Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April through October, 2004

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

August 2005

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Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April through October, 2004

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

by

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August 2005

Waterbody Numbers:
Thornton Creek WA-08-1020, Spring Creek WA-37-1014,
Marion Drain WA-37-1025, Sulphur Creek Wasteway WA-37-1030

Ecology Publication No. 05-03-025

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Abstract

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) designed a three-year monitoring study to characterize pesticide concentrations in salmonid-bearing streams during the typical pesticide-use season. This report presents data from the second year, 2004, in the study.

Two index watersheds, representing urban and agricultural land-use patterns, were sampled from March through October 2004. Thornton Creek in the Cedar-Sammamish watershed was chosen as the urban drainage. Marion Drain, Spring Creek, and Sulphur Creek Wasteway in the Lower Yakima watershed were chosen as the agricultural drainage.

Five conventional water quality parameters – discharge, temperature, pH, conductivity, and total suspended solids – were measured to characterize water quality of the streams and to investigate pesticide fate and toxicity.

Concentrations of all pesticides were generally low and close to analytical detection limits. In the agricultural basin, 2,4-dichlorophenylacetic acid (2,4-D) was the most commonly detected pesticide. Dichlobenil was most commonly detected in the urban watershed.

Pesticide detections were compared to Washington State promulgated and EPA recommended aquatic life criteria. Detections were also compared to acute and chronic toxicological endpoints used for pesticide registration by the EPA, Office of Pesticide Programs, Environmental Fate and Effects Division.

Five pesticides – azinphos-methyl, chlorpyrifos, diazinon, malathion, and 4,4’-DDE – were above the numeric component of various standards, but the weekly sampling frequency of this study did not allow for assessment of the temporal component of these standards. A single detection of malathion (3.05 µg/L) approached the acute LC_{50} for rainbow trout (4 µg/L) in the Marion Drain.

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Acronyms and Abbreviations

AED	Atomic Emission Detection
ALPQL	Average Lower Practical Quantitation Limit
CCC	Criteria Continuous Concentration
CFR	Code of Federal Regulations
CMC	Criteria Maximum Concentration
DPS	Distinct Population Segment
Ecology	Washington State Department of Ecology
EFED	Environmental Fate and Effects Division (EPA)
EIM	Environmental Information Management (Ecology)
EPA	United States Environmental Protection Agency
ESA	Endangered Species Act
ESU	Evolutionary Significant Unit
GC	Gas Chromatography
LCS	Laboratory Control Sample
LC_{50}	Lethal Concentration for 50% of a Population
LOC	Level of Concern
MDL	Method Detection Limit
MEL	Manchester Environmental Laboratory
MS	Mass Spectrometry
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NAWQA	National Water Quality Assessment Program (USGS)
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observable Effect Concentration
NRWQC	National Recommended Water Quality Criteria (EPA)
OP	Organophosphate
PQL	Practical Quantitation Limit
QA/QC	Quality Assurance/Quality Control
RED	Registration Eligibility Decision
RPD	Relative Percent Difference
SE	Sulfite Ester
TSS	Total Suspended Solids
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area
WSDA	Washington State Department of Agriculture

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Introduction

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) are conducting a three-year monitoring effort to characterize pesticide concentrations in surface waters during the typical pesticide-use season (Johnson and Cowles 2003). The data collected will allow WSDA and the U.S. Environmental Protection Agency (EPA) to refine exposure assessments for pesticides registered for use in Washington State. Understanding the fate and transport of pesticides used in Washington allows regulators to make appropriate decisions to protect endangered species while minimizing the economic impacts to agriculture.

Results from this second year of surface water monitoring, March 30 through October 27, 2004, for one urban and one agricultural watershed are presented in this report. The first year results, April through October 2003, are presented in Anderson et al. (2004).

Thornton Creek, located in the Cedar-Sammamish Water Resource Inventory Area (WRIA) 8 (Figure 1), 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 2005a). Three sub-basins of the Lower Yakima WRIA 37 were selected to represent agricultural land use: Marion Drain, Sulphur Creek Wasteway, and Spring Creek (Figure 2). These three sub-basins were selected because they have the highest percentage of land with crops and a diversity of agriculture within the drainage (Johnson and Cowles 2003).

In this 2004 study, registered and historical-use pesticides and herbicides were analyzed, including organochlorine, organophosphorus, and carbamate pesticides. 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.

Limited comparison is made between 2003 and 2004 results. After the 2005 sampling has occurred, the data will be evaluated in greater depth to assess trends over time and potential impacts on listed species.

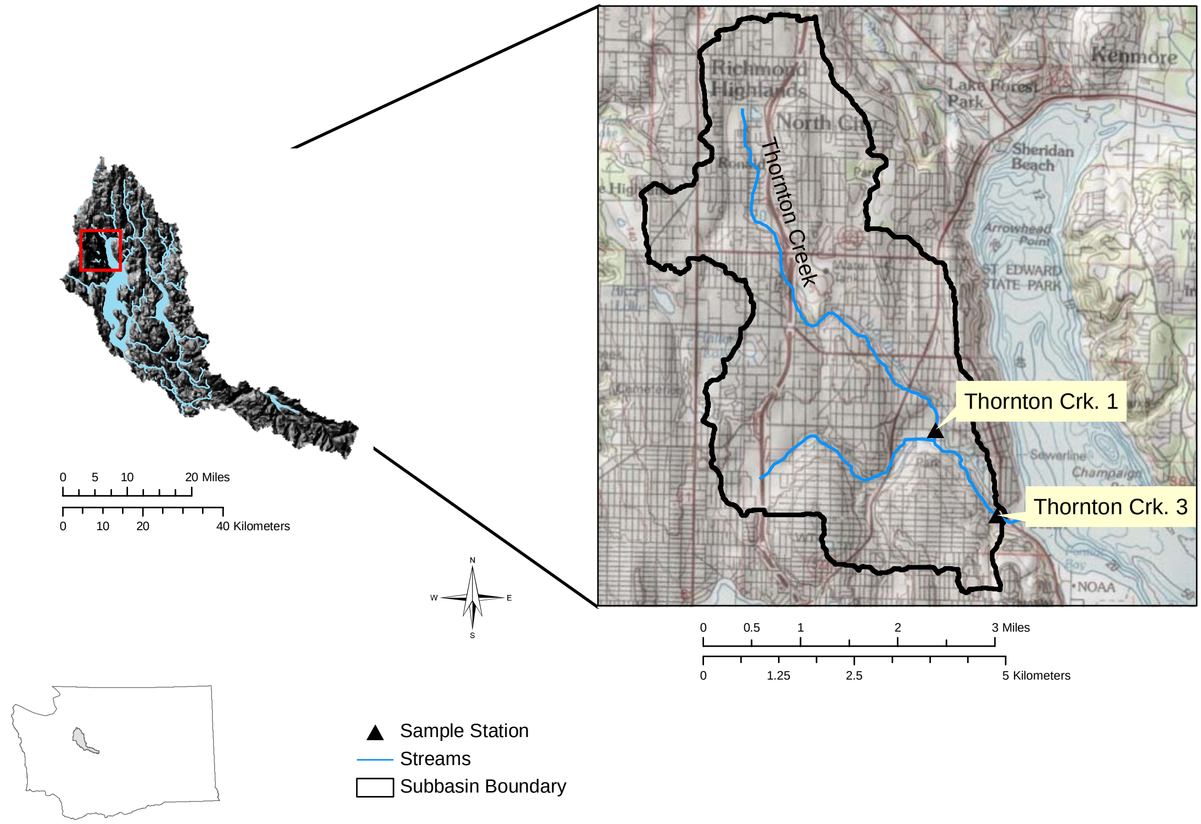

Figure 1. Sampling stations in Thornton Creek in the Cedar-Sammamish watershed.

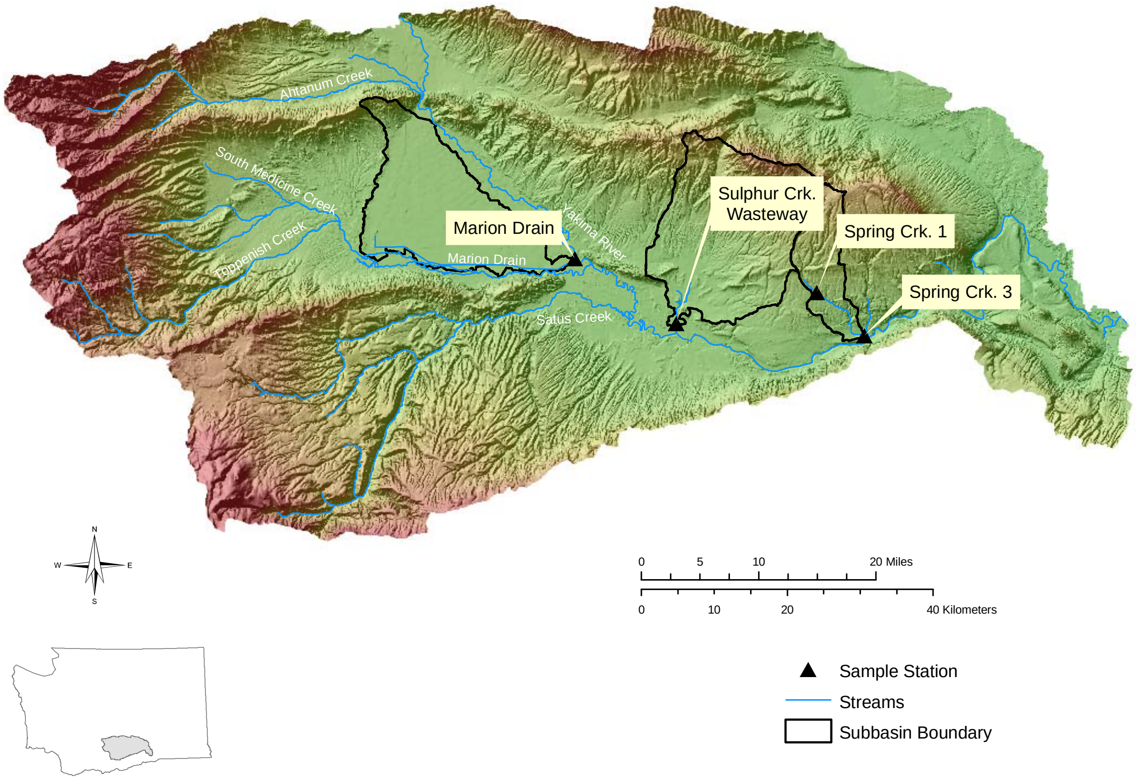

Figure 2. Sampling stations in Marion Drain, Sulphur Creek Wasteway, and Spring Creek in the Lower Yakima watershed.

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Methods

Study Design

This study is designed to measure pesticide residues in Endangered Species Act (ESA)-listed, salmonid-bearing streams during typical pesticide use periods. Site selection and sampling frequency are described below, and were previously described in the quality assurance project plan for this study (Johnson and Cowles 2003). Site locations are presented in Appendix A.

Two watersheds were selected for this study. Both watersheds are within ESA-listed geographic boundaries as designated by the National Atmospheric and Oceanic Administration (NOAA) Fisheries and the U.S. Fish and Wildlife Service (NOAA Fisheries 2005b, NOAA Fisheries and USFWS 2005). A summary of fisheries information is provided in Appendix B.

The urban stream, Thornton Creek, is within the Puget Sound Chinook Salmon Evolutionary Significant Unit (ESU) and the Puget Sound Bull Trout Distinct Population Segment (DPS), both designated threatened status. Essential Fish Habitat has been designated for chinook, coho and Puget Sound sockeye salmon under the Sustainable Fisheries Act (Magnuson-Stevens act as amended) for the Thornton Creek watershed (50 CFR Part 600 2002, NOAA Fisheries 2004b).

The three agricultural streams are within the Middle Columbia Steelhead ESU and the Columbia Basin Bull Trout DPS, both designated threatened status. Additionally, Essential Fish Habitat has been designated for chinook and coho salmon in the Lower Yakima watershed (50 CFR Part 600 2002, NOAA Fisheries 2004b).

All four streams selected for the study have documented presence of a listed threatened species (Ecology 2005, Haring 2001, Kerwin 2001, PFMC 2000, PSMFC 2005, Tyler 2004, WCC 2005, WDFW 2002, WDFW 2005, WDFW et al. 1993). Additionally, all streams and sites (except the upstream site on Thornton Creek) are subject to pesticide buffer restrictions as determined by the United States District Court, Western District of Washington (WDC Case C01-0132C http://agr.wa.gov/PestFert/EnvResources/docs/FinalOrder01-22-04.pdf, EPA 2005a).

Watercourses were named according to the USGS Geographic Names Information System (GNIS). The GNIS is the official repository of domestic geographic names information for the United States (http://geonames.usgs.gov/gnishome.html).

Frequency

The sample design was modified in 2004, based on 2003 sample results, to better characterize pesticide occurrence during the typical pesticide-use season. Three upstream sites were eliminated (Thornton 2, Marion 1, and Spring 2) which allowed for increased sampling frequency at the remaining six sites. Upstream sites were sampled every other week, and downstream sites were sampled weekly. Semivolatile organic compounds were eliminated to focus on pesticide fate and occurrence. Organochlorine pesticide analyses were eliminated in areas of limited detections (Thornton Creek) or during periods of no or few detections (July-October). Similarly, carbamate analyses were eliminated in Thornton Creek and during periods of low detection in the agricultural watersheds (July-October). Sample frequency is presented in Table 1.

Table 1. Sample frequency and analysis conducted.

Watershed	Urban: Cedar-Sammamish		Agricultural: Lower Yakima			
Drainage	Thornton Creek		Marion Drain	Sulphur Creek Wasteway	Spring Creek	
Site	Thornton 1 (Upstream)	Thornton 3 (Downstream)	Marion	Sulphur	Spring 1 (Upstream)	Spring 3 (Downstream)
Frequency	Every other week	Weekly	Weekly	Weekly	[1]Weekly (Mar-June) Every other week (July-Oct)	Weekly
[2]Pesticide Suite						
March-June	A	A	B	B	B	B
July-October	A	A	B	B	A	C

[1]Spring 1 was sampling weekly from March through June, and every other week June through October.

[2]Pesticide Suite (See Appendix D)

A	SW846 Method 8085 and SW846 Method 8270 for herbicides
B	SW846 Method 8085 with chlorinated pesticides, SW846 Method 8318 for carbamate pesticides, and SW846 Method 8270 for herbicides
C	SW846 Method 8085, SW846 Method 8318 for carbamate pesticides, and SW846 Method 8270 for herbicides

There were a total of 156 sampling events in 2004 including:

- 47 in Thornton Creek (16 at Thornton 1, and 31 at Thornton 3)
- 30 in Marion Drain
- 31 in the Sulphur Creek Wasteway
- 46 in Spring Creek (15 at Spring 1, and 31 at Spring 3)

Temperature, pH, conductivity, and streamflow were measured in the field. Chemical analyses, including total suspended solids (TSS) and pesticides, were conducted at Ecology's Manchester Environmental Laboratory (MEL) or commercial laboratories contracted by MEL.

Site Selection

Consistent with the 2003 study, the criteria applied in site selection included location within an ESA-listed (threatened or endangered) salmonid ESU, documented ESA-listed salmonid presence, land use, and historical pesticide detections. Salmonid ESA listing, presence, historical pesticide detection, and supporting references are summarized by stream and site in Appendix B. Extensive review of site selection procedures is presented in Johnson and Cowles (2003) and Anderson et al. (2004).

Urban Sites

Thornton Creek is located in the Cedar-Sammamish watershed (WRIA 8), which lies within the Puget Sound basin. WRIA 8 is encompassed by the Puget Sound Chinook ESU (threatened), the Coastal Puget Sound Bull Trout DPS (threatened), and the Puget Sound/Straight of Georgia Coho ESU (candidate for threatened status).

In 2003, there were three stations established along Thornton Creek and its tributaries. One station was located at the mouth, just upstream of the limit of influence from Lake Washington (Thornton 3). Additional stations were sited near the mouth of the south fork of Thornton Creek (Thornton 2), and near the mouth of the north fork of Thornton Creek (Thornton 1). The station located on the south fork (Thornton 2) was dropped in 2004 so weekly sampling could be conducted over the entire summer in Thornton Creek. In addition, the north fork site (Thornton 1) was relocated to a more accessible location closer to the confluence of the two forks. Therefore, for 2004, there were two sites on Thornton Creek, upstream and downstream (Figure 1).

The majority of the Thornton Creek watershed is comprised of single-family residences. Other major land uses include a golf course, shopping centers and malls, multifamily apartment complexes, and parks (Johnson and Cowles 2003)

Agricultural Sites

The agricultural basin is represented by three drainages within the Lower Yakima watershed (WRIA 37): Marion Drain, Sulphur Creek Wasteway, and Spring Creek. WRIA 37 is within the Middle Columbia Steelhead ESU (threatened) and the Columbia Basin Bull Trout DPS (threatened). While the three streams selected for this study all have documented steelhead presence, the overall quality of habitat within these drainages ranges from providing good habitat with excellent spawning gravels, to reaches that are poor habitat not capable of supporting naturally spawning populations (Romey and Cramer 2001 and personal communication, Marnie Tyler, WDFW Salmonid Recovery Coordinator).

In addition to the specifics cited below, all downstream stations (Marion 2, Sulphur 1, and Spring 3) represent reaches that terminate at the confluence with the Yakima River. The agricultural drainages have numerous minor crops such as currants, cherries, alfalfa, mint, and asparagus. See Appendix C for cropping information. The diversity of cropping, and consequently pesticide use, was the reason for choosing the Lower Yakima WRIA as an index watershed.

Marion Drain

Marion Drain is located within Yakama Indian Nation lands and has a watershed area of 85,786 acres. Fifty-five percent of the drainage is cropped; see Appendix C for commodities grown and approximate acreages. In 2003, this drainage was evaluated through an upstream station, Marion 1, and a downstream station, Marion 2. Marion 1 was not monitored in 2004; therefore in 2004, the only site on the Marion Drain was downstream near the confluence of the Yakima River (Figure 2).

Sulphur Creek Wasteway

Sulphur Creek Wasteway originates as drainage from the Roza Canal. It is a highly channelized agricultural conveyance, and is represented by one station, Lower Sulphur Creek. Salmonids are attracted to Sulphur Creek Wasteway by the high volume of irrigation return flows. Sulphur Creek Wasteway does not contain suitable spawning gravels to permit successful reproduction. The Yakama Nation, Irrigation Districts, and WDFW are working to secure funding to prevent adult salmonids from entering Sulphur Creek Wasteway. The Sulphur Creek Wasteway watershed is 103,010 acres and is 34% cropped; see Appendix C for commodities grown and approximate acreages.

Spring Creek

In the 2003 study, Spring Creek[1] was represented by three stations: Spring 1 upstream, Spring 2 midstream, and Spring 3 downstream. In 2004, the Spring 2 site was dropped and Spring 1 was moved to a location further upstream. Spring 1 was moved because of stream modification just upstream of the site. Therefore, in 2004, two sites were monitored on Spring Creek: upper and lower Spring Creek (Figure 2). The Spring Creek drainage is 27,372 acres with 54% of the area cropped; see Appendix C for commodities grown and approximate acreages.

Sampling Procedures

Pesticides

All pesticide samples were collected by hand-compositing grab samples from quarter-point transects across each stream. These transects were conducted by wading across the stream, hand-dipping a transfer container while facing upstream, and avoiding the collection of excessive particulates. A 1-L sized transfer container was used to dip into the stream and pour water into the actual sample containers. During collection of all water samples, field personnel wore non-talc nitrile gloves. Quarter point compositing was not used at Sulphur Creek (stream depths are over 5 feet). In lieu of using a bridge sampler and possibly introducing dust into samples from the road or bridge, Sulphur Creek Wasteway was sampled by hand dipping containers from the east bank (facing upstream). All sample/transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA 1990).

Each sample container was labeled with the project name, station name, laboratory number, collection date, collection time, and analyses required. All samples were placed on ice immediately after collection and held at 4ºC until extraction. Samples were transported in a secure cooler, and chain-of-custody was maintained between the field and the laboratory.

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[1] Spring Creek (Wasteway). The Washington Department of Fish and Wildlife (WDFW) and the Sunnyside Valley Irrigation District (SVID) disagree on the designation of Spring Creek as a creek vs. a constructed wasteway for irrigation return flows. SVID prevailed with designating it as a constructed wasteway in a court decision in 2002. WDFW is engaging SVID in negotiations over the designation of Spring Creek at the time this report was prepared.

Temperature, pH, and Conductivity

Temperature, pH, and conductivity were measured in the field. All meters were calibrated according to the quality assurance project plan for this project (Johnson and Cowles 2003), Environmental Assessment Program sampling protocols (Cusimano 1993, Ward 2001, Bilhimer and LeMoine 2004), USGS methods (Radtke et al. 2004), and manufacturer specifications (Thermo Electron Corporation 2004a,b).

Temperature was measured using a precision alcohol thermometer (0-50^{o}C), pH meter (Orion 250A+), and Stowaway TidbiT (hereafter referred to as *tidbit*) temperature data loggers. Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Radtke et al. 2004). Tidbit data loggers were tested and found within their acceptable accuracy range of ±0.2˚C (Bilhimer and LeMoine 2004).

Tidbit data loggers were placed at each station, near the water collection site, using the field measurement protocols of Bilhimer and LeMoine (2004). The data loggers provided 30-minute temperature measurements for the duration of the 2004 project. Tidbit data loggers are the primary source of temperature data, and are reference checked weekly against the precision alcohol and Orion 250 A+ temperature measurements. Temperature measurements were downloaded monthly from the data loggers.

pH was measured using an Orion 250 A+ handheld meter (Thermo Electron Corporation 2004a,b). At the beginning of each sampling day, the pH meter was calibrated using a three-point calibration with pH 4.01, 7.00, and 10.01 buffered standards. pH calibration follows a linear response and may be evaluated through determination of slope. Calibration was considered successful if the slope was between 97 and 100%. Recalibration of pH due to slope was not necessary in 2004. At each subsequent sampling station, the calibration drift was checked against a pH 7.00 buffer. If the measured value was within 0.05 pH units, the calibration was considered valid. If the probe deviated by more than this amount, the pH meter was recalibrated.

Conductivity was also measured in the field using a Beckman model RB-5 conductivity bridge. This meter required manual compensation to the instream temperature. The temperature measured by the precision thermometer was used for the conductivity bridge. Calibration of the conductivity bridge was periodically verified with 100 and 300 µmho/cm standards.

Discharge

Discharge is the product of velocity and cross-sectional area of a stream. Stream width was measured using an engineering tape, standard units, and divided into approximately 10 to 20 sections. Velocity and depth measurements were taken for each section using a Marsh-McBirney flow meter and top-setting rod, respectively. Velocity was measured at 60% of the total depth when depths were less than 2.0 feet. When stream depths exceeded 2.0 feet, velocity was measured at 20% and 80% of total depth and averaged. A stream segment as close as possible to the sampling site and with a relatively flat and even bottom contour was chosen for discharge evaluation. Discharge (Q in cubic feet per second) was calculated according to USGS procedures (Rantz et al. 1982).

Discharge data for Sulphur Creek were obtained from an adjacent U.S. Bureau of Reclamation gaging station, "SUCW – Sulphur Creek Wasteway at Holaday Road Near Sunnyside". Fifteen-minute discharges were available during the sampling period. The record closest to the actual sampling time was used in lieu of field measurements.

Analysis

The analytical methods used in this project are listed in Table 2. Analytical procedures are on-line at the EPA website (www.epa.gov/epaoswer/hazwaste/test/main.htm). Detailed quality assurance information is provided in Appendix D.

Table 2. Analytical methods.

Analyte	Analytical Method		Reference	Lab
	Extraction	Analysis		
pH	n/a	pH meter	n/a	Field
Temperature	n/a	pH meter	n/a	Field
Conductivity	n/a	conductivity meter	n/a	Field
Total suspended solids (TSS)	n/a	Gravimetric	EPA 160.2	MEL
Pesticides (*except carbamates*)	SW846 Method 3510	GC/AED and GC/MS	SW846 Method 8085	MEL
Carbamates	SW846 Method 8318	HPLC	SW846 Method 8318	PSC

n/a – not applicable
GC/AED - gas chromatography/atomic emission detection
GC/MS - gas chromatography/mass spectrometry
HPLC - high performance liquid chromatography
MEL - Manchester Environmental Laboratory
PSC - Philip Services Corporation

Quality Assurance/Quality Control

Conventional Water Quality Parameters

Five conventional water quality parameters were measured for this study. Of the conventional parameters, discharge, temperature, pH, and conductivity were measured in the field. Total suspended solids (TSS) were measured in the laboratory.

Discharge, Temperature, pH, and Conductivity

Field procedure QA/QC was achieved through adherence to the quality assurance project plan developed for this study (Johnson and Cowles 2003), Ecology Standard Operating Procedures (Cusimano 1993, Ward 2001), EPA methods (EPA 2004), USGS methods (Rantz et al. 1982, Radtke et al. 2004), and manufacturer specifications (Thermo Electron Corporation 2004a,b).

Total Suspended Solids

All method blanks were non-detect for these analyses. Relative percent difference for laboratory and field duplicates was within 0 to 20%. Laboratory control sample recoveries were all within the acceptance limits of 80 to 120%. Some samples were flagged as estimated due to the presence of fast settling sands. Other than this potential variation, all method QA/QC parameters were met for TSS samples.

Pesticides

Data Review

All data generated for this project were passed through multiple levels of quality review. For laboratory analyses conducted at Ecology's Manchester Environmental Laboratory (MEL), each data package generated by the analytical chemist was reviewed for quality by another independent MEL chemist prior to distribution to the project officer. In the case of carbamate pesticides, each data package delivered from the contract laboratory was evaluated for compliance with method performance criteria by MEL's quality assurance chemist prior to distribution to the project officer.

The project officer compared all of the project's case narratives to the generated data. Case narratives are provided for each analysis. They describe the method, calibration, quality assurance and quality control (QA/QC) results, and data qualification applicable to the specific analytical run (e.g., week 14 sample analysis). Data qualification describes the amount of confidence that may be placed on a single data point and is calculated according to the EPA National Functional Guidelines for Organic Data Review (EPA 1999, 2005b). A complete description of QA/QC used for this project may be found in Appendix D (Anderson et al. 2004, and Johnson and Cowles 2003).

Recovery and Qualification of Results

Sampling efforts in the urban and agricultural watersheds resulted in 574 pesticide (and degradate) detections out of 156 sampling events. Each sampling event was tested for 144 pesticides. Thus, 22,464 (156×144) chemical analyses were run in 2004. Chemical and conventional parameter results are presented in Appendix E. Many of the chemicals in the pesticide screens are not known or suspected of being used in any of the watersheds, but are part of the analytical methodology. Care should be used in evaluating a detection percentage based on the number of chemical analysis. The water samples were not filtered prior to extraction, thus the analytical results reported represent the dissolved phase as well as dislodgeable residues from any suspended solids in the sample. Analytical results are not corrected for recovery.

Most of the data collected for this project are considered usable, with qualification, as reported. Performance practical quantitation limits (PQL) were developed for this study and are reported in Appendix D. The PQL is the minimum reporting level for a constituent and is frequently established by the lowest standard used in calibration of the analytical instrument. Target performance method detection limits (MDL) and estimated detection limits (EDT) are reviewed in comparison to PQL in Appendix D**.** The MDL is generally assumed to be the minimum detection associated with an analytical method. The MDL is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the sample standard deviation estimate with n-1 degrees of freedom (Appendix D, 40 CFR Part 136 2005, EPA 1996). The EDT for the Atomic Emission Detector is based on a detector signal/noise ratio of 3:1 (MEL 2000). Practical quantitation and method detection limits are experimentally determined and will vary according to analytical run.

Of the pesticide detections, 73 were not qualified and are summarized in Appendix F. The absence of a data qualifier means the reported concentration was above the PQL, and no analytical factors are present which may influence data use. The highest degree of confidence may be placed in the 73 unqualified values. A 'J' data flag was assigned to 501 of the pesticide detections. MEL defines the 'J' flag as: The analyte is positively identified; the numerical result is an estimate (Feddersen and Magoon 2003). The 'J' flagged value is frequently an estimated concentration between the method detection limit (MDL) and practical quantitation limit (PQL). The use of 'J' qualified data in regulatory decision making is acceptable with proper consideration of analytical confidence (Appendix D; EPA 1991, EPA 2005b, NJDEP 2004). Embrey and Frans (2003), of the USGS, used estimated values for comparison to aquatic life standards. Additionally, qualified data are routinely reported within the USGS database (Mohrman 2002, Williams 1998a,b).

'NJ' flagged data are defined as: There is evidence that the analyte is present, the reported number is an estimate (Feddersen and Magoon 2003). 'NJ' designations normally result when there is not an exact match in chemical signature, or the result was detected on the AED but not confirmed on the GC/MS. 'NJ' qualified data are assigned a lower degree of confidence, are not used in summary tables or treated as detections, but are presented in Appendix E for reference. California regulations regard the 'NJ' qualification as non-detections (CSWRCB 2002), and the EPA does not support their use in regulatory decision-making (EPA 1991, 1994). A total of 307 pesticide results were ‘NJ’ flagged. The few rejected results (REJ) were not used for any purpose.

Quality Assurance and Control Measures

Field, or transport, blank samples were collected for pesticides. These samples were created by field decanting laboratory-supplied deionized water into a transfer container and then filling appropriate sample containers. Field blanks are used to assess contamination due to transport and processing of samples. No pesticides were detected in field blanks during the 2004 sample season.

Matrix spike and matrix spike duplicates (MS/MSD) were performed by collecting a duplicate volume of water at the sample site and then spiking with a known amount of analyte (i.e., concentrations of pesticide compounds) at Manchester Environmental Laboratory. Three spiking mixtures, applied on a rotating basis, were required to account for all analytes of the pesticide analyses. Only one spiking mixture was required for herbicides. MS/MSDs are an excellent measure of the complete analytical process. Results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. The average relative percent difference between MS and MSD was 6.9%. MS/MSD results are presented in Appendix D.

Field replicate samples were also conducted for pesticides. A field replicate consists of two samples collected sequentially at the same location. Collecting field replicates is a method of looking at the precision and reproducibility of the entire process of sampling and analysis. Differences between results of replicate samples may arise from the collection process, sample containers, and/or the analytical procedures. The replicate sample was labeled with a different site name than the original. These are referred to as “blind” field replicates, since the laboratory analysts are not made aware that they are field replicates (Feddersen and Magoon 2003).

The rate of consistent to inconsistent replicate sets is similar to results of USGS-NAWQA replicate analysis (1992-1997 samples) when the average pesticide concentration was less than 0.1 µg/L (~20%; Martin 2002). A replicate set is considered ‘consistent’ when both the sample and its duplicate result in a positive detection. The average relative percent difference (RPD) of consistent replicate sets was 9.46%. The median pooled standard deviation of consistent replicate sets was 7.58%. This value is lower than the NAWQA median pooled relative standard deviation of 15% at concentrations < 0.01µg/L, 13% at concentrations near 0.1 µg/L, and 12% at concentrations near 0.1 µg/L. Replicate results are presented in Appendix D.

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Results

Urban – Thornton Creek

Conventional Water Quality Parameters

2004 summary statistics for conventional water quality parameters measured in Thornton Creek are listed in Table 3. Chemical and conventional parameter results for all sites are referenced in Appendix E. Based on median values, total suspended solids (TSS) measurements were 4 mg/L higher at the station near the mouth (3-76 mg/L) of Thornton Creek than the upstream station (1-13 mg/L) during the sampling season. This difference in upstream and downstream TSS concentrations was similar to 2003 results. The maximum TSS value reported for Thornton Creek was at the downstream site and occurred following a storm event.

The upstream station had continuous discharge ranging from 1.4 – 4.1 cubic feet per second (cfs). Discharge decreased with the progression of summer. The lowest water volumes were reached at the end of August. The downstream station had consistently higher flow measurements (2.6 – 17.0 cfs) than the upstream station.

Table 3. Conventional parameters for Thornton Creek, 2004.

Parameter	n	Minimum	Median	Maximum
Thornton 1 (upstream)				
TSS (mg/L)	16	1	3	13
Temperature (˚C)	10,081	7.4	14.5	20.2
pH	16	7.3	8.0	8.2
Conductivity (µmhos/cm)	16	205	239	260
Discharge (cfs)	16	1.4	2.6	4.1
Thornton 3 (downstream)				
TSS (mg/L)	31	3	7	76
Temperature (˚C)	10,081	7.4	14.8	21.9
pH	31	7.1	7.8	8.2
Conductivity (µmhos/cm)	31	165	248	291
Discharge (cfs)	31	2.6	5.0	17.0

Pesticides

A total of 47 sampling events were conducted within Thornton Creek (16 upstream and 31 downstream) between March 30 and October 27, 2004. As in 2003, herbicides dominate the detection profile (Table 4). Dichlobenil was the most commonly detected compound (0.0039 – 0.12 µg/L), followed by 2,4-D (0.0047 – 0.21 µg/L) and triclopyr (0.011 – 0.085 µg/L). The most commonly detected organophosphorus insecticide, diazinon, was detected in 12.8% of the samples with a maximum value of 0.101 µg/L.

Table 4. Pesticide detections for Thornton Creek, 2004.

Chemical	Category	[1]Detections	[2]Det. Freq.	[3]ALPQL	Concentration (µg/L) Min	Median	[4]Max
Dichlobenil	Herbicide	36	76.6%	0.063	0.0039	0.012	0.12
2,4-D	Herbicide	19	40.4%	0.079	0.0047	0.035	0.21*
Triclopyr	Herbicide	19	40.4%	0.079	0.011	0.033	0.085*
MCPP (Mecoprop)	Herbicide	18	38.3%	0.079	0.0076	0.024	0.1*
Pentachlorophenol	Wood Preservative	17	36.2%	0.079	0.0069	0.014	0.078
Prometon (Pramitol 5p)	Herbicide	13	27.7%	0.031	0.0019	0.0056	0.025
Diazinon	Insecticide/OP	6	12.8%	0.026	0.01	0.0205	0.101
Ethoprop	Insecticide/OP	1	2.1%	0.025	0.036	0.036	0.036
Sample Events	16 at T1 and 31 at T3 = 47						

Results as reported by Manchester Environmental Laboratory.
[1] Number of detections based on unqualified and 'J' qualified data.
[2] Detection Frequency is calculated as Detections/Total number of sample events (47).
[3] ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix D.
[4] Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified.
Insecticide/OP: Insecticide Organophosphate

Dichlobenil was consistently detected at both stations from March 30 through September 1. Prometon was not detected at either station until June and was not detected after August. Pentachlorophenol and MCPP (Mecoprop) were detected throughout the entire sampling period at the downstream station. However, both residue detections did not follow any pattern. Both stations on Thornton Creek had consistent detection patterns of triclopyr over the sampling period from March to October.

Agricultural – Marion Drain, Sulphur Creek Wasteway, and Spring Creek

Conventional Water Quality Parameters

Summary statistics for conventional water quality parameters measured in the agricultural basin are presented in Table 5. TSS results were variable in the sampled drainages with values ranging from 1 to 180 mg/L. The highest median value (37 mg/L) was measured at the downstream Spring Creek station. The lowest values were measured in the Marion Drain and the upstream station of Spring Creek. Conductivity measurements were variable across all agricultural stations. The maximum conductivity values were measured on the last day of the sampling period at the downstream Spring Creek station (605 µmhos/cm) and Sulphur Creek Wasteway (651 µmhos/cm). The maximum values were 300 µmhos/cm greater than the median value for each respective station and were taken when irrigation had been discontinued for the year in the respective watersheds.

Discharge measurements were variable across all stations. Sulphur Creek Wasteway typically had the highest discharge except during the last two months of the sampling period when Marion Drain's discharge was greater. Median water temperatures were similar across all stations with the exception of the upper station on Spring Creek. This station had water temperatures at least one degree higher than the other stations. The highest water temperatures of the Lower Yakima watershed were measured in Spring Creek (Table 5).

Table 5. Conventional parameters for the Lower Yakima watershed, 2004.

Parameter	n	Minimum	Median	Maximum
Marion Drain				
TSS (mg/L)	30	1	7	62
Temperature (˚C)	10,076	9.4	16.6	24.0
pH	30	7.5	8.1	9.0
Conductivity (µmhos/cm)	30	159	257	365
Discharge (cfs)	28	3.0	79.4	303.6
Sulphur Creek Wasteway				
TSS (mg/L)	31	7	24	180
Temperature (˚C)	10,075	7.8	16.8	24.3
pH	31	7.9	8.2	8.8
Conductivity (µmhos/cm)	31	210	319	651
Discharge (cfs)	31	79.9	201.4	509.0
Spring Creek (upstream)				
TSS (mg/L)	23	1	5	23
Temperature (˚C)	9,501	9.5	18.2	27.5
pH	23	7.3	7.7	8.9
Conductivity (µmhos/cm)	23	95	154	480
Discharge (cfs)	23	0.3	0.9	2.4
Spring Creek (downstream)				
TSS (mg/L)	31	7	37	86
Temperature (˚C)	10,075	7.8	17.1	27.0
pH	31	7.7	8.3	9.1
Conductivity (µmhos/cm)	31	170	226	605
Discharge (cfs)	31	8.4	36.9	88.6

Pesticides

A total of 107 sample events were conducted within the Lower Yakima watershed between March 31 and October 27 of 2004. Herbicides were the most commonly detected compounds. 2,4-D, atrazine, and bromacil were the most frequently detected chemicals at all agricultural stations except Marion Drain. In Marion Drain, terbacil was detected more frequently than bromacil. Chlorpyrifos, malathion, and azinphos-methyl (Guthion) were the most frequently detected organophosphorus pesticides. Relative to other sample results, singular high concentrations of malathion (3.05 µg/L), bentazon (2.5µg/L), and propargite (2.144 µg/L) were detected in the Marion Drain. The majority of pesticide/herbicide results were assigned a ‘J’ data flag as their concentrations were estimated between the method detection and practical quantitation limits.

Marion Drain

A total of 30 samples were taken from Marion Drain. All samples were collected at the downstream station which is located near the confluence of the Yakima River. Summary statistics for pesticide detections in Marion Drain are presented in Table 6.

A total of 23 pesticides were detected in Marion Drain. Herbicides account for 81% of the chemical detections. 2,4-D, terbacil, and atrazine were detected in 77%, 67%, and 63% of the sampling events, respectively. Organophosphorus pesticides made up 18% of detected pesticides and included chlorpyrifos, malathion, and ethoprop.

Table 6. Pesticide detections for the Marion Drainage, site Marion 2, 2004.

Chemical	Category	[1]Detections	[2]Det. Freq.	[3]ALPQL	Concentration (µg/L) Min	Median	[4]Max
2,4-D	Herbicide	23	76.7%	0.079	0.016	0.045	0.22
Terbacil	Herbicide	20	66.7%	0.093	0.0069	0.088	0.37
Atrazine	Herbicide	19	63.3%	0.032	0.0031	0.016	0.142*
Bentazon	Herbicide	16	53.3%	0.079	0.017	0.125	2.5*
Chlorpyrifos	Insecticide/OP	11	36.7%	0.025	0.002	0.02	0.1*
Eptam	Herbicide	8	26.7%	0.063	0.0028	0.008	0.027
Bromoxynil	Herbicide	7	23.3%	0.079	0.02	0.034	0.081*
MCPA	Herbicide	7	23.3%	0.079	0.022	0.032	0.297*
Bromacil	Herbicide	7	23.3%	0.126	0.0041	0.0072	0.052
Malathion	Insecticide/OP	6	20.0%	0.025	0.0067	0.0275	3.05*
Ethoprop	Insecticide/OP	6	20.0%	0.025	0.013	0.0485	0.18*
Simazine	Herbicide	5	16.7%	0.031	0.0075	0.022	0.031
Pendimethalin	Herbicide	4	13.3%	0.046	0.007	0.046	0.126*
Dimethoate	Insecticide/OP	4	13.3%	0.025	0.014	0.0305	0.14
Alachlor	Herbicide	3	10.0%	0.112	0.0029	0.005	0.04
Hexazinone	Herbicide	3	10.0%	0.047	0.0056	0.009	0.036
Treflan (Trifluralin)	Herbicide	2	6.7%	0.047	0.0076	0.0153	0.023
Prometon (Pramitol 5p)	Herbicide	2	6.7%	0.031	0.0076	0.0218	0.036
Metolachlor	Herbicide	2	6.7%	0.127	0.0009	0.00235	0.0038
Chlorpropham	Herbicide	1	3.3%	0.127	0.032	0.032	0.032
Propargite	Insecticide/SE	1	3.3%	0.063	2.144	2.144	2.144
Disulfoton (Di-Syston)	Insecticide/OP	1	3.3%	0.019	0.023	0.023	0.023*

Sample Events	30 (29-carbamates)

Results as reported by Manchester Environmental Laboratory.
[1] Number of detections based on unqualified and 'J' qualified data.
[2] Detection Frequency is calculated as Detections/Total number of sample events (30, 29-Carbamates).
[3] ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix D.
[4] Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified.
Insecticide/OP: Insecticide Organophosphate
Insecticide/SE: Insecticide Sulfite Ester

Sulphur Creek Wasteway

The Sulphur Creek Wasteway had one sampling station located near its confluence with the Yakima River. Summary statistics for the pesticides detected during the 31 sampling events during 2004 are presented in Table 7.

The majority of the 28 pesticides detected in Sulphur Creek Wasteway were herbicides (84%). 2,4-D, bromacil, and atrazine were the most frequently detected herbicides with 84%, 71%, and 48% detection frequencies, respectively. Organophosphorus pesticides made up 12% of the 142 chemical detections. The most frequently detected organophosphorus pesticide was chlorpyrifos (19%).

Table 7. Pesticide detections for the Sulphur Creek Wasteway, 2004.

			[2]Det.		Concentration (μg/L)		
Chemical	Category	[1]Detections	Freq.	[3]ALPQL	Min	Median	[4]Max
2,4-D	Herbicide	26	83.9%	0.079	0.033	0.0805	0.41
Bromacil	Herbicide	22	71.0%	0.126	0.023	0.036	0.141
Atrazine	Herbicide	15	48.4%	0.032	0.0035	0.0088	0.029
Bentazon	Herbicide	13	41.9%	0.079	0.017	0.031	0.04
Hexazinone	Herbicide	12	38.7%	0.047	0.0022	0.0135	0.15
Terbacil	Herbicide	8	25.8%	0.093	0.0039	0.0185	0.063
4,4'-DDE	Degradate	3	21.4%	0.079	0.0009	0.002	0.0028
Chlorpyrifos	Insecticide/OP	6	19.4%	0.025	0.006	0.011	0.047
MCPA	Herbicide	5	16.1%	0.079	0.0083	0.011	0.015
Norflurazon	Herbicide	5	16.1%	0.063	0.026	0.042	0.048
Azinphos (Guthion)	Insecticide/OP	4	12.9%	0.050	0.013	0.0295	0.042
Malathion	Insecticide/OP	4	12.9%	0.025	0.0095	0.0155	0.024
Treflan (Trifluralin)	Herbicide	3	9.7%	0.047	0.0013	0.0079	0.012
Simazine	Herbicide	2	6.5%	0.031	0.013	0.014	0.015
Carbaryl	Insecticide/Carbamate	1	3.3%	0.13	0.16	0.16	0.16*
3,5-Dichlorobenzoic Acid	Degradate	1	3.2%	0.079	0.0038	0.0038	0.0038
Diazinon	Insecticide/OP	1	3.2%	0.026	0.0082	0.0082	0.0082
Dicamba I	Herbicide	1	3.2%	0.079	0.016	0.016	0.016
Dichlobenil	Herbicide	1	3.2%	0.063	0.0047	0.0047	0.0047
Dimethoate	Insecticide/OP	1	3.2%	0.025	0.018	0.018	0.018
Disulfoton (Di-Syston)	Insecticide/OP	1	3.2%	0.019	0.16	0.16	0.16*
Eptam	Herbicide	1	3.2%	0.063	0.002	0.002	0.002
MCPP (Mecoprop)	Herbicide	1	3.2%	0.079	0.021	0.021	0.021
Pendimethalin	Herbicide	1	3.2%	0.046	0.025	0.025	0.025
Pentachlorophenol	Wood Preservative	1	3.2%	0.079	0.0054	0.0054	0.0054
Pronamide (Kerb)	Herbicide	1	3.2%	0.127	0.154	0.154	0.154*
Triclopyr	Herbicide	1	3.2%	0.079	0.032	0.032	0.032
Sample Events	31 (30 for carbamates, 14 for 4,4'-DDE)						

Results as reported by Manchester Environmental Laboratory.
[1] Number of detections based on unqualified and 'J' qualified data.
[2] Detection Frequency is calculated as Detections/Total number of sample events (31, 30-Carbamates, 14 for 4,4'-DDE).
[3] ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix D.
[4] Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified.
Insecticide/OP: Insecticide Organophosphate

Spring Creek

Samples were collected at two stations in the Spring Creek drainage during 46 sampling events. Fifteen samples were collected at the upstream station, and 31 samples were collected at the downstream station. The downstream monitoring location is near the confluence of the Yakima River. Summary statistics for Spring Creek are presented in Table 8.

Twenty pesticides were detected in the Spring Creek drainage with the majority being herbicides (82%). 2,4-D, atrazine, and bromacil were detected in 78%, 44%, and 37% of the samples, respectively. Organophosphorus pesticides were detected in 14% of the samples. The most commonly detected organophosphorus pesticides were chlorpyrifos and malathion.

Table 8. Pesticide detections for the Spring Creek watershed, 2004.

					Concentration (µg/L)		
Chemical	Category	[1]Detections	[2]Det. Freq.	[3]ALPQL	Min	Median	[4]Max
2,4-D	Herbicide	36	78.3%	0.079	0.016	0.0605	0.73*
Atrazine	Herbicide	20	43.5%	0.032	0.0009	0.00705	0.024
Bromacil	Herbicide	17	37.0%	0.126	0.0066	0.023	0.086
Bentazon	Herbicide	12	26.1%	0.079	0.012	0.02	0.049
Pendimethalin	Herbicide	10	21.7%	0.046	0.016	0.0535	0.21*
Chlorpyrifos	Insecticide/OP	10	21.7%	0.025	0.005	0.012	0.077*
MCPA	Herbicide	8	17.4%	0.079	0.0073	0.0124	0.024
Malathion	Insecticide/OP	7	15.2%	0.025	0.01	0.014	0.03*
Norflurazon	Herbicide	5	10.9%	0.063	0.0079	0.032	0.058
Simazine	Herbicide	4	8.7%	0.031	0.0073	0.0105	0.032
Azinphos (Guthion)	Insecticide/OP	4	8.7%	0.050	0.014	0.019	0.023
Terbacil	Herbicide	3	6.5%	0.093	0.0094	0.032	0.055
4,4'-DDE	Degradate	1	4.8%	0.079	0.0015	0.0015	0.0015
Dicamba I	Herbicide	2	4.3%	0.079	0.021	0.0325	0.044
Pentachlorophenol	Wood Preservative	2	4.3%	0.079	0.0032	0.00415	0.0051
Oxyfluorfen	Herbicide	2	4.3%	0.127	0.021	0.031	0.041
4-Nitrophenol	Degradate	1	2.2%	0.079	0.014	0.014	0.014
Dichlobenil	Herbicide	1	2.2%	0.063	0.015	0.015	0.015
Metribuzin	Herbicide	1	2.2%	0.031	0.004	0.004	0.004
Sample Events	46 (44 for carbamates, 21 for 4,4'-DDE)						

Results as reported by Manchester Environmental Laboratory.

[1] Number of detections based on unqualified and 'J' qualified data.

[2] Detection Frequency is calculated as Detections/Total number of sample events (46, 44-Carbamates, 21 for 4,4'-DDE).

[3] ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix D.

[4] Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified.

Insecticide/OP: Insecticide Organophosphate

Discussion

Conventional Water Quality Parameters

Conventional parameters analyzed during 2004 include discharge, total suspended solids (TSS), conductivity, pH, and temperature. These parameters are useful in understanding the transport and fate of a pesticide. Additionally, multiple parameters may be combined to evaluate habitat and cumulative stresses to aquatic organisms.

The hydrologic regime, characterized by timing and magnitude of precipitation and discharge, is indicative of the physical and chemical dynamics operating within a stream. Increases in discharge, especially following a storm event, are normally the result of increased overland and subsurface storm flow. The increased force exerted by greater flows extracts dissolved and particulate matter from soils and sediments, and transports constituents to the nearest channel. Rapid increases in flow rate (i.e., storm flow) are associated with increased pesticide transport to stream channels.

TSS, conductivity, pH, and temperature influence pesticide transport and fate. Some pesticides, e.g., total DDT (t-DDT = DDT + DDE + DDD), have low solubilities and are frequently sorbed to particulate matter (TSS). Additionally, the effectiveness of several herbicides (Paraquat, Diquat, Glyphosate) is reduced in elevated TSS environments (Ross and Lembi 1999). pH can indicate the potential degradation pathway of a pesticide. Many pesticides (e.g., azinphos-methyl, carbaryl, diazinon) have shorter half-lives at higher pH levels (alkaline hydrolysis at pH 8-9). Also, temperature directly affects a pesticides solubility, chemical degradation, and microbial metabolism.

The temperature sampling regime was modified from 2003 to 2004. In 2003 data were collected during sample events. During the 2004 sampling period, temperature data were recorded every half-hour from March 31 through October 27 using instream data loggers. This continuous recording of temperature measurements provided sufficient data to calculate consecutive daily averages which more accurately characterize the temperature profile of the stream.

As shown in Figure 3, water temperature increases through the summer and eventually exceeds the 2003 Chapter 173-201A WAC temperature standard of 17.5 ºC (7-day average maximum) at all sites. The Eastern Washington sites exceeded the standard from mid-May to mid-September, and the urban site exceeded the standard from early July to early September. Given the historical data and current study results, the attainability of the promulgated standard (WAC 1997, 2003) is questionable[2]. The complete set of temperature results are presented in Appendix G.

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[2] There is a component of Washington’s 2003 temperature standard that provides for a use attainability analysis (UAA) to determine if a particular waterbody can physically meet the specified temperature standard. In order to take advantage of a UAA to raise the temperature standard of a waterbody, accurate, high-quality data must be collected for a basis to verify that current standards cannot be attained, and that a reasonable alternative is appropriate.

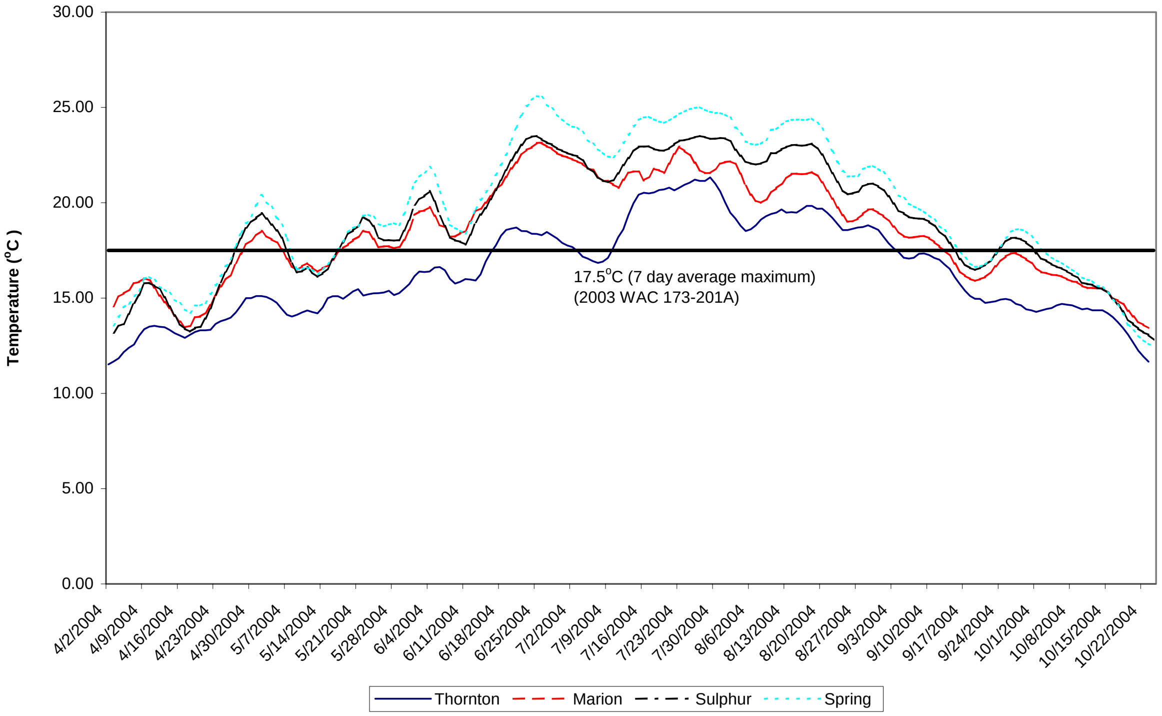

Figure 3. Seven-day average daily maximum temperature data for downstream stations.

Pesticides

Comparison of Detections to Water Quality Values

Three sets of water quality values were chosen for comparison with the results of the pesticide analysis:

- EPA National Recommended Water Quality Criteria: 2002.
- EPA Pesticide Registration Eligibility Document assessment endpoints, including the endangered species Level of Concern (LOC) which is 0.05 the LC_{50} and the chronic toxicity No Observable Effect Concentration (NOEC).
- Washington State water quality standards for the protection of aquatic life.

These standards and toxicity values were chosen because they represent either federal or state regulatory values, standards used for aquatic life protection, or the pesticide registration process in the United States. Washington State water quality standards are established in the Washington Administrative Code (WAC), Chapter 173-201A. These standards were designed to protect beneficial uses such as public enjoyment, fish, shellfish, and wildlife. EPA Registration Eligibility Documents describe toxicological endpoints used for determining the registration status of a pesticide. Of the commonly detected compounds, only pentachlorophenol, chlorpyrifos, and 4,4’-DDE as a degradate of DDT have promulgated Washington State water quality criteria. The aquatic life standards and toxicological endpoints included in Table 9 are provided to place the observed concentrations into context. A comprehensive list of available criteria is presented in Appendix H. Discharge and temporal detection relationships are presented in Appendix I.

Table 9. Results above numeric criteria, 2003 and 2004. Additional information and results are presented in Appendices D, E and F. Standards information is presented in Appendix H.

	Values above numeric criteria (n) and maximum concentration (µg/L)				Aquatic Life Standards (µg/L)				Toxicological Endpoints (µg/L)		
					[1]WAC Promulgated		[2]EPA NRWQC Recommended		[3]EPA RED		
	2003		2004								
Chemical	n	Max	n	Max	Acute	Chronic	CMC	CCC	Chronic (NOEC)	Endangered Species LOC	Species
Azinphos methyl (Guthion)	6	0.025	8	0.042	–	–	–	0.01	0.44	0.15	R
Chlorpyrifos	2	0.085	5	0.1	0.083[a]	0.041[b]	0.083	0.041	<0.12	0.15	FM/R
Diazinon	2	0.21	1	0.101	–	–	0.1	0.1	<0.55	4.5	BT/R
DDT (and [4]met.)	4	0.017	3	0.0028	1.1[c]	0.001[d]	1.1	0.001	–	–	–
Endosulfan	1	0.36	–	–	0.22[c]	0.056[d]	–	–	0.11	0.042	R
Malathion	–	–	1	3.05	–	–	–	0.1	21	0.2	R

Results as reported by Manchester Environmental Laboratory.

[1]WAC: Promulgated standards according to Chapter 173-201A WAC.

[2]EPA National Recommended Water Quality Criteria (EPA-822-R-02-047).

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

[3]EPA Registration Eligibility Document. Toxicological endpoints used in determining registration status of a pesticide.

NOEC: No observable effects concentration.

ESLOC: Endangered species level of concern. Equal to $0.05 \times \text{Acute}\,\text{LC}_{50}$

R: Rainbow Trout; FM/R Flathead Minnow used for chronic value and LOC based on Rainbow Trout; BT/R Brook Trout used for chronic value and LOC based on Rainbow Trout.

[4]Criteria applies to DDT and its metabolites (ΣDDT). 4,4'DDE is applied in this instance.

[a]A 1-hour average concentration not to be exceeded more than once every three years on average.

[b]A 4-day average concentration not to be exceeded more than once every three years on average.

[c]An instantaneous concentration not to be exceeded at any time.

[d]A 24-hour average not to be exceeded.

Five pesticides or degradates had estimated concentrations above water quality values. Although five compounds were above the numeric criteria of the various water quality standards, they do not necessarily indicate the water quality criteria have been exceeded. There is typically a temporal duration of exposure criteria in addition to numeric criteria for a water quality standard. For example, the proposed acute aquatic life criteria for diazinon reads *"…freshwater aquatic life and their uses should not be affected unacceptably if the one-hour average concentration of diazinon does not exceed 0.10 µg/L more than once every three years on the average."* (EPA 2003). Also, toxicity values such as those used for pesticide registration are determined from continuous exposure over time (e.g., LC_{50} freshwater fish acute toxicity tests are run for

96 hours at a constant concentration). Therefore, when comparing the monitoring data either to the aquatic life criteria or directly to a toxicity endpoint, one must consider the duration of exposure as well as the numeric toxicity value.

This monitoring study is designed to assess exposure of aquatic organisms to pesticides by compiling a minimum of three years of monitoring data collected weekly and every other week, and subsequently looking for trends across years (i.e., a weight of evidence approach). It is not possible to determine if an aquatic life criterion has been exceeded based solely on an individual sample because the sampling frequency is at best weekly which does not allow for assessment of the temporal component of the standard.

The relationship between frequently detected pesticides, discharge, water quality criteria for Washington State, and recommended EPA national recommended water quality criteria (NRWQC) are presented in Appendix H.

Urban – Thornton Creek

Thirteen pesticide and degradate compounds were detected in Thornton Creek during 2003, compared to eight in 2004. Of the eight detected compounds, only the organophosphorus insecticide diazinon was found to be above the recommended numeric water quality criteria. A single diazinon result of 0.101 µg/L was numerically above the EPA recommended chronic and acute concentrations of 0.1 µg/L. The result is a 'J' qualified estimate (Appendix D).

Diazinon was present in 46% of the samples in 2003 and 12.8% of the samples in 2004. Similarly, two diazinon results were above the EPA recommended criterion values in 2003 and one was above in 2004. The highest concentrations of diazinon were found at the upstream location on Thornton Creek in 2003 and 2004 (0.13 and 0.101 µg/L respectively). The decline in diazinon detections may be linked to the prohibition of diazinon sales for home owner use as of December 31, 2004. It is expected diazinon detections should diminish as existing stocks are used.

Agricultural – Marion Drain, Sulphur Creek Wasteway, and Spring Creek

A total of 37 pesticide and degradate compounds were detected in the agricultural watershed in 2004, compared to 42 in 2003. The agricultural chemical profile detected in 2003 was similar to 2004 results. Of the 37 compounds detected in 2004, four compounds were numerically above water quality criteria and included the organophosphorus insecticides azinphos-methyl, chlorpyrifos, and malathion as well as the DDT metabolite 4,4'-DDE. The DDE residues observed are the result of historical DDT use, which was banned in 1972.

Azinphos methyl

Azinphos methyl was detected eight times in 2004, and all detections were numerically above the EPA recommended chronic concentration of 0.01 µg/L. No detections approached the EPA endangered species level of concern of 0.15 µg/L used in pesticide registration decisions. The eight detections were evenly split between the Sulphur Creek Wasteway and Spring Creek. The highest concentrations were found in the Sulphur Creek Wasteway on May 26 (0.036 µg/L) and June 2 (0.042 µg/L). Maximum Spring Creek detections occurred during June 23 (0.02 µg/L) and July 28 (0.023 µg/L) at the upstream site. All azinphos methyl concentrations are 'J' qualified estimates as their concentration was below the average lower practical quantitation limit of 0.050 µg/L.

Chlorpyrifos

Chlorpyrifos was the most commonly detected insecticide in the agricultural watershed. Chlorpyrifos was detected 37 times and at all sample stations. Of the 37 detections, five results were above the numeric WAC promulgated and EPA recommended chronic criterion of 0.041 µg/L (four-day average). One result (0.1 µg/L) was above the acute numeric criterion of 0.083 µg/L (WAC and EPA – one-hour average). This result also approaches the RED ESLOC (0.15 µg/L) and chronic NOEC of < 0.12 µg/L (see Appendix H).

Chlorpyrifos results, above numeric criterion, were split between Marion Drain (three detections), the downstream Spring Creek location (March 31, 0.077 µg/L) and Sulphur Creek Wasteway (August 11, 0.047 µg/L). The Marion Drain detections occurred on consecutive sampling events (Sept 8, 0.052 µg/L; Sept 15, 0.1 µg/L; and Sept 22, 0.074 µg/L). Four of the five elevated chlorpyrifos results were unqualified and one result was 'J' qualified.

Malathion

Malathion was detected 17 times, and in all agricultural watersheds. In the Marion Drain, malathion was detected on five sampling events from April through June at concentrations ranging from 0.0067 – 0.084 µg/L before a single high concentration of 3.05 µg/L was detected on July 21. The acute LC_{50} for rainbow trout and coho salmon reported in the EPA Registration Eligibility Document (RED) for malathion are 4 and 170 µg/L respectively (Appendix H). The concentration of malathion detected on July 21 is above the EPA recommended Criteria Continuous Concentration (CCC) of 0.1 µg/L, and the endangered species level of concern (ESLOC) of 0.2 µg/L reported in the Malathion RED (Appendix H). The CCC is an estimate of the highest concentration of a pollutant an aquatic community can be exposed to indefinitely without an adverse effect. The ESLOC is calculated as $1/20^{th}$ of the acute LC_{50}.

4,4'-DDE

4,4-DDE was detected in Spring Creek and Sulphur Creek Wasteway. Three of the four detections were above the WAC and EPA recommended chronic concentration of 0.001 µg/L for DDT metabolites. Overall, the 4,4'-DDE detections were near analytical detection limits, ranging from 0.0009 µg/L (June 16, Sulphur Creek Wasteway) to 0.0028 µg/L (June 9, Sulphur Creek Wasteway). The single Spring Creek detection of 0.0015 µg/L occurred at the downstream monitoring location on June 9. The two higher June 9 detections occurred during a storm event and were likely due to sediment re-suspension. All concentrations were below the method estimated and practical quantitation limits and, as such, were 'J' qualified.

Differences over the Sampling Period

Many chemicals were detected during the sampling period, March 30 through October 27, 2004, but only a few showed a pattern or were detected more or less frequently during particular times of the season.

- 2,4-D was the only chemical detected throughout the sampling period at all stations.
- Malathion was detected at all stations during June. However, the highest concentration of malathion was detected in the Marion Drain during the third week of July.
- Pendimethalin was detected from mid-April to early June at all stations except for Sulphur Creek Wasteway.
- MCPA was detected at all stations from April 21 through early June. MCPA detections dropped off sharply after mid-May.
- Chlorpyrifos was detected at both Spring Creek stations and Sulphur Creek Wasteway from March 30 through mid-May. Chlorpyrifos was detected in Marion Drain early (April 7 – June 2) and late in the sampling period (September 8 – October 13).

Summary

This report presents results from Year 2 of a three-year study to assess the occurrence of pesticides in streams from an urban basin and an agricultural basin. The study includes monitoring data for registered pesticides and degradates as well as historically used pesticides such as DDT. Sampling occurred weekly at four downstream stations, and every other week at two upstream stations.

During 2004, eight pesticides were detected in the urban watershed during 47 sampling events. Thirty-seven pesticides were detected in the agricultural watershed during 107 sampling events. In general, concentrations of pesticides detected were between the limit of detection and the practical quantitation limit.

Detected chemicals were compared with Washington State Water Quality Standards, EPA National Recommended Water Quality Criteria for the protection of aquatic life, as well as acute and chronic toxicological endpoints used for pesticide registration by EPA.

A total of 18 detections exceeded the numeric component of water quality criteria. All elevated detections, except diazinon, occurred in the agricultural watershed. The majority of chemicals do not have water quality criteria established, and, in some cases, toxicological endpoints from EPA were not available for comparison. Although azinphos methyl, chlorpyrifos, diazinon, 4,4’-DDE, and malathion exceeded the numeric component of various standards, it is not possible to determine if an aquatic life criterion has been exceeded based solely on an individual sample. A single detection of malathion (3.05 µg/L) in the Marion Drain approached the acute LC_{50} for rainbow trout (4 µg/L), as reported in the EPA Registration Eligibility Document (Appendix H).

All four streams exceeded the 2003 Washington State temperature criterion of 17.5°C (7-day average maximum). The downstream Thornton Creek site exceeded the temperature criterion from early July to early September. The downstream sites in the three agricultural streams exceeded the temperature criterion from mid-May to mid-September.

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Appendices

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Appendix A. Monitoring Locations

Table A-1. Station location and description.

Site	Latitude*	Longitude*	Description
Thornton 1	47 42' 43.68"	122 17' 18.94"	On NE 110th Street upstream of footbridge
Thornton 3	47 41' 46.18"	122 16' 28.94"	Downstream of footbridge near Mathews Park
Marion 2	46 19' 50.39"	120 11' 56.04"	Upstream of bridge at Indian Church Road
Spring 1	46 17' 17.04"	119 46' 06.06"	Downstream side of culvert below Evans Road
Spring 3	46 14' 03.79"	119 41' 04.06"	10' downstream of the Chandler Canal overpass
Sulphur 1	46 15' 04.57"	120 01' 08.30"	Downstream side of bridge at Holaday Road

Datum = NAD 83
* Positions shown in degrees/minutes/seconds

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Appendix B. Fisheries Habitat and History of Pesticide Occurrence

Two federal statutes apply to fisheries and fisheries habitat in Washington State:

1. Endangered Species Act of 1973, as amended (PL 93-205; 16 U.S.C. 1531 et seq.)
2. Magnuson-Stevens Fishery Conservation and Management Act (16 U.S.C. 801 et seq.), as amended (Sustainable Fisheries Act PL 104-297).

Both statutes require consultation by either NOAA Fisheries or USFWS for actions affecting classified, or listed, species (and habitat, where designated).

Table B-1. Fisheries classification and historical pesticide occurrence in Thornton Creek.

WRIA	WRIA 8: Cedar-Sammamish Watershed	
Sub-Watershed	Thornton Creek	
Sites	Thornton 1	Thornton 3
Description	Northwest – Upstream	Lower
[1]Fisheries Classification		
MSA Essential Fish Habitat	Chinook, Coho, and Puget Sound Sockeye Salmon – Lake Washington	
ESA Listing – Threatened	Puget Sound Chinook ESU and Coastal Puget Sound Bull Trout DPS	
ESA Critical Habitat	Chinook CH proposed November 2004, economic exemption (proposed)	
[2]Stock Status	FCh-H, Coho-D, So-D	FCh-H, Coho-D, So-D
[3]Fish Distribution	Coho-Sp, FCh-P	FCh-Sp, So-Sp, Coho-R
[4]History of Pesticide Occurrence – Partial Listing		
Prometon, dichlobenil, atrazine, simazine, metolachlor, carbaryl, chlorpyrifos, diazinon, lindane, and malathion.		

MSA - Magnuson-Stevens Fishery Conservation and Management Act
ESA - Endangered Species Act
ESU - Evolutionary Significant Unit
DPS - Distinct Population Segment

[1] References: 50 CFR Part 226 2004, 50 CFR Part 226 2005, 50 CFR Part 402 2004, 50 CFR Part 600 2002, Ecology 2005, Kerwin 2001, NOAA 2004a, NOAA 2004b, NOAA 2005a, NOAA 2005b, NOAA et al. 2005, PFMC 2000, PSMFC 2005, WCC 2005, WDFW 1998, WDFW 2002, WDFW 2005, WDFW et al. 1993.

[2] Stock Status. FCh-H Healthy stock of Fall Chinook, Coho-D Depressed stock of Coho, So-D Depressed stock of Sockeye.

[3] Fish Distribution. Coho-Sp Spawning Coho, Coho-R Rearing Coho, FCh-P Documented presence of Fall Chinook, FCh-Sp Spawning Fall Chinook, So-Sp Spawning Sockeye.

[4] Pesticide Detections: Anderson et al. 2004, Ecology 2005, Embrey and Frans 2003.

Table B-2. Fisheries classification and historical pesticide occurrence in Marion Drain.

WRIA	WRIA 37: Lower Yakima Watershed
Sub-Watershed	Marion Drain
Sites	Marion 2
Description	Downstream
[1]**Fisheries Classification**	
MSA Essential Fish Habitat	Chinook and Coho Salmon - Lower Yakima River
ESA Listing - Threatened	Mid-Columbia River Steelhead ESU, Mid-Columbia Bull Trout DPS
ESA Critical Habitat	Steelhead proposed December 2004
[2]Stock Status	FCh-H, SuSt-D, SpCh-M
[3]Fish Distribution	FCh-Sp, Coho-P, SuSt-P
[4]**History of Pesticide Occurrence – Partial Listing**	
Parathion, dieldrin, 4,4;-DDE, terbacil, atrazine, simazine, carbaryl, metolachlor, malathion, and trifluralin.	

MSA - Magnuson-Stevens Fishery Conservation and Management Act
ESA - Endangered Species Act
ESU - Evolutionary Significant Unit
DPS - Distinct Population Segment

[1] References: 50 CFR Part 17 2002, 50 CFR Part 226 2004, 50 CFR Part 226 2005, 50 CFR Part 402 2004, 50 CFR Part 600 2002, Ecology 2005, Haring 2001, NOAA 2004a, NOAA 2004b, NOAA 2005a, NOAA 2005b, NOAA et al. 2005, PFMC 2000, PSMFC 2005, WCC 2005, WDFW 1998, WDFW 1998, WDFW 2002, WDFW 2005, WDFW et al. 1993.

[2] Stock Status. FCh-H Healthy stock of Fall Chinook, SuSt-D Depressed stock of Summer Steelhead, SpCh-M Migrating Spring Chinook.

[3] Fish Distribution. FCh-Sp Spawning Fall Chinook, Coho-P Documented presence of Coho, SuSt-P Documented presence of Summer Steelhead.

[4] Pesticide Detections: Anderson, et al. 2004, Ebbert and Embrey 2002, Ecology 2004.

Table B-3. Fisheries classification and historical pesticide occurrence in Sulphur Creek Wasteway.

WRIA	WRIA 37: Lower Yakima Watershed
Sub-Watershed	Sulphur Creek Wasteway
Sites	Sulphur 1
Description	Downstream
[1]**Fisheries Classification**	
MSA Essential Fish Habitat	Chinook and Coho Salmon - Lower Yakima River
ESA Listing - Threatened	Mid-Columbia River Steelhead ESU, Mid-Columbia Bull Trout DPS
ESA Critical Habitat	Steelhead proposed December 2004
[2]Stock Status	FCh-M, SpCh-M, SuSt-D
[3]Fish Distribution	Coho-Sp, SuSt-P, FCh-P, SpCh-P
[4]**History of Pesticide Occurrence – Partial Listing**	
4,4’-DDD, 4,4’-DDE, DDT, dieldrin, azinphos-methyl, terbacil, disulfoton, diazinon, atrazine, bromacil, chlorpyrifos, dimethoate, and carbaryl.	

MSA - Magnuson-Stevens Fishery Conservation and Management Act
ESA - Endangered Species Act
ESU - Evolutionary Significant Unit
DPS - Distinct Population Segment

[1] References: 50 CFR Part 17 2002, 50 CFR Part 226 2004, 50 CFR Part 226 2005, 50 CFR Part 402 2004, 50 CFR Part 600 2002, Ecology 2005, Haring 2001, NOAA 2004a, NOAA 2004b, NOAA 2005a, NOAA 2005b, NOAA et al. 2005, PFMC 2000, PSMFC 2005, WCC 2005, WDFW 1998, WDFW 1998, WDFW 2002, WDFW 2005, WDFW et al. 1993.

[2] Stock Status. FCh-M Migratory Fall Chinook. SpCh-M Migratory Spring Chinook, SuSt-D Depressed stock of Summer Steelhead.

[3] Fish Distribution. Coho-Sp Spawning Coho, SuSt-P Documented presence of Summer Steelhead, FCh-P Documented presence of Fall Chinook, SpCh-P Documented presence of Spring Chinook.

[4] Pesticide Detections: Anderson, et al. 2004, Ebbert and Embrey 2002, Ecology 2004.

Table B-4. Fisheries classification and historical pesticide occurrence in Spring Creek.

WRIA	WRIA 37: Lower Yakima Watershed	
Sub-Watershed	Spring Creek	
Sites	Spring 1	Spring 3
Description	Upstream	Downstream
[1]Fisheries Classification		
MSA Essential Fish Habitat	Chinook and Coho Salmon - Lower Yakima River	
ESA Listing - Threatened	Mid-Columbia River Steelhead ESU, Mid-Columbia Bull Trout DPS	
ESA Critical Habitat	None	Steelhead proposed December 2004
[2]Stock Status	SuSt-D	FCh-M, SpCh-M, Coho-M, SuSt-D
[3]Fish Distribution	SuSt-PP	Coho-Sp, SpCh-R, FCh-P, SuSt-P
[4]History of Pesticide Occurrence		
DDT, 4,4’-DDE, 4,4’-DDD, chlorpyrifos, dieldrin, malathion, atrazine, azinphos-methyl, carbaryl, prometon, simazine, terbacil, and EPTC.		

MSA - Magnuson-Stevens Fishery Conservation and Management Act
ESA - Endangered Species Act
ESU - Evolutionary Significant Unit
DPS - Distinct Population Segment

[1] References: 50 CFR Part 17 2002, 50 CFR Part 226 2004, 50 CFR Part 226 2005, 50 CFR Part 402 2004, 50 CFR Part 600 2002, Ecology 2005, Haring 2001, NOAA 2004a, NOAA 2004b, NOAA 2005a, NOAA 2005b, NOAA et al. 2005, PFMC 2000, PSMFC 2005, WCC 2005, WDFW 1998, WDFW 1998, WDFW 2002, WDFW 2005, WDFW et al. 1993.

[2] Stock Status. SuSt-D Depressed stock of Summer Steelhead FCh-M, Migratory Fall Chinook, SpCh-M Migratory Spring Chinook, Coho-M Migratory Coho.

[3] Fish Distribution. SuSt-PP Probably presence of Summer Steelhead, Coho-Sp Spawning Coho, SpCh-R Rearing Spring Chinook, FCh-P Presence of Fall Chinook, SuSt-P Presence of Summer Steelhead.

[4] Pesticide Detections: Anderson, et al. 2004, Ebbert and Embrey 2002, Ecology 2004.

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Appendix C. Crop Area Estimation

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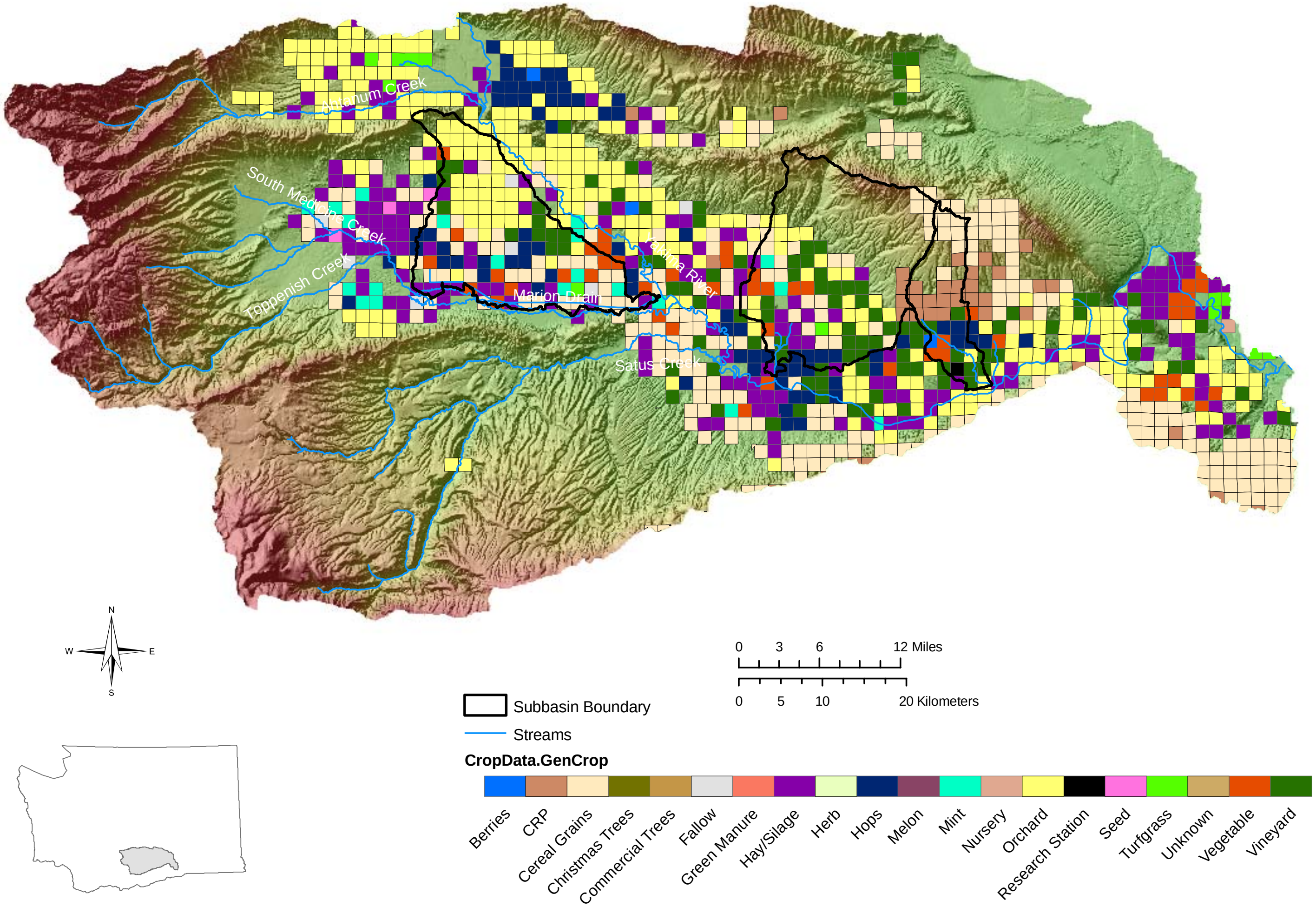

Figure C-1. Crops of the Lower Yakima watershed.

Table C-1. Marion Drain

Crop	Area (acres)	Watershed Area (%)
Apples	9602	11.19
Hops	7814	9.11
Corn	6413	7.48
Wheat	5875	6.85
Alfalfa/Grass	3800	4.43
Grapes – Concord	3747	4.37
Mint	3180	3.71
Asparagus	1452	1.69
Peaches	994	1.16
Potatoes	885	1.03
Pears	851	0.99
Cherries	620	0.72
Grass	515	0.60
Fallow	339	0.40
Barley	230	0.27
Beans	190	0.22
Onions	136	0.16
Cabbage	130	0.15
Peas	130	0.15
Oats	112	0.13
Carrots	100	0.12
Nursery	100	0.12
Turfgrass	80	0.09
Squash	63	0.07
Dill	50	0.06
Christmas Trees	40	0.05
Peppers	2.5	< 0.01
Bluegrass	0.6	< 0.01
Apricots	0.6	< 0.01
	Estimated Crop Area	47,452
	Watershed Area	85,786
	Percent Agriculture	55

Table C-2. Sulphur Creek Wasteway

Crop	Area (acres)	Watershed Area (%)
Grapes – Concord	8326	8.08
Corn	5923	5.75
Apples	5092	4.94
Alfalfa/Grass	2993	2.91
Grapes – Wine	2800	2.72
Wheat	2256	2.19
Hops	1551	1.51
Asparagus	1502	1.46
CRP	1469	1.43
Cherries	797	0.77
Mint	595	0.58
Grass	540	0.52
Pears	265	0.26
Peaches	160	0.16
Rye	155	0.15
Barley	120	0.12
Beans	120	0.12
Turfgrass	110	0.11
Sorghum	79	0.08
Squash	75	0.07
Nursery	60	0.06
Pumpkins	40	0.04
Oats	35	0.03
Apricots	25	0.02
Triticale	20	0.02
Beets	10	0.01
Turfgrass	5	< 0.01
	Estimated Crop Area	35,123
	Watershed Area	103,010
	Percent Agriculture	34

Table C-3. Spring Creek

Crop	Area (acres)	Watershed Area (%)
CRP	4614	16.85
Wheat	3089	11.28
Grapes – Wine	1676	6.12
Grapes –Concord	1386	5.06
Apples	1255	4.59
Hops	955	3.49
Research Station	625	2.28
Cherries	293	1.07
Alfalfa/Grass	193	0.70
Corn	185	0.68
Potatoes	171	0.63
Squash	165	0.60
Fallow	100	0.37
Currants	50	0.18
Peas	40	0.15
Asparagus	30	0.11
Nursery	10	0.04
Peaches	3	0.01
Pears	1	< 0.01
	Estimated Crop Area	14,841
	Watershed Area	27,372
	Percent Agriculture	54

Appendix D. Sample Analysis

Procedure and Quantitation

Pesticides, including Acidic Herbicides

Pesticide water samples were collected in organic-free, one-gallon glass jars with Teflon-lined lids, cooled to 4^{o}C for preservation, and delivered to Ecology's Manchester Environmental Laboratory (MEL) for analysis. Samples were extracted *in situ* with methylene chloride according to EPA SW-846 Method 3510 and analyzed by capillary gas chromatography/atomic emission detection (GC/AED) per SW-846 Method 8085. Confirmation and/or identification of compounds were performed by gas chromatography/mass spectrometry (GC/MS). Herbicides were analyzed by GC/MS per SW-846 Method 8270. Retention times are updated for both the MS and AED at the beginning of each analytical run. Extraction and analysis were conducted within the 7-day and 40-day holding times, respectively (EPA 2005). MEL standard operating procedures were followed for all analyses.

Analytical structure (batch sequencing) for this study is consistent between years. The number of samples in a batch varied from 3 to 6 samples**.** A typical pesticide analytical sequence constitutes:

- Conditioning shot (to remove any active sites in the inlet or column)
- CIC, injected three times to yield multipoint calibrations for the different elements
- Organophosphorus pesticide standard 1
- Organophosphorus pesticide standard 2
- Nitrogen pesticide standard 1
- Nitrogen pesticide standard 2
- Nitrogen pesticide standard 3
- Chlorinated pesticide standard 1
- Chlorinated pesticide standard 2
- Surrogate spike dilution
- Method blank 1
- Sample 1
- Sample 2
- Sample 3
- Sample 4
- Sample 5
- Sample 6
- Matrix spike dilution
- Laboratory control sample (LCS)
- Matrix spike (MS)
- Matrix spike duplicate (MSD)
- Method blank 2

- CIC, injected three times to yield multipoint calibrations for the different elements
- Organophosphorus pesticide standard 1
- Organophosphorus pesticide standard 2
- Nitrogen pesticide standard 1
- Nitrogen pesticide standard 2
- Nitrogen pesticide standard 3
- Chlorinated pesticide standard 1
- Chlorinated pesticide standard 2

MEL conducted compound independent calibrations (CIC) and single point calibrations (SPC) at both the beginning and the end of each analytical batch. The CIC is a multi-level elemental calibration for sulphur, nitrogen, chlorine, and phosphorus. CIC and SPC solutions are certified, used prior to the expiration date, and periodically evaluated to assure concentration consistency. Standards are purchased as certified solutions from AccuStandard Company.

Quantitation is performed on the Atomic Emission Detector (AED). Results below the practical quantitation limit (PQL) are quantitated with the SPC, and above the PQL are quantitated with CIC. Target analyte criteria for quantifiable residues were followed according to SW-846, Method 8085 Sections 10.2.3.1 and 10.2.3.3. Data are not corrected for recovery.

To be reported as a valid concentration, the SPC and CIC must agree within ±20%, and the percent relative standard deviation (%RSD) of the CIC elemental response factors may not exceed 10% for all compounds except phosphorus. Phosphorus may not exceed 20%. A compound receives a 'J' qualification if its identification has been MS confirmed but the concentration is below the PQL. If the compound does not have MS confirmation and the concentration is below the PQL, the value is 'NJ' qualified. Similarly, if the concentration of a confirmed compound is above the PQL but does not have %RSD agreement between SPC and CIC: the lower value is reported and 'J' qualified. If the same compound is below the PQL, the lower value is reported and 'NJ' qualified.

Carbamate Pesticides

Carbamate pesticides were collected, preserved, and analyzed separately from other samples. These pesticide samples were collected in EPA-certified clean 1-L amber glass jars. Immediately after collection, the samples were preserved to approximately pH 3 to 3.5 using chloroacetic acid.

The pH of these samples was periodically verified using test paper. These jars were stored in closed coolers away from light, on ice at 4ºC, with other samples. After delivery to MEL, the samples were shipped to Philip Services Corporation Analytical, a contract laboratory in Sidney, British Columbia, via overnight courier for analysis.

Samples were received by the contract laboratory in good condition, at a pH of less than 4 and a temperature of 3-6ºC. Rarely, samples were broken in transport or arrived above the 6°C control temperature. Broken samples were discarded and samples with temperatures above 6°C were appropriately qualified.

Samples were extracted and analyzed within a 28-day holding time per American Public Health Association (APHA) Standard Method 6610.

A five-point calibration was used for the carbamate analysis. The calibration, expressed as a water concentration, spanned the range of 0.13 to 1.75 µg/L. No surrogate compounds were used in the analysis of carbamate pesticides, but laboratory control samples (LCS) were run with every batch. The LCS was composed of deionized water spiked with all analytes of interest. Matrix Spike/Matrix Spike Duplicates (MS/MSD) and field blanks were periodically presented to the laboratory. Control limits for LCS and MS/MSD samples are 60 to 120% recovery. Performance outside of this window results in qualified data. No analytes were detected in the field blanks. The carbamate LCS, MS/MSD, and field blank samples were used to evaluate extraction efficiency, field degradation, matrix interference, and sample contamination.

Total Suspended Solids

Total suspended solids were analyzed at each station by APHA Standard Method SM2540D. One-liter polyethylene bottles, pre-washed by MEL, were used to collect waters for analysis. This method uses 1.5 µm glass fiber filters to remove particulates from the samples. After drying, the mass of solids is gravimetrically determined.

Quality Assurance and Quality Control

Field and Method Blanks

No target compounds were detected in method blanks performed with every sample batch. The method blank is produced by extracting carbon-free water in the same manner as the samples. In addition to the method blanks, two field blanks were performed using deionized water, transferred in the field from laboratory-supplied carboys, through a transfer jar, into sampling containers. Quantifiable pesticide concentrations were not found in either method or field blanks, indicating the system was free of contamination.

Surrogate Analysis

Water samples were fortified with surrogate compounds to assess potential matrix effects on analytical method performance. Recovery is used to evaluate sample specific performance, and the relative standard deviation (RSD) is used to assess precision.

When surrogate recoveries violated their respective control limits, the analyst flagged results with a data qualifier. Control limits for surrogates are presented in Table D-1. Criteria were set and modified according to EPA Contract Laboratory Program methodologies (EPA 1999, 2005). Contract Laboratory Program limits for pesticides in general are 30% to 150% (EPA 1999, 2005). Surrogate data for the 2004 analytical results are presented in Tables D-2 through D-7.

Table D-1. Control limits for pesticide surrogate recoveries.

Surrogate compound	Minimum allowable recovery	Maximum allowable recovery
2,4-Dichlorophenylacetic acid	40%	130%
2,4,6-Tribromophenol	40%	130%
Triphenyl phosphate	30%	145%
1,3 Dimethyl-2-nitrobenzene	30%	104%
Dibutylchlorendate	50%	150%
Decachlorobiphenyl	50%	120%

Table D-2. 2,4-Dichlorophenylacetic acid, herbicide surrogate.

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Thornton 1	0.5	0.446	0.099	0.221	89.3	16
Thornton 3	0.5	0.446	0.097	0.217	89.3	31
Marion 2	0.5	0.442	0.108	0.244	88.4	30
Sulphur 1	0.5	0.385	0.119	0.309	77.0	31
Spring 3	0.5	0.414	0.084	0.203	82.7	31
Spring 1	0.5	0.409	0.081	0.198	81.8	15

SD- standard deviation
RSD-relative standard deviation

Table D-3. 2,4,6-Tribromophenol, herbicide surrogate.

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Thornton 1	0.5	0.441	0.160	0.363	88.1	16
Thornton 3	0.5	0.464	0.153	0.330	92.8	31
Marion 2	0.5	0.436	0.151	0.346	87.3	30
Sulphur 1	0.5	0.451	0.143	0.317	90.2	31
Spring 3	0.5	0.470	0.122	0.260	94.0	31
Spring 1	0.5	0.475	0.079	0.165	95.0	15

SD- standard deviation
RSD-relative standard deviation

Table D-4. Triphenyl phosphate, pesticide surrogate for phosphorus-containing compounds .

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Thornton 1	1	0.986	0.252	0.256	98.6	16
Thornton 3	1	0.939	0.274	0.292	93.9	31
Marion 2	1	0.982	0.250	0.255	98.2	30
Sulphur 1	1	0.993	0.267	0.269	99.3	31
Spring 3	1	0.988	0.283	0.286	98.8	31
Spring 1	1	1.019	0.290	0.284	101.9	15

SD- standard deviation
RSD-relative standard deviation

Table D-5. 1,3-Dimethyl-2-nitrobenzene, pesticide surrogate for nitrogen-containing compounds.

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Thornton 1	1	0.528	0.208	0.394	52.8	16
Thornton 3	1	0.514	0.253	0.491	51.4	31
Marion 2	1	0.475	0.234	0.493	34.8	30
Sulphur 1	1	0.531	0.225	0.424	53.1	31
Spring 3	1	0.507	0.263	0.519	50.7	31
Spring 1	1	0.626	0.586	0.935	62.6	15

SD- standard deviation
RSD-relative standard deviation

Table D-6. Dibutylchlorendate, pesticide surrogate for chlorinated compounds.

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Marion 2	1	0.785	0.150	0.191	78.5	14
Sulphur 1	1	0.801	0.148	0.185	80.1	14
Spring 3	1	0.837	0.095	0.113	83.7	14
Spring 1	1	0.843	0.095	0.113	84.3	7

SD- standard deviation
RSD-relative standard deviation

Table D-7. Decachlorobiphenyl, pesticide surrogate for chlorinated compounds.

Sites	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
Marion 2	1	0.788	0.211	0.268	78.8	14
Sulphur 1	1	0.811	0.193	0.238	81.1	14
Spring 3	1	0.863	0.164	0.190	86.3	14
Spring 1	1	0.864	0.067	0.078	86.4	7

SD- standard deviation
RSD-relative standard deviation

Laboratory Control Samples

Laboratory control samples (LCS) contain deionized water and target analytes. LCS were performed for all compounds of interest at least once, and their concentrations were reported by the laboratory as a percent recovery. LCS determine the potential to correctly quantify an analyte, without matrix effects, and are often used to assess analytical precision and error.

The percent recovery for select laboratory control samples are presented in Table D-8. Due to interference and coelution issues, an LCS for all compounds was not conducted during every analytical run. In all instances, the average analyte recovery was < 100%. Normal analyte recoveries ranged form 70 to 105%. In one instance, the recovery of 2,4-D and malathion were less than 50% and 30%, respectively.

Table D-8. Laboratory Control Sample (LCS) percent recoveries for selected pesticides.

Analytes	Nominal Fortified Concentration (µg/L)	Mean Recovery (µg/L)	SD	RSD	Average Recovery (%)	n
2,4-D	0.25	0.203	0.051	0.252	81.3	30
4,4'-DDE	0.125	0.100	0.018	0.175	30.0	3
Azinphos-methyl	0.25	0.229	0.035	0.154	91.7	9
Carbaryl	1.25	1.185	0.106	0.090	94.8	31
Chlorpyrifos	1	0.944	0.112	0.119	94.4	9
Diazinon	1	0.942	0.010	0.011	94.2	9
Dichlobenil	1	0.959	0.118	0.123	95.9	8
Malathion	1	0.817	0.306	0.375	81.7	9

SD- standard deviation
RSD-relative standard deviation

Matrix Spike and Matrix Spike Duplicates

Matrix spike and matrix spike duplicates (MS/MSD) were performed by collecting a volume of water, in duplicate, and spiking with a MEL standard mixture. Pesticide analysis required three spiking mixtures, which were applied on a rotating basis. Only one spiking mixture was required for herbicides. MS/MSDs are an excellent measure of the complete analytical process. Results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. LCS and MS/MSD are best used in combination to evaluate analytical bias. MS/MSD results are presented in Table D-9.

Overall, the average recovery of MS/MSD samples was high and the relative percent difference (RPD) between samples very low. The average recovery of MS/MSD samples was 98%. The average RPD of MS/MSD was 6.9%. The highest RPDs tended to be for analytes whose recoveries were at the extremes of the recovery spectrum.

Table D-9. MS/MSD results, RPD, and mean RPDs for selected pesticides (µg/L).

Chemical	MS	MSD	RPD
2,4-D	66	80	19
	80	72	11
	64	55	15
	133	135	1
		Mean =	12
4,4-DDE	62	66	6
Azinphos (Guthion)	73	75	3
	108	125	15
		Mean =	9
Carbaryl	102	102	0
	98	105	7
	95	96	1
	97	100	3
	91	94	3
		Mean =	3
Chlorpyrifos	62	64	3
	111	112	1
	115	137	17
	106	102	4
		Mean =	6
Diazinon	127	130	2
	108	118	9
	89	95	7
		Mean =	6
Dichlobenil	83	95	13
	109	103	6
	86	87	1
		Mean =	7
Malathion	57	57	0
	126	138	9
	133	153	14
	111	102	8
		Mean =	8

MS – matrix spike
MSD – matrix spike duplicate
RPD – relative percent difference

Replicate Samples

Replicate sampling is useful in determining the overall variability of field and laboratory procedures. Variability may be analyzed in terms of sample qualification and quantitation.

Twenty-six replicate sets were analyzed. Of those, 20 were consistently identified at the sample qualification level (unqualified; J and NJ qualified estimates) and are presented in Table D-10. One sample, included in Table D-10, is an inconsistent replicate set where the sample was J qualified and the replicate was NJ qualified. Six of 26 replicate sets had inconsistent detections (detection/non-detection) and are presented in Table D-11.

Table D-10. Consistently detected, replicate results, RPD, and mean RPDs for selected pesticides (µg/L).

Chemical	Sample		Replicate		RPD
2,4-D	0.022	J	0.026	J	16.67
	0.097		0.097		0.00
	0.065	J	0.064	J	1.55
	0.035	J	0.036	J	2.82
	0.14		0.14		0.00
			Mean =		4.21
Atrazine	0.107		0.082		26.46
	0.0035	J	0.0071	J	67.92
	0.0049		0.0044		10.75
	0.0055	J	0.0058	NJ	5.31
			Mean =		27.61
Bentazon	0.031	J	0.031	J	0.00
	0.019	J	0.02	J	5.13
			Mean =		2.56
Bromacil	0.026	J	0.024	J	8.00
	0.03	J	0.031	J	3.28
	0.035	J	0.032	J	8.96
			Mean =		6.74
Bromoxynil	0.044	J	0.043	J	2.30
Dicamba I	0.021	J	0.023	J	9.09
Eptam	0.008	J	0.009	J	11.76
MCPA	0.297		0.276		7.33
Simazine	0.029	J	0.026	J	10.91
Terbacil	0.197	J	0.196	J	0.51
	0.012	J	0.012	J	0.00
			Mean =		0.25

RPD – relative percent difference

Table D-11. Inconsistently detected, replicate results, RPD, and mean RPDs for select pesticides (µg/L).

Chemical	Sample		Replicate		RPD
Bromacil	0.125	U	0.019	J	147.22
Hexazinone	0.047	U	0.003	J	176.00
Hexazinone	0.048	UJ	0.011	J	125.42
Pendimethalin	0.007	J	0.047	U	148.15
Terbacil	0.098	U	0.011	J	159.63
				Mean =	151.28

RPD – relative percent difference

The rate of consistent to inconsistent replicate sets is similar to results of USGS-NAWQA replicate analysis (1992-1997 samples) when the average pesticide concentration was less than 0.1 µg/L (~20%, Martin 2002). In the USGS study, and this analysis, the associated error of inconsistent replicate sets preclude use in variability analysis. Inconsistent replicate sets had a very high mean RPD, 151.28%.

The RPD of atrazine was higher than other analytes. Atrazine RPD ranged from 5.31% to 67.92%. This is probably due to estimation of values at very low levels (<0.008 µg/L). Chemical specific RPDs for other analytes ranged from 0 to 17%.

Overall, the average RPD of consistent replicate sets was very low, 9.46%. Similarly, the median pooled standard deviation is 7.58%. This value is lower than NAWQA median pooled relative standard deviation of 15% at concentrations < 0.01µg/L, 13% at concentrations near 0.1 µg/L, and 12% at concentrations near 0.1 µg/L (Martin 2002)

Summary

Overall, the QA/QC results for 2004 indicate an accurate, precise, and consistent quantitation of pesticides. No target compounds were found in method and field blanks, indicating the system was free of contamination. Surrogates, LCS, and MS/MSDs yielded recoveries that generally were biased low but within established control limits. Analysts and managers have several choices for analytical adjustment when the data appear biased low. An analyst may correct the reported concentration for percent recovery. At the next level of review, managers may employ EPA guidelines for applying adjustment factors to low biased, ‘J’ qualified data (EPA 1991, 1994). Both processes would increase the reported concentration.

MS/MSD and field replicates yielded very low RPDs among samples with an average MS/MSD RPD of 6.9% and average replicate RPD of 9.46%. No correction or statistical treatment of data, with respect to variability, is necessary.

Method, Estimated, and Practical Quantitation Limits

Method, estimated, and performance practical quantitation limits were determined for this study (Table D-12). Method detection limits (MDLs) were calculated by EPA and Manchester Environmental Laboratory (MEL) procedures according to 40CFR Part 136 (see EPA 1996, 2000, 2005, and MEL 2000). The target MDL provided by EPA is for illustrative purposes only; actual MDLs will vary by laboratory. The MDL is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom (40 CFR Part 136).

The estimated detection limit (EDL) is calculated by dividing the approximate amount of primary elements (nitrogen, phosphorus, chlorine) needed to obtain a detector signal/noise ratio of 3:1 by the fraction of primary element contained in the analyte, and then extrapolating to the sample concentration (MEL 2000).

The lower performance practical quantitation limit (LPQL) is determined by averaging the lower reporting values, per analyte, for all batches over each study year (U and UJ qualified values).

In some instances, MEL analysts were able to detect pesticides below the EPA method, MEL method, and MEL estimated detection limits. This was due to the use of larger volume injections during the 2003-2004 analyses.

Table D-12. Method detection, estimated detection, and practical quantitation limits (µg/L).

	[1]EPA	[2]Manchester		[3]WSDA	
				2003	2004
Chemical	MDL	MDL	EDL	LPQL	LPQL
1-Napthtol				0.19	0.13
2,3,4,5-Tetrachlorophenol	0.022	0.022	0.014	0.087	0.079
2,3,4,6-Tetrachlorophenol	0.023	0.018	0.014	0.087	0.079
2,4,5-T	0.033	0.018	0.017	0.125	0.079
2,4,5-TP (Silvex)	0.033	0.0099	0.022	0.125	0.079
2,4,5-Trichlorophenol	0.025	0.02	0.017	0.500	0.079
2,4,6-Trichlorophenol	0.025	0.019	0.017	0.495	0.079
2,4-D	0.042	0.019	0.028	0.160	0.079
2,4-DB	0.05	0.022	0.031	0.190	0.079
2,4'-DDD	0.02	0.02	0.038	0.018	0.079
2,4'-DDE	0.01	0.01	0.037	0.018	0.079
2,4'-DDT	0.02	0.02	0.033	0.018	0.079
3,5-Dichlorobenzoic Acid	0.042	0.017	0.024	0.160	0.079
3-Hydroxycarbofuran				0.19	0.13
4,4'-DDD	0.02	0.02	0.038	0.018	0.079
4,4'-DDE	0.02	0.02	0.03	0.018	0.079
4,4'-DDT	0.03	0.03	0.033	0.018	0.079
4-Nitrophenol	0.073	0.023	0.036	0.290	0.079
Acephate					1.594
Acifluorfen (Blazer)	0.15	0.15	0.088	0.640	0.079
Alachlor	0.1	0.1	0.16	0.335	0.112
Aldicarb				0.19	0.13
Aldicarb sulfoxide+s				0.19	0.13
Aldrin	0.006	0.006	0.029	0.018	0.079
Alpha-BHC	0.03	0.03	0.023	0.018	0.079
Ametryn	0.04	0.04	0.03	0.033	0.031
Atraton	0.13	0.13	0.03	0.052	0.047
Atrazine	0.05	0.05	0.03	0.039	0.032
Azinphos (Guthion)	0.025	0.02	0.01	0.053	0.050
Azinphos Ethyl	0.02	0.025	0.01	0.053	0.050
Bendiocarb				0.19	0.13
Benefin	0.15	0.15	0.07	0.050	0.047
Bensulide					14.187
Bentazon	0.006	0.0064	0.038	0.235	0.079
Benzamide, 2,6-dichloro-				0.22	
Beta-BHC	0.03	0.03	0.023	0.018	0.079
Bolstar (Sulprofos)	0.011	0.02	0.01	0.023	0.022
Bromacil	0.27	0.27	0.08	0.135	0.126
Bromoxynil	0.042	0.022	0.015	0.160	0.079
Butachlor	0.16	0.16	0.19	0.199	0.189
Butylate	0.14	0.14	0.13	0.066	0.063
Captafol	0.25	0.25	0.041	0.063	0.394
Captan	0.18	0.18	0.048	0.089	0.213
Carbaryl				0.19	0.13

(continued)

Table D-12 continued.

Chemical	[1]EPA	[2]Manchester		[3]WSDA	
				2003	2004
	MDL	MDL	EDL	LPQL	LPQL
Carbofuran				0.19	0.13
Carbophenothion	0.009	0.009	0.01	0.033	0.031
Carboxin	0.41	0.41	0.14	0.199	0.189
Chlorothalonil (Daconil)	0.18	0.18	0.08	0.079	0.075
Chlorpropham	0.26	0.26	0.13	0.132	0.127
Chlorpyrifos	0.004	0.004	0.011	0.026	0.025
Cis-Chlordane (Alpha-Chlordane)	0.04			0.017	0.079
Cis-Nonachlor	0.035			0.018	0.079
Coumaphos	0.01	0.010	0.011		1.504
Cyanazine	0.06	0.06	0.02	0.050	0.047
Cycloate	0.19	0.19	0.13	0.066	0.063
Dacthal (DCPA)	0.033	0.008	0.019	0.125	0.079
Delta-BHC	0.035	0.03	0.023	0.018	0.079
Demeton-O	0.021	0.021	0.008	0.033	0.022
Demeton-S	0.07	0.08	0.008	0.033	0.022
Di-allate (Avadex)	0.17	0.17	0.16	0.345	0.221
Diazinon	0.014	0.014	0.009	0.027	0.026
Dicamba I	0.042	0.022	0.028	0.160	0.079
Dichlobenil	0.06	0.06	0.1	0.065	0.063
Dichlorprop	0.046	0.014	0.029	0.170	0.079
Diclofop-Methyl	0.063	0.013	0.042	0.240	0.079
Dieldrin	0.02	0.02	0.037	0.018	0.079
Dimethoate	0.05	0.05	0.007	0.027	0.025
Dinoseb	0.063	0.016	0.038	0.240	0.079
Dioxacarb				0.19	0.13
Diphenamid	0.13	0.13	0.14	0.099	0.094
Disulfoton (Di-Syston)	0.016	0.016	0.008	0.020	0.019
Diuron	0.21	0.21	0.11	0.195	0.189
Endosulfan I	0	0	0.032	0.018	0.079
Endosulfan II	0	0	0.032	0.018	0.079
Endosulfan Sulfate	0.03	0.03	0.033	0.018	0.079
Endrin	0.03	0.03	0.03	0.018	0.079
Endrin Aldehyde	0.02	0.02	0.02	0.018	0.079
Endrin Ketone	0.01	0.01	0.03	0.018	0.079
EPN	0.008	0.008	0.01	0.033	0.031
Eptam	0.22	0.22	0.11	0.066	0.063
Ethalfluralin (Sonalan)	0.08	0.08	0.07	0.050	0.047
Ethion	0.006	0.006	0.006	0.023	0.022
Ethoprop	0.012	0.012	0.007	0.027	0.025
Fenamiphos	0.03		0.009	0.050	0.047
Fenarimol	0.23	0.23	0.1	0.099	0.094
Fenitrothion	0.004	0.004	0.008	0.023	0.022
Fensulfothion	0.08	0.12	0.009	0.033	0.031

(continued)

Table D-12 continued.

	[1]EPA	[2]Manchester		[3]WSDA	
				2003	2004
Chemical	MDL	MDL	EDL	LPQL	LPQL
Fenthion	0.011	0.011	0.008	0.023	0.022
Fluridone	0.66	0.66	0.2	0.199	0.189
Fonofos	0.004	0.004	0.007	0.020	0.019
Gamma-BHC (Lindane)	0.03	0.03	0.023	0.018	0.079
Heptachlor	0.01	0.01	0.025	0.018	0.079
Heptachlor Epoxide	0.008	0.008	0.026	0.018	0.079
Hexachlorobenzene	0.04	0.04	0.069	0.018	0.079
Hexazinone	0.05	0.05	0.04	0.050	0.047
Imidan	0.007	0.007	0.01	0.036	0.035
Ioxynil	0.042	0.0063	0.019	0.160	0.079
Kelthane	0.17			0.051	0.315
Malathion	0.01	0.01	0.01	0.027	0.025
MCPA	0.083	0.022	0.05	0.315	0.079
MCPP (Mecoprop)	0.083	0.029	0.054	0.315	0.079
Merphos (1 & 2)	0.024	0.06	0.009	0.040	0.038
Metalaxyl	0.35	0.35	0.17	0.199	0.189
Methamidophos					1.594
Methidathion					1.594
Methiocarb				0.19	0.13
Methomyl				0.19	0.13
Methoxychlor	0.03	0.03	0.054	0.088	0.079
Methyl Chlorpyrifos	0.008	0.008	0.01	0.027	0.025
Methyl Parathion	0.005	0.005	0.008	0.023	0.022
Metolachlor	0.15	0.15	0.17	0.133	0.127
Metribuzin	0.02	0.02	0.03	0.033	0.031
MGK264	0.26	0.26	0.16	0.263	0.252
Mirex	0.04	0.04	0.021	0.018	0.079
Molinate	0.17	0.17	0.11	0.066	0.063
Naled					1.594
Napropamide	0.11	0.11	0.16	0.099	0.094
Norflurazon	0.07	0.07	0.06	0.066	0.063
Oxamyl				0.19	0.13
Oxychlordane	0.035			0.018	0.079
Oxyfluorfen	0.1	0.1	0.22	0.134	0.127
Parathion	0.009	0.009	0.009	0.027	0.025
Pebulate	0.11	0.11	0.12	0.066	0.063
Pendimethalin	0.06	0.06	0.06	0.050	0.046
Pentachloroanisole	0.035			0.018	0.079
Pentachlorophenol	0.021	0.007	0.013	0.080	0.079
Phorate	0.006	0.006	0.008	0.023	0.022
Picloram	0.042	0.004	0.02	0.160	0.079
Profluralin	0.07	0.07	0.07	0.079	0.075
Promecarb				0.19	0.13
Prometon (Pramitol 5p)	0.04	0.04	0.03	0.032	0.031

(continued)

Table D-12 continued.

Chemical	[1]EPA	[2]Manchester		[3]WSDA	
				2003	2004
	MDL	MDL	EDL	LPQL	LPQL
Prometryn	0.04	0.04	0.03	0.033	0.031
Pronamide (Kerb)	0.13	0.13	0.15	0.169	0.127
Propachlor (Ramrod)	0.12	0.12	0.13	0.079	0.075
Propargite	0.14	0.14	0.02	0.066	0.063
Propazine	0.05	0.05	0.03	0.033	0.031
Propoxur				0.19	0.13
Ronnel	0.005	0.005	0.01	0.023	0.022
Simazine	0.05	0.05	0.02	0.033	0.031
Sulfotepp	0.006	0.006	0.005	0.020	0.019
Tebuthiuron	0.03	0.03	0.03	0.050	0.047
Terbacil	0.13	0.13	0.06	0.099	0.093
Terbutryn (Igran)	0.05	0.05	0.03	0.033	0.031
Trans-Chlordane (Gamma)	0.03			0.018	0.079
Trans-Nonachlor	0.035			0.018	0.079
Treflan (Trifluralin)	0.09	0.09	0.07	0.050	0.047
Triadimefon	0.13	0.13	0.06	0.086	0.082
Triallate	0.26	0.26	0.18	0.099	0.094
Triclopyr	0.035	0.0091	0.02	0.130	0.079
Vernolate	0.22	0.22	0.12	0.066	0.063

[1]Environmental Protection Agency. Target method detection limits (MDLs). Provided for comparative purposes only.
Actual MDL for a specific matrix will vary. Each laboratory should determine its own MDL.
Lowest detection level abstracted from Tables 1-8 (EPA 2000).
MDL – Method detection limit is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom. (Appendix B to 40 CFR Part 136).
EPA 1996, 2000, 2005.

[2]Manchester Environmental Laboratory.
MDL – Method detection limit is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom. (Appendix B to 40 CFR Part 136).
EDL – Estimated detection limit is calculated by dividing the approximate amount of primary elements (nitrogen, phosphorus, chlorine) to obtain a detector signal/noise ratio of 3:1 by the fraction of primary elements contained in the analyte, and then extrapolating to the sample concentration (MEL 2000).

[3]WSDA Pesticides Study, 2003-2004
LPQL: Lower performance practical quantitation limit. Average of lower performance (reporting) values, per analyte for all batches over each study year (14-31 batches per year).

Data Qualification

Data may be qualified if one or more analytical factors effect confidence in the prescribed data value. Manchester Environmental Laboratory qualifies data according to the National Functional Guidelines for Organic Data Review (EPA 1999, 2005). Data qualification is presented in Table D-13.

Table D-13. Data qualification.

Qualifier	Definition
U	The analyte 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 (due either to the quality of the data generated because 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 inaccurate or 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 represents its approximate concentration.
NC	Not calculated

MEL 2000, EPA 2005

The multitude of reasons for data qualification are explained in the National Functional Guidelines documents (EPA 1999, 2005). The most frequent reason for a ‘J’ qualification involves a confirmed sample which has an estimated value below the practical quantitation limit (PQL). ‘NJ’ designation is most frequently assigned when confirmation between the AED and GC/MS is not successful. Of 881 quantified chemical results; 73 were unqualified, 501 received a ‘J’ qualification, and 307 received a ‘NJ’ qualification (Table D-14).

Some pesticides and herbicides are typically poor analytical performers. Questionable pesticide performers include 2,4’-DDT, 4,4’-DDT, captafol, captan, kelthane, and methoxychlor. These chlorinated pesticides are susceptible to degradation as the GC inlet gets dirty. Additionally, the original PQL for these compounds was very low and often unachievable, thus the samples were frequently rejected. Subsequently, the PQL was raised. The chlorophenoxy herbicides, dinoseb and picloram, typically experience highly variable recoveries and are routinely qualified in samples and method blanks. Demeton-s, oxyfluorfen, norflurazon, fluridone, cyanazine, hexazinone, and dimethoate historically do not perform well because of the uncertainty of the analytical behavior of these compounds, and they are normally qualified as estimates.

Diuron and linuron break down to the same product when analyzed by the AED and GC/MS. As such, we cannot be sure that what we are observing is diuron, although that is the most frequently used urea pesticide. When found, diuron and linuron are always reported with an ‘NJ’ qualifier. Confirmation may be achieved through the use of High Performance Liquid Chromatography (HPLC).

Table D-14. Pesticide data qualification summary for chemical results.

			Data Qualification		
Chemical	Classification	Results	No Qualification	J	NJ
2,4-D	Herbicide	114	33	71	10
Atrazine	Herbicide	77	3	51	23
Diuron	Herbicide	74	0	0	74
Bromacil	Herbicide	59	0	46	13
Dichlobenil	Herbicide	52	0	38	14
Pentachlorophenol	Wood Preservative	47	0	20	27
Bentazon	Herbicide	45	10	31	4
Terbacil	Herbicide	38	0	31	7
Simazine	Herbicide	35	0	11	24
Chlorpyrifos	Insecticide/OP	33	6	21	6
Prometon (Pramitol 5p)	Herbicide	32	0	15	17
MCPP (Mecoprop)	Herbicide	29	1	18	10
Triclopyr	Herbicide	27	1	19	7
MCPA	Herbicide	23	1	19	3
Norflurazon	Herbicide	20	0	10	10
Hexazinone	Herbicide	19	0	15	4
Malathion	Insecticide/OP	19	3	14	2
Pendimethalin	Herbicide	17	6	9	2
Azinphos (Guthion)	Insecticide/OP	16	0	8	8
Treflan (Trifluralin)	Herbicide	14	0	5	9
4,4'-DDE	Degradate	11	0	4	7
Bromoxynil	Herbicide	10	1	6	3
Eptam	Herbicide	10	0	9	1
Diazinon	Insecticide/OP	8	0	7	1
Dicamba I	Herbicide	8	0	3	5
Ethoprop	Insecticide/OP	8	4	3	1
Dimethoate	Insecticide/OP	7	0	5	2
Alachlor	Herbicide	6	0	3	3
Dinoseb	Herbicide	5	0	0	5
Chlorpropham	Herbicide	3	0	1	2
Metolachlor	Herbicide	3	0	2	1
4-Nitrophenol	Degradate	2	0	1	1
Disulfoton (Di-Syston)	Insecticide/OP	2	2	0	0
Oxyfluorfen	Herbicide	2	0	2	0
3,5-Dichlorobenzoic Acid	Herbicide	1	0	1	0
Carbaryl	Insecticide/Carbamate	1	1	0	0
Metalaxyl	Fungicide	1	0	0	1
Metribuzin	Herbicide	1	0	1	0
Pronamide (Kerb)	Herbicide	1	1	0	0
Propargite	Insecticide/SE	1	0	1	0
Totals		881	73	501	307

Data qualification assigned by Manchester Environmental Laboratory

Insecticide/OP:	Insecticide Organophosphate
Insecticide/SE:	Insecticide Sulfite Ester

Poor performing analytes were normally rejected, UJ or NJ qualified. The preceding qualifications excluded the value from analysis in the main body of this report. Questionable data were not compared to promulgated or recommended aquatic life criteria values.

Application of 'J' qualified values

The use of 'J' qualified values in regulatory decisions has had limited discussion among agencies, and there is little consensus of appropriateness. In this report, 'J' qualified values have been compared to promulgated and recommended criterion. The comparison is for illustrative purposes. Most compounds do not meet the time component for criteria exceedance.

Application of 'J' qualified data has been investigated through the following documents: CSWRCB 2002, Embrey and Frans 2003 (USGS), EPA 1991, EPA 1994, EPA 2005 and NJDEP 2004. All references approve of the use of 'J' qualified data with proper consideration of the qualification. The California standards document (CSWRCB 2002) considers the use of 'J' qualified data that are above the method detection limit but below the reporting limit. Direct comparison of estimated values to criteria concentrations is presented in Embrey and Franz (2003). Additional information may be gained from an analysis of potential bias.

Five considerations lend support to the application of 'J' qualified results within this data set.

1. Study results appear to be biased low (see Tables D-2 through D-8). The WSDA has taken a conservative approach to data reporting by not applying percent recovery or qualified data adjustment.
2. 'J' designation is primarily applied to confirmed data near the low end of the linear range of the instrument. 'J' qualified data provide definitive analyte identification.
3. Historical presence of identified analytes in Thornton Creek and the Lower Yakima watershed.
4. Comparable studies and guidelines that use qualified data.
5. This study uses a weight-of-evidence approach. While discussion and data are analyzed, the majority of data do not meet the time requirement for criteria exceedance, and comparisons are for illustrative uses.

Specific treatment of values above numeric criteria is presented in the *Discussion* section of this report.

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Appendix E. Chemical and Conventional Parameter Results

All sample results are available for download as a comma-delimited file from Ecology's Internet site at: http://apps.ecy.wa.gov/eimreporting/

Data are also available by parameter name, Chemical Abstract Service (CAS) number, and location. Flow, pH, conductivity, and total suspended solids (TSS) values are also available from the same website.

Appendix F. Pesticide Summaries; Unqualified and NJ Qualified Results

Table F-1. Thornton Creek pesticide summary. Unqualified values reported.

Chemical	Category	Detections	Concentration (µg/L) Min	Median	Max
2,4-D	Herbicide	1	0.21	0.21	0.21
MCPP (Mecoprop)	Herbicide	1	0.1	0.1	0.1
Triclopyr	Herbicide	1	0.085	0.085	0.085

Sample Events: 16 at T1 and 31 at T3 = 47

Table F-2. Marion Drain pesticide summary. Unqualified values reported.

Chemical	Category	Detections	Concentration (µg/L) Min	Median	Max
Bentazon	Herbicide	10	0.053	0.16	2.5
2,4-D	Herbicide	6	0.027	0.089	0.18
Ethoprop	Insecticide/OP	4	0.038	0.0645	0.18
Chlorpyrifos	Insecticide/OP	4	0.038	0.063	0.1
Atrazine	Herbicide	3	0.034	0.107	0.142
Pendimethalin	Herbicide	2	0.071	0.0985	0.126
Malathion	Insecticide/OP	1	3.05	3.05	3.05
MCPA	Herbicide	1	0.297	0.297	0.297
Bromoxynil	Herbicide	1	0.081	0.081	0.081
Disulfoton (Di-Syston)	Insecticide/OP	1	0.023	0.023	0.023

Sample Events: 30 (29-carbamates)

Table F-3. Sulphur Creek Wasteway pesticide summary. Unqualified values reported.

Chemical	Category	Detections	Concentration (µg/L) Min	Median	Max
2,4-D	Herbicide	14	0.078	0.1035	0.25
Carbaryl	Insecticide/Carbamate	1	0.16	0.16	0.16
Disulfoton (Di-Syston)	Insecticide/OP	1	0.16	0.16	0.16
Pronamide (Kerb)	Herbicide	1	0.154	0.154	0.154
Chlorpyriphos	Insecticide/OP	1	0.035	0.035	0.035
Malathion	Insecticide/OP	1	0.018	0.018	0.018

Sample Events: 31 (30-carbamates, 14 for 4,4'-DDE)

Table F-4. Spring Creek pesticide summary. Unqualified values reported.

Chemical	Category	Detections	Concentration (µg/L) Min	Median	Max
2,4-D	Herbicide	12	0.071	0.125	0.73
Pendimethalin	Herbicide	4	0.1	0.1525	0.21
Chlorpyrifos	Insecticide/OP	1	0.077	0.077	0.077
Malathion	Insecticide/OP	1	0.03	0.03	0.03
Azinphos (Guthion)	Insecticide/OP	1	0.023	0.023	0.023

Sample Events: 46 (44-carbamates, 21 for 4,4'-DDE)

Table F-5. Thornton Creek pesticide summary. NJ qualified values reported.

			Concentration (µg/L)		
Chemical	Category	Detections	Min	Median	Max
Pentachlorophenol	Wood Preservative	18	0.0043	0.0105	0.023
Diuron	Herbicide	15	0.0032	0.0086	0.17
MCPP (Mecoprop)	Herbicide	9	0.0061	0.01	0.024
Simazine	Herbicide	8	0.0032	0.00495	0.012
Triclopyr	Herbicide	7	0.0028	0.011	0.041
Prometon (Pramitol 5p)	Herbicide	6	0.0019	0.00465	0.012
2,4-D	Herbicide	5	0.0047	0.018	0.028
Diazinon	Insecticide/OP	1	0.049	0.049	0.049
Treflan (Trifluralin)	Herbicide	1	0.028	0.028	0.028
Atrazine	Herbicide	1	0.0092	0.0092	0.0092

Sample Events: 16 at T1 and 31 at T3 = 47

Table F-6. Marion Drain pesticide summary. NJ qualified values reported.

			Concentration (µg/L)		
Chemical	Category	Detections	Min	Median	Max
Diuron	Herbicide	16	0.0022	0.0255	0.16
Simazine	Herbicide	9	0.0042	0.0076	0.015
Prometon (Pramitol 5p)	Herbicide	6	0.0016	0.00525	0.019
Treflan (Trifluralin)	Herbicide	5	0.0019	0.0072	0.076
Chlorpyrifos	Insecticide/OP	5	0.0028	0.0044	0.0088
Atrazine	Herbicide	5	0.0052	0.0059	0.0068
Pentachlorophenol	Wood Preservative	4	0.0036	0.004	0.0086
Hexazinone	Herbicide	4	0.0009	0.0066	0.0085
Azinphos (Guthion)	Insecticide/OP	3	0.012	0.023	0.042
Alachlor	Herbicide	3	0.0026	0.0047	0.0075
Dichlobenil	Herbicide	2	0.0046	0.0098	0.015
Chlorpropham	Herbicide	2	0.0042	0.0086	0.013
Bromoxynil	Herbicide	2	0.0058	0.00705	0.0083
Bentazon	Herbicide	2	0.0065	0.0068	0.0071
Bromacil	Herbicide	2	0.0016	0.00265	0.0037
Terbacil	Herbicide	1	0.045	0.045	0.045
2,4-D	Herbicide	1	0.021	0.021	0.021
MCPA	Herbicide	1	0.0095	0.0095	0.0095
Eptam	Herbicide	1	0.0072	0.0072	0.0072
Ethoprop	Insecticide/OP	1	0.0053	0.0053	0.0053
Norflurazon	Herbicide	1	0.0053	0.0053	0.0053
Pendimethalin	Herbicide	1	0.0051	0.0051	0.0051
Dicamba I	Herbicide	1	0.004	0.004	0.004
Malathion	Insecticide/OP	1	0.0027	0.0027	0.0027
Metolachlor	Herbicide	1	0.0006	0.0006	0.0006

Sample Events: 30 (29-carbamates)

Table F-7. Sulphur Creek Wasteway pesticide summary. NJ qualified values reported.

			Concentration (µg/L)		
Chemical	Category	Detections	Min	Median	Max
Diuron	Herbicide	19	0.0074	0.052	0.171
Atrazine	Herbicide	7	0.0026	0.005	0.0066
Dichlobenil	Herbicide	6	0.0006	0.00775	0.031
Dinoseb	Herbicide	5	0.041	0.047	0.053
Terbacil	Herbicide	5	0.0022	0.005	0.02
Simazine	Herbicide	5	0.0038	0.0046	0.015
Azinphos (Guthion)	Insecticide/OP	4	0.013	0.0235	0.039
Bromacil	Herbicide	3	0.036	0.038	0.052
Treflan (Trifluralin)	Herbicide	3	0.0032	0.0047	0.014
Prometon (Pramitol 5p)	Herbicide	3	0.0043	0.005	0.0053
Norflurazon	Herbicide	2	0.032	0.052	0.072
Dicamba I	Herbicide	2	0.0038	0.00665	0.0095
Pentachlorophenol	Herbicide	2	0.0035	0.0042	0.0049
Dimethoate	Insecticide/OP	2	0.0016	0.0032	0.0048
4,4'-DDE	Degradate	2	0.0013	0.0014	0.0015
MCPA	Herbicide	1	0.013	0.013	0.013
Chlorpyrifos	Insecticide/OP	1	0.008	0.008	0.008

Sample Events: 31 (30-carbamates, 14 for 4,4'-DDE)

Table F-8. Spring Creek pesticide summary. NJ qualified values reported.

			Concentration (µg/L)		
Chemical	Category	Detections	Min	Median	Max
Diuron	Herbicide	24	0.0034	0.032	0.22
Atrazine	Herbicide	10	0.0022	0.00525	0.014
Bromacil	Herbicide	8	0.0031	0.0205	0.053
Norflurazon	Herbicide	7	0.0013	0.0047	0.027
Dichlobenil	Herbicide	6	0.0006	0.0058	0.049
4,4'-DDE	Degradate	5	0.0009	0.001	0.0016
2,4-D	Herbicide	4	0.009	0.0185	0.042
Azinphos (Guthion)	Insecticide/OP	4	0.011	0.0175	0.039
Pentachlorophenol	Wood Preservative	3	0.0029	0.0036	0.0041
Dicamba I	Herbicide	2	0.0025	0.00775	0.013
Bentazon	Herbicide	2	0.0083	0.00965	0.011
Prometon (Pramitol 5p)	Herbicide	2	0.007	0.0085	0.01
Simazine	Herbicide	2	0.0038	0.0049	0.006
4-Nitrophenol	Degradate	1	0.02	0.02	0.02
Malathion	Insecticide/OP	1	0.013	0.013	0.013
MCPP (Mecoprop)	Herbicide	1	0.0089	0.0089	0.0089
MCPA	Herbicide	1	0.0067	0.0067	0.0067
Pendimethalin	Herbicide	1	0.0058	0.0058	0.0058
Bromoxynil	Herbicide	1	0.0052	0.0052	0.0052
Metalaxyl	Fungicide	1	0.0038	0.0038	0.0038
Terbacil	Herbicide	1	0.0021	0.0021	0.0021

Sample Events: 46 (44-carbamates, 21 for 4,4'-DDE)

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Appendix G. Temperature Results

Temperature probes (and data loggers), called TidbiTs, were placed at each of the six stations for the duration of the sampling period from March 30 through October 27. Before placement in the streams, all temperature sensors went through a calibration check with a primary calibration reference. In this case, the primary reference was a National Institute of Science and Technology (NIST) thermometer. This calibration check ensures that all temperature sensors are measuring temperatures within the accuracy range of ± 0.2 ˚C. To further check the instruments accuracy, reference temperatures were recorded on a weekly basis using a thermometer. After calibration, the sensors were programmed to record temperature every 30 minutes. Once programmed, the temperature sensors were placed in locations that would provide representative instream water temperatures throughout the sampling period. In order to minimize solar influence, the sensors were placed inside short pieces of gray PVC tubing.

To ensure that large amounts of data were not lost due to theft or sensor failure, the temperature sensors were downloaded in the field on a monthly basis. Once downloaded, the data could be entered into a database. Upon completion of the field season, all continuous temperature data were used to calculate minimum and maximum daily averages as well as 7-day average daily temperatures (7DAD). The following graphs are output from the database and show the continuous temperature data, reference check points, and 7DAD minimum and maximum temperatures. All of the graphs have the same scale for ease of comparison.

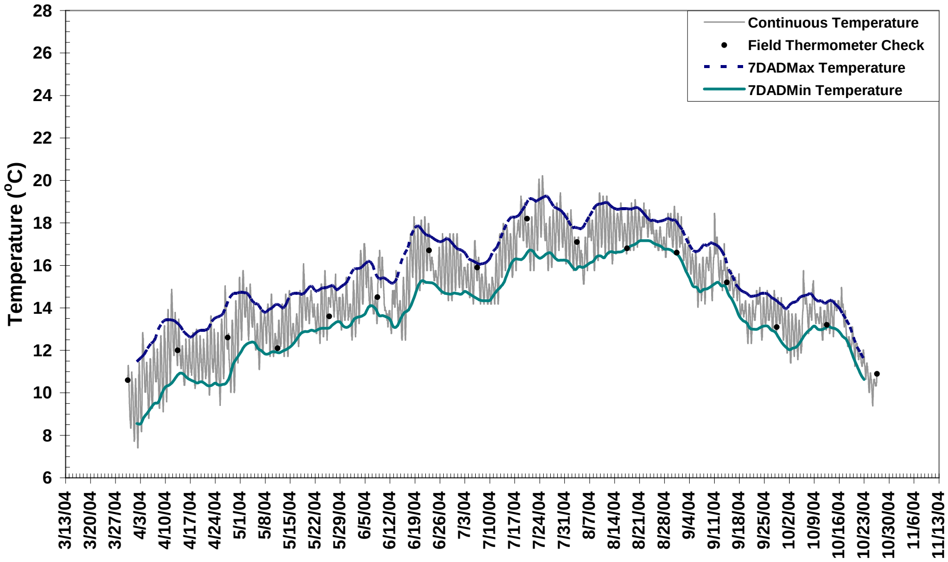

Figure G-1. Temperature results for Thornton 1.

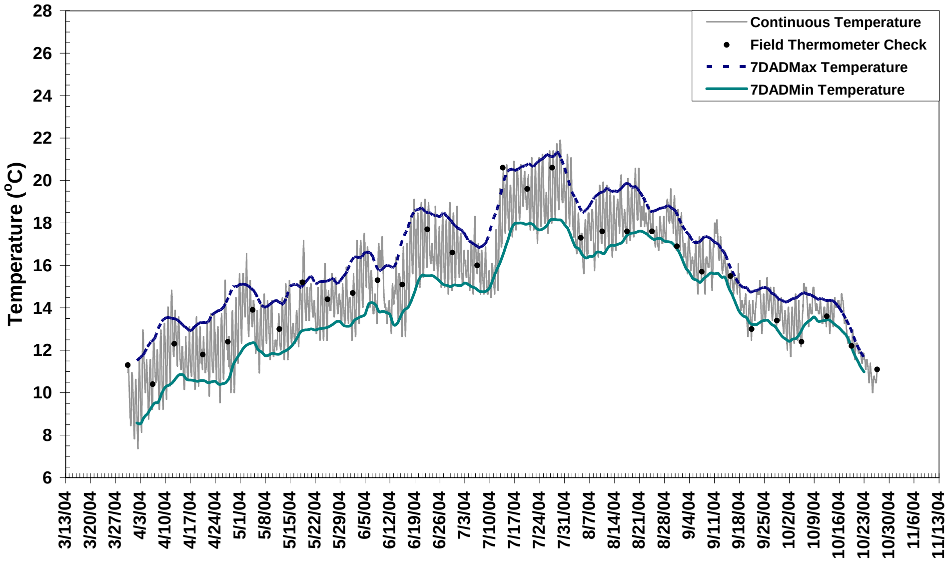

Figure G-2. Temperature results for Thornton 3.

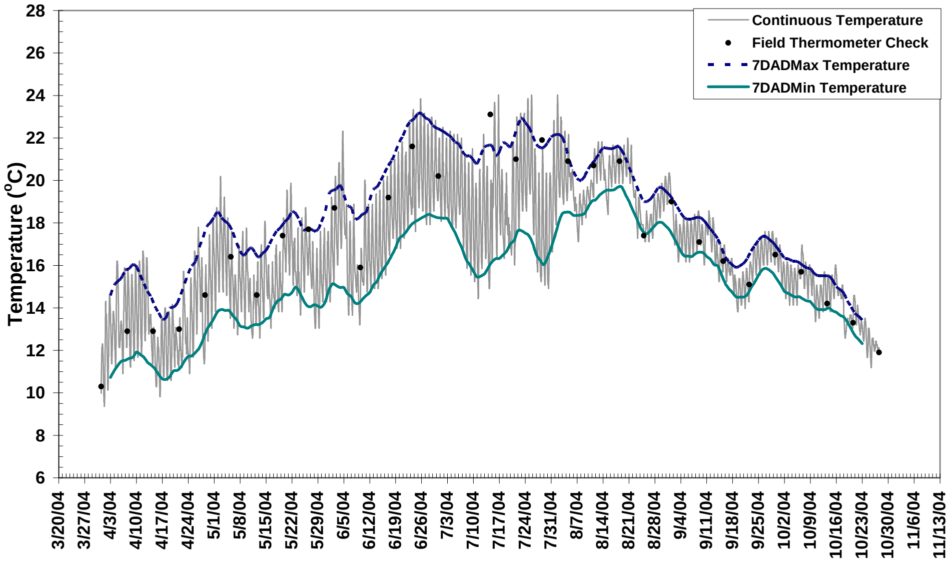

Figure G-3. Temperature results for Marion 2.

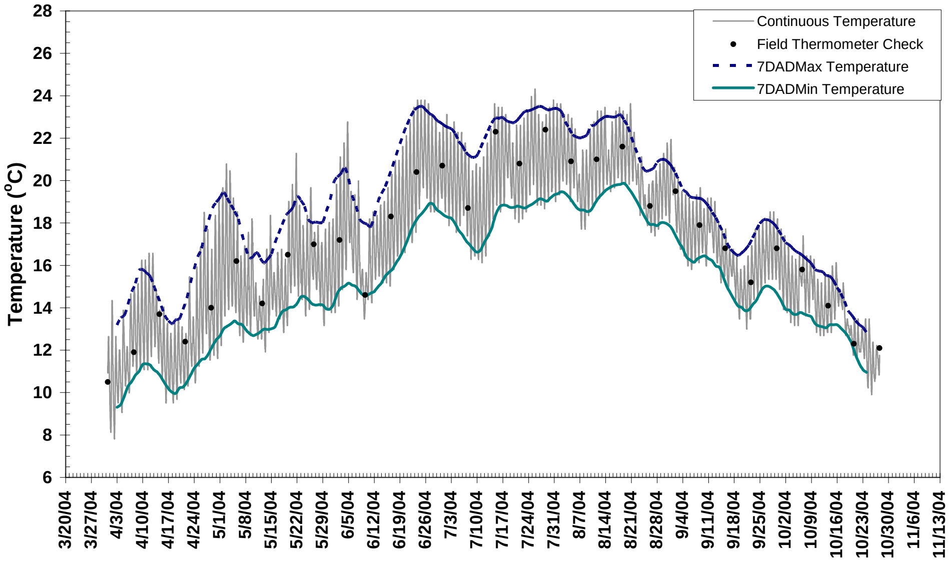

Figure G-4. Temperature results for Sulphur 1.

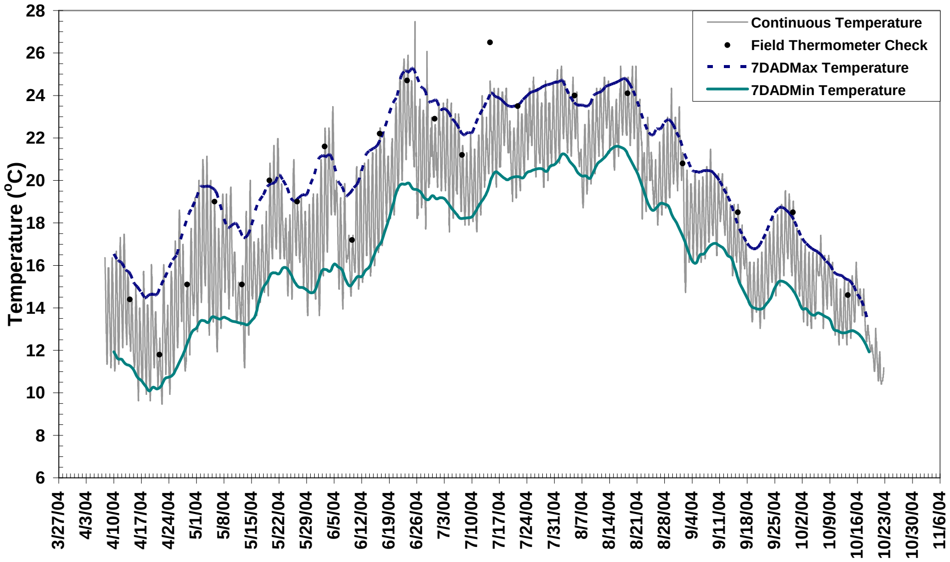

Figure G-5. Temperature results for Spring 1.

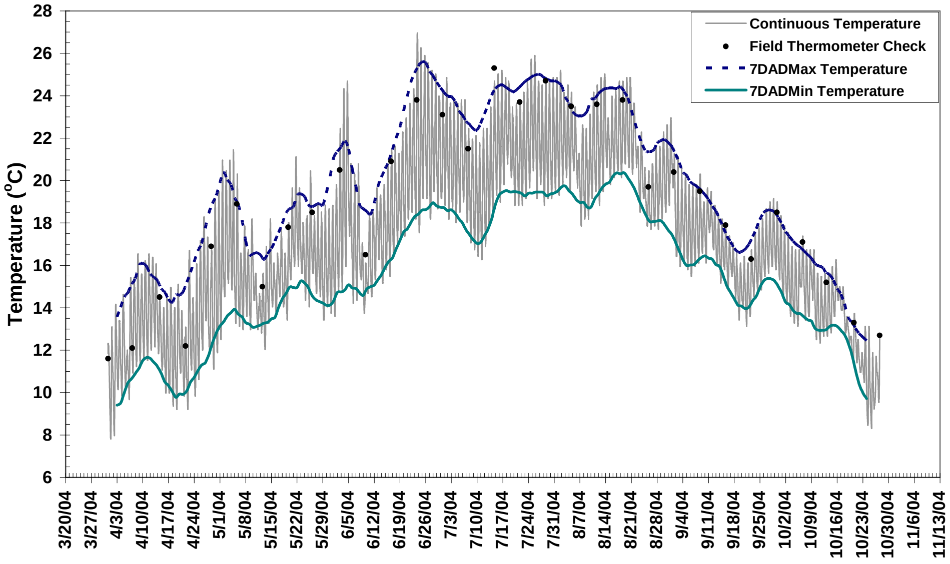

Figure G-6. Temperature results for Spring 3.

Appendix H. Available Freshwater Aquatic Life Standards

Table H-1. Available freshwater standards (μg/L) for the protection of aquatic life.

	Aquatic Life Standards				Toxicological Endpoints				
	[1]WAC Promulgated		[2]EPA NRWQC Recommended		[3]EPA RED Registration Status				
Chemical	Acute	Chronic	CMC	CCC	Acute	Chronic (NOEC)	Endangered Species LOC	Species	Ref.
Alachlor					1400	187	70	R	3a
Aldrin			3.0						
[4]Aldrin/Dieldrin	2.5[a]	0.0019[b]							
Atrazine			1500[h]		5300	65	265	R	3b
Azinphos methyl (Guthion)				0.01	2.9	0.44	0.15	R	3c
Bentazon					>100000			R	3d
Bromacil					36000		1800	R	3e
Bromoxynil					50	18	2.5	FM/R	3f
Carbaryl					1200	210	60	FM/R	3g
Chlordane	2.4[a]	0.0043[b]	2.4	0.0043					
Chlorpropham					5700		285	R	3h
Chlorpyrifos	0.083[c]	0.041[d]	0.083	0.041	3	<0.12	0.15	FM/R	3i
Demeton				0.1					
Diazinon			0.1[i]	0.1[i]	90	<550	4.5	BT/R	3j
Dichlobenil					4930	<330	246.5	BT/R	3k
DDT (and [5]metabolites)	1.1[a]	0.001[b]	1.1	0.001					
Dieldrin			0.24	0.056[j]					
[4]Dieldrin/Aldrin	2.5[a]	0.0019[b]							
Dimethoate					6200	430	310	R	3l
Diuron					710	26	35.5	FM/CT	3m
Endosulfan (Σα and β)			0.22[k]	0.056[k]	0.83	0.11	0.042	R	3n
Endosulfan [6](unspecified)	0.22[a]	0.056[b]							
Endrin	0.18[a]	0.0023[b]	0.086	0.036[j]					
Eptam					14000		700	NI	3o
Ethoprop					1020	24	51	FM/R	3p
Heptachlor	0.52[a]	0.0038[b]	0.52	0.0038					
Hexachlorocyclo-hexane (Lindane)	2.0[a]	0.08[b]							
Hexazinone					>320000	17000	>16000	FM/R	3q
Imidan (PHOSMET)					230	3.2	11.5	R	3r

continued

Table H-1 continued.

	Aquatic Life Standards				Toxicological Endpoints				
	[1]WAC Promulgated		[2]EPA NRWQC Recommended		[3]EPA RED Registration Status				
Chemical	Acute	Chronic	CMC	CCC	Acute	Chronic (NOEC)	Endangered Species LOC	Species	Ref.
Malathion				0.1	4	21	0.2	R	3s
Metalaxyl					18400	9100	920	R/FM	3t
Methoxychlor				0.03					
Metolachlor					3900	780	195	NI	3u
Metribuzin					42000		2100	R	3v
Mirex				0.001					
Norflurazon					8100	1500	405	R	3w
Oxyfluorfen					250	38	12.5	FM/R	3x
Parathion	0.065[c]	0.013[d]	0.065	0.013					
Pendimethalin					138	6.3	6.9	FM/R	3y
Pentachlorophenol	20[e,c]pH	13[f,d]pH	19[l]pH	15[m]pH					
Pronamide (Kerb)					72000		3600	R	3z
Propargite					118	16	5.9	FM/R	3aa
Tebuthiuron					143000		7150	R	3bb
Terbacil					46200		2310	R	3cc
Toxaphene	0.73[c,g]	0.0002[d]	0.73	0.0002					
Treflan (Trifluralin)					41	1.14	2	R	3dd
Tributyltin (TBT)			0.46	0.063					
Triclopyr Acid					117000	>104000	5850	FM/R	3ee
Triclopyr TEA					613000	>104000		R	3ee
Triclopyr BEE					650			R	3ee

[1] WAC: Promulgated standards according to Chapter 173-201AWAC

[2] EPA National Recommended Water Quality Criteria (EPA-822-R-02-047)

CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.

CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

[3] EPA Registration Eligibility Document. Toxicological endpoints used in determining registration status of a pesticide.

NOEC: No observable effects concentration.

ESLOC: Endangered species level of concern. Equal to 0.05*Acute Value (LC$_{50}$).

R: Rainbow Trout; FM/R Flathead Minnow used for chronic value and LOC based on Rainbow Trout; FM/CT Flathead Minnow used for chronic value and LOC based on Cutthroat Trout; BT/R Brook Trout used for chronic value and LOC based on Rainbow Trout. NI Species not indicated.

3a Environmental Fate and Effects Division (EFED): Alachlor Registration Eligibility Document (RED) 9-30-1998
3b EFED Atrazine RED 4-22-2002
3c EFED Azinphos methyl RED 7-15-1999
3d EFED Bentazon RED 1-27-1995
3e EFED Bromacil RED 8-1996
3f EFED Bromoxynil RED 9-23-1998
3g EFED Carbaryl RED 3-18-2003
3h EFED Chlorpropham RED 10-1996
3i EFED Chlorpyrifos RED 6-1-2000
3j EFED Diazinon RED 10-2000; <550 µg/L active ingredient
3k EFED Dichlobenil RED 10-1998

3l EFED Dimethoate RED 2-4-1999
3m EFED Diuron RED 9-2003
3n EFED Endosulfan RED 4-13-2001
3o EFED Eptam RED 12-1999
3p EFED Ethoprop RED addendum 8-30-99
3q EFED Hexazinone RED 9-1994
3r EFED Phosmet (Imidan) RED 4-24-1998
3s EFED Malathion RED 11-9-2000
3t EFED Metalaxyl RED 9-1994
3u EFED Metolachlor RED 5-1995
3v EFED Metribuzin RED 2-1998
3w EFED Norflurazon RED No Date
3x EFED Oxyfluorfen RED 12-11-2001
3y EFED Pendimethalin RED 6-1997
3z EFED Pronamide RED 6-28-1994
3aa EFED Propargite 6-7-2000
3bb EFED Tebuthiuron RED 6-15-1994
3cc EFED Terbacil RED 1-1998
3dd EFED Trifluralin RED 4-1996
3ee EFED Triclopyr RED 9-30-1997; TEA = Triethylammonium, BEE = Butoxyethyl Ester; In this study, Triclopyr is reported as Total (ΣAcid+TEA+BEE)

[4] Aldrin is metabolically converted to Dieldrin. Therefore, the sum of the Aldrin and Dieldrin concentrations are compared with the Dieldrin criteria.

[5] Criteria applies to DDT and its metabolites (ΣDDT). 4,4'DDE is applied in this instance.

[6] Chemical form of Endosulfan is not defined in WAC 173-201A. Endosulfan sulfate is applied in this instance.

[a] An instantaneous concentration not to be exceeded at any time.

[b] A 24-hour average not to be exceeded.

[c] A 1-hour average concentration not to be exceeded more than once every three years on average.

[d] A 4-day average concentration not to be exceeded more than once every three years on average.

[e] $\leq e^{[1.005(pH)-4.830];}$ pH = 7.8 for table.

[f] $\leq e^{[1.005(pH)-5.290];}$ pH = 7.8 for table.

[g] Channel Catfish may be more acutely sensitive.

[h] www.epa.gov/waterscience/criteria/atrazine/atrazinefacts.html

[i] www.epa.gov/waterscience/criteria/diazinon/draft-fs.htm

[j] The derivation of the CCC for this pollutant did not consider exposure through the diet, which is probably important for aquatic life occupying upper trophic levels.

[k] This value was derived from data for endosulfan and is most appropriately applied to the sum of alpha-endosulfan and beta-endosulfan.

[l] $\leq e^{[1.005(pH)-4.869}$]; pH = 7.8 for table.

[m] $\leq e^{[1.005(pH)-5.134}$]; pH = 7.8 for table.

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Appendix I. Discharge Relationships of Frequently Detected Pesticides

The following figures illustrate the temporal relationship of detected pesticide residues to discharge. Pesticide results are presented for all stations which:

1. Contain more than one detection and;
2. Exceed or approach a numeric criterion.

A discussion of criteria is presented in the main body of the report, and Appendix H.

Thornton Creek

The upstream station (Figure I-1) was sampled twice monthly and the downstream station (Figure I-2) was sampled weekly.

Diazinon was the only pesticide residue that approached, or was above, a numeric water quality criterion in Thornton Creek. Diazinon was detected twice at the upstream station and four times at the downstream station. All detections occurred between April 6 and May 11. On May 11, diazinon was detected upstream at a concentration of 0.101 µg/L and downstream at 0.095 µg/L, indicating a sustained exposure of diazinon throughout this segment of Thornton Creek on this day. A prohibition on diazinon sales for homeowner use became effective December 31, 2004. It is expected diazinon detections should diminish as existing stocks are used.

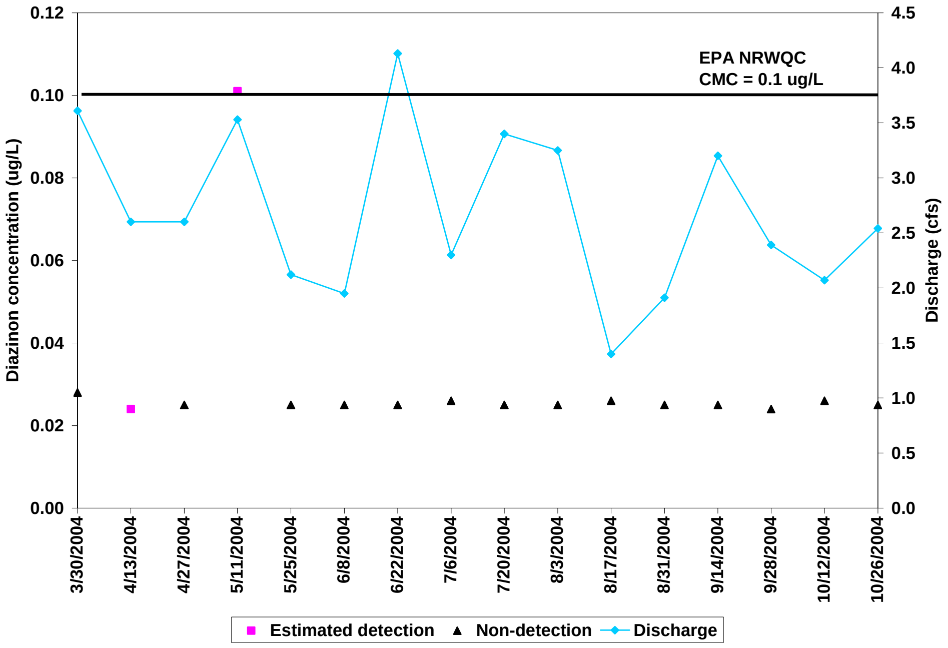

Figure I-1. Diazinon detections and discharge at the upstream Thornton Creek site.

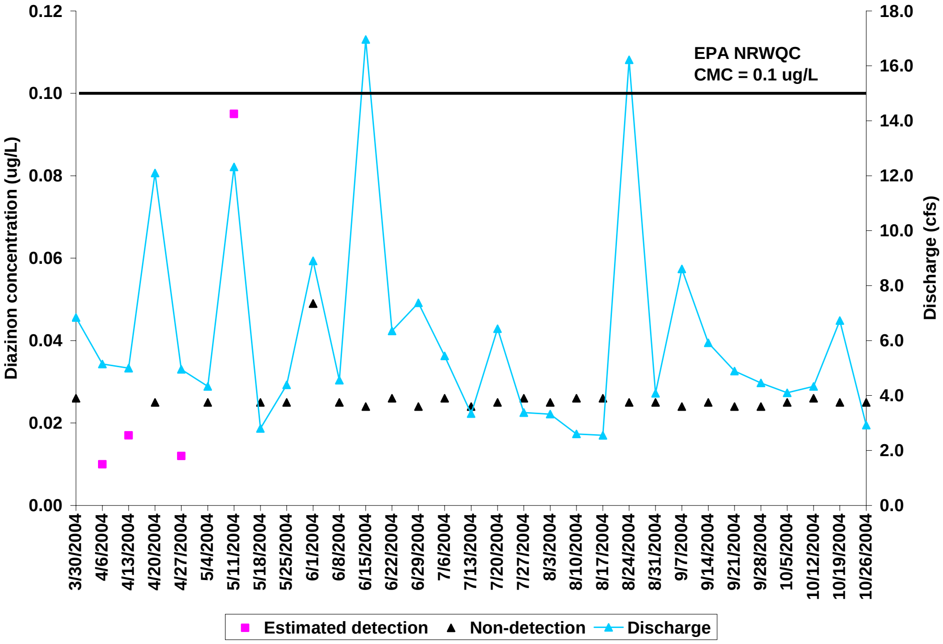

Figure I-2. Diazinon detections and discharge at the downstream Thornton Creek site.

Lower Yakima Watershed

Three sub-basins comprise the Lower Yakima watershed: Marion Drain, Sulphur Creek Wasteway, and Spring Creek. Four pesticide residue results were numerically above a water quality criterion: chlorpyrifos, azinphos-methyl, malathion, and 4,4-DDE.

Marion Drain

Chlorpyrifos and malathion residues were numerically above a water quality criterion in Marion Drain.

Chlorpyrifos (Figure I-3) was detected 11 times with detections clustered in the spring (April 7-June 2) and fall (Sept 8-Oct 13). During three consecutive sampling events in the fall, chlorpyrifos concentrations were above the numerical water quality standard.

Malathion (Figure I-4) was detected six times in Marion Drain. Five of six detections occurred during June and July of 2004. A single detection (3.04 µg/L), above the Endangered Species Level of Concern value (0.2 µg/L), and approaching the EPA RED acute toxicological value (4 µg/L) for rainbow trout, occurred on July 21, 2004. All malathion detections occurred during the low-flow period from April 29 to July 29.

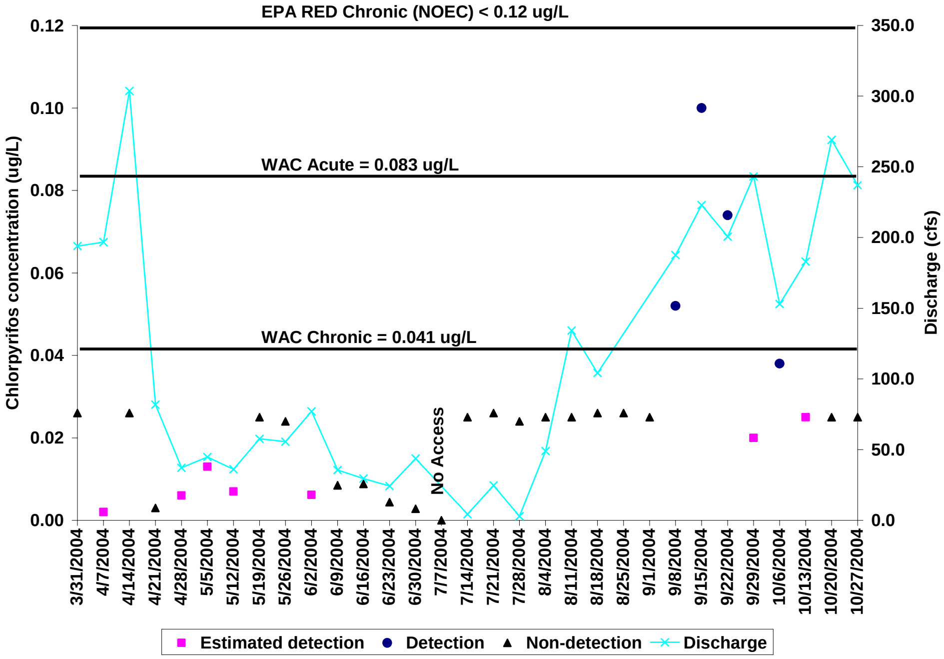

Figure I-3. Chlorpyrifos detections and discharge in Marion Drain.

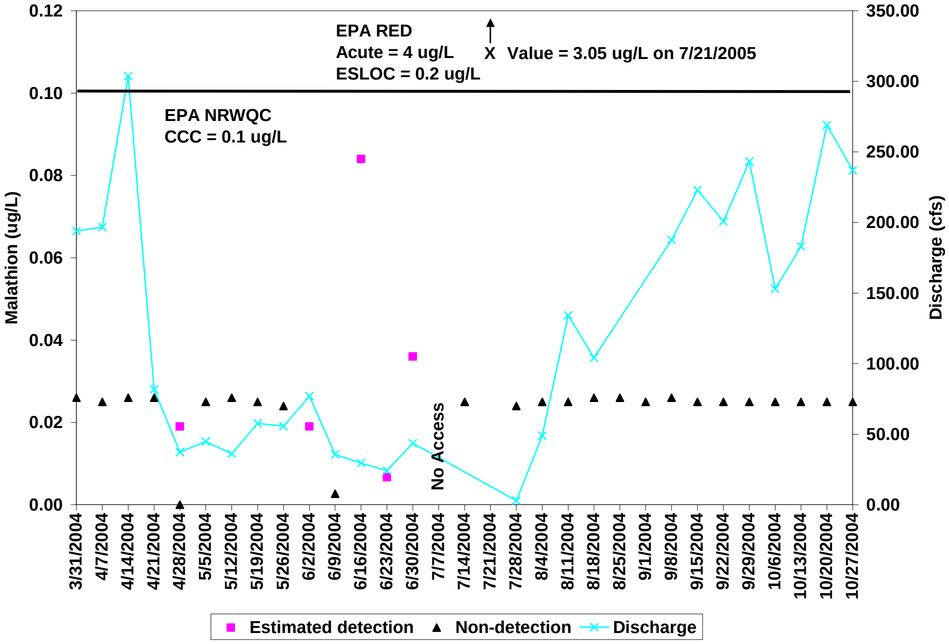

Figure I-4. Malathion detections and discharge in Marion Drain.

Sulphur Creek Wasteway

Sulphur Creek Wasteway drains Roza and lateral canals near the city of Sunnyside, and was sampled weekly during the 2004 investigation. Chlorpyrifos, azinphos-methyl, and 4,4'-DDE residues were numerically above water quality criterion.

Four of five chlorpyrifos detections in Sulphur Creek Wasteway occurred during the spring between March 31 and April 19 (Figure I-5). A single detection of chlorpyrifos above the numerical criterion occurred on August 4, 2004. Four detections of azinphos-methyl residues occurred during May-June of 2004 (Figure I-6). 4,4'-DDE exceeded WAC promulgated numeric chronic criterion of 0.001 µg/L (Figure I-7) three times during the weekly sampling of Sulphur Creek Wasteway. In general, the detections of 4,4'-DDE were correlated with increased concentrations of total suspended solids. 4,4'-DDE is the breakdown product of the legacy pesticide DDT, banned in 1972. Organochlorine residue analysis, which includes 4,4'-DDE, was conducted from April to June.

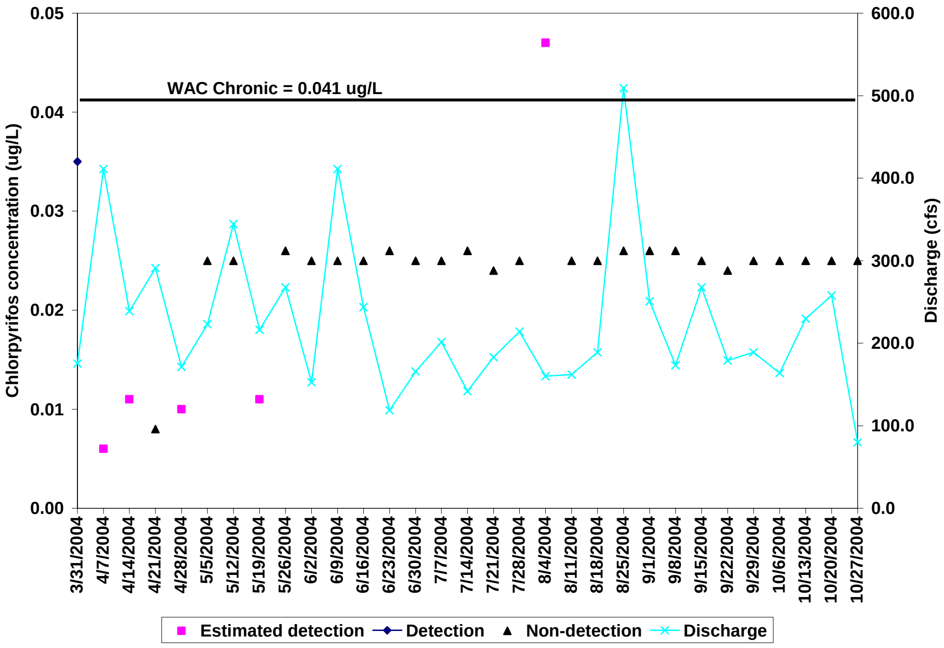

Figure I-5. Chlorpyrifos detections and discharge in Sulphur Creek Wasteway.

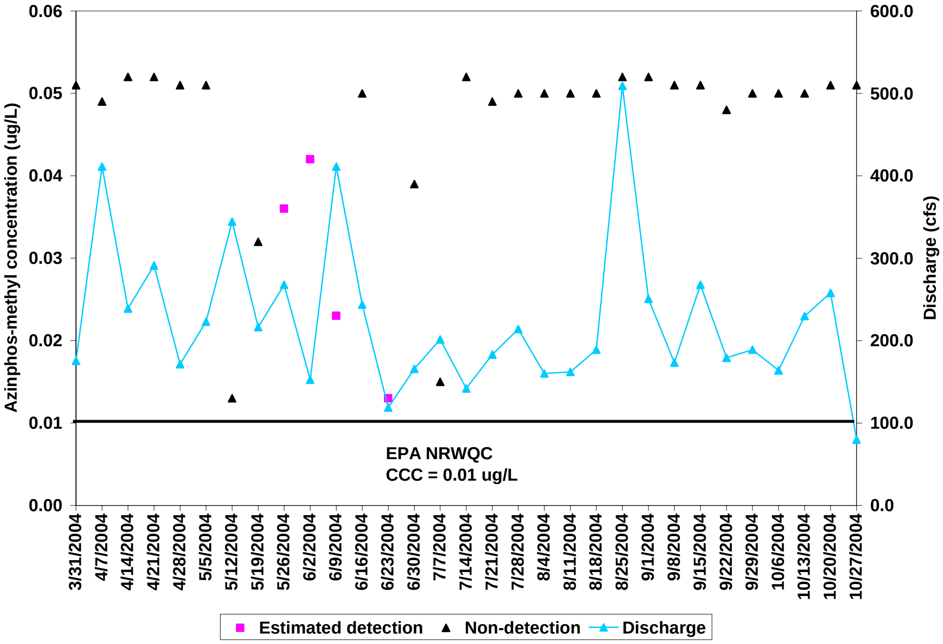

Figure I-6. Azinphos-methyl detections and discharge in Sulphur Creek Wasteway.

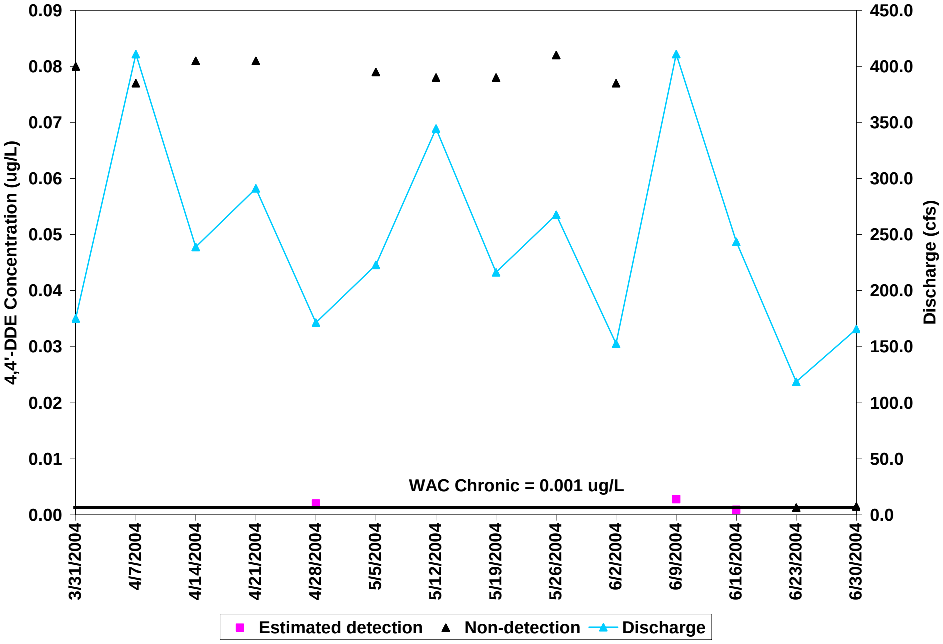

Figure I-7. 4,4'-DDE detections and discharge in Sulphur Creek Wasteway.

Spring Creek

Spring Creek was sampled twice monthly at the upstream station and weekly at the downstream station. Chlorpyrifos was detected at both Spring Creek sites (Figures I-8 and I-9, respectively). A single residue result above water quality criterion occurred at the downstream site on March 31, 2004. Both sites are illustrated to show the temporal relationship of chlorpyrifos detections in Spring Creek. All detections of chlorpyrifos in Spring Creek occurred between March 31 and May 12.

Azinphos-methyl was detected above the numeric water quality criterion three times at the downstream monitoring site on Spring Creek (Figure I-10) between June 9 and July 28, 2004.

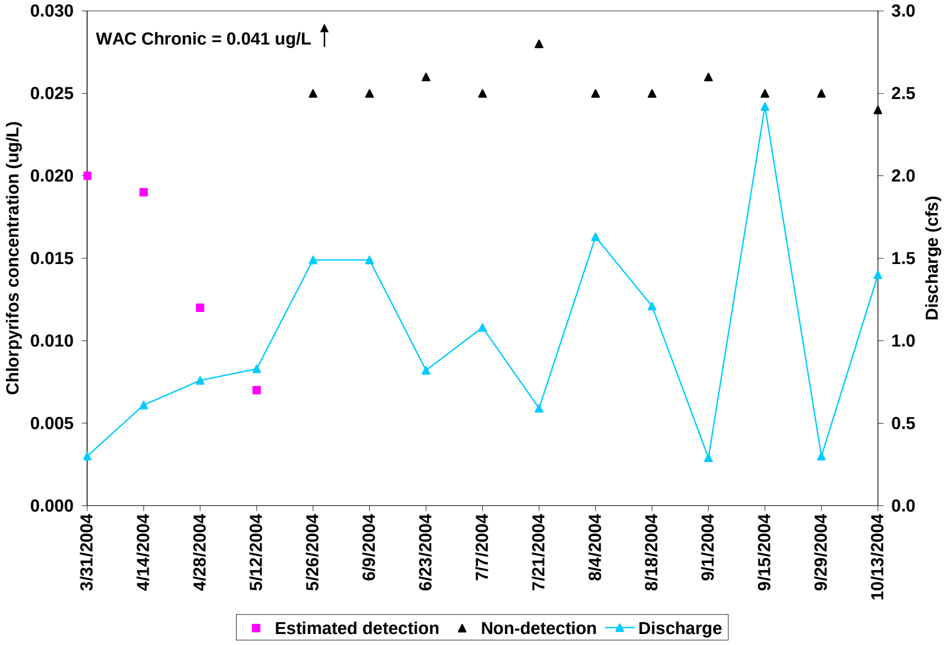

Figure I-8. Chlorpyrifos detections and discharge at Spring Creek (upstream).

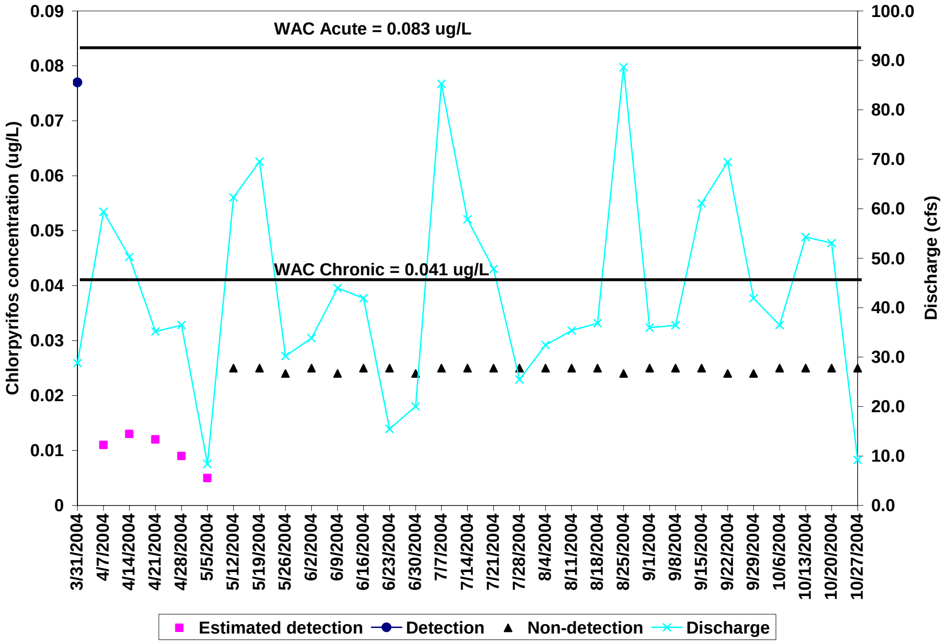

Figure I-9. Chlorpyrifos detections and discharge at Spring Creek (downstream).

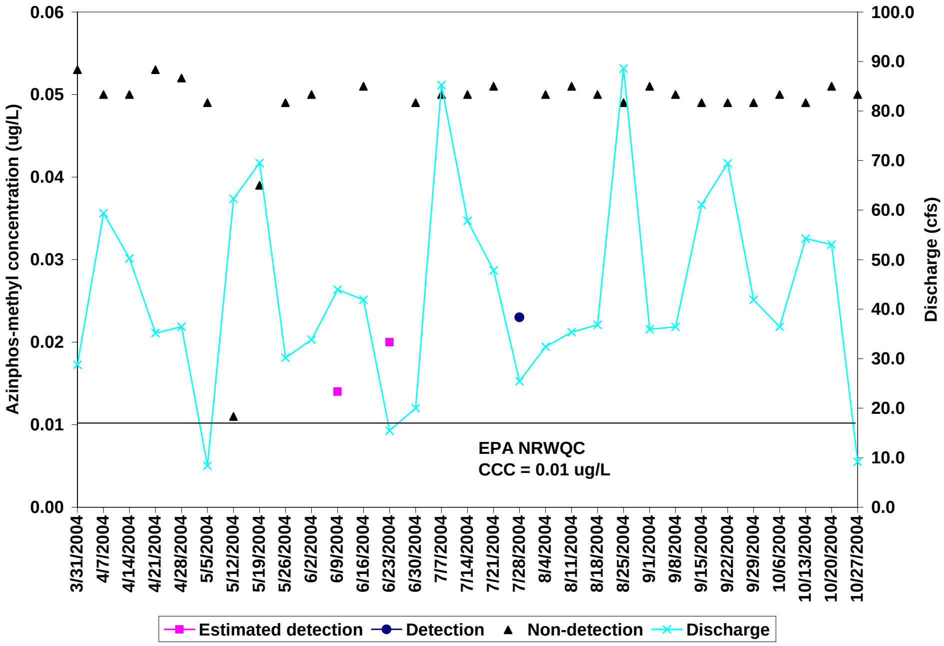

Figure I-10. Azinphos-methyl detections and discharge at Spring Creek (downstream).