



Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April to December, 2003

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

November 2004

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Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, April to December 2003

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

by

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November 2004

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

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Abstract

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) designed a multi-year monitoring effort to characterize pesticide concentrations in salmonid-bearing surface waters during the typical pesticide use season. 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.

Two index watersheds, representing urban and agricultural land-use patterns, were sampled from April through December 2003. 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 represented agricultural land-use patterns. Sampling frequencies included weekly, every other week, and during storm events.

Concentrations of all chemicals were generally low and close to analytical detection limits. 2,4-dichlorophenylacetic acid (2,4-D) was the most commonly detected chemical; however, pentachlorophenol 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 EPA Environmental Fate and Effects Division acute and chronic toxicological endpoints. One detection of endosulfan sulfate exceeded a Washington State water quality standard. Azinphos-methyl, chlorpyrifos, diazinon, and 4,4'-DDE results were above the numeric component of various standards, but data were insufficient to characterize the time component of these standards. Most chemicals had limited or no criteria available with which to compare concentrations.

Urban run-off frequently contains other chemicals in addition to pesticides and, therefore, semivolatile organic compounds (SVOCs) were analyzed in Thornton Creek. Thirty-eight compounds were detected; the majority of detections occurred during three storm events. Phthalates and polynuclear aromatic hydrocarbons were the most frequently detected compounds in the SVOC analyses.

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 - Art Johnson for preparing the quality assurance project plan and reviewing the final report.
 - Joan LeTourneau for editing and formatting the final report.

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)
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
SVOC	Semivolatile Organic Compounds
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) designed a multi-year monitoring effort to characterize pesticide concentrations in surface waters (Johnson and Cowles 2003). This effort is focused on assessing pesticides found in salmonid-bearing streams during the typical pesticide use season. The data collected will allow WSDA and the US 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.

This project is designed to evaluate pesticide residues in surface water over multiple years. The results from the first season of monitoring (April through December 2003) from two index watersheds are presented in this report. Thornton Creek, located in the Cedar-Sammamish Water Resource Inventory Area (WRIA) 8 (Figure 1), was selected as the urban watershed due to prior salmonid habitat enhancement efforts and the occurrence of pre-spawning mortality in Coho salmon. Three sub-basins of the Lower Yakima WRIA 37 were selected to represent agricultural land use: Marion Drain, Sulphur Creek Wasteway, and Spring Creek. These three sub-basins were selected because they have the highest percent area cropped and a diversity of agriculture within the drainage (Johnson and Cowles 2003).

A wide range of pesticides that included both current and historical usage were analyzed in both watersheds; these included herbicides, organochlorine, organophosphorous, and carbamate pesticides. To better understand factors influencing pesticide concentrations, conventional water quality parameters (total suspended solids, pH, conductivity, temperature, and flow) were also measured.

Urban run-off frequently contains other chemicals in addition to pesticides and, therefore, limited sampling was conducted to evaluate concentrations of other common urban organic contaminants. Semivolatile organic compounds (SVOCs) were analyzed biweekly (every other week) and during three fall storm events in the Thornton Creek watershed at all stations.

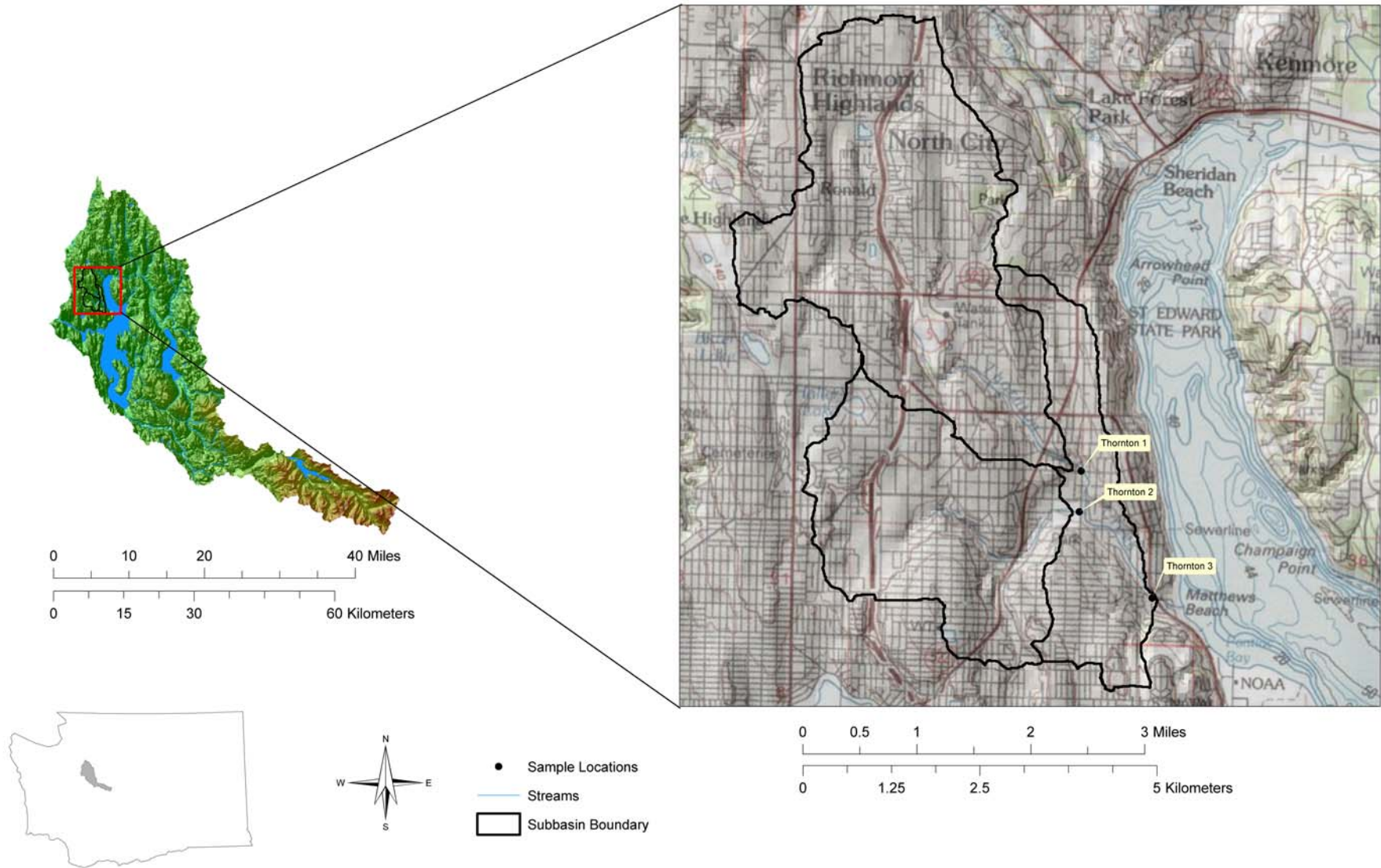


Figure 1. Sampling stations on Thornton Creek in the Cedar-Sammamish watershed.

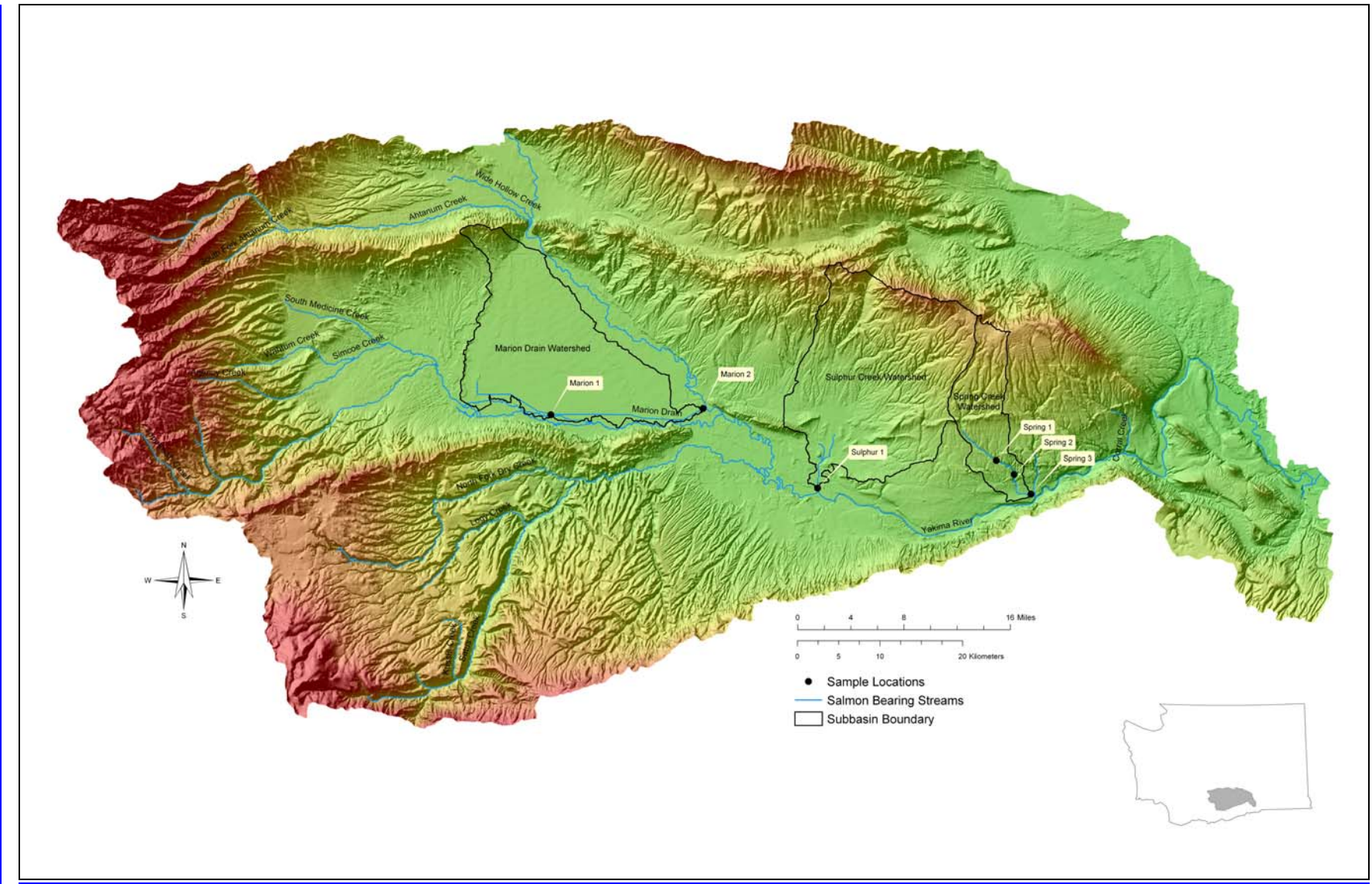


Figure 2. Sampling stations on Marion Drain, Spring Creek, and Sulphur Creek Wasteway in the Lower Yakima watershed.

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Methods

Sample Design

Sampling was designed to address the potential for pesticide movement into 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).

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 US Fish and Wildlife Service. The urban watershed, 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. The agricultural watersheds are within the Middle Columbia Steelhead ESU and the Columbia Basin Bull Trout DPS – both designated threatened status. Finally, all four streams selected for the study have documented presence of a listed threatened species, as documented by the Washington Department of Fish and Wildlife (SalmonScape database, <http://wdfw.wa.gov/mapping/salmonscape/> and Marnie Tyler, WDFW Salmonid Recovery Coordinator, personal communication).

All watercourses were named according to the USGS Geographic Names Information System (GNIS). The GNIS is our nation's official repository of domestic geographic names information. <http://geonames.usgs.gov/gnishome.html>

Site Selection

The primary 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 listings, pesticide detections, and supporting references are summarized, by stream and site, in Appendix A. Unless specified, fisheries classification and pesticide occurrence information were amalgamated from a literature review referenced in Appendix A.

Urban Sites

Thornton Creek is located in the Cedar-Sammamish WRIA 8, in the Puget Sound basin. WRIA 8 is within 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).

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

Collectively, Thornton Creek supports a healthy Fall Chinook stock and depressed Coho and Sockeye stocks. Spawning habitat has been documented in Thornton 1 (Coho), Thornton 2 (Sockeye) and Thornton 3 (Fall Chinook and Sockeye). Coho rearing habitat exists in Thornton 2 and Thornton 3. Although Thornton Creek supports a healthy stock of Fall Chinook, the stream is located within the Puget Sound Chinook ESU, which is threatened.

Thornton Creek has been previously monitored for pesticides. A total of 20 pesticides and transformation compounds were detected in samples collected from Thornton Creek from March 1996 to April 1998 (Embrey and Frans 2003). The most common detections included herbicides (prometon, simazine, and dichlobenil) and insecticides (carbaryl, chlorpyrifos, diazinon, lindane, and malathion).

Agricultural Sites

The agricultural basin is represented by three drainages within the Lower Yakima 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 drainages selected for this study all have documented threatened steelhead presence, the overall quality of the habitat within these drainages ranges from reaches that provide 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). However, as stated in the site selection section above, sites were chosen based on land use and previous pesticide detections, as well as fish presence.

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. All of the agricultural drainages have numerous minor crops such as currants, cherries, alfalfa, mint, and asparagus (Appendix B). The diversity of cropping, and consequently pesticide use, was the impetus for choosing the Lower Yakima WRIA as an index watershed.

Marion Drain

Marion Drain is located within Yakama Indian Nation lands and was evaluated through an upstream station, Marion 1, and downstream station, Marion 2. Marion Drain supports a healthy stock of Fall Chinook, depressed stock of Summer Steelhead, and migratory stock of Spring Chinook. Spawning habitat is present in Marion 1 (Fall Chinook and Summer Steelhead) and Marion 2 (Fall Chinook).

The Marion Drain has approximately 55% of its drainage area in agricultural crops. The majority of this acreage is in apple (11%) and hops (9%) production. A subset of historical pesticide detections within Marion Drain includes currently registered pesticides (atrazine, simazine, carbaryl, and trifluralin) and cancelled pesticides (parathion, dieldrin, 4,4'-DDE, and DDT).

Sulphur Creek Wasteway

Sulphur Creek Wasteway is a highly channelized agricultural conveyance and is represented by one station, Sulphur 1. Sulphur Creek Wasteway supports a depressed stock of Summer Steelhead and migratory stocks of Fall Chinook and Spring Chinook. The fish distribution in Sulphur Creek Wasteway includes spawning Coho; however, the habitat does not support the resulting emerging fry. 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. WSDA will closely monitor the status of Sulphur Creek Wasteway and make all future sampling decisions in close coordination with the Washington Department of Fish and Wildlife. Currently, Summer Steelhead, Fall Chinook, and Spring Chinook have all been documented as present in Sulphur Creek Wasteway.

The Sulphur Creek Wasteway drainage is about 34% cropped, with the major crop being grapes (11%). Sulphur Creek Wasteway has been monitored for pesticides previously as well. Prior pesticides detected include currently registered pesticides (azinphos-methyl, diazinon, atrazine, carbaryl, endosulfan, and others) as well as cancelled pesticides (dieldrin, DDT, and its metabolites).

Spring Creek

Spring Creek¹ is represented by three stations: Spring 1 upstream, Spring 2 midstream and Spring 3 downstream. Spring 1 and Spring 2 support depressed Summer Steelhead stocks. The lower portion of Spring Creek, near entry to the Yakima River, is represented by Spring 3. This reach supports a depressed stock of Summer Steelhead and migratory stocks of Fall Chinook, Spring Chinook, and Coho. The fish distribution in the reach of Spring 3 includes spawning coho and Spring Chinook rearing. The presence of Coho, Spring Chinook, Fall Chinook, and Summer Steelhead has been documented at Spring 3.

The Spring Creek drainage is 54% cropped, with wheat (11%), grapes (11%), and apples (5%), being the principle crops. Historical pesticide detections in Spring Creek include currently registered pesticides (malathion, chlorpyrifos, azinphos-methyl, carbaryl, prometon, and others) and cancelled pesticides (dieldrin, DDT, and its metabolites).

¹ 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 in a court decision in 2002 regarding this matter. WDFW is engaging SVID in negotiations over the designation of Spring Creek at the time this report was prepared.

Frequency

To characterize pesticide concentrations during peak application periods, weekly sampling was conducted from April through June 2003 at three sites each on Thornton and Spring creeks. Two locations within Marion Drain and one at the mouth of Sulphur Creek Wasteway were also sampled weekly April through June. Between July and September 2003, biweekly sampling was conducted at the three Lower Yakima sites. Sampling in the Thornton Creek watershed was focused on a single creek, based on the assumption that pesticide use is similar among urban watersheds.

To evaluate contaminant transport during fall run-off events, Thornton Creek was sampled during three storm events. Sampling for each storm event occurred at the beginning of the storm and later during the same storm. A storm was defined as at least four days of dry weather followed by sufficient precipitation to produce visible turbidity and an increase in stream discharge. The sampling schedule for 2003 is presented in Appendix A.

There were a total of 153 sampling events in 2003 including:

- 54 in the Thornton Creek watershed (18 each at Thornton 1, 2, and 3),
- 45 in the Spring Creek drainage (12 at Spring 1, 12 at Spring 2, and 21 at Spring 3),
- 33 in the Marion drainage (12 at Marion 1, and 21 at Marion 2)
- 21 within Sulphur Creek Wasteway

Temperature, pH, conductivity, and streamflow were measured in the field. All other metrics and analyses were conducted at Ecology's Manchester Environmental Laboratory (MEL) or commercial laboratories contracted by MEL.

Sampling Procedures

Pesticide/Semivolatile Organics

All pesticide and organic samples were collected by hand-compositing grab samples from quarter-point transects across each stream. These transects were conducted by wading across the stream and 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 the collection of all water samples, field personnel wore non-talc nitrile gloves. Quarter point compositing was not used at Sulphur-1 (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-1 was sampled by hand dipping containers from the east bank. Water samples are not filtered, and analytical results are presented as total pesticides.

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

All containers for analyses were delivered pre-cleaned by the manufacturer to EPA specifications (EPA 1990). Each station and sampling event used a dedicated transfer container that was pre-cleaned following EPA specifications (EPA 1990).

The transfer containers were cleaned by:

1. Washing with hot tap water and brushing with Liquinox detergent
2. Rinsing with 10% nitric acid
3. Rinsing with deionized water
4. Rinsing with acetone
5. Air drying in a fume hood
6. Wrapping with aluminum foil until ready for use

Two field blank samples were collected for pesticides only. These samples were created by field decanting laboratory-supplied deionized water into a transfer container and then filling appropriate sample containers.

To evaluate sample degradation during transport, fortified field blanks were also analyzed. These samples were composed of laboratory-supplied deionized water combined with an acetone-based fortification mixture supplied by MEL. The fortification mixture contains a known quantity of a group of pesticides. Three fortification mixtures were required to avoid coelution problems. Elution is the process of extracting a single pesticide (or other chemical parameter) from a compound mixture; coelution occurs when more than one pesticide (or compound) is extracted.

The three fortification mixtures are the same as those used by MEL for laboratory control samples (LCS) and matrix spike/matrix spike duplicates (MS/MSD). The LCS contains the fortification mixture, yet is exposed solely to analytical processing within the laboratory. MS/MSD includes the fortification mixture and a specific sample volume. The MS/MSD are used to determine chemical degradation (similar to LCS and fortified field blanks) and interferences due to interactions between the sample and analytical matrices (sample constituents, fortification mixture, and analytical processing).

The fortification mixtures were kept frozen at -20°C until used. A gas-tight syringe was used to remove 1 mL of fortification solution from the vial and injected into 900 mL of deionized water. These samples were then chilled to 4°C on ice and carried into the field. The fortified blanks were exposed to typical field storage conditions for two days along with other collected samples and then delivered to the laboratory for analysis.

Field replicate samples were collected for pesticides. A field replicate consists of two samples collected from the same location at the same time. Collecting field replicates is a method of

looking at the precision of the entire process of sampling and analysis. Differences between the results of replicate samples can arise from variations in the sample location, 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).

Temperature, pH, and Conductivity

Temperature and pH were measured in the field using an Orion 250A+ handheld meter. Calibrations were conducted according to the quality assurance project plan for this project (Johnson and Cowles 2003), Ecology Standard Operating Procedures (SOP) (Cusimano 1993, Ward 2001) and manufacturer specifications (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. Calibrations were considered successful if the slope was between 97 and 100%. Investigation and recalibration of pH due to slope was not necessary in 2003. At each subsequent sampling station, the calibration drift was checked against the 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 hand calibration to the current temperature. The temperature recorded by the pH meter was used to calibrate the conductivity bridge. Calibration of the Beckman model RB-5 conductivity bridge was periodically checked with 100 and 300 $\mu\text{mho/cm}$ standards. A field notebook was maintained with all field measurements, including discharge.

Discharge

Discharge data for Sulphur 1 was obtained from an adjacent US Bureau of Reclamation gauging station “SUCW – Sulphur Creek Wasteway at Holiday Road Near Sunnyside”. Fifteen-minute discharges were available during the period of sampling. The record closest to the actual sampling time was used in lieu of field measurements.

Stream discharge was calculated from depth and velocity measurements obtained through the use of a March-McBirney flow meter and top-setting rod at all stations except “Sulphur-1”. 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. Approximately 10 velocity/depth measurements were conducted across each stream. A stream segment as close as possible to the sampling site and with a relatively flat and even bottom contour was chosen. Discharge volume (Q) was calculated according to US Geological Survey procedures (Rantz et al. 1982) and is equal to velocity multiplied by the cross-sectional area of the stream.

Analysis

The analytical methods used in this project are listed in Table 1. Analytical procedures are on-line at the EPA website (<http://www.epa.gov/epaoswer/hazwaste/test/main.htm>). Detailed quality assurance information is provided in Appendix C.

Table 1. Summary of 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
TSS	n/a	Gravimetric	EPA 160.2	MEL
Pesticides (<i>except carbamates</i>)	SW846 Method 3510	GC/AED	SW846 Method 8085	MEL
Carbamates	SW846 Method 8318	HPLC	SW846 Method 8318	PSC
Semivolatiles	SW846 Method 3510	GC/MS	SW846 Method 8270	MEL

n/a – not applicable

TSS - total suspended solids

MEL - Manchester Environmental Laboratory

GC/AED - gas chromatography/atomic emission detection

GC/MS - gas chromatography/mass spectrometry

HPLC - high performance liquid chromatography

PSC - Philip Services Corporation

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Quality Assurance/Quality Control

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.

Following this, the project officer compared all of the project's case narratives to the generated data. Case narratives are provided for each analysis and describe the method, calibration, 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). Qualification for pesticide and SVOC detections are presented in Appendix C. Case narrative review compared each week's data with ongoing MS/MSD and LCS results to look for sampling and/or analytical system degradation.

Pesticide

Data Recovery

Sampling efforts in the urban and agricultural watersheds resulted in 644 pesticide (and degradate) detections out of 153 sampling events. Each sampling event was tested for 144 pesticides. Thus, 22,032 (153×144) chemical analyses were run in 2003. Chemical and conventional parameter results are presented in Appendix D. 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 tests.

All reported results are for total pesticides and SVOCs. Dissolved fractions were not measured. Additionally, chemical results were not adjusted for percent recovery.

Most of the data collected for this project are considered usable, with qualification, as reported. Practical quantitation limits (PQL) were developed for this study and appear in Appendix C. 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 C. 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 C, 40 CFR Part 136, 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. In some instances, MEL was able to detect pesticides below the MDL and EDL. This is due to the use of larger volume injections during the 2003 analysis season.

Of the pesticide detections, 31 were not qualified and are summarized in Appendix E. 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 31 unqualified values. A 'J' data flag was assigned to 613 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 C, EPA 1991, 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, Williams 1998b).

'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 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 in the main body of the report but are presented in Appendix E. 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). 218 pesticide data points were 'NJ' flagged. The few rejected results (REJ) are not used for any purpose. QA/QC results are discussed in this section of the report and in Appendix C.

Control Sample Recoveries

A variety of metrics are available to monitor pesticide recoveries and gauge sampling, storage, extraction, and analytical performance. LCS were applied in a rotating schedule, once every three weeks, for pesticides. The chemicals used in sample extraction and processing determine probable coelution interferences. The analytical process used for pesticides has three potential coeluting matrices. As such, LCS must be analyzed with each matrix. Herbicide and carbamate analyses have fewer coelution interferences, and LCS were analyzed weekly.

Selected LCS results are available in Appendix C. Of the selected compounds, dichlobenil (94%) and carbaryl (94%) were most effectively recovered. 2,4-dichlorophenylacetic acid (2,4-D) had the lowest recovery range (25 to 71%). Based on LCS from laboratory and field fortification for 2,4-D, bromacil, and MCP, reported concentrations probably underestimate actual environmental levels (Appendix C, Bias Estimation, EPA 1991).

Matrix Spike Recoveries

All pesticide matrix spike/matrix spike duplicates (MS/MSD) were reviewed by both the analytical chemist and the project officer. Recoveries of matrices with 2,4-D had the greatest range of variation (51-183%) yet the average 2,4-D matrix recovery was 103%. Fortification mixtures are developed according to observed sample concentrations and the calibration standards used for analysis (Carrell, personnel communication, 2004). The fortification mixture was appropriate to the data previously observed yet was not ideal for concentrations observed later in the season. Thus, the predictive capacity of the fortification mixture was limited and, as a result, the matrix recoveries had a higher degree of variation. The degree of precision, accuracy, and statistical confidence in pesticide results will increase with the expanding data set. MS/MSD results were generally within data quality objective parameters (Johnson and Cowles 2003) and are presented in Appendix C.

Surrogate Recoveries

Surrogate recoveries were assessed by the analytical chemist and data reviewers to evaluate analytical performance of the method in relation to a specific sample run. Allowable control limits for surrogates are presented in Appendix C. Surrogate recoveries outside of their acceptable range indicate under- or over-estimation of the analyte concentration. Analytical results associated with out-of-range surrogate results were 'J' flagged. Generally, surrogate recoveries were within control limits.

Field Spikes

Several field spikes were prepared using deionized water and pesticide spiking mixtures supplied by MEL. While these samples were carried in the field and exposed to conditions similar to environmental samples, they are more closely related to LCS samples than MS/MSDs. This is due to the absence of matrix effects from particulates and organic carbon. For those chemicals used in the field spike, 2,4-D, bromacil, chlorpyrifos, and MCPP were found to have lower recoveries ranging from 46.5 to 64%. Low field spike recovery indicates reported values are probably underestimated (EPA 1991). Field spike results were more efficient for carbaryl (91%), dichlobenil (82%), and pentachlorophenol (87.5%).

Field Replicates

Field replicates were collected during most sample runs (weeks) and submitted as blind samples to the laboratory. All field replicate results were below their corresponding PQL. There is a higher level of uncertainty when compounds are detected above the MDL but below the PQL. Field replicates had mean relative percent differences (RPD) ranging from 19 – 30 % (Appendix C). The average RPD of field replicates was 25.5%. Similar RPD values have been reported for field replicate sampling (sequential) in Washington State (Embrey and Frans 2003). The replicate samples showed good reproducibility at the low levels detected.

Conventional Parameters

Five conventional water quality parameters were collected in this study. Of the conventional parameters, discharge, pH, conductivity, and temperature 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 (SOP) (Cusimano 1993, Ward 2001), USGS methodologies (Rantz et al. 1982), 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.

Results

Urban – Thornton Creek

Conventional Water Quality Parameters

Summary statistics for conventional water quality parameters measured in the Thornton Creek watershed are listed in Table 2. Chemical and conventional parameter results for all sites are presented in Appendix D. Based on median values, total suspended solids (TSS) measurements were 4 mg/L higher at the station near the mouth (3-16 mg/L) of the creek than the two upstream stations (1-3 mg/L) during the spring (April through June). The maximum values reported for TSS reflect the levels found during storm events (October through December). During the summer sampling period, the two upstream stations had consistently lower discharge measurements than the station near the mouth.

During the spring and summer, Station 1 on the tributary to the north fork ranged from 0.05 – 0.32 cubic feet per second (cfs) and was nearly dry after the fourth week of sampling (5/6/03). Station 2 on the south fork ranged from 1.41 – 3.58 cfs, and station 3 near the mouth ranged from 3.12 – 7.15 cfs. Station 1 nearly went dry while the station at the mouth had consistent discharge; therefore, groundwater input is the source of flow for Thornton Creek in the summer months. Maximum values reported for discharge reflect levels found during storm events (October through December).

Table 2. Summary of conventional parameters for the Thornton Creek watershed.

Parameter	n	Minimum	Median	Maximum
Thornton 1				
TSS (mg/L)	18	1	1	123
Temperature (°C)	16	7.7	11.95	14.3
pH	16	6.63	7.5	7.88
Conductivity (µmhos/cm)	15	73	230	265
Discharge (cfs)	8	0.05	0.54	11.13
Thornton 2				
TSS (mg/L)	18	1	1	211
Temperature (°C)	16	8.1	11.4	14.9
pH	16	7.05	7.72	8.22
Conductivity (µmhos/cm)	15	71	240	270
Discharge (cfs)	16	1.41	2.2	56.7
Thornton 3				
TSS (mg/L)	18	3	5	257
Temperature (°C)	16	7.5	11.8	16.1
pH	16	7.23	7.67	8.04
Conductivity (µmhos/cm)	15	120	241	269
Discharge (cfs)	16	3.12	4.83	37.8

Pesticides

Fifty-four sampling events were conducted within Thornton Creek (18 at each of Thornton 1, 2, and 3) between April and December 2003 (Table 3). Herbicides comprise the majority of the chemical profile. However, pentachlorophenol (0.0047 – 0.083 µg/L), a wood preservative, was the most commonly detected compound, followed by dichlobenil (0.0038 – 0.34 µg/L) and triclopyr (0.0094 – 0.19 µg/L). The most common organophosphorous insecticide, diazinon, was detected in 46% of the samples, and the maximum concentration was 0.21 µg/L at Thornton 2.

Table 3. Summary of pesticide detections in the Thornton Creek watershed.

Chemical	Category	¹ Detections	² Det. Freq.	³ ALPQL	Concentration (µg/L)		
					Min	Median	⁴ Max
Pentachlorophenol	Wood Preservative	48	88.9%	0.080	0.0047	0.0155	0.083*
Dichlobenil	Herbicide	39	72.2%	0.065	0.0038	0.019	0.34*
Triclopyr	Herbicide	30	55.6%	0.130	0.0094	0.0385	0.19
Diazinon	Insecticide/OP	25	46.3%	0.027	0.0025	0.029	0.21
MCPP (Mecoprop)	Herbicide	19	35.2%	0.315	0.012	0.033	0.15
2,4-D	Herbicide	18	33.3%	0.160	0.01	0.04	0.16
Prometon	Herbicide	12	22.2%	0.032	0.0032	0.0125	0.027
Benzamide, 2,6-dichloro-	Degradate	6	11.1%	0.220	0.047	0.06	0.091
Simazine	Herbicide	3	5.6%	0.033	0.01	0.014	0.025
4-Nitrophenol	Degradate	2	3.7%	0.290	0.011	0.131	0.25
Tebuthiuron	Herbicide	2	3.7%	0.050	0.014	0.087	0.16
Dicamba I	Herbicide	1	1.9%	0.160	0.083	0.083	0.083
Bromacil	Herbicide	1	1.9%	0.135	0.008	0.008	0.008

Sample Events 18 weeks at 3 stations = 54

Results as reported by Manchester Environmental Laboratory.

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

²Detection Frequency is calculated as Detections/Total number of sample events (54).

³ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix C.

⁴Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified. Unqualified and 'NJ' qualified values are summarized in Appendix E.

Insecticide/OP: Insecticide Organophosphate

Upstream versus Downstream

Thornton Creek was the only watershed to have regular sampling at all sample stations (18 each). Thornton 2 had the least number of detections, 46. Thornton 1 had a greater number of detections (76) and, as expected, the downstream station had the highest number of detections, 83. The number of species detected between sites was very similar (10 for Thornton 1, 9 for Thornton 2, and 10 for Thornton 3).

Diazinon and dichlobenil were detected more frequently, at all three stations, during the dry period from April to September than during the storm sampling period from October to December. For the station on the south fork and the station at the mouth of Thornton Creek,

diuron was detected often in the dry period and was not detected during the wet period. Prometon followed the same pattern for station 1 on the north fork tributary and station 3 at the mouth of Thornton Creek. Pentachlorophenol was present at all stations over the duration of the sampling period.

Semivolatile Organic Compounds

The majority of detected SVOCs were polynuclear aromatic hydrocarbons (PAH). Most PAHs detected are associated with incomplete combustion of fossil fuels as well as urban street dust (Cubbage 1994). One source of this incomplete combustion is emissions from motorized vehicles. Most of the remaining compounds were phthalates. About 80% of all phthalates manufactured are used as plasticizers. Plasticizers make plastics flexible; their chief use is in the manufacture of vinyl.

Summary statistics and detection frequency for SVOC results are presented in Table 4. Thirty-eight chemical species and 394 detections resulted from 36 SVOC sampling events in Thornton Creek. Of the 394 detections, 190 values were not qualified and 204 received 'J' qualifications (Appendix C). Two of the 39 detected chemicals were present at a frequency greater than 60%. These two chemicals were bis(2-ethylhexyl) phthalate (0.1 – 16 µg/L) and caffeine (0.02 – 0.99 µg/L).

Semivolatile detections did not follow any of the patterns found for pesticides. The majority of SVOC detections occurred during the fall runoff events (334). Thornton 1 had the greatest number of detections (121), followed by Thornton 3 (107) and Thornton 2 (106). Runoff events were bounded by sampling at the beginning of the storm and sampling near the end. The difference between beginning samples (166 detections) and end samples (168 detections) was minimal. A "first flush" type event occurred between sample events as a whole. The first event, October 15, yielded a total of 167 detections. Subsequent storm events yielded less detections: 96 on November 15-16 and 71 on December 10. The first flush event is characterized by a buildup of chemicals during a long dry period followed by a surface flow event. Subsequent storm events do not contribute the same magnitude of chemicals, as the dry periods tend to be shorter in duration. Bis(2-ethylhexyl) phthalate was the only compound that was commonly detected throughout the entire sampling period from April to December.

A comparison between the three stations for semivolatile chemicals showed that all stations had the same 32 of 38 compounds detected. In addition, the concentration ranges for these compounds were similar, except for three compounds at Thornton 1. Bis(2-ethylhexyl) phthalate, 4-methylphenol, and di-n-butyl phthalate were detected at higher concentrations at least one time during the sampling period.

Table 4. Summary of semivolatile chemicals detected in the Thornton Creek watershed.

Chemical	¹ Detections	² Det. Freq.	³ ALPQL	Concentration (µg/L)		
				Min	Median	⁴ Max
Bis(2-Ethylhexyl) Phthalate	35	97.2%	0.28	0.1	0.47	16*
Caffeine	25	69.4%	0.13	0.02	0.14	0.99
Fluoranthene	20	55.6%	0.06	0.01	0.055	0.58*
Butylbenzylphthalate	19	52.8%	0.13	0.1	0.33	0.91*
Pyrene	19	52.8%	0.07	0.01	0.06	0.46*
Acenaphthene	18	50.0%	0.07	0.01	0.02	0.03
Diethylphthalate	17	47.2%	0.08	0.02	0.11	0.79*
2-Methylphenol	15	41.7%	0.07	0.03	0.14	0.4*
4-Methylphenol	15	41.7%	0.13	0.04	0.18	3.1*
Di-N-Butylphthalate	15	41.7%	0.17	0.02	0.19	2*
Chrysene	14	38.9%	0.07	0.02	0.06	0.27*
Phenanthrene	14	38.9%	0.07	0.01	0.05	0.26*
2,4-Dimethylphenol	13	36.1%	0.13	0.03	0.125	0.24*
2-Methylnaphthalene	13	36.1%	0.06	0.01	0.05	0.68*
Phenol	13	36.1%	0.13	0.03	0.15	0.52
1-Methylnaphthalene	10	27.8%	0.06	0.01	0.05	0.45*
Benzyl Alcohol	10	27.8%	0.64	0.34	0.985	3.1*
Benzo(b)fluoranthene	9	25.0%	0.13	0.09	0.2	0.34*
Benzo(k)fluoranthene	9	25.0%	0.13	0.01	0.06	0.18*
Benzo(a)pyrene	8	22.2%	0.07	0.07	0.115	0.23
Benzo(ghi)perylene	8	22.2%	0.13	0.08	0.11	0.21*
Indeno(1,2,3-cd)pyrene	8	22.2%	0.13	0.19	0.24	0.35*
Anthracene	7	19.4%	0.07	0.01	0.02	0.05
Benzo(a)anthracene	7	19.4%	0.07	0.03	0.1	0.17*
Carbazole	7	19.4%	0.17	0.02	0.05	0.09
Fluorene	7	19.4%	0.07	0.01	0.01	0.03
Pentachlorophenol	7	19.4%	1.30	0.23	0.27	0.63
Benzoic Acid	6	16.7%	2.6	2.1	2.6	15
Naphthalene	6	16.7%	0.07	0.05	0.075	0.71*
3B-Coprostanol	5	13.9%	1.3	1.1	1.6	2.3*
Retene	5	13.9%	0.13	0.01	0.03	0.07
Dimethylphthalate	3	8.3%	0.13	0.04	0.05	0.07
N-Nitrosodiphenylamine	2	5.6%	0.07	0.03	0.03	0.03
2-Nitrophenol	1	2.8%	0.26	0.11	0.11	0.11
Acenaphthylene	1	2.8%	0.07	0.01	0.01	0.01
Dibenzo(a,h)anthracene	1	2.8%	0.13	0.16	0.16	0.16
Dibenzofuran	1	2.8%	0.07	0.01	0.01	0.01
Di-N-Octyl Phthalate	1	2.8%	0.20	0.57	0.57	0.57

Sample Events 12 weeks at 3 stations = 36

Results as reported by Manchester Environmental Laboratory.

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

²Detection Frequency is calculated as Detections/Total number of sample events (36).

³ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix C.

⁴Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified. Unqualified and 'NJ' qualified values are summarized in Appendix E.

Pentachlorophenol was included in both the pesticide and SVOC analyses. The GC/MS (SVOC method 8270) method detected pentachlorophenol at a minimum of 0.23 µg/L, median of 0.27 µg/L, and maximum of 0.63 µg/L. Pesticide quantitation by AED (method 8085) yielded a minimum of 0.0047 µg/L, median of 0.016 µg/L and maximum of 0.086 µg/L. The pesticide AED method is more sensitive than GC/MS in detecting and quantifying pentachlorophenol. The practical quantitation limit for pentachlorophenol is 0.080 µg/L by the AED method and 1.3 µg/L by the GC/MS (SVOC) method. Pentachlorophenol results should be evaluated with respect to quantitative sensitivity.

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

Conventional Water Quality Parameters

Summary statistics for conventional water quality parameters measured at all of the sampling sites in the agricultural basin are presented in Table 5. TSS were variable in the sampled creeks with values ranging from 1 to 100 mg/L. The highest median value (35 mg/L) was measured at Spring Creek station 3. The lowest levels were measured in the Marion Drain and the upstream station on Spring Creek. Conductivity measurements were found to have a similar median value with the exception of two stations. The middle Spring Creek station and the Sulphur Creek Wasteway station had conductivity values a minimum of 75 µmhos/cm higher than the other sampling stations. Discharge was variable across all stations during all sampling events with Sulphur Creek Wasteway typically having the highest measurements. Median water temperatures were similar across all stations with the exception of the upper two stations on Spring Creek. These two stations had water temperatures two degrees lower than the other stations. The highest water temperatures were measured at the mouth of Marion Drain (23.2 °C) and the mouth of Spring Creek (23.8 °C).

Table 5. Summary of conventional parameters for the Lower Yakima watershed.

Parameter	n	Minimum	Median	Maximum
Marion 1				
TSS (mg/L)	12	10	13	22
Temperature (°C)	12	13	16	19.5
pH	12	7.29	8.06	8.46
Conductivity (µmhos/cm)	11	212	240	288
Discharge (cfs)	12	129.91	183.18	230.9
Marion 2				
TSS (mg/L)	21	1	16	46
Temperature (°C)	21	13.4	16.2	23.2
pH	21	7.11	8.32	8.99
Conductivity (µmhos/cm)	20	195	239	375
Discharge (cfs)	21	26.49	104.74	251.13
Spring 1				
TSS (mg/L)	12	7	16	24
Temperature (°C)	12	11.7	14.3	19.9
pH	12	7.04	7.63	8.08
Conductivity (µmhos/cm)	11	180	211	251
Discharge (cfs)	12	1.81	4.75	6.32
Spring 2				
TSS (mg/L)	12	18	27	45
Temperature (°C)	12	11.1	14	18.7
pH	12	7.67	7.95	8.09
Conductivity (µmhos/cm)	11	268	340	395
Discharge (cfs)	12	4.77	9.51	15.53
Spring 3				
TSS (mg/L)	21	19	35.5	94
Temperature (°C)	21	10.1	16.8	23.8
pH	21	7.03	8.04	8.34
Conductivity (µmhos/cm)	20	180	205	280
Discharge (cfs)	21	20.93	44.35	67.6
Sulphur 1				
TSS (mg/L)	21	11	26.5	100
Temperature (°C)	21	11.5	16.1	20.3
pH	21	7.58	8.23	8.58
Conductivity (µmhos/cm)	20	189	315	450
Discharge (cfs)	21	115.54	191.06	386.5

Pesticides

Ninety-nine sample events were conducted within the Lower Yakima watershed between April and October 2003. Several chemical classes were detected, including organophosphate and chlorinated and carbamate pesticides.

Herbicides were the most frequently detected compounds. 2,4-D, atrazine, and bromacil were detected in 87%, 58%, and 52% of all agricultural samples, respectively. Chlorpyrifos and azinphos-methyl (Guthion) were the most frequently detected organophosphate pesticides and had a detection rate of 38% and 13%, respectively. Marion Drain samples differed slightly from the average. Terbacil was the most frequently detected herbicide within Marion Drain and was present in 73% of samples. Similarly, dimethoate was the second most common organophosphate pesticide and was present in 24% of samples within the Marion drainage. Chlorinated pesticides are principally represented by α -endosulfan and its degradate endosulfan sulfate. Relative to other samples collected, singular high concentrations of carbaryl (1.8 $\mu\text{g/L}$ at Spring 2 and 10 $\mu\text{g/L}$ at Spring 1) and 2,4-D (1.9 $\mu\text{g/L}$ at Marion 1) were detected. The majority of pesticide/herbicide results were estimated between the method detection limit and the practical quantitation limit. These values were assigned a 'J' data flag.

Marion Drain

A total of 33 samples were taken from the Marion Drain. Twelve samples were taken from the upstream site, Marion 1, and 21 samples were taken from the downstream site, Marion 2. Marion 2 represents the reach terminating at the confluence with the Lower Yakima River.

Herbicides account for 82% of the chemical detections within the Marion Drain. Terbacil, 2,4-D, and atrazine were detected in 73%, 70%, and 67% of the sampling events, respectively. Organophosphorous pesticides comprise 16% of chemical detections. Organophosphorous pesticides are primarily represented by chlorpyrifos, dimethoate, and azinphos-methyl (Guthion) and were detected in 36%, 24%, and 9% of the sampling events, respectively.

Table 6. Summary of pesticide detections in the Marion drainage.

Chemical	Category	¹ Detections	² Det. Freq.	³ ALPQL	Concentration (µg/L)		
					Min	Median	⁴ Max
Terbacil	Herbicide	24	72.7%	0.335	0.0046	0.066	0.41
2,4-D	Herbicide	23	69.7%	0.050	0.011	0.057	1.9*
Atrazine	Herbicide	22	66.7%	0.033	0.0019	0.0055	0.017
Pendimethalin	Herbicide	15	45.5%	0.135	0.004	0.039	0.1
Chlorpyrifos	Insecticide/OP	12	36.4%	0.027	0.0016	0.0073	0.085
Bromoxynil	Herbicide	12	36.4%	0.315	0.001	0.012	0.052
MCPA	Herbicide	12	36.4%	0.160	0.022	0.043	0.076
Dimethoate	Insecticide/OP	8	24.2%	0.195	0.0014	0.0112	0.13
Dicamba I	Herbicide	6	18.2%	0.018	0.0037	0.0105	0.079
Treflan (Trifluralin)	Herbicide	5	15.2%	0.160	0.003	0.0062	0.016
Bromacil	Herbicide	5	15.2%	0.050	0.0036	0.007	0.013
Azinphos (Guthion)	Insecticide/OP	3	9.1%	0.066	0.0003	0.0031	0.0064
Malathion	Insecticide/OP	3	9.1%	0.132	0.0031	0.015	0.024
Bentazon	Herbicide	3	9.1%	0.080	0.02	0.053	0.063
Simazine	Herbicide	2	6.1%	0.039	0.0016	0.0018	0.002
Alachlor	Herbicide	2	6.1%	0.099	0.002	0.0041	0.0061
Endosulfan II	Insecticide	1	3.0%	0.065	0.004	0.004	0.004
Diazinon	Insecticide/OP	1	3.0%	0.066	0.007	0.007	0.007
Pentachlorophenol	Wood Preservative	1	3.0%	0.235	0.01	0.01	0.01
Propargite	Insecticide	1	3.0%	0.053	0.015	0.015	0.015
Chlorpropham	Herbicide	1	3.0%	0.027	0.037	0.037	0.037
Eptam	Herbicide	1	3.0%	0.027	0.038	0.038	0.038*
Ethoprop	Insecticide/OP	1	3.0%	0.026	0.046	0.046	0.046
Diphenamid	Herbicide	1	3.0%	0.099	0.093	0.093	0.093
Endosulfan Sulfate	Degradate	1	3.0%	0.160	0.36	0.36	0.36
Dichlobenil	Herbicide	1	3.0%	0.018	0.5	0.5	0.5*
Sample Events	12 weeks at M1, 21 weeks at M2 = 33						

Results as reported by Manchester Environmental Laboratory.

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

²Detection Frequency is calculated as Detections/Total number of sample events (33).

³ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix C.

⁴Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified. Unqualified and 'NJ' qualified values are summarized in Appendix E.

Insecticide/OP: Insecticide Organophosphate

Spring Creek

Forty-five sampling events were conducted in the Spring Creek drainage: 12 samples from Spring 1 (upstream), 12 samples from Spring 2 (midstream), and 21 samples from Spring 3 (downstream). Spring 3 represents the reach terminating at the confluence with the Lower Yakima River.

Herbicides account for the majority of detections, 79%, and were dominated by 2,4-D, bromacil, and atrazine. 2,4-D and bromacil were the most frequently detected chemicals and were present in 73% and 62% of the samples, respectively. Organophosphorous pesticides made up 15% of the chemical detections. The most abundant organophosphorous pesticide, chlorpyrifos, was detected in 36% of the samples.

Table 7. Summary of pesticide detections in the Spring Creek drainage.

Chemical	Category	¹ Detections	² Det. Freq.	³ ALPQL	Concentration (µg/L)		
					Min	Median	⁴ Max
2,4-D	Herbicide	33	73.3%	0.160	0.01	0.05	0.31*
Bromacil	Herbicide	28	62.2%	0.135	0.0022	0.026	0.17
Atrazine	Herbicide	20	44.4%	0.039	0.0016	0.0032	0.012
Chlorpyrifos	Insecticide/OP	16	35.6%	0.026	0.0013	0.0062	0.05
Pendimethalin	Herbicide	15	33.3%	0.050	0.0031	0.018	0.088
Terbacil	Herbicide	13	28.9%	0.099	0.0063	0.019	0.21
Norflurazon	Herbicide	11	24.4%	0.066	0.0028	0.016	0.065
Simazine	Herbicide	7	15.6%	0.033	0.0012	0.0031	0.017
Azinphos (Guthion)	Insecticide/OP	5	11.1%	0.053	0.0032	0.01	0.025
Malathion	Insecticide/OP	3	6.7%	0.027	0.0032	0.013	0.076
4,4'-DDE	Degradate	3	6.7%	0.018	0.0029	0.0035	0.017
Carbaryl	Insecticide/Carbamate	2	4.4%	0.190	1.75	5.88	10*
MCPA	Herbicide	2	4.4%	0.315	0.018	0.0275	0.037
Hexazinone	Herbicide	2	4.4%	0.050	0.0044	0.0237	0.043
Endosulfan Sulfate	Degradate	2	4.4%	0.018	0.016	0.0175	0.019
Bromoxynil	Herbicide	2	4.4%	0.160	0.0056	0.0173	0.029
Pentachlorophenol	Wood Preservative	2	4.4%	0.080	0.014	0.016	0.018
Dimethoate	Insecticide/OP	2	4.4%	0.027	0.0028	0.0159	0.029
Dicamba I	Herbicide	2	4.4%	0.160	0.0042	0.0076	0.011
4-Nitrophenol	Degradate	2	4.4%	0.290	0.0054	0.0066	0.0077
Dichlobenil	Herbicide	2	4.4%	0.065	0.0013	0.0027	0.0041
Oxyfluorfen	Herbicide	1	2.2%	0.134	0.238	0.238	0.238
Di-allate (Avadex)	Herbicide	1	2.2%	0.345	0.23	0.23	0.23*
Carboxin	Herbicide	1	2.2%	0.199	0.2	0.2	0.2*
Hexachlorobenzene	Insecticide	1	2.2%	0.018	0.16	0.16	0.16*
Imidan	Insecticide/OP	1	2.2%	0.036	0.076	0.076	0.076
Fenamiphos	Insecticide/OP	1	2.2%	0.050	0.049	0.049	0.049*
Diphenamid	Herbicide	1	2.2%	0.099	0.048	0.048	0.048
Bentazon	Herbicide	1	2.2%	0.235	0.022	0.022	0.022
Metolachlor	Herbicide	1	2.2%	0.133	0.017	0.017	0.017
Endosulfan I	Insecticide	1	2.2%	0.018	0.016	0.016	0.016
Propargite	Insecticide	1	2.2%	0.066	0.009	0.009	0.009
Ronnel	Insecticide/OP	1	2.2%	0.023	0.0071	0.0071	0.0071
Alachlor	Herbicide	1	2.2%	0.335	0.0032	0.0032	0.0032
Pronamide (Kerb)	Herbicide	1	2.2%	0.169	0.0031	0.0031	0.0031
Treflan (Trifluralin)	Herbicide	1	2.2%	0.050	0.0019	0.0019	0.0019

Sample Events 12 weeks at S1 and S2, 21 weeks at S3 = 45

Results as reported by Manchester Environmental Laboratory.

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

²Detection Frequency is calculated as Detections/Total number of sample events (45).

³ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix C.

⁴Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified. Unqualified and 'NJ' qualified values are summarized in Appendix E.

Insecticide/OP: Insecticide Organophosphate

Sulphur Creek Wasteway

The Sulphur Creek Wasteway drainage had one sampling station located near the confluence of the Lower Yakima River. Sulphur 1 was tested on 21 different occasions for pesticides.

Herbicides account for 81% of the chemical detections within Sulphur Creek Wasteway. 2,4-D, bromacil, and atrazine were detected in 95%, 67%, and 48% of the sampling events, respectively. Organophosphorous insecticides make up 13% of the chemical detections. The frequency of organophosphorous detection is spread between chlorpyrifos (14%), azinphos-methyl (14%), diazinon (10%), and dimethoate (10%).

Table 8. Summary of pesticide detections in the Sulphur Creek Wasteway drainage.

Chemical	Category	¹ Detections	² Det. Freq.	³ ALPQL	Concentration (µg/L)		
					Min	Median	⁴ Max
2,4-D	Herbicide	20	95.2%	0.099	0.013	0.082	0.25*
Bromacil	Herbicide	14	66.7%	0.315	0.0096	0.0165	0.07
Atrazine	Herbicide	10	47.6%	0.080	0.0019	0.0054	0.013
Pendimethalin	Herbicide	5	23.8%	0.053	0.0041	0.0066	0.016
Terbacil	Herbicide	4	19.0%	0.160	0.0041	0.018	0.029
Bentazon	Herbicide	4	19.0%	0.066	0.019	0.025	0.032
Chlorpyrifos	Insecticide/OP	3	14.3%	0.195	0.0025	0.0038	0.013
Azinphos (Guthion)	Insecticide/OP	3	14.3%	0.050	0.017	0.017	0.023
2,4,6-Trichlorophenol	Herbicide	2	9.5%	0.050	0.0033	0.0041	0.0048
Diazinon	Insecticide/OP	2	9.5%	0.027	0.0057	0.0062	0.0066
Pentachlorophenol	Wood Preservative	2	9.5%	0.039	0.0049	0.0064	0.0078
Dimethoate	Insecticide/OP	2	9.5%	0.027	0.0033	0.0142	0.025
Norflurazon	Herbicide	2	9.5%	0.235	0.0031	0.0381	0.073
Treflan (Trifluralin)	Herbicide	1	4.8%	0.495	0.0003	0.0003	0.0003
4,4'-DDE	Degradate	1	4.8%	0.033	0.0029	0.0029	0.0029
Simazine	Herbicide	1	4.8%	0.018	0.0089	0.0089	0.0089
4-Nitrophenol	Degradate	1	4.8%	0.066	0.01	0.01	0.01
MCPP (Mecoprop)	Herbicide	1	4.8%	0.135	0.019	0.019	0.019
Malathion	Insecticide/OP	1	4.8%	0.160	0.02	0.02	0.02
Bromoxynil	Herbicide	1	4.8%	0.027	0.02	0.02	0.02
Propargite	Insecticide	1	4.8%	0.290	0.158	0.158	0.158
Sample Events	21 weeks at 1 station = 21						

Results as reported by Manchester Environmental Laboratory.

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

²Detection Frequency is calculated as Detections/Total number of sample events (21).

³ALPQL: Average Lower Practical Quantitation Limit as determined in Appendix C.

⁴Values with an asterisk, *, are not qualified. All other maximum values are 'J' qualified. Unqualified and 'NJ' qualified values are summarized in Appendix E.

Insecticide/OP: Insecticide Organophosphate

Upstream versus Downstream

Marion Drain and Spring Creek have upstream and downstream stations. The Marion Drain had 15 chemicals that were detected at both the upper and the lower stations. Marion 2 near the mouth was found to have 11 additional chemicals that were not detected at Marion 1 near the headwaters. The reason for this difference may be attributed to the small amount of cultivated land upstream of Marion 1 compared to the large amount above Marion 2. The 15 pesticides detected at both Marion sampling stations had similar concentrations. The only exception included a single high detection of 2,4-D (1.9 µg/L) at Marion 1.

Spring Creek displayed a pattern opposite to that of Marion Drain with the upstream station having more detections than the station at the mouth. The upstream station had a total of 33 detected pesticides, well in excess of the 22 pesticides detected at the lower station. A reason for the increased frequency of detection at the upstream sampling location may be the proximity of cultivated land adjacent to this site. Similar to Marion Drain, the 17 pesticides detected at both Spring Creek stations had analogous concentrations. The only exception was carbaryl, which was detected at 10 µg/L at the upstream location and at 1.7 µg/L at the midstream station during the same sampling event (6/18/2003).

Differences over Sampling Period

2,4-D, atrazine, and bromacil were consistently detected at all stations between April and October 2003. Spring Creek and Sulphur Creek Wasteway had detections of chlorpyrifos and pendimethalin during the beginning of the sampling season, and the detection rate decreased markedly with the onset of summer. Ten of 11 Azinphos-methyl detections occurred during two sample weeks (week 22-5/27 and week 25-6/17). Bentazon was not detected until week 21 (5/21) and detections continued throughout the sampling season. The wide variation in detections during the sampling period is likely due to the differences in cropping patterns, application periods, and chemical fate characteristics in each of the watersheds. For example, pendimethalin is an herbicide typically applied in the fall to ditch banks and rights of way or pre-emergence in the spring for a variety of crops. Pendimethalin has an aerobic soil half-life over one year but can dissipate in less than 35 days in aquatic environments based on hydrolysis and aquatic metabolism studies (EPA 1997).

Discussion

Comparison to Applicable Water Quality Values

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

- EPA National Recommended Water Quality Criteria: 2002.
- EPA Registration Eligibility Document assessment endpoints, including the endangered species Level of Concern (LOC) which is 0.05 the LC₅₀ 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 or standards used for aquatic life protection and 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. Regulatory values are not available for all compounds detected. Of the commonly detected compounds, only pentachlorophenol, endosulfan, chlorpyrifos, and 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 F.

Five pesticides or degradates had estimated concentrations above promulgated or recommended numeric water quality values. Although several of the results are 'J' qualified estimates, each of the five compounds detected were positively identified. The use of 'J' qualified data in regulatory decision making is acceptable with proper consideration of analytical confidence (Appendix C, CSWRCB 2002, EPA 1991, NJDEP 2004). Embrey and Frans (2003), of the USGS, used estimated values for comparison to aquatic life standards. 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 G.

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. With the exception of endosulfan, which has an instantaneous acute criterion, there is typically a 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.*, LC₅₀ 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 by compiling three years of monitoring data collected weekly or biweekly and subsequently looking for trends across years to assess water quality, *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 this sampling schedule is weekly and biweekly.

Table 9. Available standards for chemicals that were above water quality values in urban and agricultural areas.

Chemical	¹ Maximum observed concentration (µg/L)	Aquatic Life Standards (µg/L)				Toxicological Endpoints (µg/L)			
		² WAC Promulgated		³ EPA NRWQC Recommended		⁴ EPA RED			
		Acute	Chronic	CMC	CCC	Chronic (NOEC)	Endangered Species LOC	Species	Ref.
Azinphos methyl (Guthion)	0.025				0.01	0.44	0.15	R	f
Chlorpyrifos	0.085	0.083 ^a	0.041 ^b	0.083	0.041	<0.12	0.15	FM/R	g
Diazinon	0.21			0.1 ^c	0.1 ^c	<0.55	4.5	R/BT	h
DDT (and ⁵ metabolites)	0.017	1.1 ^c	0.001 ^d	1.1	0.001				
Endosulfan ⁶	0.36	0.22 ^c	0.056 ^d			0.11	0.042	R	i

¹All maximum observed concentrations were 'J' qualified. Qualification of maximum values is presented in Appendix C.

²WAC: Promulgated standards according to Chapter 173-201A

³EPA 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

⁴EPA 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 (LC₅₀)

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

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

⁶Chemical form of Endosulfan is not defined in WAC 173-201A. Endosulfan sulfate is applied in this instance. The sum of α and β endosulfan did not exceed EPA water quality criteria.

^aA 1-hour average concentration not to be exceeded more than once every three years on average

^bA 4-day average concentration not to be exceeded more than once every three years on average

^cAn instantaneous concentration not to be exceeded at any time

^dA 24-hour average not to be exceeded

^e<http://www.epa.gov/waterscience/criteria/diazinon/draft-fs.htm>

^fEnvironmental Fate and Effects Division (EFED): Azinphos methyl Registration Eligibility Document (RED) 7-15-1999

^gEFED Chlorpyrifos RED 6-1-2000

^hEFED Diazinon RED 10-2000

ⁱEFED Endosulfan RED 4-2001

Urban – Thornton Creek

Of the 13 pesticides and degradates detected in Thornton Creek throughout the sampling period from April to December 2003, only diazinon was found to be above the recommended numeric water quality criteria and both data results were ‘J’ qualified. Diazinon was present in 46% of the urban samples in this study, and peak values included 0.21 µg/L (5/14, Thornton 2) and 0.13 µg/L (11/16, Thornton 1).

During the sampling period, 38 semivolatile compounds were detected. These detections were compared to the Washington State Water Quality Standards (WAC 173-201A), and none of the chemicals exceeded an available standard.

Agricultural Basin

Forty-two pesticides and degradates were detected in the agricultural watershed; however, only endosulfan exceeded a water quality standard. Although other compounds were periodically detected above the numeric criteria for a water quality standard, it is not possible to evaluate the duration of exposure from the data collected to date. Washington State has promulgated criteria for chlorpyrifos, endosulfan, and DDT metabolites.

Azinphos-methyl was detected 11 times during the sampling period and was present in all agricultural sample stations. Six of 11 detections were ‘J’ qualified estimates and above the EPA criterion continuous concentration (CCC) of 0.01 µg/L. Three detections were above the numeric criteria for azinphos-methyl at Sulphur 1, and one detection at each of Spring 1, 2, and 3 were above the numeric criteria. Additionally, three of these detections occurred during week 22 (5/27-5/28) at Spring 1, Spring 3, and Sulphur 1 with concentrations of 0.025, 0.022 and 0.023 µg/L, respectively. The maximum concentration of azinphos-methyl (0.025 µg/L) is six times below the EPA RED endangered species level of concern for rainbow trout (0.15 µg/L).

Chlorpyrifos was detected in 31 samples and was present at all agricultural sample stations. The first water sample collected near the mouth of Marion Drain had a chlorpyrifos concentration of 0.085 µg/L, slightly above the Washington State numeric acute water quality criterion of 0.083 µg/L. Similarly, the first water sample collected at the upstream Spring Creek station was above the numeric Washington State chronic water quality criteria (0.041 µg/L) with a concentration of 0.050 µg/L. Both results were ‘J’ qualified estimates.

Endosulfan sulfate was detected three times: once each at Marion 2, Spring 2, and Spring 3. One sample (downstream Marion Drain, 8/20, 0.36 µg/L) exceeded the WAC acute aquatic life standard of 0.22 µg/L. The detected value was a ‘J’ qualified estimate. No other detected values exceeded available water quality standards.

4,4’-DDE was detected four times. Three detections occurred during week 21 (5/21) and one during week 15 (4/9). 4,4’-DDE was found twice in the upstream Spring Creek station, once at the downstream station and once in Sulphur Creek Wasteway. All detections were above the numeric WAC chronic and EPA CCC aquatic life criteria (0.001 µg/L). Additionally, all

detections were ‘J’ qualified estimates. Depending on the analytical run, 4,4’-DDE detection limits are frequently above numeric aquatic life standards (EPA SW-846, Methods 8085 and 8270). The 4,4’-DDE detections are the result of historical applications and DDT metabolism, not present activities.

The highest detected concentration of carbaryl occurred at Spring 1 (10 µg/L, 6/18) and is likely associated with a second elevated concentration found in Spring 2 (1.7 µg/L, 6/18). However, these concentrations do not exceed a water quality criterion or the EPA endangered species LOC for rainbow trout (60 µg/L).

Comparison to Other Environmental Quality Data

For perspective, data from this study were compared to historical environmental quality data from previous Department of Ecology and USGS National Water Quality Assessment (NAWQA) monitoring in Washington. Information was gathered from Ecology’s Environmental Information Management (EIM) database on pesticide results by WRIA (urban watershed) and county (agricultural watershed), and the NAWQA data warehouse was queried for selected pesticides. No data was available for pentachlorophenol in the urban basin (USGS). Comparison data are shown in Tables 10 (urban basin) and 11 (agricultural basin).

These historic samples span a wide range of streams, rivers, and lakes, with varying detection limits; therefore, the median of the detected concentrations was chosen to compare to the median of current sample detections. Tables 10 and 11 also report minimum and maximum detected concentrations from EIM, NAWQA, and the current data set.

Urban - Thornton Creek

Data from the current study, Ecology EIM, and USGS NAWQA are summarized in Table 10. NAWQA data are summarized from results for the Puget Sound basin, WRIA 8.

Table 10. Comparison of selected pesticide data from the present study to Ecology and USGS data for the Puget Sound basin.

Chemical	Current Study (µg/L)				Ecology EIM (µg/L)				USGS – NAWQA (µg/L)			
	n	Min	Median	Max	n	Min	Median	Max	n	Min	Median	Max
Pentachlorophenol	48	0.0047	0.0155	0.083	81	0.0069	0.060	2	-	-	-	-
Dichlobenil	39	0.0038	0.019	0.34	86	0.0015	0.034	0.7	18	0.0003	0.035	1.200
Triclopyr	30	0.0094	0.0385	0.19	78	0.0060	0.062	0.98	-	-	-	-
Diazinon	25	0.0025	0.029	0.21	51	0.0016	0.036	0.42	93	0.002	0.032	0.501

¹ Puget Sound data only

"-" = no data available

n = number of detections

EIM = Environmental Information Management system

USGS = United States Geological Survey

NAWQA - National Water Quality Assessment

In general, the median concentrations of compounds detected in 2003 are comparable to those found in EIM and previous NAWQA studies as presented in Table 10. Although similar, all 2003 Thornton Creek median concentrations are lower than historical Ecology and USGS studies presented. The maximum concentrations detected in 2003 were lower than those previously observed. This trend was also observed when directly comparing the results of this project and a recent study on Thornton Creek, conducted by the USGS from 1995-98 (Embrey and Frans 2003). Between March 1996 and April 1998, the USGS sampled Thornton Creek 46 times, compared to 54 sampling events on Thornton Creek during 2003. Diazinon, dichlobenil, and prometon were commonly detected in both studies with similar median concentrations; however, the maximum observed concentration values were higher in the USGS study.

Reduced median concentrations are likely a result of homeowner education and organic techniques for pest control in the urban environment. Of note was the detection of atrazine in the USGS study. Atrazine was not detected in this study yet was present in 19 of 46 samples collected by the USGS. Historically there was a weed and feed product for specialty grasses containing atrazine available for retail sale in Washington; however, this registration was canceled in 2003.

A possible explanation for differences in the maximum concentrations observed in 2003 compared to other previous studies may be related to changing use patterns and/or precipitation in the Thornton Creek watershed during the summer of 2003. According to data collected by the National Weather Service (NWS), the average total precipitation for the Puget Sound basin during the sampling period from April to June 2003 was 1.44 inches, 0.51 inches less than normal (NWS 2004). Figure 3 illustrates the deviation from normal beginning in May with rainfall 0.70 inches below average, and ending in September with rainfall 0.72 inches below average. Conversely, rainfall in March, April, late September, and October was several inches higher than the monthly precipitation average. The spring and fall events coincide with the greatest delivery of pesticides (number of chemicals) and lower concentrations, likely a result of dilution.

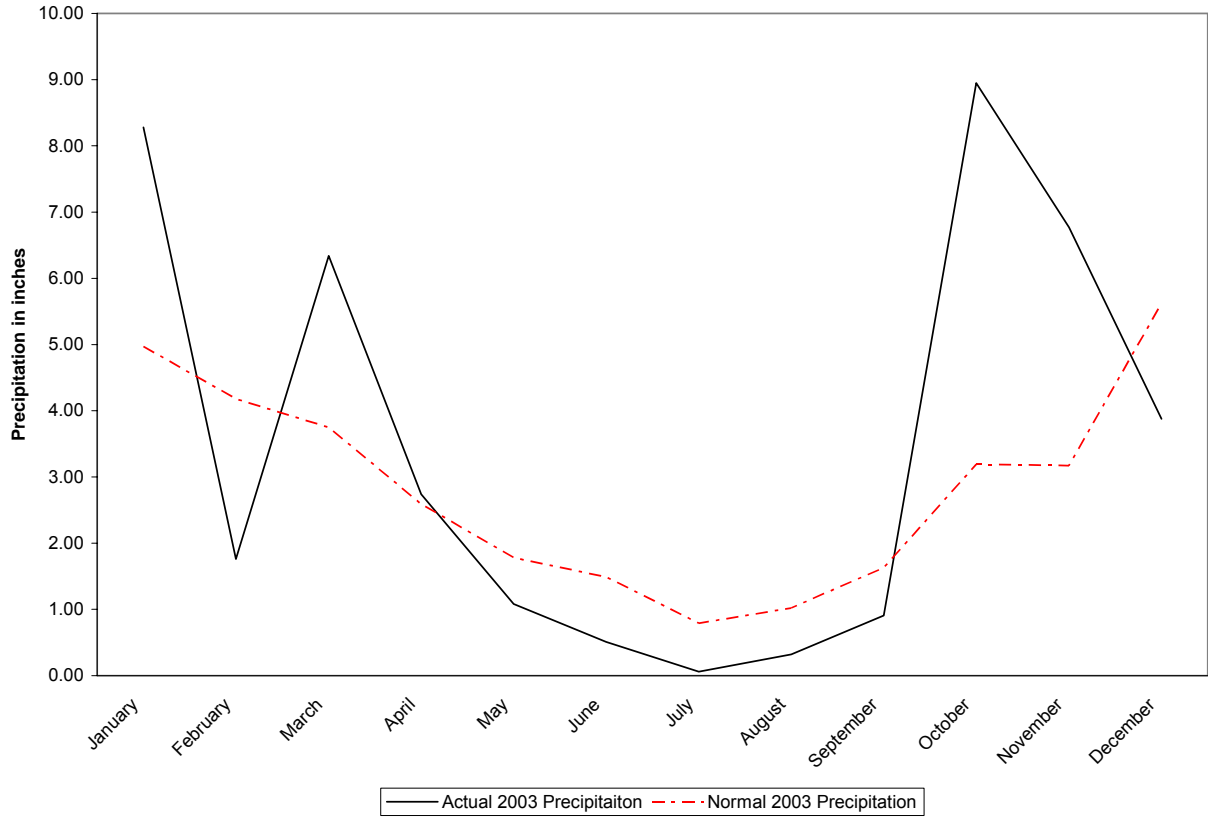


Figure 3. Year 2003 and average precipitation for the Puget Sound basin.

Lower Yakima Watershed

Data from the current study, Ecology EIM, and USGS NAWQA are summarized in Table 11. NAWQA data are summarized from results from Benton, Franklin, Grant, Lincoln, Whitman, and Yakima counties.

Table 11. Comparison of selected pesticide data from the present study to Ecology and USGS data for six counties in Eastern Washington.

Chemical	Current Study (µg/L)				Ecology EIM (µg/L)				USGS – NAWQA (µg/L)			
	n	Min	Median	Max	n	Min	Median	Max	n	Min	Median	Max
2,4-D	76	0.01	0.064	1.90	37	0.001	0.056	0.98	102	0.0083	0.080	1.80
Atrazine	52	0.0016	0.0047	0.017	42	0.0032	0.0135	0.24	540	0.001	0.012	0.208
Chlorpyrifos	31	0.0013	0.0065	0.085	22	0.004	0.0485	0.48	123	0.0009	0.006	0.120

n = number of detections

EIM = Environmental Information Management system

USGS = United States Geological Survey

NAWQA = National Water Quality Assessment

¹ Benton, Franklin, Grant, Lincoln, Whitman, and Yakima counties.

Monitoring data from the agricultural basins in the current study are similar to the data from EIM and the USGS. The median 2,4-D value for the current study is between EIM and USGS median concentrations. The 2,4-D maximum detected value, which occurred in the Marion Drain, is equivalent to the maximum USGS value. Median chlorpyrifos concentrations are similar between this study and the USGS summary. Median and maximum values for atrazine are less than the EIM and USGS summaries. Atrazine results from USGS – NAWQA are based on a greater number of detections. The lower concentrations of atrazine observed in the current study may be attributed to lower use, changes in agricultural practices, and hydrological characteristics in the drainages of this study. A detailed review of the agricultural watershed will be conducted at the end of the three-year study period.

Conventional Water Quality Parameters

Conventional parameters analyzed during 2003 include discharge, total suspended solids (TSS), conductivity, pH, and temperature. These secondary 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 critical species (e.g., salmonids).

The hydrologic regime, characterized by timing and magnitude of precipitation and discharge, is indicative of the physical (temperature) and chemical (TSS, pesticides) 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 (TSS, pesticides) 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 pesticide species, especially 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) are reduced in elevated TSS environments (Ross and Lembi 1999). Measurement of TSS assesses the solids in solution and provides an indication of sediment-associated chemicals. Conductivity is the measurement of the ability of water to carry a charge and is directly related to the concentration of dissolved substances. The pH of water can determine chemical speciation, degradation rate, and pathway of a pesticide. Many pesticides (azinphos-methyl, carbaryl, diazinon) have shorter half-lives at higher pH levels (alkaline hydrolysis at pH 8-9). Temperature directly affects pesticide solubility, chemical degradation, and microbial metabolism. Depth, velocity, substrate, dissolved oxygen, and temperature are principal parameters in the evaluation and designation of salmonid habitat.

Consistent with historical temperature data, Thornton Creek temperatures ranged from 7.5°C to 16.1°C, and were not above promulgated temperature criteria. Temperature results for the lower sites of Sulphur Creek Wasteway, Spring Creek, and Marion Drain are presented in Figure 4. Historical temperature data collected by the USGS in Spring Creek between 1997-2000 are consistent with the 2003 results reported here. Temperature values in both studies are consistently between 8-17°C in the spring and fall, and increase to a maximum of 23°C during the summer.

As illustrated in Figure 4, all waterbodies were above the numeric Washington temperature criterion promulgated in 2003. However, the temperature data collected in 2003 are not sufficient to calculate consecutive daily averages required for the 2003 temperature standards. Given the historical data and current study's results, the attainability of the recently promulgated standard is questionable².

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.

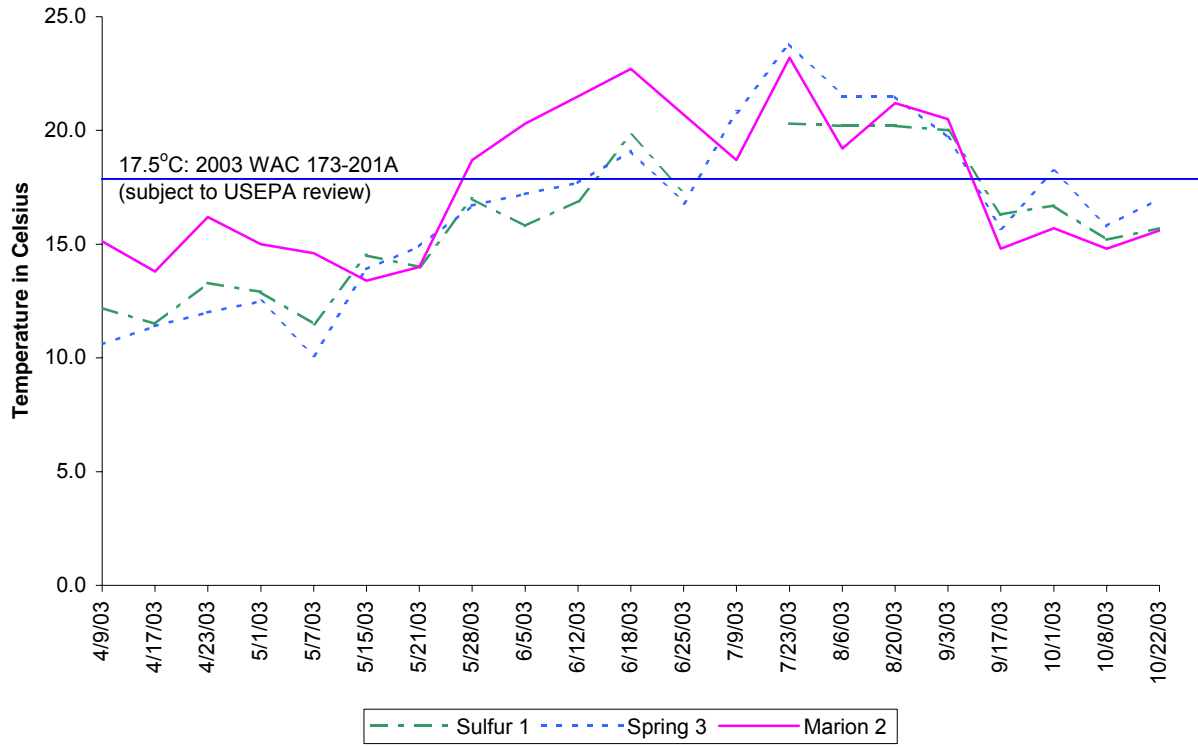


Figure 4. Seasonal water temperatures for the downstream station of study creeks in the agricultural basin.

Summary

Results from year one of a three-year study to assess the occurrence of pesticides in surface water from an urban and an agricultural basin are reported. This report includes monitoring data for 87 registered pesticides and degradates as well as historically used compounds such as DDT. In addition to the pesticides, semivolatile organic compounds (SVOCs) are reported for the urban basin. Pesticides in ambient surface waters at all stations were sampled weekly throughout the spring (April through June, 2003). In the agricultural watershed, biweekly sampling of the mouths of the three sub-drainages continued through the summer. Also, sampling occurred during three Thornton Creek storm events in the fall of 2003.

Thirteen pesticides were detected in the urban watershed during 54 sampling events. Forty-two chemicals were found in the agricultural basin in 99 sampling events. In general, concentrations of pesticides detected were between the limit of detection and the practical quantitation limit, with the median concentration detected below 0.03 µg/L (0.03 ppb). Concentrations of SVOCs in Thornton Creek were more prevalent during storm events in the fall compared to sampling events in the spring and early summer.

Detected chemicals were compared with Washington State water quality standards, EPA National Recommended Water Quality Criteria for the protection of aquatic life, and acute and chronic toxicological endpoints used for pesticide registration by EPA. The majority of chemicals do not have water quality criteria established, and in some cases toxicological endpoints from EPA were not readily available for comparison. Only endosulfan, detected as its degradate endosulfan sulfate, exceeded a Washington State water quality standard.

Although azinphos methyl, chlorpyrifos, diazinon, and DDE 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. Since this sampling schedule is weekly and biweekly, it is not possible to assess the temporal component of the criteria. This monitoring study is designed to assess exposure by compiling three years of monitoring data collected weekly or biweekly and subsequently looking for trends across years to assess water quality, *i.e.*, a weight of evidence approach.

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Appendices

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Appendix A. Summary of Sampling Stations

Table A-1. Station locations and descriptions for Thornton Creek, Marion Drain, Spring Creek, and Sulphur Creek Wasteway (Positions shown in degrees/minutes/seconds).

Site	Latitude	Longitude	Location Description
Thornton 1	47 42' 43.68"	122 17' 18.94"	On NE 115th Street upstream of culvert
Thornton 2	47 42' 24.95"	122 17' 19.60"	Foot bridge upstream of culvert
Thornton 3	47 41' 46.18"	122 16' 28.94"	Downstream of footbridge near Mathews Park
Marion 1	46 19' 30.15"	120 26' 16.65"	Downstream side of bridge at Campbell Rd
Marion 2	46 19' 50.39"	120 11' 56.04"	Upstream of bridge at Indian Church Rd
Spring 1	46 16' 34.76"	119 44' 45.32"	On upstream side of crossing with Crosby Rd
Spring 2	46 15' 29.90"	119 42' 36.52"	~25' downstream of the crossing with McCready Rd
Spring 3	46 14' 03.79"	119 41' 04.06"	10' downstream of the Sunnyside Canal overpass
Sulphur 1	46 15' 04.57"	120 01' 08.30"	Downstream side of bridge at Holiday Rd

Datum = NAD 83

Table A-2. Fisheries classification and historical pesticide occurrence in Thornton Creek.

Site	Thornton 1	Thornton 2	Thornton 3
Description	Northwest	Southwest	Lower
WRIA	8	8	8
Township/Range	26N 4E	26N 4E	26N 4E
Sections	27, 28, 21, 20, 17, 8	27, 28, 29, 33	34, 27

¹Fisheries Classification

² ESA Listing Unit	Puget Sound Chinook ESW and Coastal Puget Sound Bull Trout DPS		
³ Stock Status	FCh-H, Coho-D, So-D	Coho-D, So-D	FCh-H, Coho-D, So-D
⁴ Fish Distribution	Coho-Sp, FCh-P	So-Sp, Coho-R, FCh-P	FCh-Sp, So-Sp, Coho-R

⁵History of Pesticide Occurrence

Prometon, dichlobenil, atrazine, simazine, metolachlor, carbaryl, chlorpyrifos, diazinon, lindane, and malathion.

¹References:

Kerwin 2001, NMFS et al. 2004, WAC 1997, WAC 2003, WDFW et al. 1993, WDFW 1998, WDFW 2004, Ecology 2004.

²ESA, Endangered Species Act, Threatened Species, Puget Sound Chinook Evolutionary Significant Unit and Coastal Puget Sound Bull Trout Distinct Population Segment.

³Stock Status. FCh-H Healthy stock of Fall Chinook, Coho-D Depressed stock of Coho, So-D Depressed stock of Sockeye.

⁴Fish 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.

⁵Pesticide Detections: Embrey and Frans 2003.

Table A-3. Fisheries classification and historical pesticide occurrence in Marion Drain.

Site	Marion 1	Marion 2
Description	Upper	Lower
WRIA	37	37
Township/Range	10N 18E: 10N 19E	10N 20E: 10N 21E
Sections	15, 14, 13: 19, 20 29, 28, 27, 26, 25	30, 29, 28, 27, 26, 25: 30, 29, 28
¹Fisheries Classification		
² ESA Listing Unit	Middle Columbia Steelhead ESU and Columbia Basin Bull Trout DPS	
³ Stock Status	FCh-H, SuSt-D	FCh-H, SpCh-M, SuSt-D
⁴ Fish Distribution	FCh-Sp, Coho-P, SuSt-Sp	FCh-Sp, Coho-P, SuSt-P
⁵History of Pesticide Occurrence in Marion Drain		
Parathion, dieldrin, 4,4-DDE, terbacil, atrazine, simazine, carbaryl, metolachlor, malathion, and trifluralin.		

¹References:

Haring 2001, NMFS et al. 2004, WAC 1997, WAC 2003, WDFW et al. 1993, WDFW 1998, WDFW 2004, Ecology 2004.

²ESA, Endangered Species Act, Threatened Species, Middle Columbia Steelhead Evolutionary Significant Unit and Coastal Puget Sound Bull Trout Distinct Population Segment.

³Stock Status. FCh-Sp Healthy stock of Fall Chinook, SuSt-D Depressed stock of Summer Steelhead, SpCh-M Migrating Spring Chinook.

⁴Fish Distribution. FCh-Sp Spawning Fall Chinook, Coho-P Documented presence of Coho, SuSt-Sp Spawning Summer Steelhead, SuSt-P Documented presence of Summer Steelhead.

⁵Pesticide Detections: Ecology's Environmental Information Management (EIM) water quality database, <http://apps.ecy.wa.gov/eimreporting/> and Ebbert and Embrey 2002.

Table A-4. Fisheries classification and historical pesticide occurrence in Sulphur Creek Wasteway.

Site	Sulphur 1
Description	Lower
WRIA	37
Township/Range	9N 22E: 9N 23E: 10N 23E
Sections	25, 24, 13, 12: 6: 31

¹Fisheries Classification

² ESA Listing Unit	Middle Columbia Steelhead ESU and Columbia Basin Bull Trout DPS
³ Stock Status	FCh-M, SpCh-M, SuSt-D
⁴ Fish Distribution	Coho-Sp, SuSt-P, FCh-P, SpCh-P

⁵History of Pesticide Occurrence

4,4'-DDD, 4,4'-DDE, DDT, dieldrin, azinphos-methyl, terbacil, disulfoton, diazinon, atrazine, bromacil, chlorpyrifos, dimethoate, and carbaryl.

¹References:

Haring 2001, NMFS et al. 2004, WAC 1997, WAC 2003, WDFW et al. 1993, WDFW 1998, WDFW 2004, Ecology 2004.

²ESA, Endangered Species Act, Threatened Species, Middle Columbia Steelhead Evolutionary Significant Unit and Coastal Puget Sound Bull Trout Distinct Population Segment.

³Stock Status. FCh-M Migratory Fall Chinook. SpCh-M Migratory Spring Chinook, SuSt-D Depressed stock of Summer Steelhead.

⁴Fish 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.

⁵Pesticide Detections: Ecology's Environmental Information Management (EIM) water quality database, <http://apps.ecy.wa.gov/eimreporting/> and Ebbert and Embrey 2002.

Table A-5. Fisheries classifications and historical pesticide occurrence in Spring Creek.

Site	Spring 1	Spring 2	Spring 3
Description	Upper	Middle	Lower
WRIA	37	37	37
Township/Range	9N 24E: 10N 24E	9N 24E: 9N 24E	9N 25E
Sections	12, 2: 34, 27	20, 17, 18, 7: 12	27, 28, 29, 20
¹Fisheries Classification			
² ESA Listing Unit	Middle Columbia Steelhead ESU and Columbia Basin Bull Trout DPS		
³ Stock Status	SuSt-D	SuSt-D	FCh-M, SpCh-M, Coho-M, SuSt-D
⁴ Fish Distribution	SuSt-PP	SuSt-PP	SuSt-P, Coho-P, Coho-Sp, SpCh-P, SpCh-R, FCh-P
⁵History of Pesticide Occurrence			
DDT, 4,4'-DDE, 4,4'-DDD, chlorpyrifos, dieldrin, malathion, atrazine, azinphos-methyl, carbaryl, prometon, simazine, terbacil, and EPTC.			

¹References:

Haring 2001, NMFS et al. 2004, WAC 1997, WAC 2003, WDFW et al. 1993, WDFW 1998, WDFW 2004, Ecology 2004.

²ESA, Endangered Species Act, Threatened Species, Middle Columbia Steelhead Evolutionary Significant Unit and Coastal Puget Sound Bull Trout Distinct Population Segment.

³Stock Status. FCh-M Migratory Fall Chinook. SpCh-M Migratory Spring Chinook, SuSt-D Depressed stock of Summer Steelhead.

⁴Fish Distribution. Coho-Sp Spawning Coho, SuSt-P Documented presence of Summer Steelhead, SuSt-PP Probably presence of Summer Steelhead, FCh-P Documented presence of Fall Chinook, SpCh-P Documented presence of Spring Chinook.

⁵Pesticide Detections: Ecology's Environmental Information Management (EIM) water quality database, <http://apps.ecy.wa.gov/eimreporting/> and Ebbert and Embrey 2002.

Table A-6. Summary of sampling conducted for each site.

	April	May	June	July	Aug	Sept	Oct	Nov	Dec
^{1,2} Urban									
Thornton 1									
Weekly	X	X	X	X					
Storm							X	X	X
Thornton 2									
Weekly	X	X	X	X					
Storm							X	X	X
Thornton 3									
Weekly	X	X	X	X					
Storm							X	X	X
³ Agricultural									
Marion 1									
Weekly	X	X	X	X					
Biweekly					X	X	X		
Marion 2									
Weekly	X	X	X	X					
Biweekly					X	X	X		
Spring 1									
Weekly	X	X	X	X					
Biweekly					X	X	X		
Spring 2									
Weekly	X	X	X	X					
Biweekly					X	X	X		
Spring 3									
Weekly	X	X	X	X					
Biweekly					X	X	X		
Sulphur 1									
Weekly	X	X	X	X					
Biweekly					X	X	X		

^{1,2}Urban

¹Chlorinated, nitrogen, organophosphorous, and carbamate pesticides; herbicides; semivolatiles (urban only)

²Nitrogen, organophosphorous, and carbamate pesticides; herbicides; semivolatiles (urban storm events)

³Agricultural

³Chlorinated, nitrogen, organophosphorous, and carbamate pesticides; herbicides (agriculture only through October)

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Appendix B. Crop Area Estimation

Table B-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 B-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 B-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

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Appendix C. Sample Analysis and Quality Assurance Information

Procedure

Pesticides

Water samples for pesticides analyzed at Ecology's Manchester Environmental Laboratory (MEL) were extracted in one-gallon glass jars with Teflon-lined lids used for sample transport. The samples were extracted with methylene chloride by SW-846 Method 3510. MEL standard operating procedures were followed for pesticide and acid herbicide analyses.

All extracts were then analyzed by capillary gas chromatography/atomic emission detection (GC/AED) per EPA SW-846 Method 8085. Confirmation of compounds and/or identification of compounds were performed by gas chromatography/mass spectrometry (GC/MS). Retention times are updated for both the MS and AED at the beginning of each analytical run.

The analytical progression for the WSDA pesticides project was fairly consistent. Special QA/QC measures (e.g., field blanks) were scheduled at regular intervals. The number of samples in a batch varied from 7 to 9 samples. A typical analytical sequence would be as follows:

- Conditioning shot (to remove any active sites in the inlet or column)
- CIC, injected three times to yield multipoint calibrations for the different elements
- Organophosphorous pesticide standard 1
- Organophosphorous 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
- Sample 7
- Sample 8
- Sample 9
- Matrix spike dilution
- LCS

- MS
- MSD
- Method blank 2
- CIC, injected three times to yield multipoint calibrations for the different elements
- Organophosphorous pesticide standard 1
- Organophosphorous pesticide standard 2
- Nitrogen pesticide standard 1
- Nitrogen pesticide standard 2
- Nitrogen pesticide standard 3
- Chlorinated pesticide standard 1
- Chlorinated pesticide standard 2

Manchester Environmental Laboratory 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 phosphorous. 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 Co.

Quantitations are performed on the Atomic Emission Detector (AED). Compounds below the practical quantitation limit (PQL) are quantitated with the SPC and above PQL are quantitated with Compound Independent Calibration (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 $\pm 20\%$, 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 it is below the PQL and has MS confirmation. If the compound is below the PQL and does not have MS confirmation, the value is 'NJ' qualified. Similarly, if 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.

Surrogates were added to the batch, and the recovery of surrogates were used to evaluate sample specific performance. When surrogate recoveries violated their respective control limits, the analyst flagged results with a data qualifier. Control limits for pesticide surrogates are presented in Table C-1. Criteria were set and modified according to EPA Contract Laboratory Program methodologies (EPA 2004). EPA CLP limits for pesticides in general are 30% to 150%.

Table C-1. Control limits for surrogate recoveries.

Surrogate compound	Minimum allowable recovery	Maximum allowable recovery
1,3 Dimethyl-2-nitrobenzene	30%	104%
Tetrachloro-m-xylene	30%	115%
4,4-Dibromooctafluorobiphenyl	30%	98%
Decachlorobiphenyl	50%	120%
Triphenyl phosphate	40%	113%
2,4-dichlorophenylacetic acid	40%	140%
2,4,6-tribromophenol	40%	140%

In addition to the calibration standards and surrogates, two other types of fortified samples were analyzed. Fortified blanks, water samples containing deionized water, and concentrations of analytes of interest were performed for all compounds of interest at least once. Most compounds had two fortified blanks analyzed. The concentrations therein were reported by the laboratory as a percent recovery. The fortified blanks represent the influence of handling, storage, and degradation on sample results without significant matrix influences. These values were compared to matrix spikes and matrix spike duplicates (MS/MSDs).

Matrix spikes and matrix spike duplicates were performed by collecting an extra volume of water at one station during each sampling event. These jars were then spiked (in duplicate) with one of MELs three standard pesticide spiking mixtures in the laboratory on a rotating basis. Unlike the pesticide analysis, only one spiking mixture was required for herbicides. Therefore MS/MSDs were able to be performed for herbicide compounds every week, instead of on a rotating schedule.

The MS/MSDs represent the recovery efficiency of the extractions and solvent exchanges from the water matrix without consideration of significant degradation. Fortified blanks and MS/MSDs were thus used together to evaluate the potential for significant bias in the results on a compound by compound basis.

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. All pesticide analyses were conducted within the 7 day holding time between collection and extraction and also within the 40-day holding time between extraction and analysis.

Carbamate Pesticides

Carbamate pesticides were collected, preserved, and analyzed separately from other samples. These pesticides 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 4°C, 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 6°C or less. The one exception was a single sample with a broken cap. This was discarded. 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 0.25 µg/L to 3.75 µg/L. No surrogate compounds were used in the analysis of carbamate pesticides, but a laboratory control sample (LCS) was run with every batch. The LCS was composed of deionized water spiked with all analytes of interest. Control limits for LCS and MS/MSD samples are 60 to 120% recovery. Performance outside of this window results in qualified data.

Matrix spikes and matrix spike duplicates were not initially performed by the contract laboratory. However after May 2003, all batches of carbamates had MS/MSDs conducted. In addition to the LCS, one fortified blank was submitted to the laboratory. The carbamate LCS, MS/MSD, and fortified blank samples have been used as with other analyses to evaluate extraction efficiency, field degradation, and matrix interference effects.

Semivolatile Organics

Semivolatile organic compounds (SVOCs) are also called base-neutral acid organics (BNAs). These compounds were analyzed only at Thornton Creek stations. Water samples were prepared by extraction with methylene chloride per SW-846,3510. Extracts were then analyzed using a GC/MS. Manchester Environmental Laboratory used EPA Method SW-846, 8270 for this analysis.

The GC/MS was calibrated using target analytes and a five-point linear calibration curve. Eight different surrogates were added to each sample, similar to the pesticide analysis, and LCS, MS/MSD, and laboratory blank samples were conducted for each sampling event. Allowable LCS and MS/MSD limits are 50-150% recovery.

Total Suspended Solids Analysis

Total suspended solids were analyzed at each station by 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.

Laboratory Control Sample, Matrix Spike, Field Spike, and Replicate Evaluation

Figures C-1 and C-2 illustrate the percent recovery for select laboratory control samples (LCSs) and MS/MSD compounds. Due to inference and coelution issues, a LCS for these compounds was not conducted during every analytical run. The parenthetical values after each compound name represent the number of LCSs performed.

The boxplots in Figure C-2 can be compared with those in Figure C-1. This indicates poor recoveries in LCSs do not necessarily lead to poor performance in environmental matrices, especially for 2,4-D and MCP. The presence of dissolved and particulate carbon and other matrix qualities may enhance recoveries of these herbicides.

The percent recoveries from the field spikes are quite similar to the LCS results, demonstrating that measurable alterations in performance due to field handling, storage, and transport are not present (Figures C-1 and C-3). The LCS, matrix spike, and field spike recoveries illustrate the range and average performance of the laboratory for these compounds. Similar data are available for most compounds. Exceptions include degradate and non-target compounds.

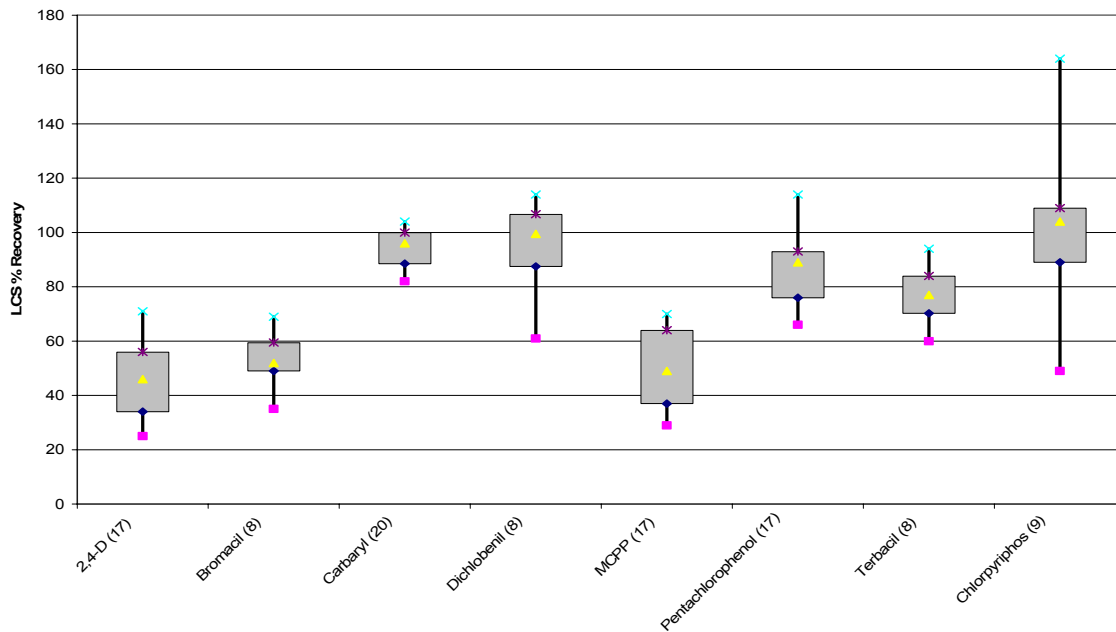


Figure C-1. Laboratory Control Sample (LCS) percent recoveries for selected pesticides. The number of samples is provided after compound name.

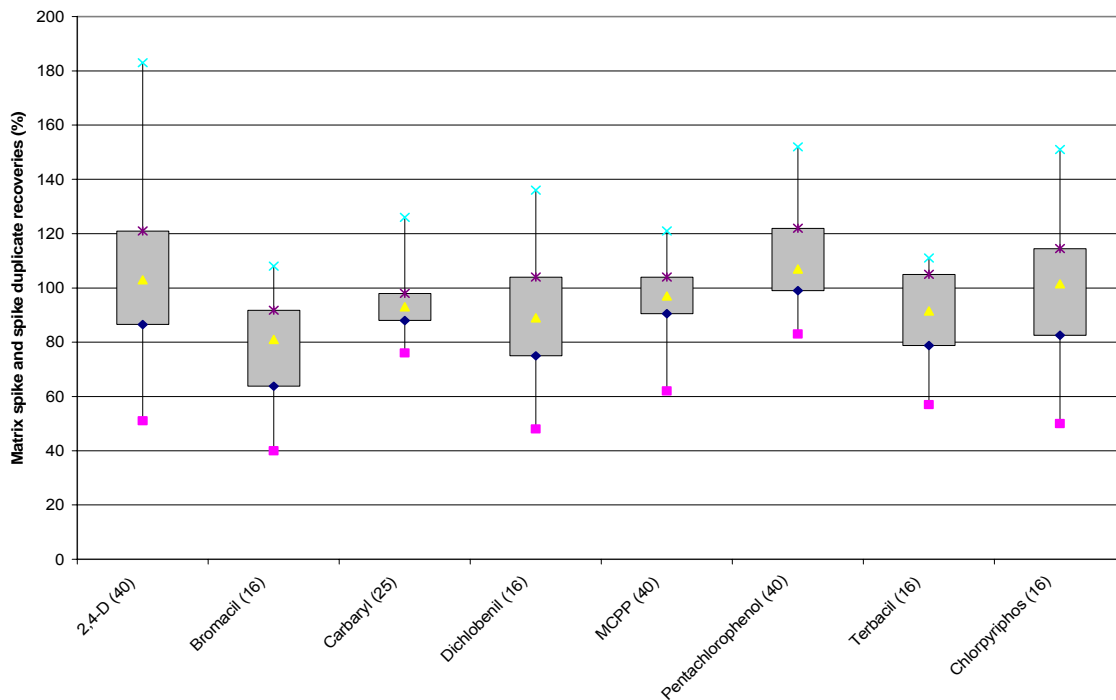


Figure C-2. Matrix spike/spike duplicate percent recoveries for selected pesticides. The number of samples is provided after compound name.

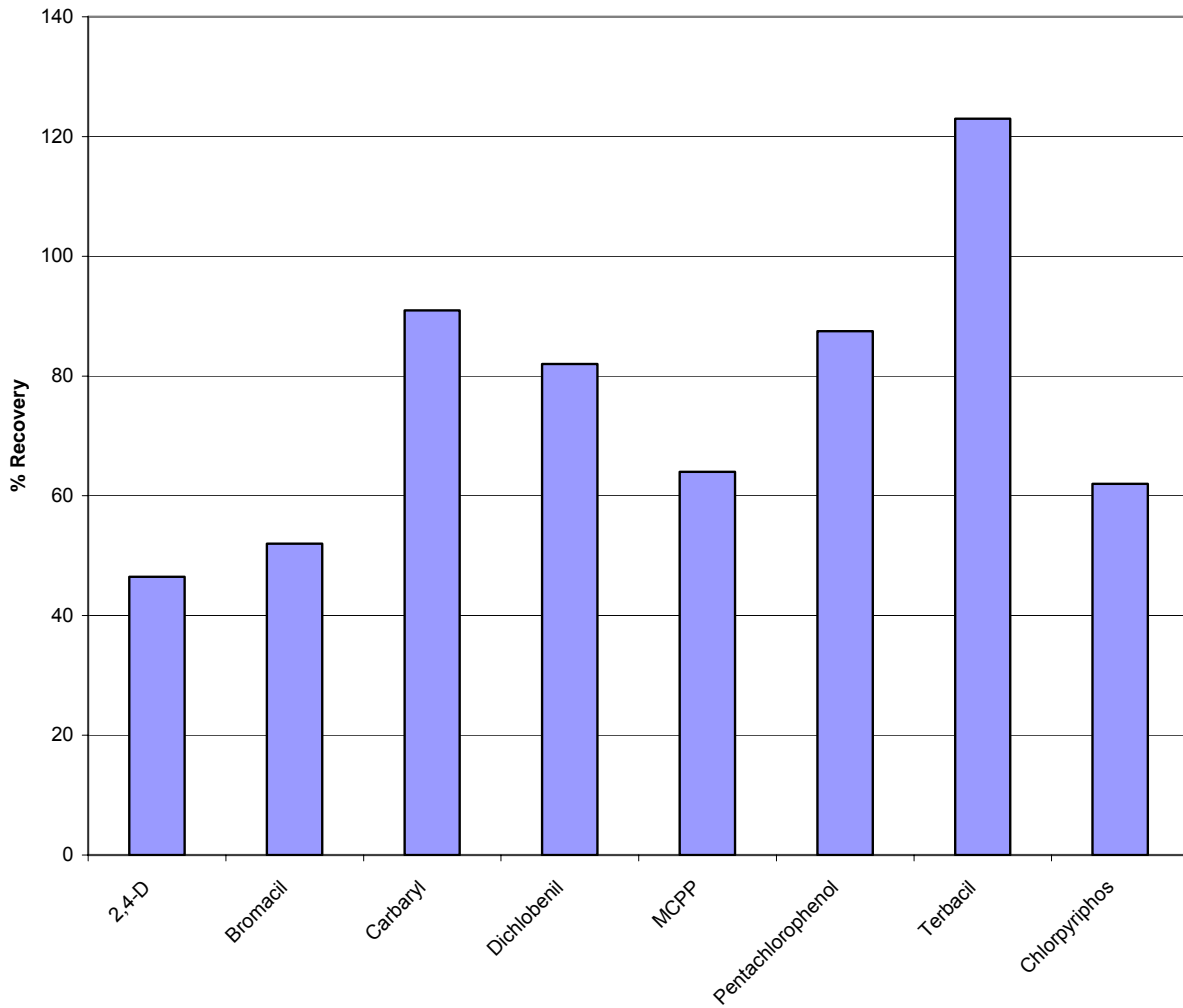


Figure C-3. Field spike arithmetic mean percent recoveries.

Table C-2. Field Replicate results, relative percent differences (RPD), and mean RPDs for selected pesticides ($\mu\text{g/L}$).

Chemical	Sample	Replicate	RPD
2,4-D	0.096	0.076	23.26
	0.063	0.064	1.57
	0.1	0.12	18.18
	0.065	0.03	73.68
	0.017	0.012	34.48
	0.029	0.043	38.89
	0.11	0.11	0.00
	0.22	0.23	4.44
	0.059	0.1	51.57
	0.026	0.02	26.09
	Mean =		27.22

Chemical	Sample	Replicate	RPD
Bromacil	0.011	0.016	37.04
	0.03	0.031	3.28
	0.01	0.013	26.09
	0.023	0.017	30.00
	0.014	0.014	0.00
	Mean =		19.28

Chemical	Sample	Replicate	RPD
Chlorpyrifos	0.002	0.0032	46.15
	0.021	0.023	9.09
	Mean =		27.62

Chemical	Sample	Replicate	RPD
Dichlobenil	0.028	0.031	10.17
	0.017	0.022	25.64
	0.0086	0.0059	37.24
	0.025	0.032	24.56
	Mean =		24.40

Chemical	Sample	Replicate	RPD
Pentachlorophenol	0.016	0.021	27.03
	0.015	0.0089	51.05
	0.011	0.01	9.52
	0.018	0.012	40.00
	0.022	0.014	44.44
	0.017	0.015	12.50
	0.015	0.012	22.22
	Mean =		29.54

Chemical	Sample	Replicate	RPD
Triclopyr	0.024	0.034	34.48
	0.025	0.031	21.43
	0.016	0.013	20.69
	0.047	0.054	13.86
	Mean =		22.62

Method, Estimated, and Practical Quantitation Limits

Method, estimated, and practical quantitation limits were determined for this study (Tables C-3 and C-4).

Method detection limits (MDL) were calculated by the EPA and Manchester Environmental Laboratory according to 40CFR Part 136 (see EPA 1996, EPA 2000, 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 element (nitrogen, phosphorous, 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).

Ranges of minimum practical quantitation limits were determined for this study. The lower and upper minimum quantitation limits (LMinQL and UMinQL) were determined by calculating the 20% and 80% minimum detection values ('U' qualified values) for each analyte.

In some instances, Manchester Laboratory was able to detect pesticides below the MDL and EDL. This is due to the use of larger volume injections during the 2003 analysis season.

Table C-3. Method detection, estimated detection, and practical quantitation limits.

Chemical	¹ EPA (µg/L)	² Manchester (µg/L)		³ WSDA Pest. (µg/L)	
	MDL	MDL	EDL	LMinQL	UMinQL
1-Naftol				0.13	0.25
2,3,4,5-Tetrachlorophenol	0.022	0.022	0.014	0.082	0.092
2,3,4,6-Tetrachlorophenol	0.023	0.018	0.014	0.082	0.092
2,4,5-T	0.033	0.018	0.017	0.12	0.13
2,4,5-TP (Silvex)	0.033	0.0099	0.022	0.12	0.13
2,4,5-Trichlorophenol	0.025	0.020	0.017	0.9	0.1
2,4,6-Trichlorophenol	0.025	0.019	0.017	0.89	0.1
2,4-D	0.042	0.019	0.028	0.15	0.17
2,4-DB	0.050	0.022	0.031	0.18	0.2
2,4'-DDD	0.02	0.02	0.038	0.016	0.019
2,4'-DDE	0.01	0.01	0.037	0.016	0.019
2,4'-DDT	0.02	0.02	0.033	0.016	0.019
3,5-Dichlorobenzoic Acid	0.042	0.017	0.024	0.15	0.17
3-Hydroxycarbofuran				0.13	0.25
4,4'-DDD	0.02	0.02	0.038	0.016	0.019
4,4'-DDE	0.02	0.02	0.030	0.016	0.019
4,4'-DDT	0.03	0.03	0.033	0.016	0.019
4-Nitrophenol	0.073	0.023	0.036	0.28	0.3
Acifluorfen (Blazer)	0.15	0.15	0.088	0.61	0.67
Alachlor	0.10	0.10	0.16	0.11	0.56
Aldicarb				0.13	0.25
Aldicarb sulfoxide+s				0.13	0.25
Aldrin	0.006	0.006	0.029	0.016	0.019
Alpha-BHC	0.03	0.03	0.023	0.016	0.019
Ametryn	0.04	0.04	0.03	0.031	0.034
Atraton	0.13	0.13	0.03	0.047	0.056
Atrazine	0.05	0.05	0.03	0.031	0.047
Azinphos (Guthion)	0.025	0.020	0.010	0.05	0.055
Azinphos Ethyl	0.020	0.025	0.010	0.05	0.055
Bendiocarb				0.13	0.25
Benefin	0.15	0.15	0.07	0.047	0.052
Bentazon	0.006	0.0064	0.038	0.22	0.25
Benzamide, 2,6-dichloro-				0.22	0.22
Beta-BHC	0.03	0.03	0.023	0.016	0.019
Bolstar (Sulprofos)	0.011	0.02	0.010	0.022	0.024
Bromacil	0.27	0.27	0.08	0.13	0.14
Bromoxynil	0.042	0.022	0.015	0.15	0.17
Butachlor	0.16	0.16	0.19	0.19	0.207
Butylate	0.14	0.14	0.13	0.063	0.069
Captafol	0.25	0.25	0.041	0.04	0.086
Captan	0.18	0.18	0.048	0.042	0.135
Carbaryl				0.13	0.25
Carbofuran				0.13	0.25
Carbophenothion	0.009	0.009	0.010	0.031	0.034
Carboxin	0.41	0.41	0.14	0.19	0.207

(Continued)

Table C-3 continued. Method detection, estimated detection, and practical quantitation limits.

Chemical	¹ EPA (µg/L)	² Manchester (µg/L)		³ WSDA Pest. (µg/L)	
	MDL	MDL	EDL	LMinQL	UMinQL
Chlorothalonil (Daconil)	0.18	0.18	0.08	0.075	0.083
Chlorpropham	0.26	0.26	0.13	0.125	0.138
Chlorpyrifos	0.004	0.004	0.011	0.025	0.027
Cis-Chlordane (Alpha-Chlordane)	0.04			0.016	0.017
Cis-Nonachlor	0.035			0.016	0.019
Cyanazine	0.06	0.06	0.02	0.047	0.052
Cycloate	0.19	0.19	0.13	0.063	0.069
Dacthal (DCPA)	0.033	0.008	0.019	0.12	0.13
Delta-BHC	0.035	0.030	0.023	0.016	0.019
Demeton-O	0.021	0.021	0.008	0.022	0.044
Demeton-S	0.070	0.080	0.008	0.022	0.044
Di-allate (Avadex)	0.17	0.17	0.16	0.22	0.47
Diazinon	0.014	0.014	0.009	0.025	0.028
Dicamba I	0.042	0.022	0.028	0.15	0.17
Dichlobenil	0.06	0.06	0.10	0.062	0.067
Dichlorprop	0.046	0.014	0.029	0.16	0.18
Diclofop-Methyl	0.063	0.013	0.042	0.23	0.25
Dieldrin	0.02	0.02	0.037	0.016	0.019
Dimethoate	0.050	0.050	0.007	0.025	0.028
Dinoseb	0.063	0.016	0.038	0.23	0.25
Dioxacarb				0.13	0.25
Diphenamid	0.13	0.13	0.14	0.094	0.103
Disulfoton (Di-Syston)	0.016	0.016	0.008	0.019	0.021
Diuron	0.21	0.21	0.11	0.19	0.2
Endosulfan I	0	0.00	0.032	0.016	0.019
Endosulfan II	0	0.00	0.032	0.016	0.019
Endosulfan Sulfate	0.03	0.03	0.033	0.016	0.019
Endrin	0.03	0.03	0.030	0.016	0.019
Endrin Aldehyde	0.02	0.02	0.020	0.016	0.019
Endrin Ketone	0.01	0.01	0.030	0.016	0.019
EPN	0.008	0.008	0.010	0.031	0.034
Eptam	0.22	0.22	0.11	0.063	0.069
Ethalfuralin (Sonalan)	0.08	0.08	0.07	0.047	0.052
Ethion	0.006	0.006	0.006	0.022	0.024
Ethoprop	0.012	0.012	0.007	0.025	0.028
Fenamiphos	0.03		0.009	0.047	0.052
Fenarimol	0.23	0.23	0.10	0.094	0.103
Fenitrothion	0.004	0.004	0.008	0.022	0.024
Fensulfothion	0.080	0.120	0.009	0.031	0.034
Fenthion	0.011	0.011	0.008	0.022	0.024
Fluridone	0.66	0.66	0.20	0.19	0.207
Fonofos	0.004	0.004	0.007	0.019	0.021
Gamma-BHC (Lindane)	0.03	0.03	0.023	0.016	0.019
Heptachlor	0.01	0.01	0.025	0.016	0.019
Heptachlor Epoxide	0.008	0.008	0.026	0.016	0.019

(Continued)

Table C-3 continued. Method detection, estimated detection, and practical quantitation limits.

Chemical	¹ EPA (µg/L)	² Manchester (µg/L)		³ WSDA Pest. (µg/L)	
	MDL	MDL	EDL	LMinQL	UMinQL
Hexachlorobenzene	0.04	0.04	0.069	0.016	0.019
Hexazinone	0.05	0.05	0.04	0.047	0.052
Imidan	0.007	0.007	0.010	0.034	0.038
Ioxynil	0.042	0.0063	0.019	0.15	0.17
Kelthane	0.17			0.032	0.069
Malathion	0.010	0.010	0.010	0.025	0.028
MCPA	0.083	0.022	0.050	0.3	0.33
MCPP (Mecoprop)	0.083	0.029	0.054	0.3	0.33
Merphos (1 & 2)	0.024	0.06	0.009	0.038	0.041
Metalaxyl	0.35	0.35	0.17	0.19	0.207
Methiocarb				0.13	0.25
Methomyl				0.13	0.25
Methoxychlor	0.03	0.03	0.054	0.016	0.16
Methyl Chlorpyrifos	0.008	0.008	0.010	0.025	0.028
Methyl Parathion	0.005	0.005	0.008	0.022	0.024
Metolachlor	0.15	0.15	0.17	0.126	0.14
Metribuzin	0.02	0.02	0.03	0.031	0.034
MGK264	0.26	0.26	0.16	0.25	0.276
Mirex	0.04	0.04	0.021	0.016	0.019
Molinate	0.17	0.17	0.11	0.063	0.069
Napropamide	0.11	0.11	0.16	0.094	0.103
Norflurazon	0.07	0.07	0.06	0.063	0.069
Oxamyl				0.13	0.25
Oxychlorthane	0.035			0.016	0.019
Oxyfluorfen	0.10	0.10	0.22	0.127	0.14
Parathion	0.009	0.009	0.009	0.025	0.028
Pebulate	0.11	0.11	0.12	0.063	0.069
Pendimethalin	0.06	0.06	0.06	0.047	0.052
Pentachloroanisole	0.035			0.016	0.019
Pentachlorophenol	0.021	0.007	0.013	0.078	0.082
Phorate	0.006	0.006	0.008	0.022	0.024
Picloram	0.042	0.004	0.020	0.15	0.17
Profluralin	0.07	0.07	0.07	0.075	0.083
Promecarb				0.13	0.25
Prometon (Pramitol 5p)	0.04	0.04	0.03	0.031	0.033
Prometryn	0.04	0.04	0.03	0.031	0.034
Pronamide (Kerb)	0.13	0.13	0.15	0.2	0.138
Propachlor (Ramrod)	0.12	0.12	0.13	0.075	0.083
Propargite	0.14	0.14	0.02	0.063	0.069
Propazine	0.05	0.05	0.03	0.031	0.034
Propoxur				0.13	0.25
Ronnel	0.005	0.005	0.010	0.022	0.024
Simazine	0.05	0.05	0.02	0.031	0.034
Sulfotepp	0.006	0.006	0.005	0.019	0.021
Tebuthiuron	0.03	0.03	0.03	0.047	0.052

(Continued)

Table C-3 continued. Method detection, estimated detection, and practical quantitation limits.

Chemical	¹ EPA (µg/L)	² Manchester E.L. (µg/L)		³ WSDA Pest. (µg/L)	
	MDL	MDL	EDL	LMinQL	UMinQL
Terbacil	0.13	0.13	0.06	0.094	0.103
Terbutryn (Igran)	0.05	0.05	0.03	0.031	0.034
Trans-Chlordane (Gamma)	0.03			0.016	0.019
Trans-Nonachlor	0.035			0.016	0.019
Treflan (Trifluralin)	0.09	0.09	0.07	0.047	0.052
Triadimefon	0.13	0.13	0.06	0.081	0.09
Triallate	0.26	0.26	0.18	0.094	0.103
Triclopyr	0.035	0.0091	0.020	0.12	0.14
Vernolate	0.22	0.22	0.12	0.063	0.069

¹Environmental Protection Agency. Target Method Detection Levels. 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.

²Manchester 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 element (nitrogen, phosphorous, chlorine) 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).

³WSDA Pesticides Study. Range of Minimum Practical Quantitation Limit.

LMinQL: Lower minimum quantitation limit.

UMinQL: Upper minimum quantitation limit.

Both parameters calculated as 20% and 80% of range of minimum detection level values for the study.

Table C-4. SVOC Practical Quantitation Limits.

Chemical	¹ WSDA Pest. (µg/L)		
	LMinQL	UMinQL	Average
1,2,4-Trichlorobenzene	0.06	0.07	0.07
1,2-Dichlorobenzene	0.06	0.07	0.07
1,2-Diphenylhydrazine	0.06	0.13	0.10
1,3-Dichlorobenzene	0.06	0.07	0.07
1,4-Dichlorobenzene	0.06	0.07	0.07
1-Methylnaphthalene	0.06	0.06	0.06
2,2'-Oxybis[1-chloropropane]	0.12	0.13	0.13
2,4,5-Trichlorophenol	0.25	0.26	0.26
2,4,6-Trichlorophenol	0.25	0.26	0.26
2,4-Dichlorophenol	0.12	0.13	0.13
2,4-Dimethylphenol	0.12	0.13	0.13
2,4-Dinitrophenol	4.9	5.2	5.1
2,4-Dinitrotoluene	0.12	0.13	0.13
2,6-Dinitrotoluene	0.25	0.26	0.26
2-Chloronaphthalene	0.06	0.07	0.07
2-Chlorophenol	0.06	0.07	0.07
2-Methylnaphthalene	0.06	0.06	0.06
2-Methylphenol	0.06	0.07	0.07
2-Nitroaniline	0.25	0.26	0.26
2-Nitrophenol	0.25	0.26	0.26
3,3'-Dichlorobenzidine	0.62	0.66	0.64
3B-Coprostanol	1.2	1.3	1.3
3-Nitroaniline	0.25	0.26	0.26
4,6-Dinitro-2-Methylphenol	1.2	1.3	1.3
4-Bromophenyl-Phenylether	0.06	0.07	0.07
4-Chloro-3-Methylphenol	0.12	0.13	0.13
4-Chloroaniline	0.12	0.13	0.13
4-Chlorophenyl-Phenylether	0.06	0.07	0.07
4-Methylphenol	0.12	0.13	0.13
4-Nitroaniline	0.62	0.66	0.64
4-Nitrophenol	0.62	0.66	0.64
Acenaphthene	0.06	0.07	0.07
Acenaphthylene	0.06	0.07	0.07
Aniline	0.12	1.5	0.81
Anthracene	0.06	0.07	0.07
Benzidine	2.5	2.6	2.6
Benzo(a)anthracene	0.06	0.07	0.07
Benzo(a)pyrene	0.06	0.07	0.07
Benzo(b)fluoranthene	0.12	0.13	0.13
Benzo(ghi)perylene	0.13	0.13	0.13
Benzo(k)fluoranthene	0.12	0.13	0.13
Benzoic Acid	2.5	2.6	2.6
Benzyl Alcohol	0.62	0.66	0.64
Bis(2-Chloroethoxy)Methane	0.06	0.07	0.07

(Continued)

Table C-4 continued. SVOC Practical Quantitation Limits.

Chemical	¹ WSDA Pest. (µg/L)		
	LMinQL	UMinQL	Average
Bis(2-Chloroethyl)Ether	0.06	0.07	0.07
Bis(2-Ethylhexyl) Phthalate	0.28	0.28	0.28
Butylbenzylphthalate	0.12	0.13	0.13
Caffeine	0.12	0.13	0.13
Carbazole	0.06	0.27	0.17
Chrysene	0.06	0.07	0.07
Dibenzo(a,h)anthracene	0.12	0.13	0.13
Dibenzofuran	0.06	0.07	0.07
Diethylphthalate	0.03	0.12	0.08
Dimethylphthalate	0.12	0.13	0.13
Di-N-Butylphthalate	0.10	0.23	0.17
Di-N-Octyl Phthalate	0.13	0.26	0.20
Fluoranthene	0.06	0.06	0.06
Fluorene	0.06	0.07	0.07
Hexachlorobenzene	0.06	0.07	0.07
Hexachlorobutadiene	0.06	0.07	0.07
Hexachlorocyclopentadiene	0.25	0.26	0.26
Hexachloroethane	0.12	0.13	0.13
Indeno(1,2,3-cd)pyrene	0.13	0.13	0.13
Isophorone	0.06	0.07	0.07
Naphthalene	0.06	0.07	0.07
Nitrobenzene	0.06	0.07	0.07
N-Nitrosodimethylamine	0.62	0.66	0.64
N-Nitroso-Di-N-Propylamine	0.06	0.07	0.07
N-Nitrosodiphenylamine	0.06	0.07	0.07
Pentachlorophenol	1.2	1.3	1.3
Phenanthrene	0.06	0.07	0.07
Phenol	0.12	0.13	0.13
Pyrene	0.06	0.07	0.07
Pyridine	0.62	0.64	0.63
Retene	0.12	0.13	0.13

¹WSDA Pesticides Study. Range of Minimum Practical Quantitation Limit.

LMinQL: Lower minimum quantitation limit.

UMinQL: Upper minimum quantitation limit.

Both parameters calculated as 20% and 80% of range of minimum detection level values for the study.

Data Qualification

Data may be qualified if one or more analytical factors effect confidence in the prescribed data value. Manchester Laboratory qualifies data according to the National Functional Guidelines for Organic Data Review (EPA 1999). Data qualifiers used in the study are presented in Table C-5.

Table C-5. Data qualifiers and definitions.

Qualifier	Definition
U	Analyte not detected at or above the reported sample quantitation limit.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
UJ	The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.
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

The multitude of reasons for data qualification are explained in the National Functional Guidelines document (EPA 1999). The most frequent reason for a ‘J’ qualification is that the sample is confirmed and the value is below the PQL. ‘NJ’ designation is most frequently assigned when confirmation between the AED and GC/MS is not successful. Out of 862 quantified chemical results, 31 were unqualified, 613 received a ‘J’ qualification, and 218 received a ‘NJ’ qualification (Table C-6).

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. The compounds demeton-s, oxyfluorfen, norflurazon, fluridone, cyanazine, hexazinone, and dimethoate historically do not perform well because of the uncertainty of the 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 C-6. Pesticide data qualification summary for chemical results.

Chemical	Results	Data Qualification		
		No Qualification	J	NJ
2,4-D	112	7	87	18
Pentachlorophenol	79	2	54	23
Atrazine	57	0	52	5
Bromacil	52	0	46	6
Diuron	49	0	0	49
Dichlobenil	44	6	36	2
Triclopyr	44	1	29	14
Terbacil	43	1	40	2
Pendimethalin	39	3	32	4
Chlorpyrifos	38	3	28	7
MCPP (Mecoprop)	32	0	20	12
Diazinon	30	2	26	2
Bentazon	26	0	8	18
Dicamba I	22	0	9	13
4-Nitrophenol	19	0	5	14
Bromoxynil	18	0	15	3
MCPA	15	0	14	1
Simazine	15	0	13	2
Prometon (Pramitol 5p)	14	0	12	2
Azinphos (Guthion)	13	0	11	2
Norflurazon	13	0	13	0
Dimethoate	12	0	12	0
Malathion	10	0	7	3
Treflan (Trifluralin)	10	0	7	3
Alachlor	6	0	3	3
Benzamide, 2,6-dichloro-	6	0	6	0
Endosulfan Sulfate	5	0	3	2
Promecarb	5	0	0	5
2,4,6-Trichlorophenol	4	0	2	2
4,4'-DDE	4	0	4	0
Propargite	3	0	3	0
Carbaryl	2	1	1	0
Diphenamid	2	0	2	0
Endosulfan I	2	0	1	1
Hexazinone	2	0	2	0
Tebuthiuron	2	0	2	0
Carboxin	1	1	0	0
Di-allate (Avadex)	1	1	0	0
Eptam	1	1	0	0
Fenamiphos	1	1	0	0
Hexachlorobenzene	1	1	0	0
Chlorpropham	1	0	1	0
Endosulfan II	1	0	1	0
Ethoprop	1	0	1	0

(Continued)

Table C-6 continued. Pesticide data qualification summary for chemical results.

Chemical	Results	Data Qualification		
		No Qualification	J	NJ
Imidan	1	0	1	0
Metolachlor	1	0	1	0
Oxyfluorfen	1	0	1	0
Pronamide (Kerb)	1	0	1	0
Ronnel	1	0	1	0
Totals	862	31	613	218

J, NJ: Data flag assigned to data points by Manchester Environmental Laboratory

J: The analyte was positively identified and the associated numerical result is an estimate

NJ: There is evidence that the analyte is present, and the reported number is an estimate

Table C-7. SVOC data qualification summary for chemical results.

Chemical	Results	Data Qualification		
		Not Qualified	J	NJ
Bis(2-Ethylhexyl) Phthalate	35	33	0	2
Caffeine	26	6	1	19
Fluoranthene	20	10	0	10
Acenaphthene	19	0	1	18
Butylbenzylphthalate	19	16	0	3
Pyrene	19	7	0	12
Diethylphthalate	17	7	0	10
2-Methylphenol	16	12	1	3
4-Methylphenol	16	9	1	6
2,4-Dimethylphenol	15	6	2	7
Di-N-Butylphthalate	15	10	0	5
Chrysene	14	6	0	8
Phenanthrene	14	6	0	8
2-Methylnaphthalene	13	6	0	7
Pentachlorophenol	13	0	6	7
Phenol	13	4	0	9
1-Methylnaphthalene	12	2	2	8
Benzyl Alcohol	11	7	1	3
Benzo(b)fluoranthene	9	8	0	1
Benzo(k)fluoranthene	9	4	0	5
Benzo(a)anthracene	8	4	1	3
Benzo(a)pyrene	8	7	0	1
Benzo(ghi)perylene	8	3	0	5
Indeno(1,2,3-cd)pyrene	8	8	0	0
Anthracene	7	0	0	7
Benzoic Acid	7	0	1	6
Carbazole	7	0	0	7
Fluorene	7	0	0	7
Naphthalene	6	4	0	2
3B-Coprostanol	5	4	0	1
Retene	5	0	0	5
Dimethylphthalate	3	0	0	3
N-Nitrosodiphenylamine	3	0	1	2
2,4-Dichlorophenol	1	0	1	0
2-Nitrophenol	1	0	0	1
Acenaphthylene	1	0	0	1
Dibenzo(a,h)anthracene	1	1	0	0
Dibenzofuran	1	0	0	1
Di-N-Octyl Phthalate	1	0	0	1
Totals	413	190	19	204

J, NJ: Data flag assigned to data points by Manchester Environmental Laboratory

J: The analyte was positively identified and the associated numerical result is an estimate

NJ: There is evidence that the analyte is present, and the reported number is an estimate

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, except for endosulfan sulfate, do not meet the time component for criteria violations.

Application of 'J' qualified data has been investigated through the following documents: CSWRCB 2002, Embrey and Frans 2003 (USGS), EPA 1991, 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. 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 violation, and comparisons are for illustrative uses.

Discussion of data bias and quality assurance associated with the endosulfan sulfate exceedance value and values above numeric criteria are explained below.

QA/QC Bias

Field spike and LCS recoveries indicate the pesticide analyses were likely biased low. According to Figure C-3, the field spike arithmetic mean percent recoveries were consistently lower than 100% in 7 out of 8 instances (except Terbacil). Similarly, the LCS for selected pesticides were consistently lower than 100% in 7 out of 8 instances. The one exception was chlorpyrifos which demonstrated a mean LCS recovery of 103%. MS/MSD recoveries were far more consistent with an average close to 100%.

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, 1996). Both processes would increase the reported concentration.

Evaluations

The five chemicals with numeric values above water quality criteria concentrations include diazinon, azinphos-methyl, chlorpyrifos, endosulfan, and 4,4'-DDE. Detection limits for affected chemicals are listed in Table C-8.

Table C-8. Method detection, estimated detection, and practical quantitation limits.

Chemical	¹ EPA (µg/L)	² Manchester (µg/L)		³ WSDA Pest. (µg/L)	
	MDL	MDL	EDL	LMinQL	UMinQL
Chlorpyrifos	0.004	0.004	0.011	0.025	0.027
Endosulfan Sulfate	0.03	0.03	0.033	0.016	0.019
Azinphos (Guthion)	0.025	0.02	0.01	0.05	0.055
Diazinon	0.014	0.014	0.009	0.025	0.028
4,4'-DDE	0.03	0.03	0.033	0.016	0.019

¹Environmental Protection Agency. Target Method Detection Levels. 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.

²Manchester 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 element (nitrogen, phosphorous, chlorine) 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).

³WSDA Pesticides Study. Range of Minimum Practical Quantitation Limit. LMinQL: Lower minimum quantitation limit. UMinQL: Upper minimum quantitation limit. Both parameters calculated as 20% and 80% of range of minimum detection level values for the study.

Chlorpyrifos

The two chlorpyrifos concentrations were above numeric water quality criteria values were ‘J’ qualified. Both values, 0.085 µg/L and 0.050 µg/L, were detected in the same analytical run and were in excess of the minimum practical quantitation limit for this run, 0.025 µg/L. The 0.085 µg/L value was ‘J’ qualified because the surrogate recovery of 120% was outside of the acceptable range of 40-113%. The 0.050 µg/L value was ‘J’ qualified because the corresponding chlorpyrifos laboratory control sample had a 30% recovery.

Endosulfan sulfate

Endosulfan sulfate was detected at a concentration of 0.36 µg/L on 8/20/2003. This data value was 'J' qualified because chlorinated surrogates, TMX (Tetra-chloro-m-xylene) and DBOB (4,4-Dibromooctafluorobiphenyl), had recoveries below 30%.

Azinphos-methyl

All azinphos-methyl detections were above the estimated detection limit, and most were above the method detection limit. The range of the six azinphos-methyl concentrations was 0.010 µg/L to 0.025 µg/L. Azinphos-methyl concentrations were 'J' qualified because they were below the practical quantitation limit (0.05 µg/L to 0.055 µg/L). Three of the azinphos-methyl concentrations were between 0.022 µg/L and 0.025 µg/L.

Diazinon

Diazinon was above the proposed numeric EPA CMC aquatic life criterion of 0.1 µg/L once at the south fork Thornton station (0.21 µg/L) and once at the north fork Thornton station (0.13 µg/L). The 0.13 µg/L value is above the estimated detection limit and very close to the method detection limit. The 0.21 µg/L value is very close to the practical quantitation limit (0.025 µg/L to 0.028 µg/L). The diazinon values were 'J' qualified because they were below the practical quantitation limit.

4,4'-DDE

All four 4,4'-DDE detections were above a numeric criterion value. The highest 4,4'-DDE detection (0.017 µg/L) was equal to the practical quantitation limit for that analytical run. The remainder of 4,4'-DDE detections were below 0.004 µg/L. All values were 'J' qualified due to their proximity to the practical quantitation limit.

Summary

Information is provided to illustrate specific reasoning used for 'J' value qualification. The qualification of several values was due to analytical considerations that would associate a low bias with the data (except for one concentration of chlorpyrifos). Except for three 4,4'-DDE values, estimated values were near or above 50% of the practical quantitation limit. As indicated in the report, the low 4,4'-DDE detections are well below associated detection limits and should be evaluated with a degree of caution.

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Appendix D. 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 TSS values are also available from the same website.

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Appendix E. Pesticide Summaries; Unqualified and 'NJ' Qualified Results

Unqualified Values

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

Chemical	Category	Detections	Concentration ($\mu\text{g/L}$)		
			Min	Median	Max
Dichlobenil	Herbicide	5	0.012	0.025	0.34
Diazinon	Insecticide/Organophosphate	2	0.027	0.039	0.05
Pentachlorophenol	Wood Preservative	2	0.08	0.082	0.083
2,4-D	Herbicide	1	0.15	0.15	0.15
Triclopyr	Herbicide	1	0.12	0.12	0.12
Sample Events	18 weeks at 3 stations = 54				

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

Chemical	Category	Detections	Concentration ($\mu\text{g/L}$)		
			Min	Median	Max
2,4-D	Herbicide	2	0.29	1.1	1.9
Pendimethalin	Herbicide	2	0.075	0.077	0.079
Dichlobenil	Herbicide	1	0.5	0.5	0.5
Eptam	Herbicide	1	0.038	0.038	0.038
Terbacil	Herbicide	1	0.099	0.099	0.099
Sample Events	12 weeks at M1, 21 weeks at M2 = 33				

Table E-3. Spring Creek pesticide summary. Unqualified values reported.

Chemical	Category	Detections	Concentration ($\mu\text{g/L}$)		
			Min	Median	Max
Chlorpyrifos	Insecticide/Organophosphate	3	0.0063	0.012	0.035
2,4-D	Herbicide	2	0.17	0.24	0.31
Carbaryl	Insecticide/Carbamate	1	10	10	10
Carboxin	Herbicide	1	0.2	0.2	0.2
Di-allate (Avadex)	Herbicide	1	0.23	0.23	0.23
Fenamiphos	Insecticide/Organophosphate	1	0.049	0.049	0.049
Hexachlorobenzene	Insecticide/Organophosphate	1	0.16	0.16	0.16
Pendimethalin	Herbicide	1	0.063	0.063	0.063
Sample Events	12 weeks at S1 and S2, 21 weeks at S3 = 45				

An unqualified value table for Sulphur Creek Wasteway is not presented due to the small number of unqualified detections. 2,4-D was detected twice in Sulphur Creek Wasteway at a concentration of 0.22 $\mu\text{g/L}$ and 0.25 $\mu\text{g/L}$.

'NJ' Qualified Results

Table E-4. Thornton Creek 'NJ' qualified results.

Chemical	Results	Concentration (µg/L)		
		Min	Median	Max
Diuron	18	0.013	0.072	0.023
Triclopyr	13	0.011	0.037	0.081
4-Nitrophenol	11	0.0053	0.15	0.42
MCP (Mecoprop)	11	0.012	0.041	0.11
2,4-D	8	0.013	0.037	0.12
Pentachlorophenol	6	0.014	0.0225	0.086
Dicamba I	3	0.0033	0.011	0.032
Bromoxynil	2	0.021	0.021	0.021
Dichlobenil	2	0.01	0.018	0.026
Prometon (Pramitol 5p)	2	0.0031	0.0047	0.0063
Diazinon	1	0.068	0.068	0.068
Pendimethalin	1	0.0095	0.0095	0.0095
Promecarb	1	0.12	0.12	0.12
Sample Events	18 weeks at 3 stations = 54			

Table E-5. Marion Drain 'NJ' qualified results.

Chemical	Results	Concentration (µg/L)		
		Min	Median	Max
Diuron	11	0.006	0.016	0.056
Bentazon	9	0.0095	0.027	0.085
2,4-D	5	0.02	0.029	0.06
Pentachlorophenol	5	0.0067	0.011	0.013
Dicamba I	3	0.0058	0.0063	0.0069
Alachlor	2	0.0064	0.0097	0.013
Pendimethalin	2	0.017	0.025	0.033
Simazine	2	0.0032	0.0041	0.005
Treflan (Trifluralin)	2	0.0032	0.00545	0.0077
4-Nitrophenol	1	0.0083	0.0083	0.0083
Atrazine	1	0.0056	0.0056	0.0056
Azinphos (Guthion)	1	0.023	0.023	0.023
Bromacil	1	0.019	0.019	0.019
Bromoxynil	1	0.01	0.01	0.01
Chlorpyrifos	1	0.0032	0.0032	0.0032
Endosulfan I	1	0.016	0.016	0.016
Endosulfan Sulfate	1	0.032	0.032	0.032
Malathion	1	0.0064	0.0064	0.0064
MCPA	1	0.01	0.01	0.01
MCP (Mecoprop)	1	0.03	0.03	0.03
Terbacil	1	0.027	0.027	0.027
Sample Events	12 weeks at M1, 21 weeks at M2 = 33			

Table E-6. Spring Creek 'NJ' qualified results.

Chemical	Results	Concentration (µg/L)		
		Min	Median	Max
Diuron	14	0.007	0.031	0.32
Pentachlorophenol	10	0.0041	0.0071	0.025
Bentazon	6	0.0036	0.015	0.03
2,4-D	5	0.016	0.041	0.05
Promecarb	4	0.15	0.15	0.15
Dicamba I	4	0.0025	0.0042	0.0079
Chlorpyrifos	3	0.0031	0.0039	0.019
Bromacil	3	0.0063	0.0072	0.01
Atrazine	3	0.0029	0.0032	0.0053
Triclopyr	1	0.0052	0.0052	0.0052
Pendimethalin	1	0.0032	0.0032	0.0032
Malathion	1	0.006	0.006	0.006
Endosulfan Sulfate	1	0.02	0.02	0.02
Azinphos (Guthion)	1	0.013	0.013	0.013
4-Nitrophenol	1	0.0098	0.0098	0.0098
Sample Events	12 weeks at S1 and S2, 21 weeks at S3 = 45			

Table E-7. Sulphur Creek Wasteway 'NJ' qualified results.

Chemical	Results	Concentration (µg/L)		
		Min	Median	Max
Pentachlorophenol	5	0.0075	0.012	0.009
Bentazon	3	0.022	0.03	0.028
Chlorpyrifos	3	0.0022	0.01	0.0063
Dicamba I	3	0.0031	0.0065	0.0046
Diuron	3	0.0013	0.0057	0.0066
2,4,6-Trichlorophenol	2	0.0025	0.013	0.00775
4-Nitrophenol	1	0.0068	0.0068	0.0068
Alachlor	1	0.0019	0.0019	0.0019
Atrazine	1	0.0025	0.0025	0.0025
Diazinon	1	0.0013	0.0013	0.0013
Malathion	1	0.01	0.01	0.01
Terbacil	1	0.0066	0.0066	0.0066
Treflan (Trifluralin)	1	0.005	0.005	0.005
Sample Events	21 weeks at 1 station = 21			

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Appendix F. Available Freshwater Aquatic Life Standards

Table F-1. Available freshwater quality standards for the protection of aquatic life.

Chemical	Aquatic Life Standards (µg/L)				Toxicological Endpoints (µg/L)				
	¹ WAC		² EPA NRWQC		³ EPA RED				
	Promulgated		Recommended		Registration Status				
	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					
Chlorpyrifos	0.083 ^c	0.041 ^d	0.083	0.041	3	<0.12	0.15	FM/R	3h
Demeton				0.1					
Diazinon			0.1 ⁱ	0.1 ⁱ	90	<0.55	4.5	BT/R	3i
Dichlobenil					4930	<330	246.5	BT/R	3j
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	3k
Diuron					710	26	35.5	FM/CT	3l
Endosulfan (Σα and β)			0.22 ^k	0.056 ^k	0.83	0.11	0.042	R	3m
Endosulfan ⁶ (unspecified)	0.22 ^a	0.056 ^b							
Endrin	0.18 ^a	0.0023 ^b	0.086	0.036 ^j					
Ethoprop					1020	24	51	FM/R	3n
Heptachlor	0.52 ^a	0.0038 ^b	0.52	0.0038					
Hexachlorocyclohexane (Lindane)	2.0 ^a	0.08 ^b							
Hexazinone					>320000	17000	>16000	FM/R	3o
Imidan (PHOSMET)					230	3.2	11.5	R	3p
Malathion				0.1	4	21	0.2	R	3q
Methoxychlor				0.03					
Mirex				0.001					

Table F-1 continued. Available freshwater quality standards for the protection of aquatic life.

Chemical	Aquatic Life Standards (µg/L)				Toxicological Endpoints (µg/L)				
	¹ WAC		² EPA NRWQC		³ EPA RED				
	Promulgated		Recommended		Registration Status				
	Acute	Chronic	CMC	CCC	Acute	Chronic (NOEC)	Endangered Species LOC	Species	Ref.
Norflurazon					8100	1500	405	R	3r
Oxyfluorfen					250	38	12.5	FM/R	3s
Parathion	0.065 ^c	0.013 ^d	0.065	0.013					
Pendimethalin					138	6.3	6.9	FM/R	3t
Pentachlorophenol	20 ^e pH	13 ^{f,d} pH	19 ^l pH	15 ^m pH					
Pronamide (Kerb)					72000		3600	R	3u
Propargite					118	16	5.9	FM/R	3v
Tebuthiuron					143000		7150	R	3w
Terbacil					46200		2310	R	3x
Toxaphene	0.73 ^{c,g}	0.0002 ^d	0.73	0.0002					
Treflan (Trifluralin)					41	1.14	2	R	3y
Tributyltin (TBT)			0.46	0.063					
Triclopyr Acid					117000	>104000	5850	FM/R	3z
Triclopyr TEA					613000	>104000		R	3z
Triclopyr BEE					650			R	3z

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

²EPA 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

³EPA 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 (LC₅₀)

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

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 Chlorpyrifos RED 6-1-2000

3i EFED Diazinon RED 10-2000

3j EFED Dichlobenil RED 10-1998

3k EFED Dimethoate RED 2-4-1999

3l EFED Diuron RED 9-2003

3m EFED Endosulfan RED 4-13-2001

3n EFED Ethoprop RED addendum 8-30-99

3o EFED Hexazinone RED 9-1994

3p EFED Phosmet (Imidan) RED 4-24-1998

3q EFED Malathion RED 11-9-2000

3r EFED Norflurazon RED No Date

3s EFED Oxyfluorfen RED 12-11-2001

3t EFED Pendimethalin RED 6-1997

3u EFED Pronamide RED 6-28-1994

3v EFED Propargite 6-7-2000

3w EFED Tebuthiuron RED 6-15-1994

3x EFED Terbacil RED 1-1998

3y EFED Trifluralin RED 4-1996

3z EFED Triclopyr RED 9-30-1997; TEA = Triethylammonium, BEE = Butoxyethyl Ester; In this study, Triclopyr is reported as Total (Σ Acid+TEA+BEE)

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

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

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

^aAn instantaneous concentration not to be exceeded at any time.

^bA 24-hour average not to be exceeded.

^cA 1-hour average concentration not to be exceeded more than once every three years on average.

^dA 4-day average concentration not to be exceeded more than once every three years on average.

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

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

^gChannel Catfish may be more acutely sensitive.

^h<http://www.epa.gov/waterscience/criteria/atrazine/atrazinefacts.html>

ⁱ<http://www.epa.gov/waterscience/criteria/diazinon/draft-fs.htm>

^jThe 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.

^kThis value was derived from data for endosulfan and is most appropriately applied to the sum of alpha-endosulfan and beta-endosulfan.

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

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

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Appendix G. Discharge Relationships of Frequently Detected Pesticides

The following figures illustrate the temporal relationship of frequently detected pesticides to discharge. Where available, water quality criteria for Washington State and the EPA national recommended water quality criteria (NRWQC) are illustrated. Extended analysis of discharge relationships will be conducted at the completion of the three-year study. All watersheds presented are illustrated through the use of the most downstream station (Thornton 3, Marion 2, Spring 3, and Sulphur 1).

Thornton Creek

Thornton Creek is represented by Figures G-1 through G-4. Chemicals used in Thornton Creek analysis include pentachlorophenol, triclopyr, dichlobenil, and diazinon.

The relationship between pentachlorophenol results, discharge, and the Washington State chronic water quality standard is presented in Figure G-1. The Washington State aquatic life standard for pentachlorophenol are calculated as:

$$\text{Acute} \leq e^{[1.005(\text{pH})-4.830]}$$
$$\text{Chronic} \leq e^{[1.005(\text{pH})-5.290]}$$

The red line in Figure G-1 is an estimation of the Washington State chronic water quality standard at the pH recorded during the time of sampling. Pentachlorophenol is characterized by pH dependent toxicity and hydrophobicity. Pentachlorophenol was routinely detected, regardless of discharge, in Thornton 3. No relationship between discharge and detection rate is apparent. All results are below Washington State aquatic life standards.

Triclopyr detections and discharge are illustrated in Figure G-2. Triclopyr concentrations appear elevated during periods of higher flow and during the springtime application season (ending at the end of May 2003).

Figure G-3 illustrates discharge and dichlobenil concentrations for lower Thornton Creek. Following early spring runoff, dichlobenil concentrations appear correlated with discharge. The association is likely due to peak application between April 15-June 24 and surface runoff events. If dichlobenil were strongly sediment associated, higher concentrations would have been expected in the early spring.

Diazinon concentrations appear correlated with the late spring application season. Several low concentrations of diazinon were reported during April, and three maximum concentrations were reported during May 2003. While diazinon concentrations were above the proposed numeric EPA NRWQC in Thornton 1 and Thornton 2, no values were above numeric criteria in the downstream station (Thornton 3).

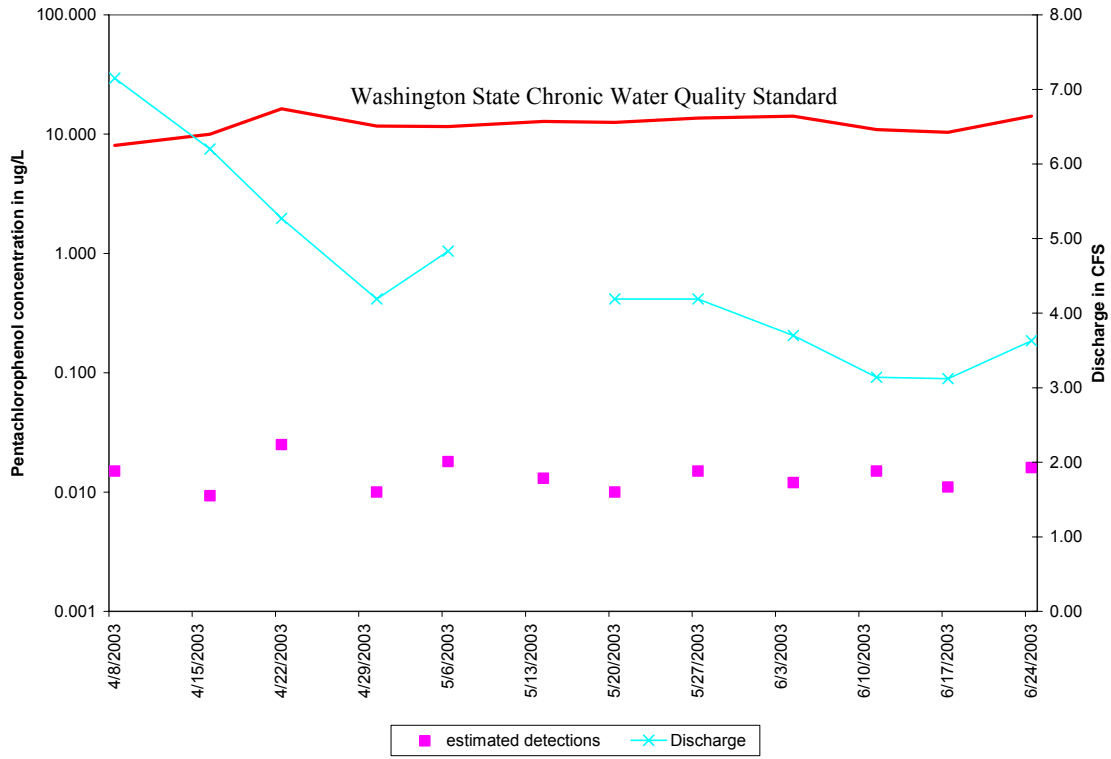


Figure G-1. Pentachlorophenol concentrations at Thornton Creek station 3.

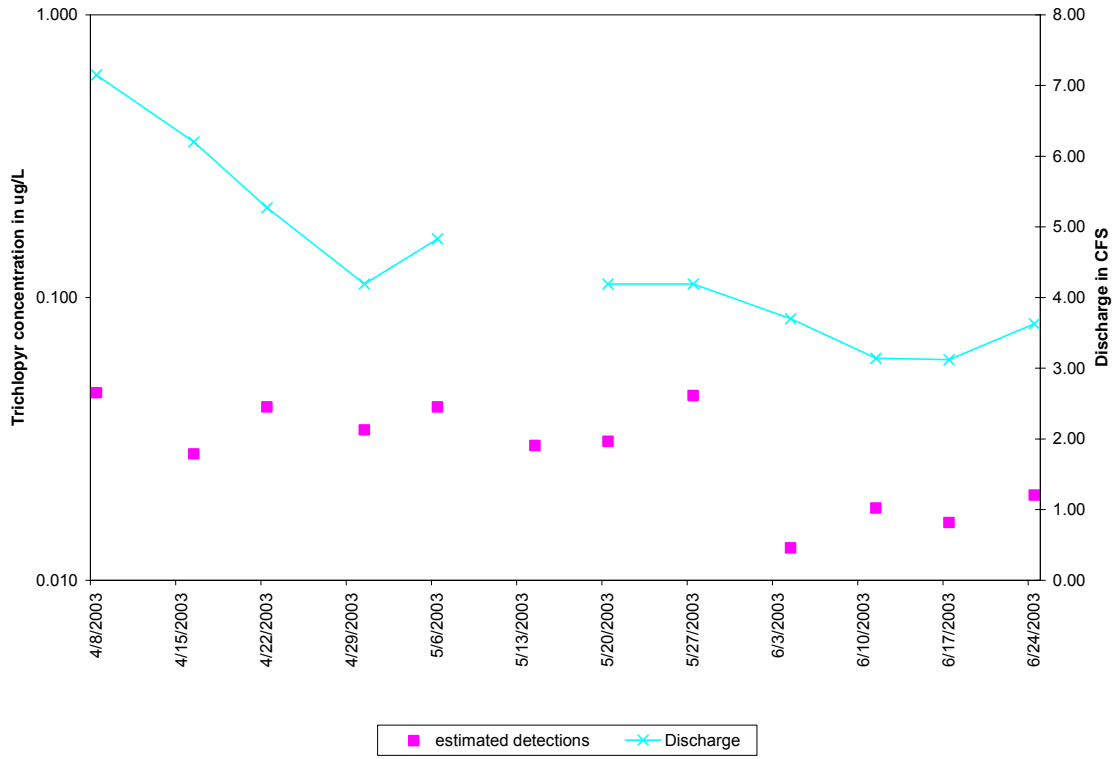


Figure G-2. Trichlopyr concentrations at Thornton Creek station 3.

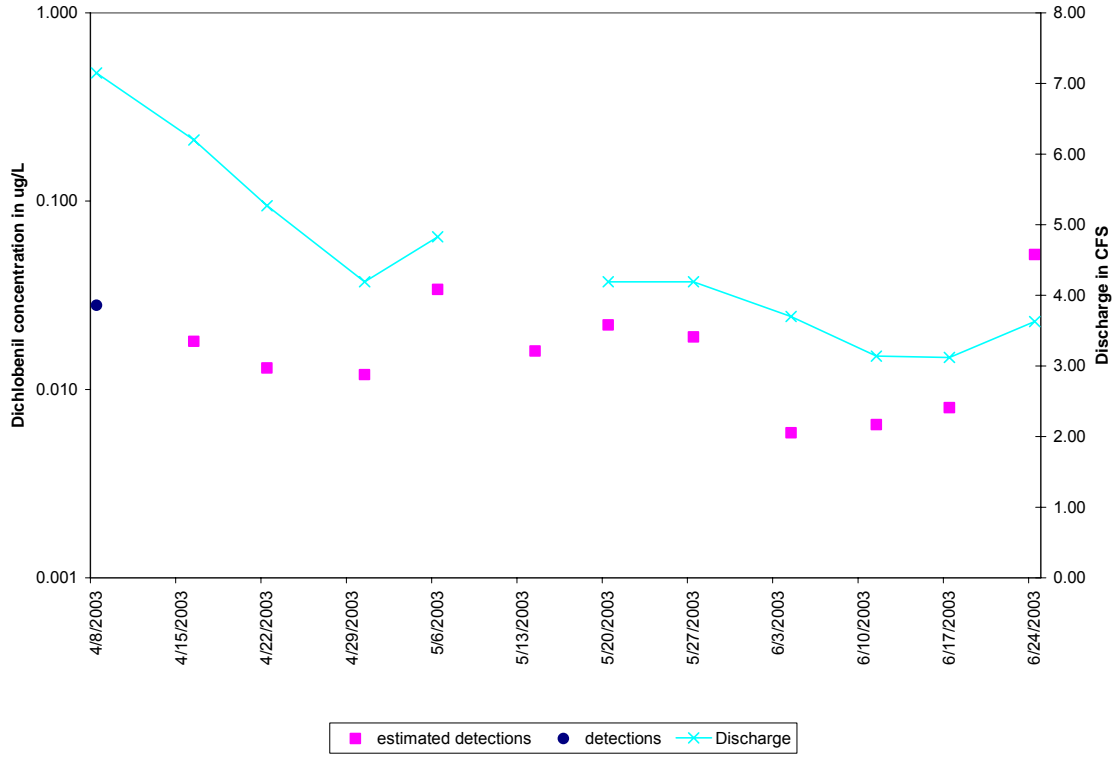


Figure G-3. Dichlobenil concentrations at Thornton Creek station 3.

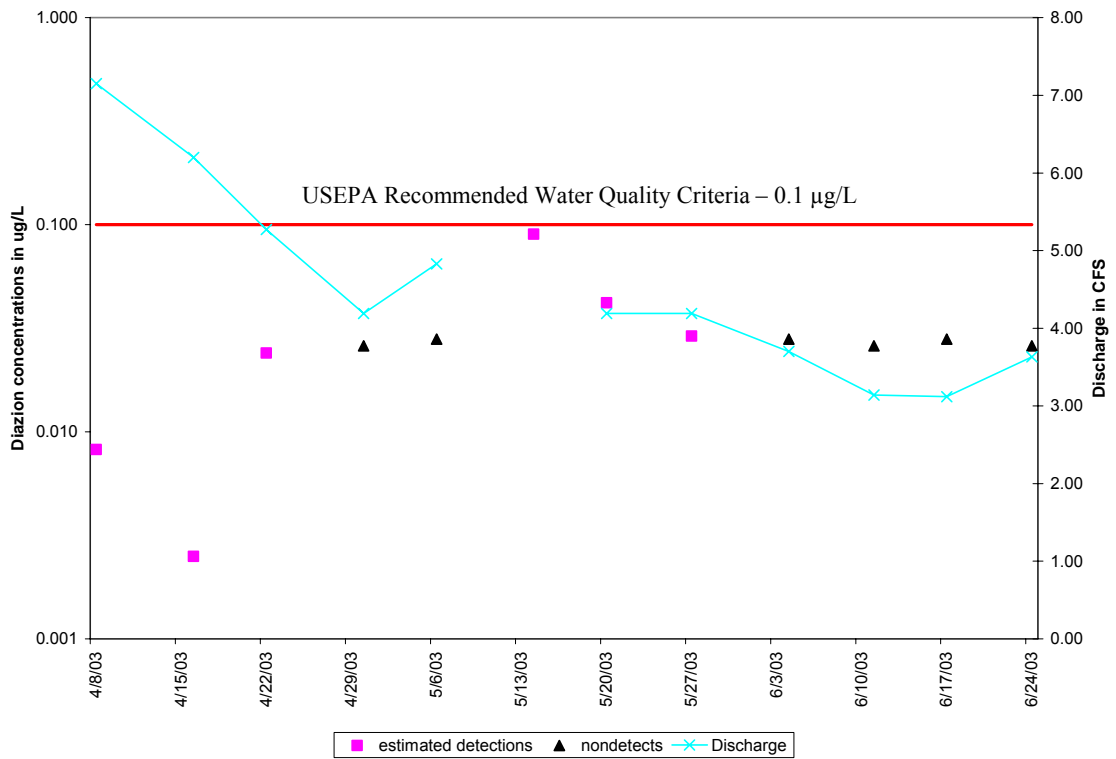


Figure G-4. Diazinon concentrations at Thornton Creek station 3.

Lower Yakima Watershed

Marion Drain, Spring Creek, and Sulphur Creek Wasteway represent three drainages within the Lower Yakima watershed. All drainages are evaluated through comparison of discharge with results for 2,4-D, atrazine, and chlorpyrifos. Discharge within Lower Yakima drainages is strongly related to agricultural conveyance and loosely associated with the natural hydraulic regime.

Marion Drain

Marion Drain discharge relationships are characterized by Figures G-5 through G-7. The 2,4-D detection profile is illustrated in Figure G-5. 2,4-D detections are associated with the herbicide use season and are not strongly correlated with discharge. Atrazine was regularly detected starting in mid-June 2003 (Figure G-6). Chlorpyrifos was regularly detected in April and September but not during the summer of 2003 (Figure G-7). One chlorpyrifos detection exceeded the Washington State Acute numeric criterion of 0.083 $\mu\text{g/L}$ on April 8, 2003. Correlations between discharge and 2,4-D, atrazine, and chlorpyrifos are not apparent.

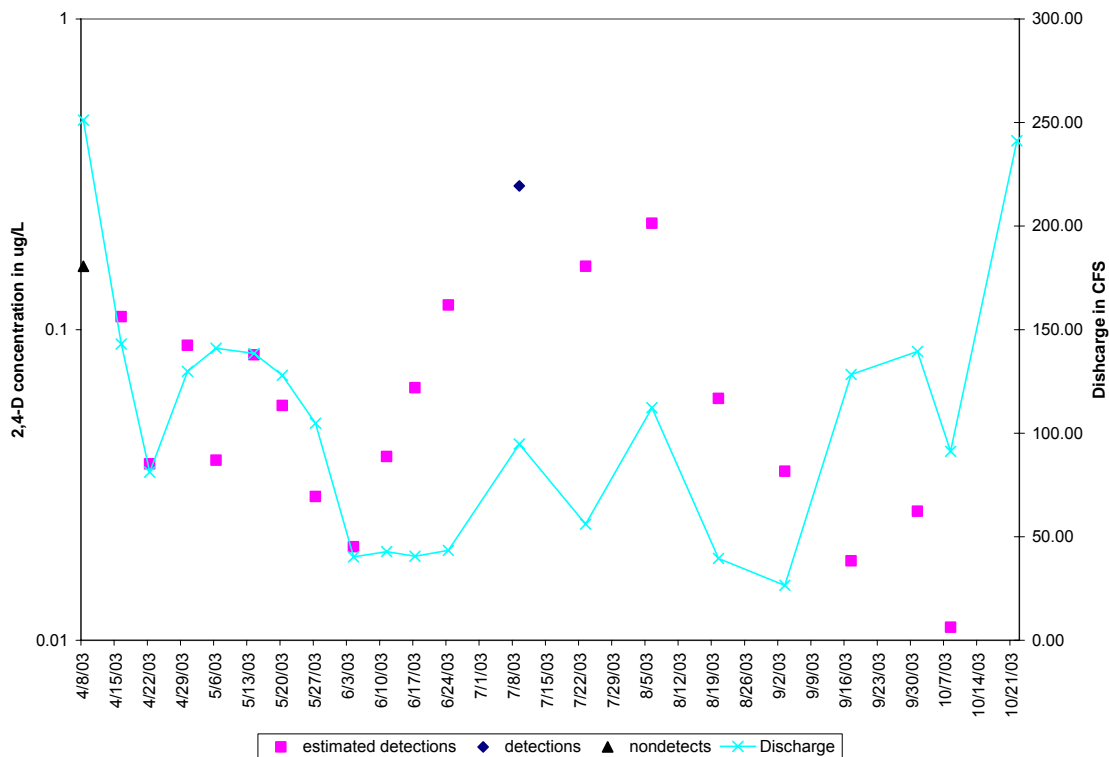


Figure G-5. 2,4-D concentrations at Marion Drain station 2.

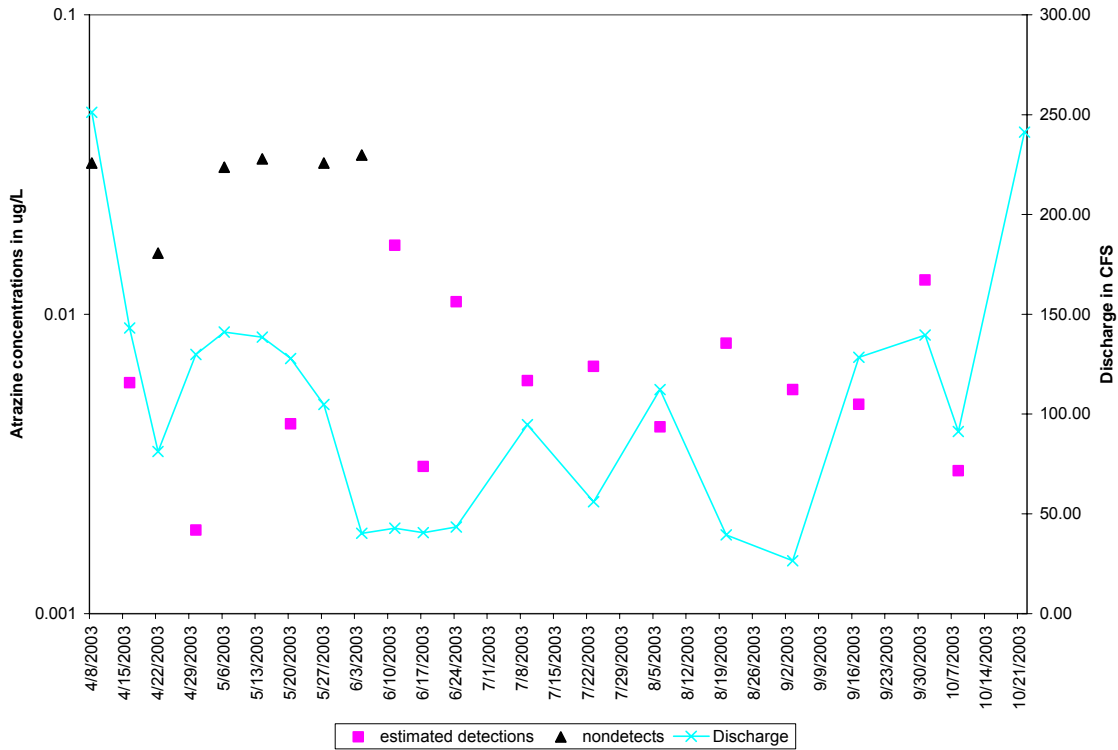


Figure G-6. Atrazine concentrations at Marion Drain station 2.

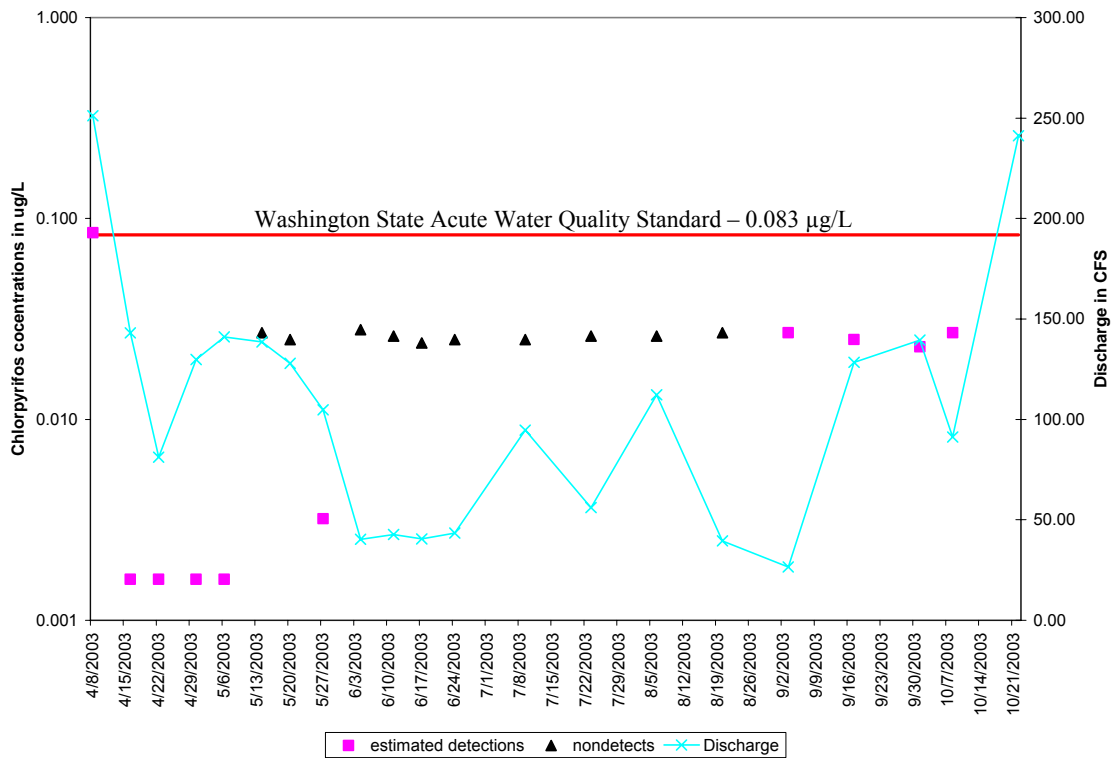


Figure G-7. Chlorpyrifos concentrations at Marion Drain station 2.

Spring Creek

Spring Creek discharge relationships are characterized by Figures G-8 through G-10. The 2,4-D detection profile is illustrated in Figure G-8. 2,4-D was consistently detected throughout the sampling season. Atrazine was occasionally detected during the spring and early summer. Chlorpyrifos was regularly detected during the spring and early summer. There were no chlorpyrifos detections following June 4, 2003. All chlorpyrifos detections are below the Washington State Acute Standard of 0.083 µg/L. Correlations between discharge and 2,4-D, atrazine, and chlorpyrifos are not apparent.

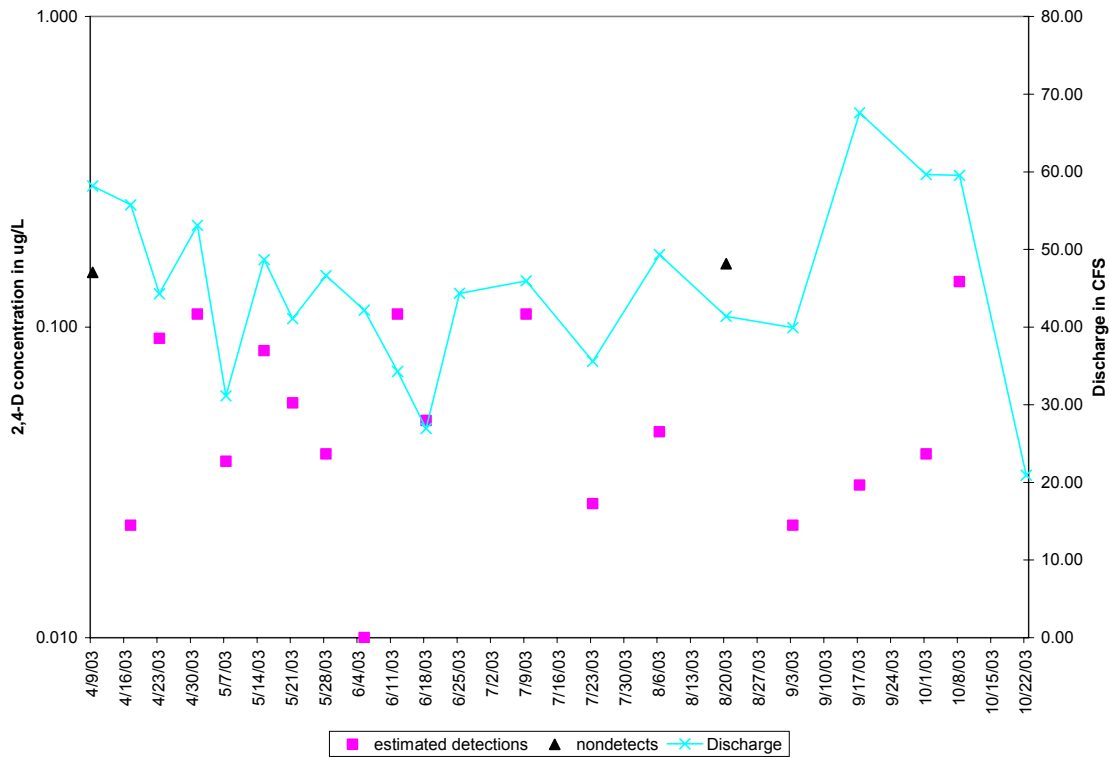


Figure G-8. 2,4-D concentrations at Spring Creek station 3.

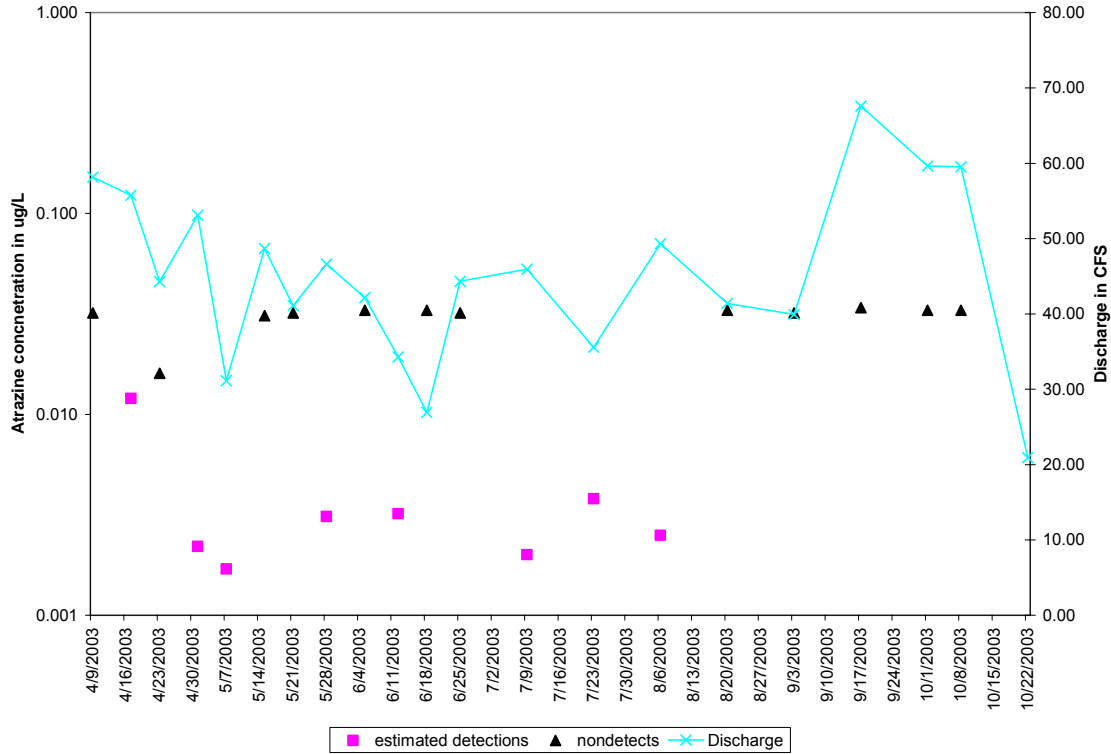


Figure G-9. Atrazine concentrations at Spring Creek station 3.

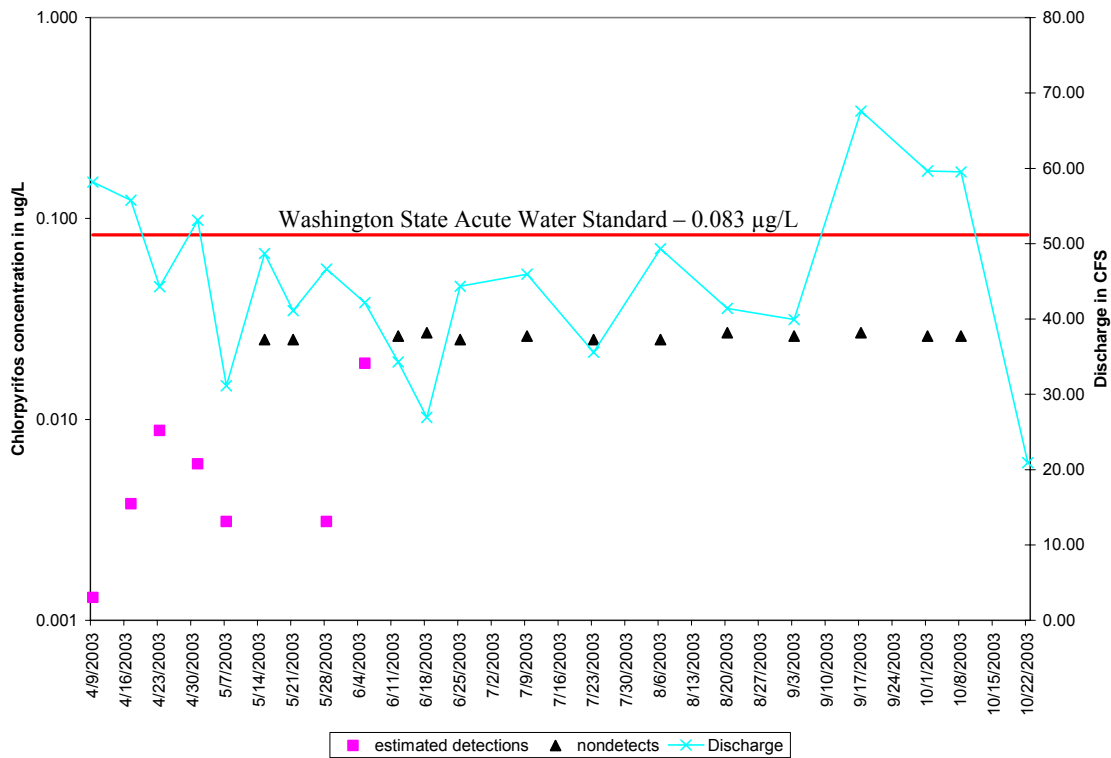


Figure G-10. Chlorpyrifos concentrations at Spring Creek station 3.

Sulphur Creek Wasteway

Sulphur Creek Wasteway discharge relationships are represented by Figures G-11 through G-13. The 2,4-D detection profile is illustrated in Figure G-11. 2,4-D was consistently detected throughout the sampling season. Atrazine was consistently detected during the spring and summer. Chlorpyrifos was regularly detected during the spring and early summer. All chlorpyrifos detections are below the Washington State Acute Standard of 0.083 $\mu\text{g/L}$. Correlations between 2,4-D, atrazine, chlorpyrifos, and discharge are not apparent.

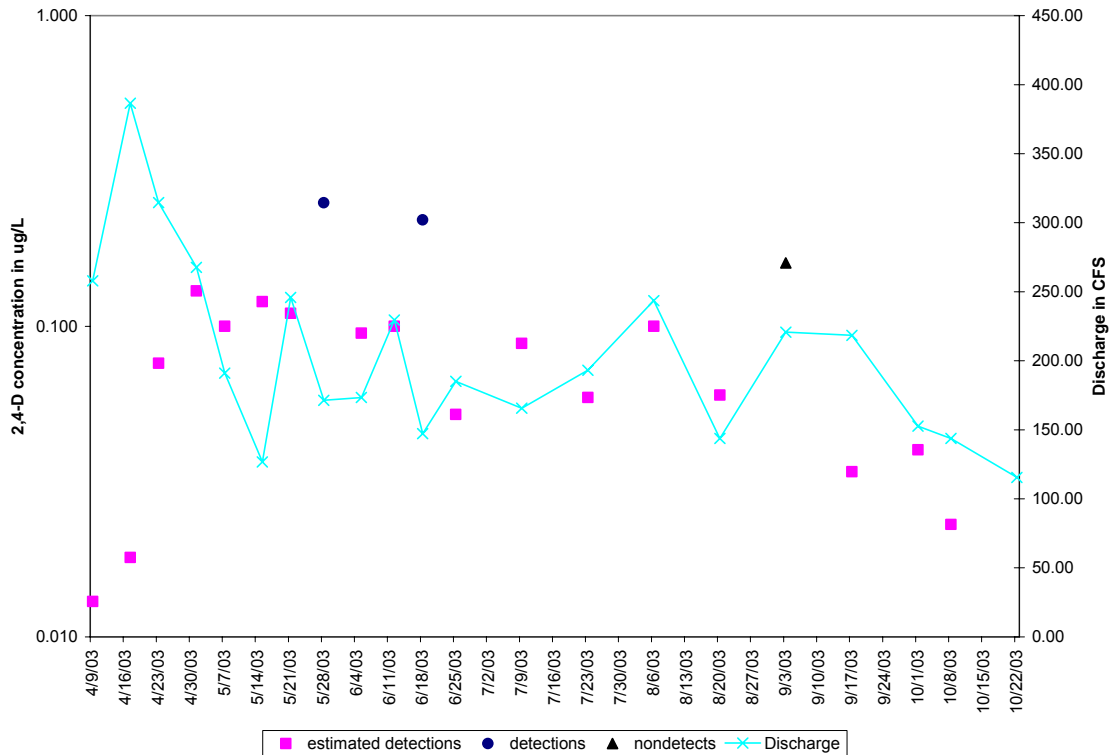


Figure G-11. 2,4-D concentrations at Sulphur Creek Wasteway station 3.

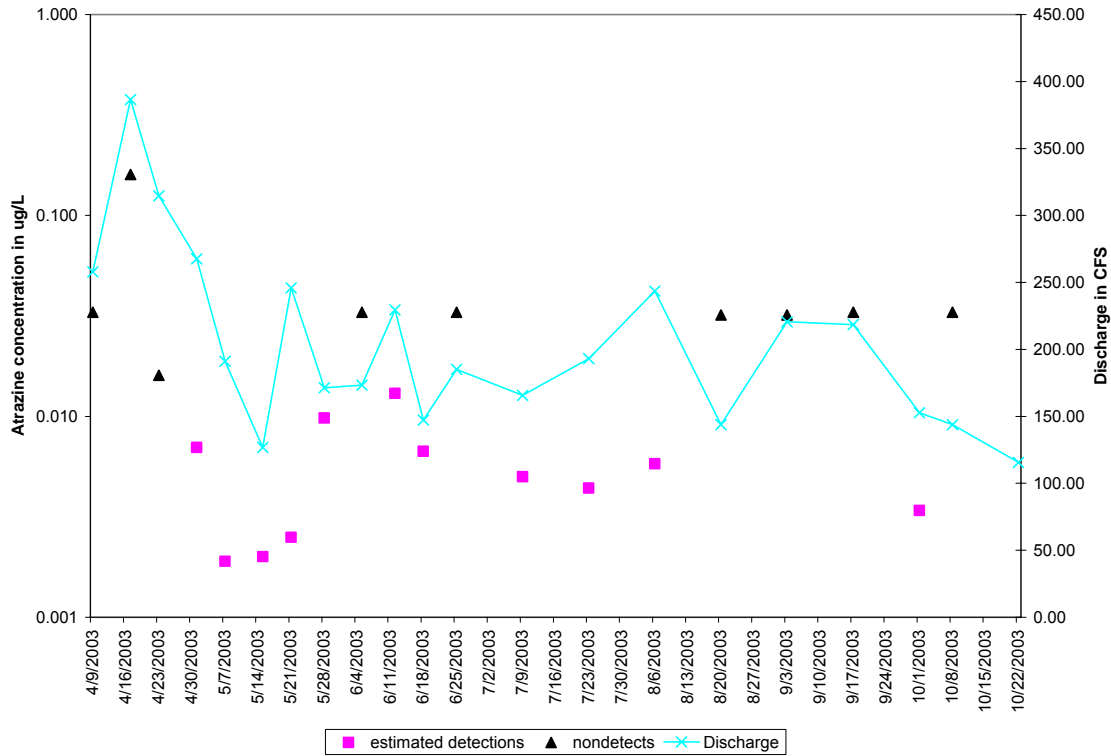


Figure G-12. Atrazine concentrations at Sulphur Creek Wasteway station 3.

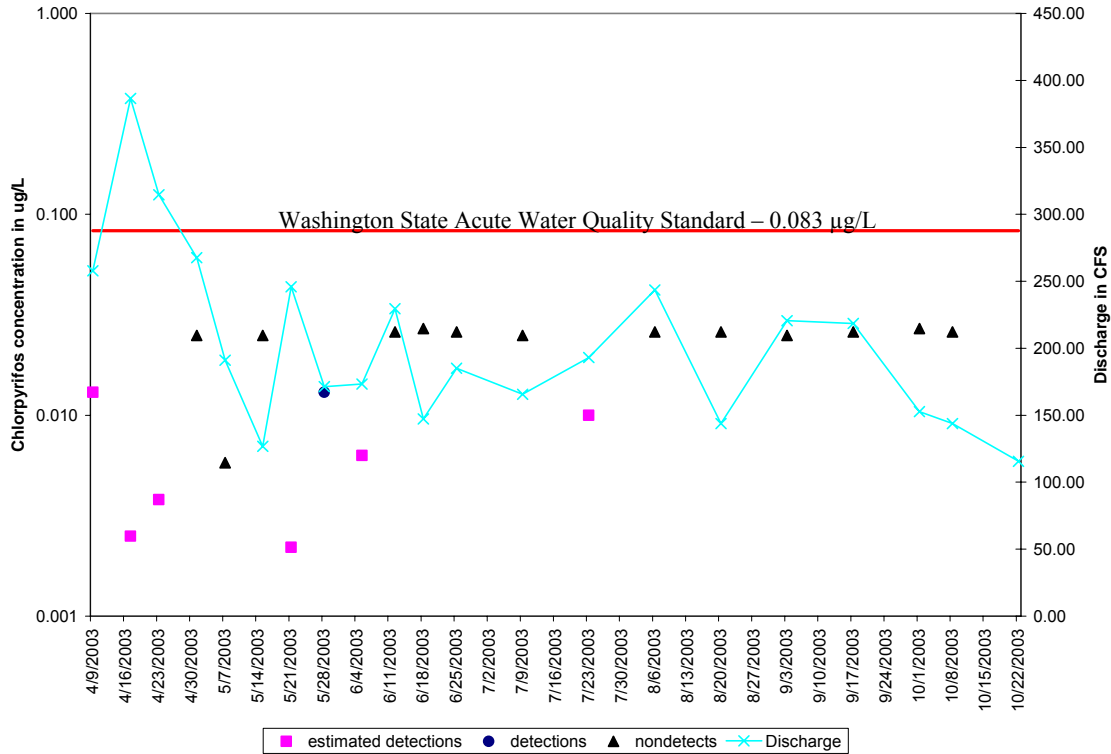


Figure G-13. Chlorpyrifos concentrations at Sulphur Creek Wasteway station 1.