	3%	0.22	0.22
Pendimethalin	Prowl	H	0.032	1	3%	0.023	0.023

Sample Events - 36
H - Herbicide
I-C - Insecticide/carbamate
I-OP - Insecticide/organophosphate
WP - Wood preservative
[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.

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

All lower Skagit-Samish sites were sampled for 29 consecutive weeks from March 2 to September 11, 2006. The results are presented in Tables 4 through 7. Samish River, Table 7, is a combination of upstream and downstream monitoring locations.

Table 4. Summary of pesticide detections in Big Ditch Slough in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
EPTC	Eptam	H	0.032	13	45%	0.045	0.47
2,4-D	(several)	H	0.079	12	41%	0.0585	0.24
Dichlobenil	Casoron	H	0.032	11	38%	0.025	0.044
Metalaxyl	Gaucho	F	0.032	11	38%	0.029	0.13
Metolachlor	Stalwart	H	0.032	10	34%	0.017	0.11
Bentazon	Basagran	H	0.079	9	31%	0.12	0.28
Triclopyr	(several)	H	0.079	7	24%	0.05	0.22
Atrazine	Aatrex	H	0.032	6	21%	0.0255	0.15
MCPA	(several)	H	0.079	6	21%	0.073	0.18
MCPP	Mecoprop	H	0.079	6	21%	0.023	0.046
Pentachlorophenol	Penta	WP	0.079	6	21%	0.0155	0.022
Diuron	Karmex	H	0.060	5	17%	0.031	0.14
Chlorpropham	Sprout Nip	H	0.032	4	14%	0.209	2.3
Tebuthiuron	Spike	H	0.032	3	10%	0.02	0.028
Chlorpyriphos	Dursban	I-OP	0.032	2	7%	0.0125	0.013
Diazinon	(several)	I-OP	0.032	2	7%	0.0455	0.07
Metribuzin	Axiom, Sencor	H	0.032	2	7%	0.1605	0.23
1-Naphthol		D	0.060	1	3%	0.13	0.13
Bromacil	Hyvar	H	0.032	1	3%	0.04	0.04
Chlorothalonil	Bravo, Daconil	F	0.032	1	3%	0.0098	0.0098
Cycloate	Ro-Neet	H	0.032	1	3%	0.017	0.017
Dicamba I	Banvel	H	0.079	1	3%	0.11	0.11
Prometon	Pramitol 5PS	H	0.032	1	3%	0.01	0.01

Sample Events - 29
D - Degradate
F - Fungicide
H - Herbicide
I-C - Insecticide/carbamate
I-OP - Insecticide/organophosphate
WP - Wood preservative
[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 5. Summary of pesticide detections in Browns Slough in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
2,4-D	(several)	H	0.079	10	34%	0.0575	0.1
Simazine	Simazine	H	0.032	10	34%	0.056	1.6
Bentazon	Basagran	H	0.079	9	31%	0.065	0.19
EPTC	Eptam	H	0.031	7	24%	0.13	1.8
Trifluralin	Treflan	H	0.031	7	24%	0.0125	0.015
Diuron	Karmex	H	0.060	4	14%	0.027	0.096
Cycloate	Ro-Neet	H	0.031	3	10%	0.056	1.2
Metalaxyl	Gaucho	F	0.031	3	10%	0.03	0.12
Pentachlorophenol	Penta	WP	0.079	2	7%	0.00945	0.017
Triclopyr	(several)	H	0.079	2	7%	0.043	0.079
1-Naphthol		D	0.060	1	3%	0.084	0.084
Atrazine	Aatrex	H	0.031	1	3%	0.037	0.037
Chlorpropham	Sprout Nip	H	0.031	1	3%	0.012	0.012
Dichlobenil	Casoron	H	0.031	1	3%	0.0028	0.0028
Metolachlor	Stalwart	H	0.031	1	3%	0.014	0.014
Metribuzin	Axiom, Sencor	H	0.031	1	3%	0.0089	0.0089

Sample Events - 29
D - Degradate
F - Fungicide
H - Herbicide
WP - Wood preservative
[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 Indian Slough in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Diphenamid		H	0.032	21	72%	0.016	0.024
2,4-D	(several)	H	0.079	16	55%	0.06	0.43
Dichlobenil	Casoron	H	0.032	14	48%	0.0155	0.13
Triclopyr	(several)	H	0.079	13	45%	0.15	0.73
Bentazon	Basagran	H	0.079	9	31%	0.042	0.053
Tebuthiuron	Spike	H	0.032	9	31%	0.068	0.31
Metolachlor	Stalwart	H	0.032	6	21%	0.0125	0.02
Pentachlorophenol	Penta	WP	0.079	6	21%	0.0145	0.019
MCPP	Mecoprop	H	0.079	5	17%	0.018	0.036
Prometon	Pramitol 5PS	H	0.032	5	17%	0.026	0.036
Diuron	Karmex	H	0.060	3	10%	0.038	0.096
MCPA	(several)	H	0.079	2	7%	0.0975	0.11
Bromacil	Hyvar	H	0.032	1	3%	0.11	0.11
Carbaryl	Sevin	I-C	0.060	1	3%	0.077	0.077
Diazinon	(several)	I-OP	0.032	1	3%	0.024	0.024
Dicamba I	Banvel	H	0.079	1	3%	0.012	0.012
EPTC	Eptam	H	0.032	1	3%	0.024	0.024
Metalaxyl	Gaucho	F	0.032	1	3%	0.034	0.034
Napropamide	Devrinol	H	0.079	1	3%	0.018	0.018
Simazine	Simazine	H	0.032	1	3%	0.035	0.035

Sample Events - 29
F - Fungicide
H - Herbicide
I-C - Insecticide/carbamate
I-OP - Insecticide/organophosphate
WP - Wood preservative
[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 the Samish River watershed in 2006 (µg/L).

Chemical	Common Name	Typ e	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
2,4-D	(several)	H	0.079	5	9%	0.12	0.22
4-Nitrophenol		D	0.078	1	2%	0.038	0.038
Dicamba I	Banvel	H	0.079	1	2%	0.029	0.029
Linuron	(several)	H	0.060	1	2%	0.03	0.03
Pentachlorophenol	Penta	WP	0.078	1	2%	0.0006	0.0006

Sample Events - 58
H - Herbicide
WP - Wood preservative
[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 24 consecutive weeks from April 5 to September 13, 2006. The results are presented in Tables 8 through 10. Spring Creek, Table 10, is a combination of upstream and downstream monitoring locations. The upstream location was sampled every two weeks during the monitoring period. Marion Drain sampling was extended through October 31, 2006.

Table 8. Summary of pesticide detections in the Marion Drain in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Terbacil	Sinbar	H	0.032	26	84%	0.096	0.68
Chlorpyrifos	Dursban	I-OP	0.032	21	68%	0.013	0.12
Atrazine	Aatrex	H	0.032	19	61%	0.011	0.078
2,4-D	(several)	H	0.079	13	42%	0.047	0.53
Trifluralin	Treflan	H	0.032	10	32%	0.015	0.034
Metolachlor	Stalwart	H	0.032	8	26%	0.011	0.033
Bentazon	Basagran	H	0.080	7	23%	0.1	0.27
Pendimethalin	Prowl	H	0.032	5	16%	0.035	0.061
Alachlor	Lasso	H	0.032	4	13%	0.014	0.11
Malathion	(several)	I-OP	0.032	4	13%	0.018	0.024
MCPA	(several)	H	0.080	3	10%	0.028	0.033
Bromoxynil	Buctril	H	0.080	2	6%	0.055	0.066
Carbaryl	Sevin	I-C	0.055	2	6%	0.0795	0.09
Diuron	Karmex	H	0.032	2	6%	0.06	0.11
EPTC	Eptam	H	0.032	2	6%	0.0185	0.022
Ethoprop	Mocap	I-OP	0.032	2	6%	0.02	0.022
Simazine	Simazine	H	0.032	2	6%	0.0175	0.018
Metribuzin	Axiom, Sencor	H	0.032	1	3%	0.049	0.049

n = 31
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 9. Summary of pesticide detections in the Sulphur Creek Wasteway in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
2,4-D	(several)	H	0.080	23	75%	0.089	1.24
Atrazine	Aatrex	H	0.031	13	42%	0.011	0.016
Chlorpyrifos	Dursban	I-OP	0.031	9	29%	0.013	0.1
Terbacil	Sinbar	H	0.031	9	29%	0.025	0.035
Bromacil	Hyvar	H	0.031	5	17%	0.0325	0.041
Diuron	Karmex	H	0.055	5	17%	0.02	0.056
Azinphos Methyl	Guthion	I-OP	0.031	4	13%	0.033	0.037
Bentazon	Basagran	H	0.080	4	13%	0.09	0.1
Norflurazon	Solicam	H	0.031	4	13%	0.056	0.13
Trifluralin	Treflan	H	0.031	4	13%	0.013	0.015
4,4'-DDE		D	0.031	3	8%	0.0044	0.0053
Diazinon	(several)	I-OP	0.031	3	8%	0.00885	0.01
Aldicarb	Temik	I-C	0.055	1	4%	0.07	0.07
Aldicarb Sulfone		D	0.100	1	4%	0.13	0.13
Dichlobenil	Casoron	I-OP	0.031	1	4%	0.0041	0.0041
Dimethoate	Dimethoate	I-OP	0.031	1	4%	0.45	0.45
Prometon	Pramitol 5ps	H	0.031	1	4%	0.015	0.015
Simazine	Simazine	H	0.031	1	4%	0.027	0.027

n = 24
D - Degradate
H - Herbicide
I-C - Insecticide/carbamate
I-OP - Insecticide/organophosphate
WP - Wood preservative
[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 Spring Creek in 2006 (µg/L).

Chemical	Common Name	Type	[1]ALPQL	Detections	[2]Det. Freq.	Concentration (µg/L)	
						Median	Max
Simazine	Simazine	H	0.032	31	86%	0.023	0.16
Atrazine	Aatrex	H	0.032	27	75%	0.011	0.017
2,4-D	(several)	H	0.079	17	47%	0.047	0.87
Norflurazon	Solicam	H	0.032	13	36%	0.027	0.057
Bromacil	Hyvar	H	0.032	11	31%	0.032	0.045
Chlorpyrifos	Dursban	I-OP	0.032	11	31%	0.015	0.06
Bentazon	Basagran	H	0.079	6	17%	0.03	0.036
Azinphos Methyl	Guthion	I-OP	0.032	5	14%	0.052	0.12
Aldicarb	Temik	I-C	0.055	2	6%	0.1125	0.16
Diazinon	(several)	I-OP	0.032	2	6%	0.0105	0.011
Malathion	(several)	I-OP	0.032	2	6%	0.015	0.017
1-Naphthol		H	0.060	1	3%	0.1	0.1
4,4'-DDE		D	0.032	1	3%	0.0031	0.0031
Aldicarb Sulfone		D	0.100	1	3%	0.13	0.13
Carbaryl	Sevin	I-C	0.050	1	3%	1.26	1.26
Diuron	Karmex	H	0.050	1	3%	0.022	0.022
Pentachlorophenol	Penta	W	0.079	1	3%	0.044	0.044
Terbacil	Sinbar	H	0.032	1	3%	0.028	0.028
Trifluralin	Treflan	H	0.032	1	3%	0.014	0.014

Sample Events - 36
D - Degradate
H - Herbicide
I-C - Insecticide/carbamate
I-OP - Insecticide/organophosphate
WP - Wood preservative
[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 monitoring results for all three watersheds are presented in:

Appendix A. Monitoring Location and Duration of Sampling

Appendix B. Quality Assurance/Quality Control

Appendix C. Continuous Temperature Profiles

Summary of Project Changes

During 2006, the following changes were made to the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams:*

- Five new sampling sites, in the Skagit-Samish watershed, were added.

- Five new pesticide residues and degradate products were added for analysis because of the addition of the LCMS method and review of all laboratory protocols (GCMS/LCMS). New functional groups added for analysis were pyrethroids and nicotinoids.

- The reporting limits of several target analytes were reduced through review.

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Appendices

Appendix A. Monitoring Locations and Duration of Sampling

Table A-1. Station locations, descriptions, and duration of monitoring for 2006.

Site	Duration	Latitude	Longitude	Location Description
Cedar-Sammamish Watershed				
Thornton 1	April - September	47.7121	122.2886	NE 110th Street upstream of bridge
Thornton 3	April - September	47.7128	122.2747	Downstream of footbridge near Mathews Beach Park
Skagit/Samish Watershed				
BD-1	March - September	48.3086	122.3473	Upstream of bridge at Milltown Rd
BS-1	March - September	48.3407	122.4141	Downstream of tidegate on Fir Island Rd
IS-1	March - September	48.4506	122.4652	Upstream of tidegate at Bayview-Edison Rd
SR-1	March - September	48.5210	122.4113	Upstream of bridge at Thomas Rd
SR-2	March - September	48.5458	122.3381	Downstream of bridge at Old Highway 99 North
Lower Yakima Watershed				
Marion 2	April - October	46.3306	120.1989	Upstream of bridge at Indian Church Rd
Spring 2	April - September	46.2583	119.7101	Downstream of the crossing with McCready Rd
Spring 3	April - September	46.2344	119.6845	10' downstream of the Chandler Canal overpass
Sulphur 1	April - September	46.2513	119.6845	Downstream side of bridge at Holaday Rd

Datum = NAD 83

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, 2007, 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
1-Naphthol	Degradate/C	Carbaryl	LCMS	0.19	0.13		0.065
3-Hydroxycarbofuran	Degradate/C	Carbofuran	LCMS	0.19	0.13	0.11	0.063
Aldicarb	Insecticide/C		LCMS	0.19	0.13	0.1	0.063
Aldicarb sulfone	Degradate/C	Aldicarb	LCMS			0.10	0.095
Aldicarb sulfoxide	Degradate/C	Aldicarb	LCMS			0.11	0.069
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
Carbofuran	Insecticide/C		LCMS	0.19	0.13	0.104	0.063
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	0.100
Methomyl	Insecticide/C		LCMS	0.19	0.13	0.12	0.055
Methomyl oxime	Degradate/C	Methomyl	LCMS				0.070
Oxamyl	Insecticide/C		LCMS	0.19	0.13	0.11	0.071
Oxamyl oxime	Degradate/C	Oxamyl	LCMS				0.092
Promecarb	Insecticide/C		LCMS	0.19	0.13	0.093	0.101
Propoxur	Insecticide/C		LCMS	0.19	0.13	0.11	0.054
2,3,4,5-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079
2,3,4,6-Tetrachlorophenol	Degradate/WP	PCP	GCMS-H	0.087	0.079	0.081	0.079
2,4,5-T	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
2,4,5-TP (Silvex)	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
2,4,5-Trichlorophenol	Fungicide		GCMS-H	0.5	0.079	0.081	0.079
2,4,6-Trichlorophenol	Fungicide		GCMS-H	0.495	0.079	0.081	0.079
2,4-D	Herbicide		GCMS-H	0.16	0.079	0.081	0.078
2,4-DB	Herbicide		GCMS-H	0.19	0.079	0.081	0.079
3,5-Dichlorobenzoic Acid	Herbicide		GCMS-H	0.16	0.079	0.084	0.079
4-Nitrophenol	Degradate/H-OP	Multiple	GCMS-H	0.29	0.079	0.238	0.079
Acifluorfen (Blazer)	Herbicide		GCMS-H	0.64	0.079	0.085	0.079
Bentazon	Herbicide		GCMS-H	0.235	0.079	0.082	0.078
Bromoxynil	Herbicide		GCMS-H	0.16	0.079	0.093	0.079
Dacthal (DCPA)	Herbicide		GCMS-H	0.125	0.079	0.081	0.079
Dicamba I	Herbicide		GCMS-H	0.16	0.079	0.081	0.078
Dichlorprop	Herbicide		GCMS-H	0.17	0.079	0.081	0.079
Diclofop-Methyl	Herbicide		GCMS-H	0.24	0.079	0.081	0.079
Dinoseb	Herbicide		GCMS-H	0.24	0.079	0.083	0.079
Ioxynil	Herbicide		GCMS-H	0.16	0.079	0.103	0.079
MCPA	Herbicide		GCMS-H	0.315	0.079	0.081	0.079
MCPP (Mecoprop)	Herbicide		GCMS-H	0.315	0.079	0.077	0.079
Pentachlorophenol	Wood Preservative		GCMS-H	0.08	0.079	0.080	0.079
Picloram	Herbicide		GCMS-H	0.16	0.079	0.081	0.079
Triclopyr	Herbicide		GCMS	0.13	0.079	0.079	0.079
2,4'-DDD	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032

Continued…

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3]			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
2,4'-DDE	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032
2,4'-DDT	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032
4,4'-DDD	Degradate/OC	DDT	GCMS	0.018	0.079	0.083	0.032
4,4'-DDE	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032
4,4'-DDT	Degradate/OC	DDT	GCMS	0.018	0.079	0.082	0.032
Acephate	Insecticide/OP		GCMS		1.594	1.500	0.032
Alachlor	Herbicide		GCMS	0.335	0.112	0.12	0.032
Aldrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Alpha-BHC	Insecticide/OC		GCMS	0.018	0.079	0.077	0.032
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
Azinphos Ethyl	Insecticide/OP		GCMS	0.053	0.05	0.06	0.032
Azinphos methyl	Insecticide/OP		GCMS	0.053	0.05	0.052	0.032
Benefin	Herbicide		GCMS	0.05	0.047	0.208	0.032
Bensulide	Herbicide/OP		GCMS		14.187	1.500	0.032
Benzamide, 2,6-dichloro-	Degradate/H-OP	Dichlobenil	GCMS	0.22			
Beta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.076	0.032
Bolstar (Sulprofos)	Insecticide/OP		GCMS	0.023	0.022	0.034	
Bromacil	Herbicide		GCMS	0.135	0.126	0.126	0.032
Butachlor	Herbicide		GCMS	0.199	0.189	0.185	
Butylate	Herbicide		GCMS	0.066	0.063	0.080	0.032
Captafol	Fungicide		GCMS	0.063	0.394	0.41	
Captan	Fungicide		GCMS	0.089	0.213	0.21	0.032
Carbophenothion	Insecticide/OP		GCMS	0.033	0.031	0.049	
Carboxin	Fungicide		GCMS	0.199	0.189	0.186	0.032
Chlorothalonil (Daconil)	Herbicide		GCMS	0.079	0.075	0.084	0.032
Chlorpropham	Herbicide		GCMS	0.132	0.127	0.121	0.032
Chlorpyrifos	Insecticide/OP		GCMS	0.026	0.025	0.029	0.032
Cis-Chlordane (Alpha-Chlordane)	Insecticide/OC		GCMS	0.017	0.079	0.083	0.032
Cis-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.258	0.032
Coumaphos	Insecticide/OP		GCMS		1.504	1.497	0.032
Cyanazine	Herbicide		GCMS	0.05	0.047	0.051	0.032
Cycloate	Herbicide		GCMS	0.066	0.063	0.067	0.032
Delta-BHC	Insecticide/OC		GCMS	0.018	0.079	0.078	0.032
Demeton (O+S)	Insecticide/OP		GCMS			0.023	
Demeton-O	Insecticide/OP		GCMS	0.033	0.022	0.022	
Demeton-S	Insecticide/OP		GCMS	0.033	0.022	0.093	
Di-allate (Avadex)	Herbicide		GCMS	0.345	0.221	0.211	0.032
Diazinon	Insecticide		GCMS	0.027	0.026	0.032	0.032
Dichlobenil	Herbicide		GCMS	0.065	0.063	0.068	0.032
Dicofol (Kelthane)	Insecticide/OC		GCMS	0.051	0.315	0.274	0.319
Dieldrin	Insecticide/OC		GCMS	0.018	0.079	0.076	0.080
Dimethoate	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032

Continued…

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3]			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
Diphenamid	Herbicide		GCMS	0.099	0.094	0.091	0.032
Disulfoton (Di-Syston)	Insecticide/OP		GCMS	0.02	0.019	0.035	0.032
Diuron	Herbicide		GCMS	0.195	0.189	0.19	0.033
Endosulfan I	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endosulfan II	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endosulfan Sulfate	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Endrin	Insecticide/OC		GCMS	0.018	0.079	0.083	0.080
Endrin Aldehyde	Degradate/OC	Endrin	GCMS	0.018	0.079	0.083	0.080
Endrin Ketone	Degradate/OC	Endrin	GCMS	0.018	0.079	0.077	0.032
EPN	Insecticide/OP		GCMS	0.033	0.031	0.036	0.032
Eptam	Herbicide		GCMS	0.066	0.063	0.064	0.032
Ethalfluralin (Sonalan)	Herbicide		GCMS	0.05	0.047	0.047	0.032
Ethion	Insecticide/OP		GCMS	0.023	0.022	0.023	0.032
Ethoprop	Insecticide/OP		GCMS	0.027	0.025	0.029	0.032
Fenamiphos	Insecticide/OP		GCMS	0.05	0.047	0.054	0.032
Fenarimol	Fungicide		GCMS	0.099	0.094	0.091	0.032
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
Fluridone	Herbicide		GCMS	0.199	0.189	0.180	0.064
Fonofos	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032
Gamma-BHC (Lindane)	Insecticide/OC		GCMS	0.018	0.079	0.082	0.032
Heptachlor	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Heptachlor Epoxide	Degradate/OC	Heptachlor	GCMS	0.018	0.079	0.083	0.032
Hexachlorobenzene	Fungicide		GCMS	0.018	0.079	0.079	0.032
Hexazinone	Herbicide		GCMS	0.05	0.047	0.048	0.080
Imidan	Insecticide/OP		GCMS	0.036	0.035	0.041	0.032
Malathion	Insecticide/OP		GCMS	0.027	0.025	0.032	0.032
Merphos (1 & 2)	Herbicide/OP		GCMS	0.04	0.038	0.055	
Metalaxyl	Fungicide		GCMS	0.199	0.189	0.34	0.032
Methamidophos	Insecticide/OP		GCMS		1.594	1.7	0.032
Methidathion	Insecticide/OP		GCMS		1.594	1.47	0.319
Methoxychlor	Insecticide/OC		GCMS	0.088	0.079	0.076	0.032
Methyl Chlorpyrifos	Insecticide/OP		GCMS	0.027	0.025	0.026	0.032
Methyl Parathion	Insecticide/OP		GCMS	0.023	0.022	0.034	0.032
Metolachlor	Herbicide		GCMS	0.133	0.127	0.121	0.032
Metribuzin	Herbicide		GCMS	0.033	0.031	0.056	0.032
MGK264	Synergist/I		GCMS	0.263	0.252	0.26	0.032
Mirex	Insecticide/OC		GCMS	0.018	0.079	0.081	0.032
Molinate	Herbicide		GCMS	0.066	0.063	0.223	
Naled	Insecticide/OP		GCMS		1.594	1.502	0.032
Napropamide	Herbicide		GCMS	0.099	0.094	0.096	0.080
Norflurazon	Herbicide		GCMS	0.066	0.063	0.071	0.032
Oxychlordane	Degradate/OC	Chlordane	GCMS	0.018	0.079	0.088	0.032

Continued…

Table B-2 continued. Mean Performance Lower Practical Quantitation Limits.

Chemical	Use[1]	Parent	Analysis Method[2]	WSDA[3]			
				2003	2004	2005	2006
				LPQL	LPQL	LPQL	LPQL
Oxyfluorfen	Herbicide		GCMS	0.134	0.127	0.121	0.032
Parathion	Insecticide/OP		GCMS	0.027	0.025	0.030	0.032
Pebulate	Herbicide		GCMS	0.066	0.063	0.064	0.032
Pendimethalin	Herbicide		GCMS	0.05	0.046	0.051	0.032
Pentachloroanisole	Degradate/WP	PCP	GCMS	0.018	0.079	0.080	
Pentachlorophenol (PCP)	Wood Preservative		GCMS	0.08	0.079	0.080	0.080
Phenothrin	Insecticide/Py		GCMS			0.061	0.032
Phorate	Insecticide/OP		GCMS	0.023	0.022	0.029	0.319
Profluralin	Herbicide		GCMS	0.079	0.075	0.081	
Prometon (Pramitol 5p)	Herbicide		GCMS	0.032	0.031	0.033	0.032
Prometryn	Herbicide		GCMS	0.033	0.031	0.043	0.032
Pronamide (Kerb)	Herbicide		GCMS	0.169	0.127	0.127	0.032
Propachlor (Ramrod)	Herbicide		GCMS	0.079	0.075	0.078	0.032
Propargite	Insecticide/SE		GCMS	0.066	0.063	0.063	0.032
Propazine	Herbicide		GCMS	0.033	0.031	0.035	0.032
Resmethrin	Insecticide/Py		GCMS			0.061	0.064
Ronnel	Insecticide/OP		GCMS	0.023	0.022	0.024	
Simazine	Herbicide		GCMS	0.033	0.031	0.031	0.032
Sulfotepp	Insecticide/OP		GCMS	0.02	0.019	0.023	0.032
Tebuthiuron	Herbicide		GCMS	0.05	0.047	0.054	0.037
Terbacil	Herbicide		GCMS	0.099	0.093	0.090	0.032
Terbutryn (Igran)	Herbicide		GCMS	0.033	0.031	0.035	
Trans-Chlordane (Gamma)	Insecticide/OC		GCMS	0.018	0.079	0.083	0.032
Trans-Nonachlor	Insecticide/OC		GCMS	0.018	0.079	0.080	0.032
Triadimefon	Fungicide		GCMS	0.086	0.082	0.087	0.032
Triallate	Herbicide		GCMS	0.099	0.094	0.098	0.032
Trifluralin (Treflan)	Herbicide		GCMS	0.05	0.047	0.054	0.032
Vernolate	Herbicide		GCMS	0.066	0.063	0.066	

[1] 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 entirety of project.

[3] 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.

The 2006 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).

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 compounds which were consistently identified in both the sample and replicate. Consistent identification refers to compounds which had a positive identification and includes all flag codes except U. 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 for selected pesticides (µg/L).

Chemical	Sample		Replicate		RPD
2,4-D	0.015	NJ	0.017	NJ	12.50
	0.022	J	0.022	J	0.00
	0.023	J	0.025	NJ	8.33
	0.05	NJ	0.049	NJ	2.02
	0.24		0.24		0.00
	0.028	NJ	0.025	NJ	11.32
				Mean =	5.70
Atrazine	0.019	NJ	0.018	J	5.41
Bentazon	0.14		0.14		0.00
	0.066	J	0.075	J	12.77
	0.041	NJ	0.044	J	7.06
	0.11	NJ	0.1	NJ	9.52
	0.029	NJ	0.03	J	3.39
				Mean =	6.55
Bromacil	0.027	J	0.029	J	7.14
Chlorpropham	2.3		2.2		4.44
Chlorpyrifos	0.27	J	0.27	J	0.00
Diphenamid	0.018	J	0.015	J	18.18
Diuron	0.023	J	0.015	J	42.11
	0.019	J	0.011	J	53.33
				Mean =	47.72
EPTC	0.13		0.12		8.00
	0.16		0.15		6.45
	0.61		0.62		1.63
				Mean =	5.36
MCPA	0.17		0.17		0.00
	0.015	NJ	0.013	NJ	14.29
				Mean =	7.14
Mecoprop	0.0055	NJ	0.006	NJ	8.70
	0.046	J	0.045	J	2.20
				Mean =	5.45
Metolachlor	0.11	J	0.11	J	0.00
Picloram	0.049	NJ	0.06	NJ	20.18
	0.026	NJ	0.027	NJ	3.77
				Mean =	11.98
Terbacil	0.16		0.17		6.06
Triclopyr	0.015	NJ	0.014	NJ	6.90
	0.043	J	0.047	J	8.89
	0.023	NJ	0.022	NJ	4.44
	0.12		0.11		8.70
	0.0088	NJ	0.0094	NJ	6.59
				Mean =	7.10

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

Chemical	Sample		Replicate		RPD
Cycloate	0.029	NJ	0.031	U	6.67
EPTC (Eptam)	0.015	J	0.032	U	72.34
4-Nitrophenol	0.037	NJ	0.078	UJ	71.30
Chlorothalonil	0.032	U	0.019	J	50.98
Metribuzin	0.031	U	0.14	J	127.49
Pentachlorophenol	0.079	U	0.0003	NJ	198.49
Pentachlorophenol	0.0028	NJ	0.079	U	186.31
Prometon	0.01	J	0.032	U	104.76
Prometon	0.031	U	0.016	NJ	63.83
				Mean =	98.02

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 (Table B-5). The median recovery of TPP standards is 107%, while 68% (σ – edges of box) of values fall within 93% to 123%, and 95% (2σ - whiskers) of values fall within 78 to 138% (Figure B-1). TPP results had higher recoveries than any other surrogate compound.

Table B-5. Surrogate compounds.

Surrogate compound	Surrogate
1,3 Dimethyl-2-nitrobenzene	N-pesticide
2,4,6-Tribromophenol	Herbicide
2,4-Dichlorophenylacetic acid	Herbicide
Decachlorobiphenyl	Cl-pesticide
Triphenyl phosphate	OP-pesticide

N = nitrogen containing
Cl = chlorinated
OP = organophosphate

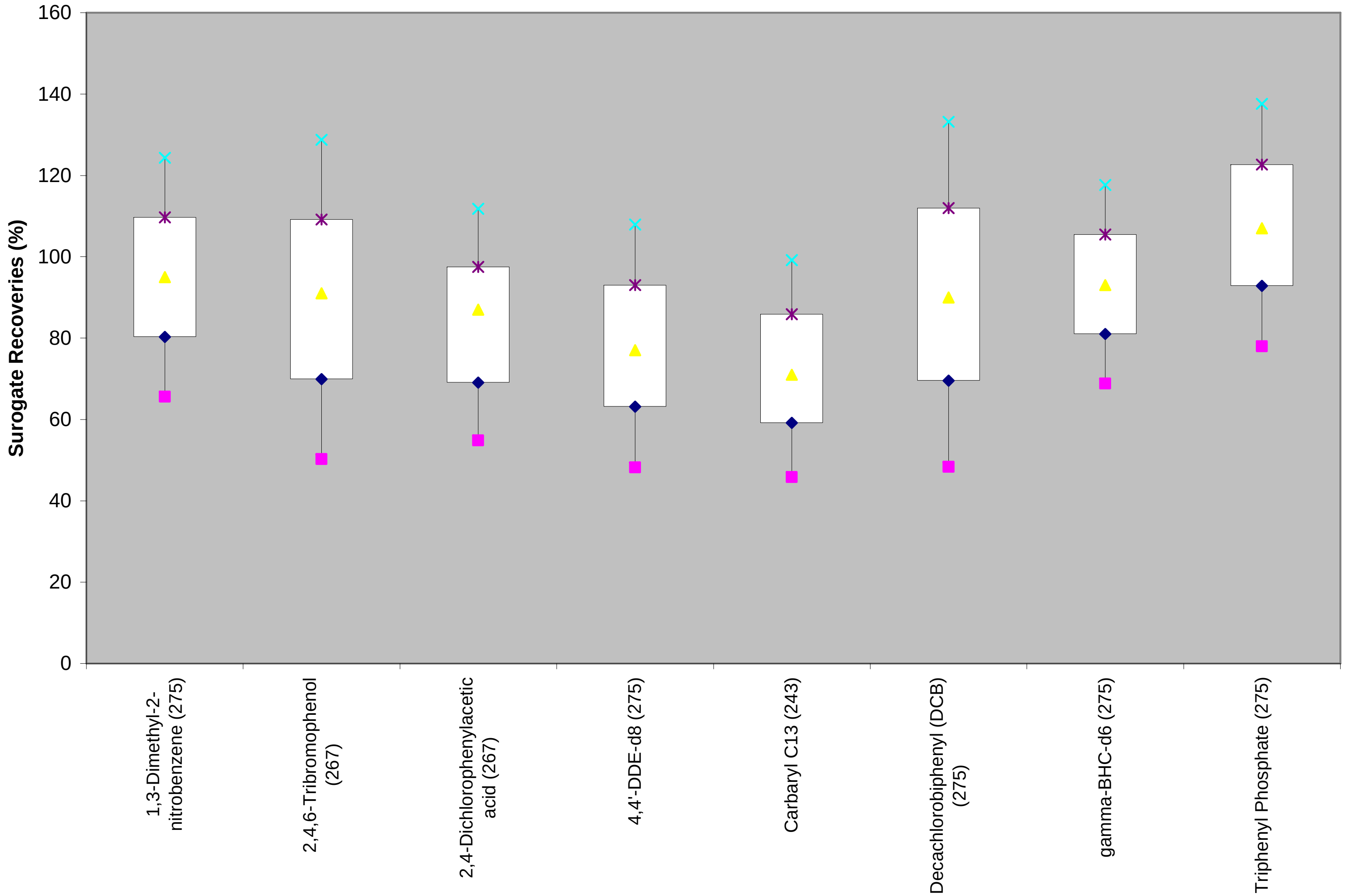

Figure B-1. Selected Surrogate Recovery Data. Triangle is median, box defines one standard deviation, and whiskers are two standard deviations.

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 11-32 LCS tests were applied for each of 150 separate pesticide residues, and residues with less than 30 tests must be evaluated as estimates – as they do not meet requirements of the central limit theorem. Two such residues include the insecticide aldicarb and one breakdown product, aldicarb sulfone. The median recoveries of both products are 70%, yet two large outliers skew the standard deviation of both products to show very 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.

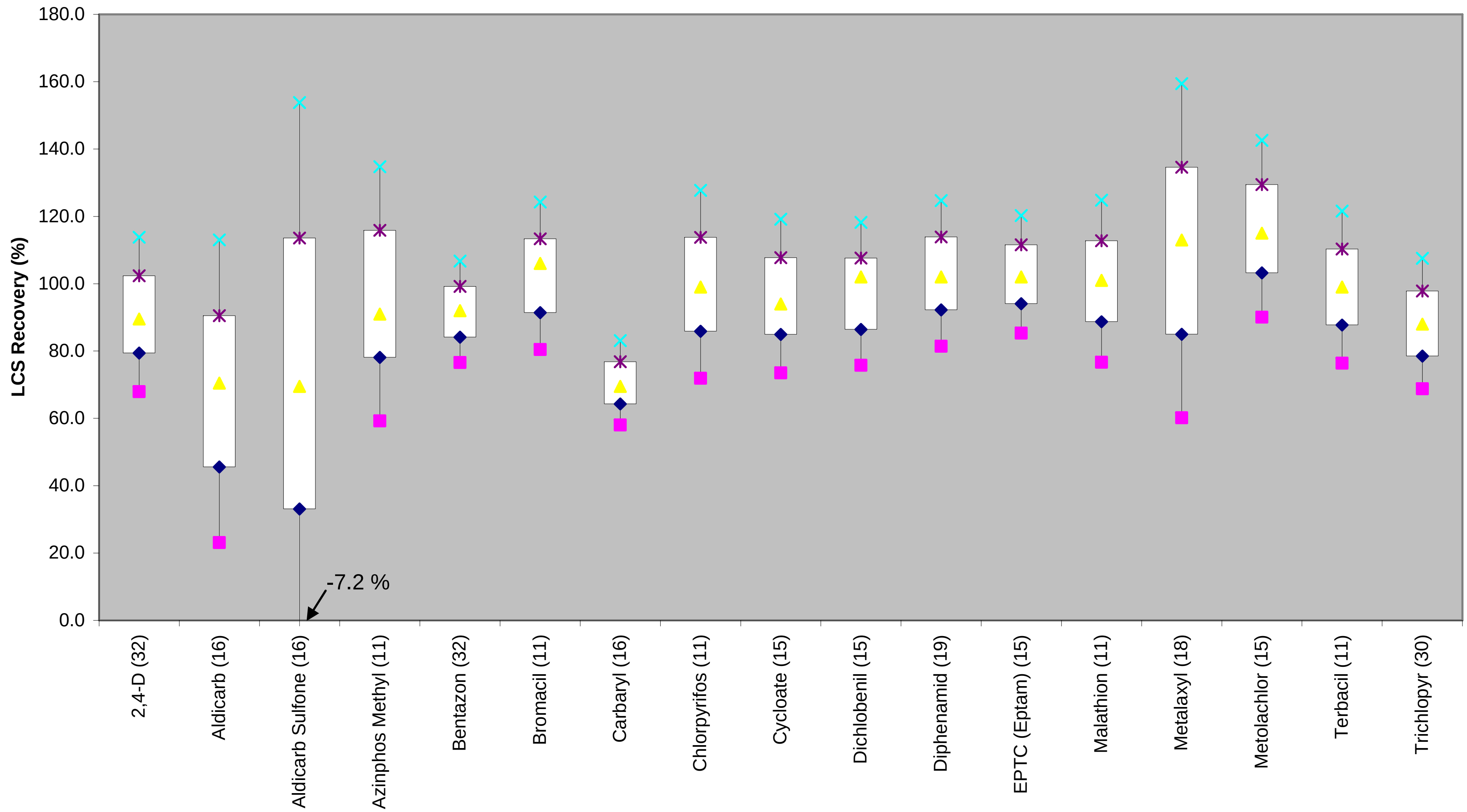

Figure B-2. Selected 2006 Laboratory Control Sample (LCS) Recovery Data. Triangle is median, box defines one standard deviation, and whiskers are two standard deviations.

Results of matrix spike/matrix spike duplicate (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. MS/MSD results and relative percent difference (RPD) for pairs for selected compounds are presented in Table B-6.

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

Chemical	MS	MSD	RPD
2,4-D	86	87	1
	57	44	26
	80	72	11
	70	62	12
	47	71	41
	127	122	4
	110	135	20
	129	125	3
	138	118	16
	132	110	18
	68	65	5
	74	61	19
	86	101	16
	146	163	11
		Mean =	15
Aldicarb	39	63	47
	130	115	12
	55	49	12
	60	60	0
		Mean =	18
Aldicarb Sulfone	48	67	33
	78	72	8
	85	85	0
	34	33	3
		Mean =	11
Azinphos Methyl	247	253	2
	190	170	11
		Mean =	7
Bentazon	85	83	2
	97	75	26
	101	122	19
	104	107	3
	71	88	21
	82	74	10
	106	96	10
	113	89	24
	90	87	3
	96	92	4
	94	111	17
	99	95	4
	110	101	9

Chemical	MS	MSD	RPD
	106	97	9
		Mean =	12
Bromacil	87	96	10
	131	105	22
	90	100	11
		Mean =	14
Carbaryl	32	86	92
	61	62	2
	67	64	5
	70	66	6
		Mean =	26
Chlorpyrifos	105	106	1
	11	95	16
	84	89	6
		Mean =	7
Cycloate	85	79	7
	99	100	1
	77	89	14
	98	110	12
		Mean =	9
Dichlobenil	96	94	2
	112	92	20
	122	101	19
	100	96	4
	105	111	6
	90	84	7
		Mean =	10
Diphenamid	87	94	8
	114	97	16
	94	100	6
	87	88	1
	111	108	3
	113	91	22
	112	108	4
	122	120	2
	105	105	0
		Mean =	7
EPTC (Eptam)	91	92	1
	113	135	18
	88	99	12
	102	112	9
		Mean =	10
Malathion	101	110	9
	124	104	18
	103	116	12
		Mean =	13
Metalaxyl	103	108	5
	120	138	14
	120	134	11

Chemical	MS	MSD	RPD
	90	90	0
	140	123	13
	129	109	17
	129	120	7
	149	147	1
Metolachlor	105	104	1
	143	143	0
	135	115	16
	120	116	3
	124	123	1
	113	113	0
		Mean =	4
Terbacil	91	98	7
	126	104	19
	72	82	13
		Mean =	13
Triclopyr	77	84	9
	73	67	9
	83	78	6
	84	82	2
	5	73	174
	97	89	9
	117	105	11
	76	79	4
	111	98	12
	113	86	27
	72	72	0
	89	74	18
	87	102	16
	98	104	6
		Mean =	22

Appendix C. Continuous Temperature Profiles

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

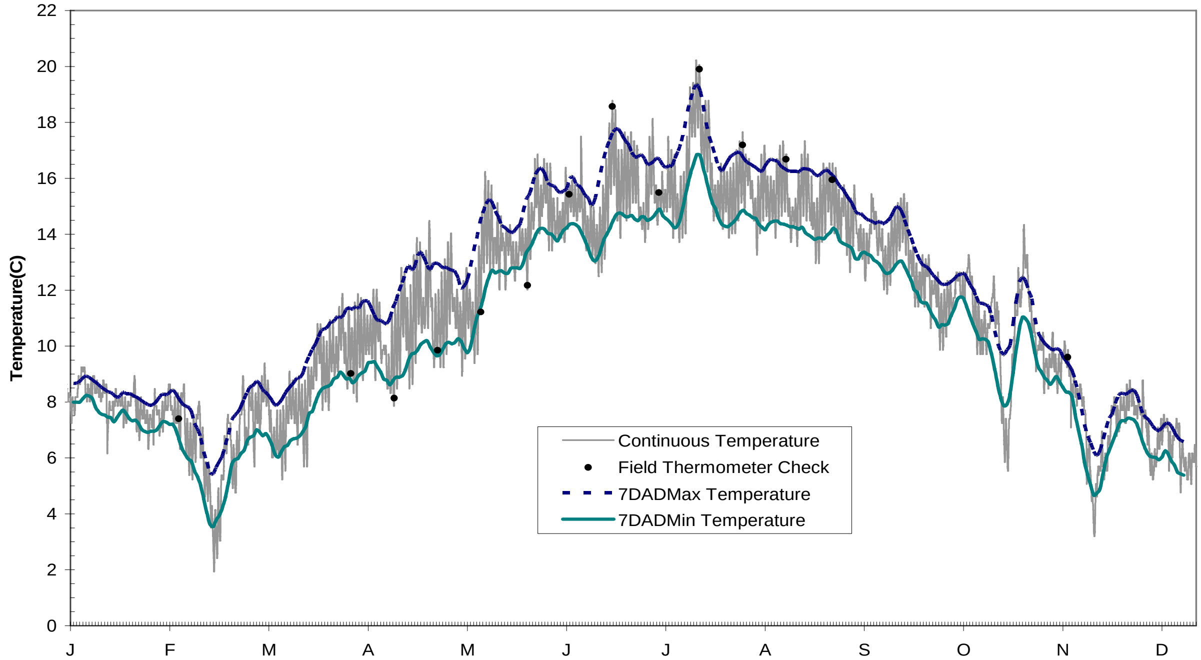

Figure C-1. 2006 continuous temperature profile for the North Fork of Thornton Creek.

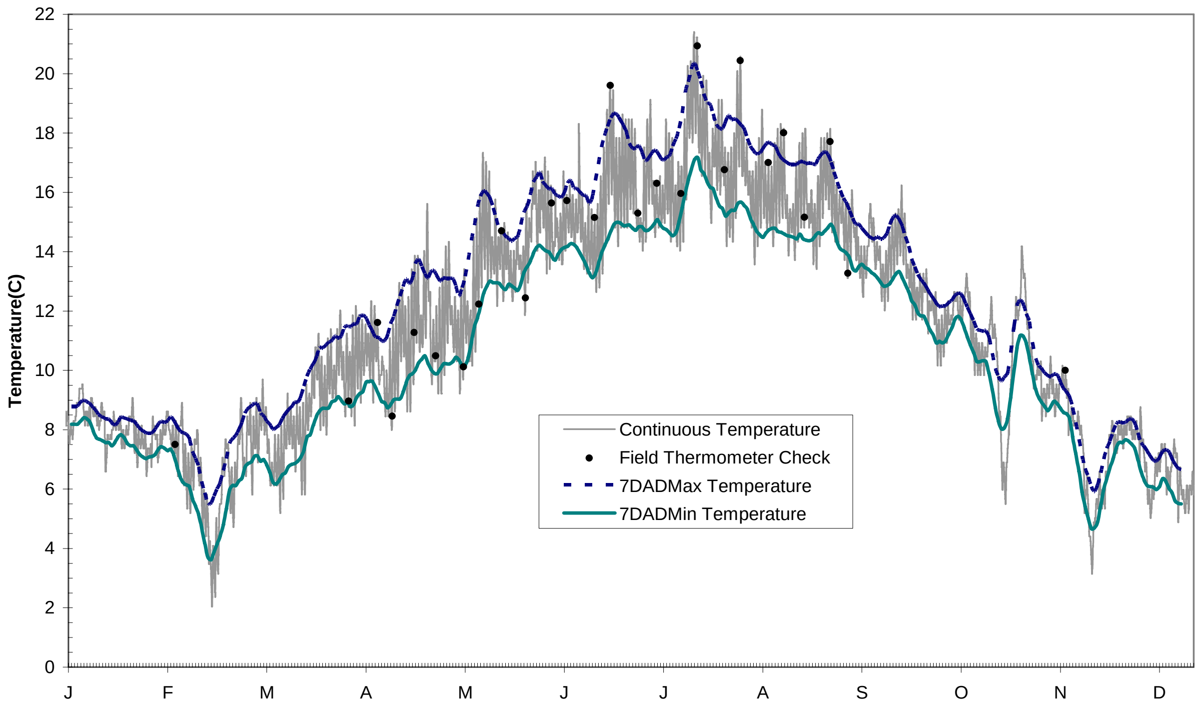

Figure C-2. 2006 continuous temperature profile for the mainstem of Thornton Creek.

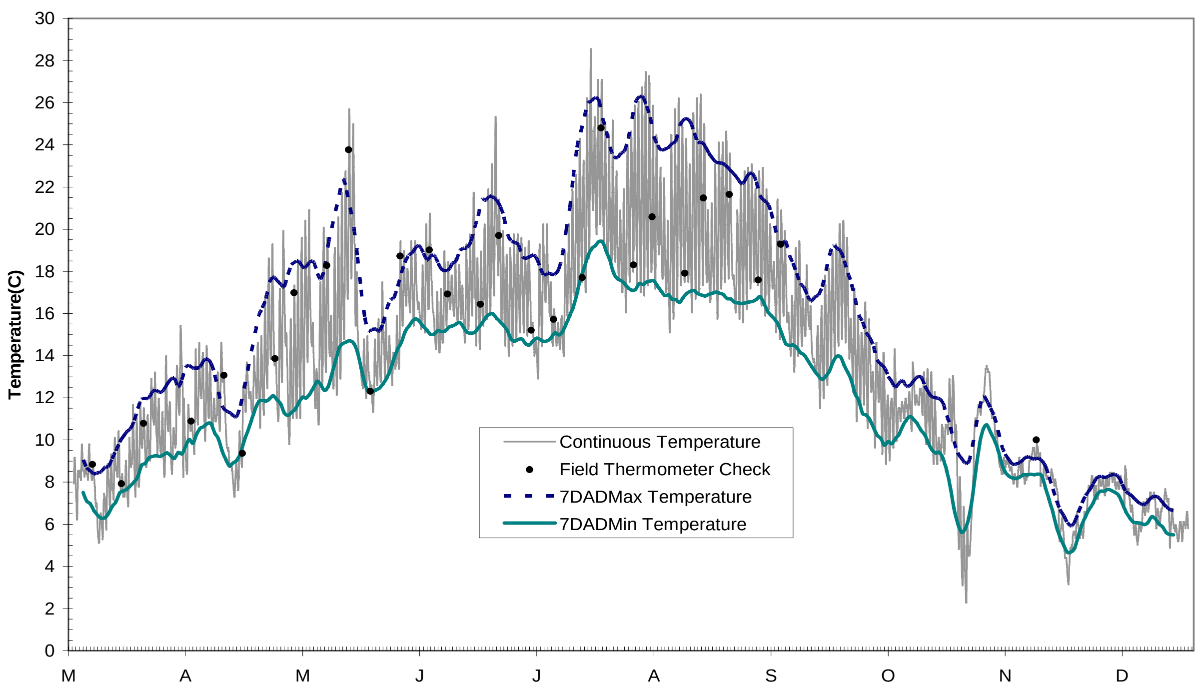

Figure C-3. 2006 continuous temperature profile for Big Ditch Slough.

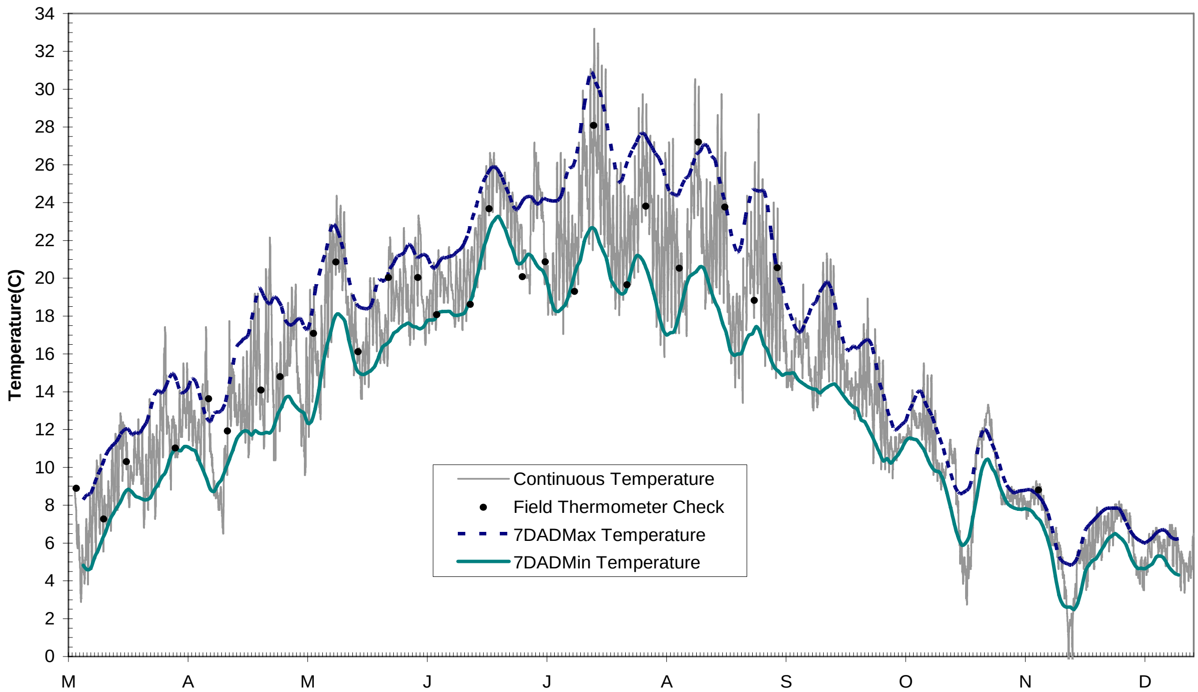

Figure C-4. 2006 continuous temperature profile for Browns Slough.

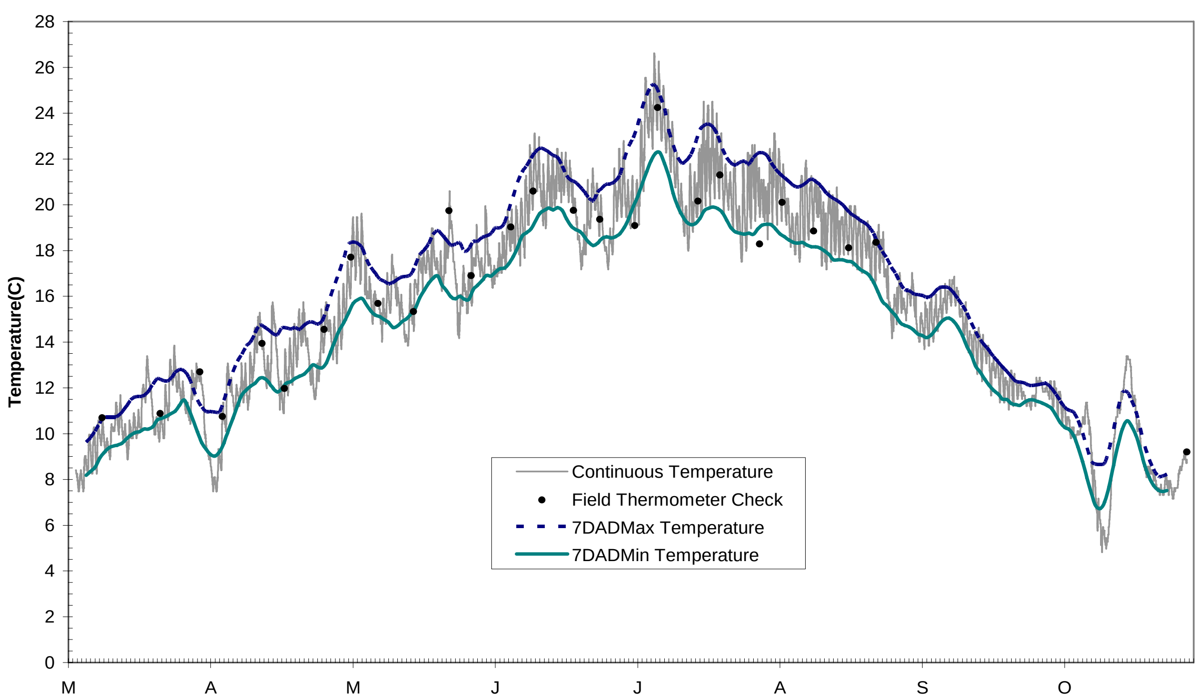

Figure C-5. 2006 continuous temperature profile for Indian Slough.

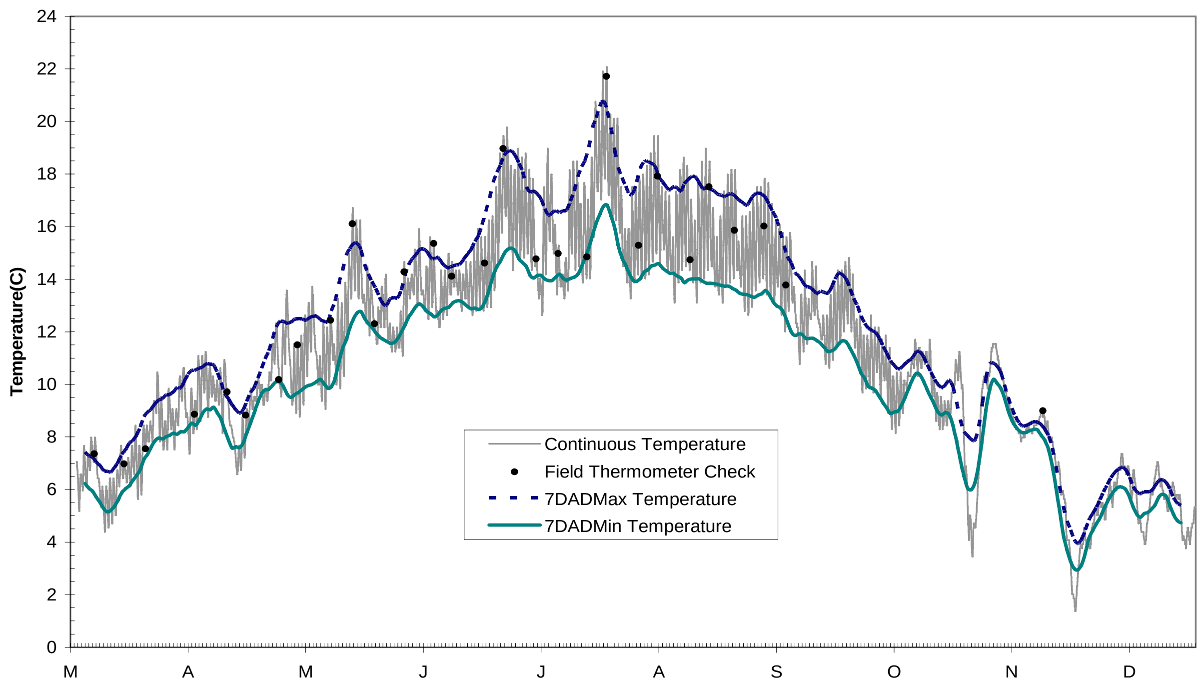

Figure C-6. 2006 continuous temperature profile for the Lower Samish River.

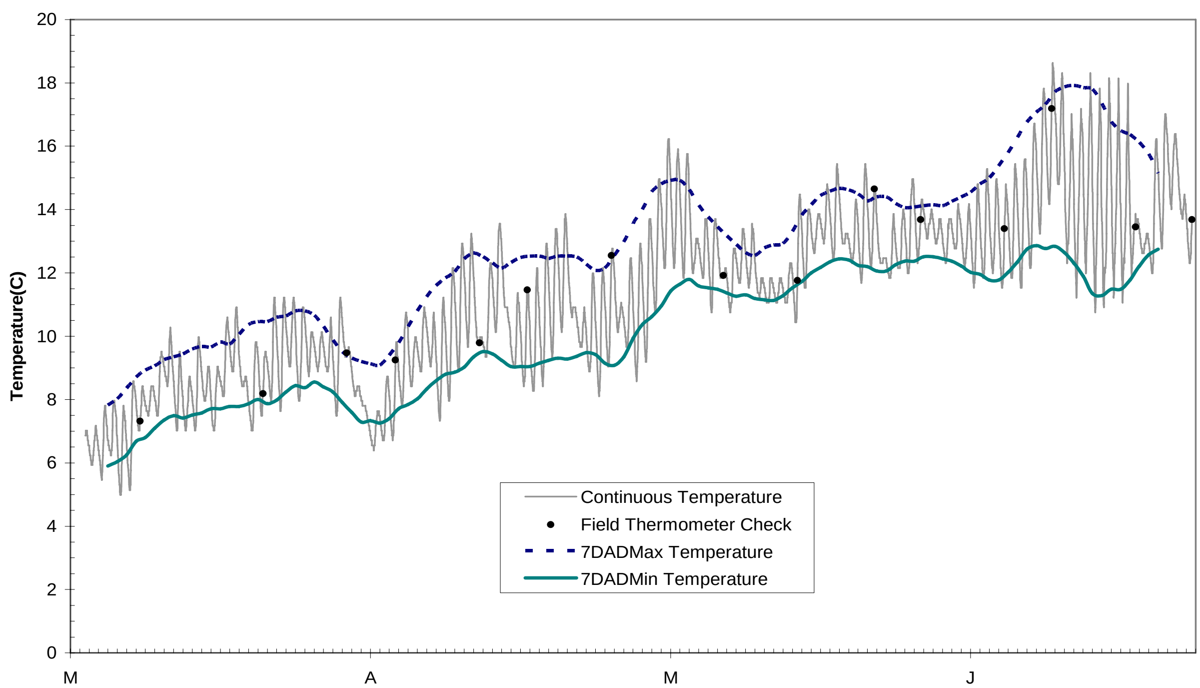

Figure C-7. 2006 continuous temperature profile for the Upper Samish River.

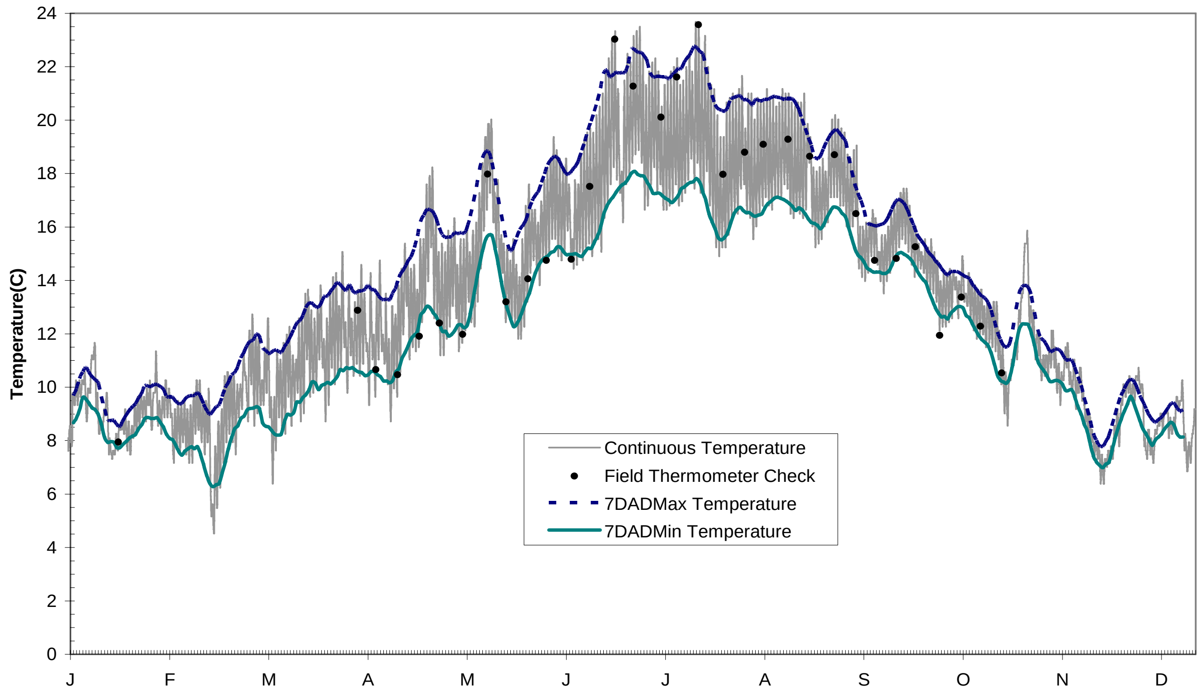

Figure C-8. 2006 continuous temperature profile for Marion Drain.

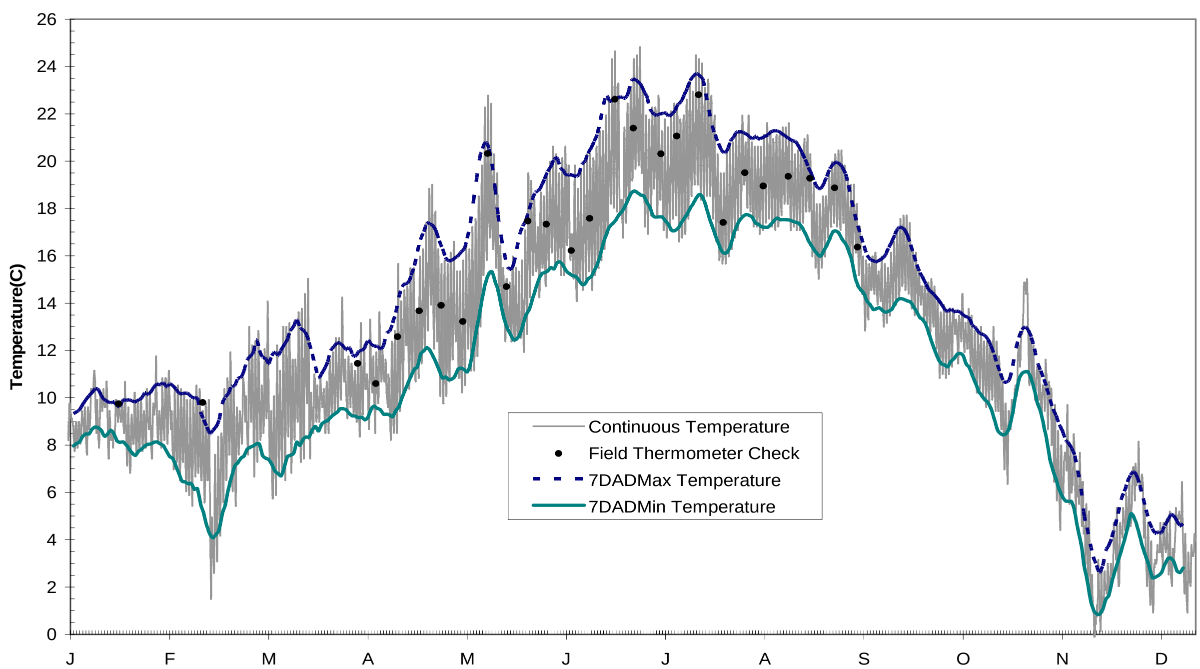

Figure C-9. 2006 continuous temperature profile for Sulphur Creek Wasteway.

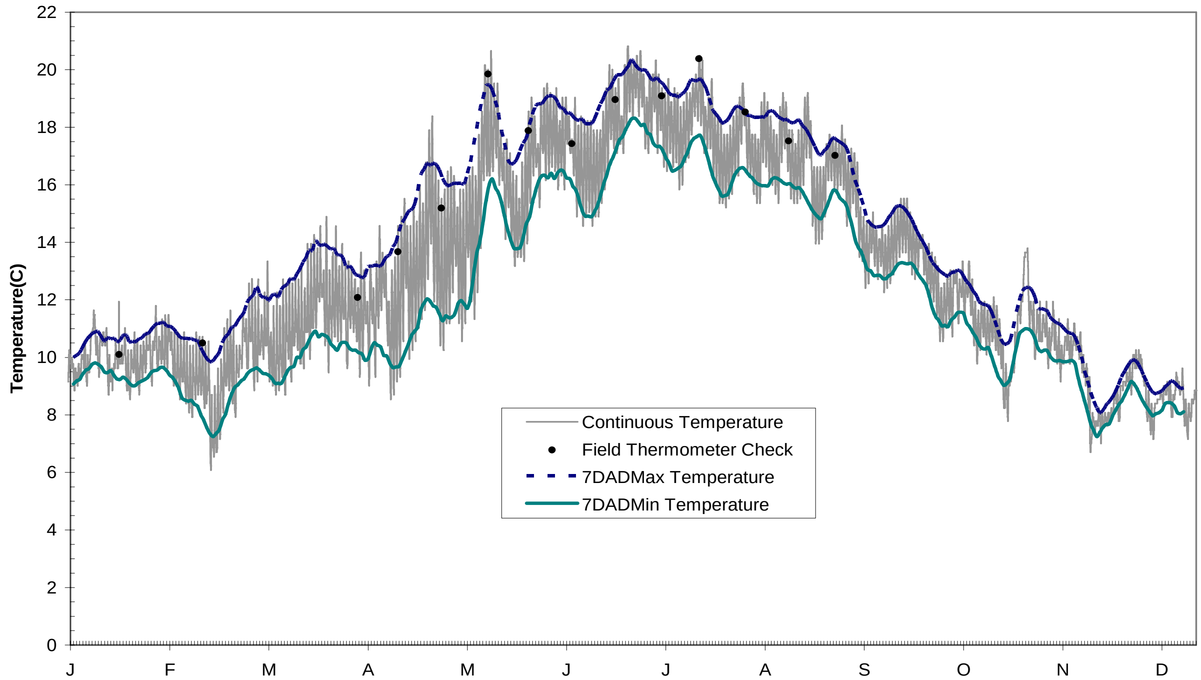

Figure C-10. 2006 continuous temperature profile for Upper Spring Creek.

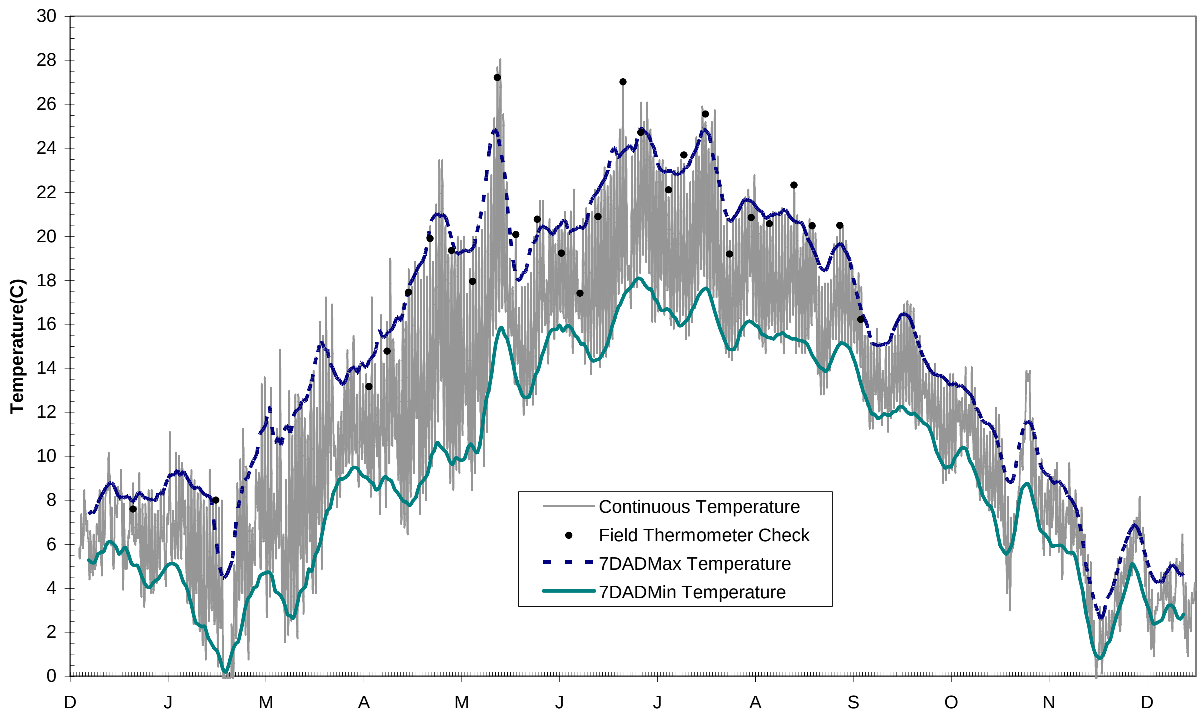

Figure C-11. 2006 continuous temperature profile for Lower Spring Creek.