Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2003-2005

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

September 2006

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Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams, 2003-2005

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

by

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September 2006

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 and the Washington State Department of Ecology conducted a multi-year monitoring study to characterize pesticide concentrations in selected salmonid-bearing streams during the typical pesticide-use season. The first three years of the study, 2003-2005, are reported.

Pesticide concentrations were measured in an urban drainage represented by Thornton Creek in the Cedar-Sammamish watershed, and in agricultural drainages represented by Marion Drain, Sulphur Creek Wasteway, and Spring Creek in the Lower Yakima watershed.

Temporal trends and potential impacts to aquatic species are investigated through comparison to (1) EPA registration toxicological criteria for fish, aquatic invertebrates, and plants, (2) Washington State Water Quality Standards, and (3) EPA National Recommended Water Quality Criteria.

A total of 51 pesticides and degradate compounds were detected in the urban and agricultural drainages. Ten of these – 4,4-DDE, 4,4-DDT, azinphos methyl, carbaryl, chlorpyrifos, diazinon, disulfoton, endosulfan sulfate, malathion, and oxyfluorfen – were above assessment criteria. Ninety-six percent of detections were below criteria.

Urban uses were restricted for chlorpyrifos in 2000, and were cancelled for diazinon in 2004. The phase out of these chemicals has resulted in reduced detection frequency and magnitude in Thornton Creek.

Chlorpyrifos, malathion, and azinphos methyl were detected in all three agricultural drainages. Chlorpyrifos residues were detected in the spring in all agricultural drainages and in the fall in Marion Drain. Azinphos methyl and malathion detections occur when summer maximum temperatures may restrict Mid-Columbia summer steelhead (Endangered Species Act-listed) occupation of monitored stream reaches. If summer steelhead are present, elevated water temperatures may make the steelhead more susceptible to pesticide toxicity.

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Acronyms and Abbreviations

AED	Atomic emission detection
CWA	Clean Water Act
EC50	Effective concentration to cause immobility in 50% of an invertebrate species, or a reduction in growth of 50% of an aquatic plant species.
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management (Ecology)
EPA	United States Environmental Protection Agency
ESA	Endangered Species Act
ESLOC	Endangered Species Level of Concern (EPA)
FR	Federal Register
GC	Gas chromatograph
LC50	Lethal concentration to cause mortality in 50% of test species
LOC	Level of concern
LPQL	Lower practical quantitation limit
MS	Mass spectrometry
MS/MSD	Matrix spike/matrix spike duplicate
NOAA	National Oceanic and Atmospheric Administration
NOEC	No observable effect concentration
NAWQA	National Water Quality Assessment Program (USGS)
NRWQC	National Recommended Water Quality Criteria (EPA)
QA/QC	Quality assurance and quality control
RQ	Risk quotient
SVOC	Semi-volatile organic compounds
TSS	Total suspended solids
USFWS	United States Fish and Wildlife Service
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) conducted a three-year monitoring study to characterize pesticide concentrations in surface waters during the typical pesticide-use season (Johnson and Cowles, 2003). Data collected are used by the WSDA and the U.S. Environmental Protection Agency (EPA) to refine salmonid exposure assessments for registered pesticides. Understanding the fate and transport of pesticides used in Washington State allows regulators to make state-based decisions to protect endangered species while minimizing the economic impacts to agriculture.

Results from the first three-year study cycle (2003-2005) are presented for an urban and agricultural watershed.

- Thornton Creek, in the Cedar-Sammamish basin (Water Resource Inventory Area [WRIA] 8), was chosen as the urban drainage (Figure 1). Thornton Creek was selected due to prior salmonid habitat enhancement efforts and the occurrence of pre-spawning mortality of coho salmon (Washington Trout, 2003; Anchor Environmental, 2004; NOAA Fisheries, 2006).
- Marion Drain, Sulphur Creek Wasteway, and Spring Creek [1] in the Lower Yakima basin (WRIA 37) were chosen due to the predominance of agriculture within these drainages (Figure 2) and their use by summer steelhead which is listed as threatened under the Endangered Species Act (ESA). Temporal trends and potential impacts to listed species are reported for downstream sites, which integrate influences of the entire watershed.

Monitoring data collected during the typical pesticide use season from 2003-2005 are evaluated against toxicity criteria used for pesticide registration under the Federal Insecticide Fungicide and Rodenticide Act (FIFRA), Washington state water quality standards, and EPA National Recommended Water Quality Criteria (NRWQC). In addition, monitoring data are compared to the life history and habitat utilization of Mid-Columbia summer steelhead. Monitoring results for 2003 and 2004 have been presented in Anderson et al., 2004, and Burke et al., 2005, respectively.

Over the three-year monitoring study, approximately 160 currently registered and historical-use pesticides and degradates were included in the analytical methods. These 160 compounds were selected based on the use of the pesticide, toxicity to non-target organisms, transport potential, and cost of analysis. Conventional water quality parameters – total suspended solids, pH, conductivity, temperature, and flow – were measured to better understand factors influencing pesticide toxicity, fate and transport, and general water quality.

[1] The Washington Department of Fish and Wildlife (WDFW) and the Sunnyside Valley Irrigation District (SVID) disagree on the designation of Spring Creek as a creek vs. a constructed wasteway for irrigation return flows. SVID prevailed with designating it as a constructed wasteway in a court decision in 2002. However, the official name for this waterway specified in the USGS Geographic Names Information System (GNIS) is Spring Creek.

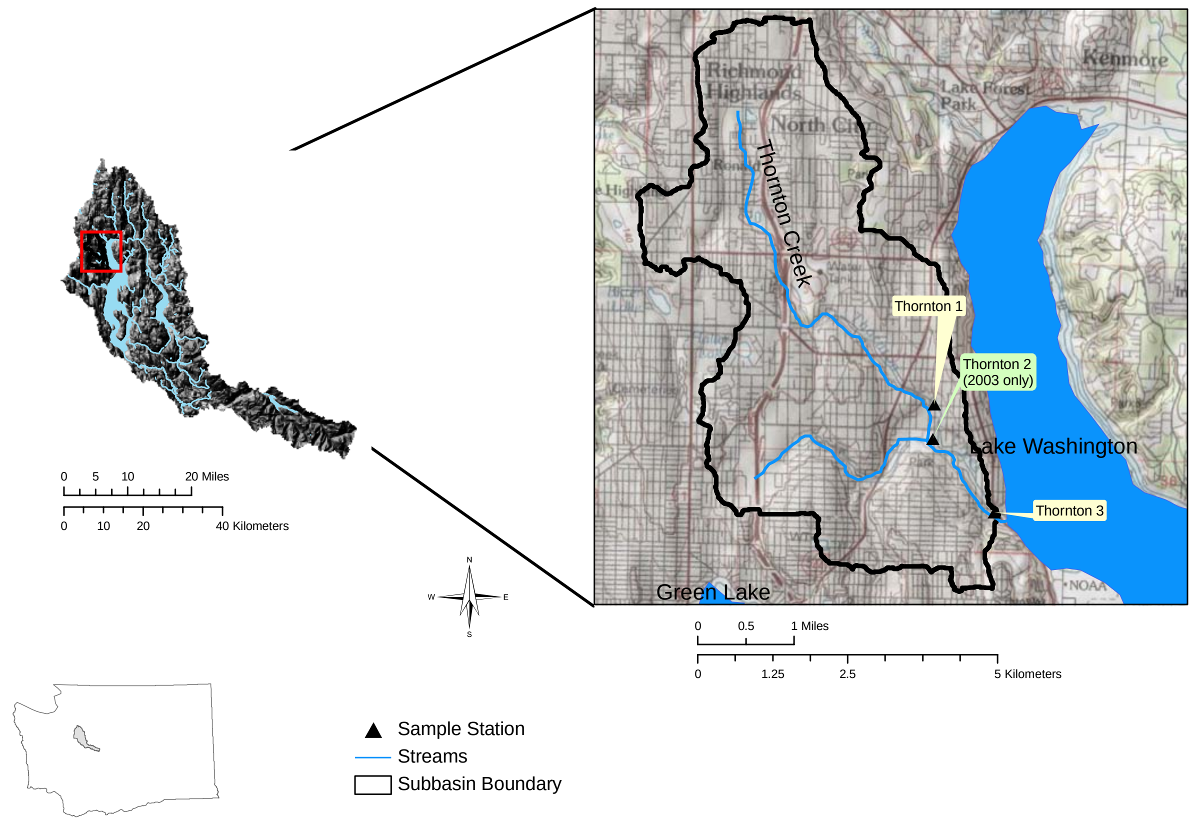

Figure 1. Sampling stations in Thornton Creek in the Cedar-Sammamish watershed.

Basin Description

Thornton Creek, located in the Cedar-Sammamish basin (Figure 1), was selected to assess pesticide exposure in an urban basin. Three sub-basins of the Lower Yakima basin were selected to represent agricultural land use: Marion Drain, Sulphur Creek Wasteway, and Spring Creek (Figure 2). These three sub-basins were selected because they have the highest percentage of land with crops and a diversity of agriculture within the drainage (Johnson and Cowles, 2003). Site location and crop area estimations are presented in Appendices A and B, respectively. Fisheries information is available in Burke et al., 2005.

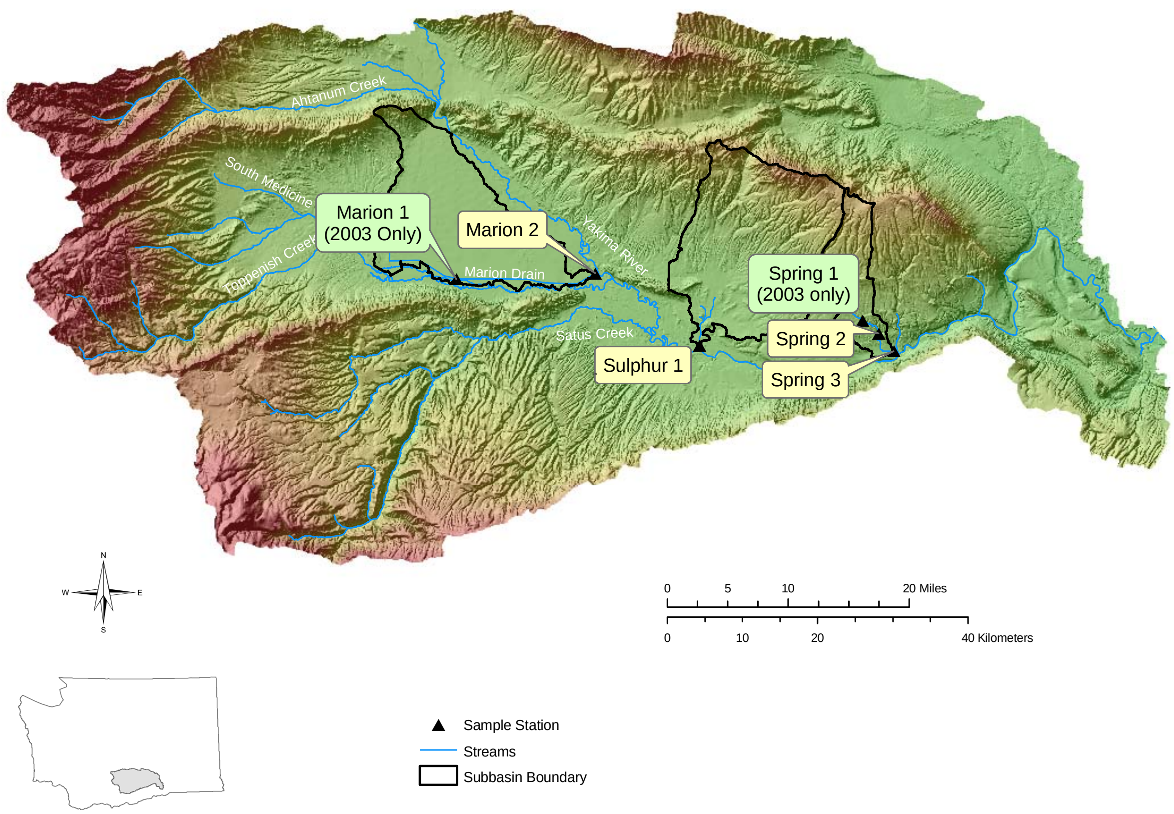

Figure 2. Sampling stations in Marion Drain, Sulphur Creek Wasteway, and Spring Creek in the Lower Yakima watershed.

Urban

Thornton Creek drains a 12.1-square-mile watershed before flowing into Lake Washington and ultimately Puget Sound. The watershed has 75,000 to 100,000 residents, thousands of daily commuters, and encompasses single-family units, multi-family apartment complexes, schools, parks, Interstate 5, a shopping mall, and a golf course (Thornton Creek Watershed Characterization Report, 2000; U.S. Census Bureau, 2000). Impervious surfaces cover approximately 50% of the watershed. The reduction of water detention and infiltration results in increased stormwater runoff, streambank erosion and sedimentation, flushing of salmon eggs and juveniles out of the stream, and reduced flows during the summer (Embrey and Frans, 2003).

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. As of March 29, 2006, the Puget Sound Steelhead DPS has been proposed for threatened status (71FR15666). Puget Sound Coho are an ESA Species of Concern.

Prior to this study pesticide residues had been detected within Thornton Creek. In a survey of agricultural and urban watersheds, Bortleson and Davis (1997) reported urban use of pesticides was three times greater than agricultural use. Voss et al. (1999), and later Embrey and Frans (2003), detected the insecticides carbaryl, chlorpyrifos, diazinon, lindane, and malathion at levels exceeding EPA National Recommended Water Quality Criterion in Thornton Creek.

Agricultural

The agricultural basin is represented by three drainages within the Lower Yakima watershed: Marion Drain, Sulphur Creek Wasteway, and Spring Creek. The three drainages encompass a total area of 216,168 acres, 47% of which is cropped (Appendix B). The most common crops are grapes (18% of cropped area), apples (14%), and wheat (13%). Other commodities include hops, mint, asparagus, cherry, potatoes, pears, and nectarines.

The Yakima and Naches rivers supply irrigation water to approximately 339,000 acres of cropland in the Lower Yakima valley. Most of the water in the Yakima River system is managed by the U.S. Bureau of Reclamation. Water distribution from canals to farms is primarily managed by irrigation districts. Greater than 50% of the water delivered to the lower basin from the Naches River and upper Yakima River is diverted for irrigation and hydropower generation during the irrigation season (Molenaar, 1985; Coffin et al., 2006).

During summer, the quality of agricultural return flows determines the quality of water in the Lower Yakima (Ebbert and Embrey, 2002). Exposure to adverse water quality constituents for fish entrained into these watercourses might significantly decrease their chances of spawning successfully later (Scholz et al., 2000). Joy and Patterson (1997) frequently detected pesticides at several sites surveyed in the Lower Yakima watershed. In surveys conducted between 1968 and 1985, Rinella et al. (1992) consistently detected pesticides including aldrin, 2-4-D, DDT and its breakdown products DDE and DDD, diazinon, dieldrin, endrin, heptachlor, heptachlor epoxide, lindane, and (2,4,5-trichlorophenoxy) acetic acid [2,4,5-T] in the water column, bed sediment, and/or tissues of resident fish.

Fish Occupation

The monitored drainages support a diverse assortment of fisheries including fall chinook, spring chinook, coho, and summer steelhead (Haring, 2001; Freudenthal et al., 2005). Of the fisheries, Mid-Columbia summer steelhead are designated threatened and have been documented in all three drainages (Haring, 2001; Freudenthal et al., 2005). The Yakima River supports ESA-listed Upper Columbia River summer/fall chinook (river-type), Mid-Columbia River spring chinook (ocean-type), and Mid-Columbia River bull trout. None of these species occupy all test drainages, and none are reviewed for potential pesticide effects in this study.

The majority of summer discharge in the Marion Drain, Sulphur Creek Wasteway, and Spring Creek is comprised of irrigation return flows or irrigation mediated exfiltration (Haring, 2001; Freudenthal et al., 2005). False attraction flows can entrain and confuse migrating adult steelhead. The Marion Drain is a constructed conveyance which intercepts a portion of historical groundwater flow to Toppenish Creek. As a result, Marion Drain steelhead are likely ancestral

Toppenish Creek fish (Freudenthal et al., 2005). Similarly, many steelhead are attracted to Sulphur Creek Wasteway due to discharge from the Roza Canal, and to Spring Creek due to discharges from the Sunnyside Canal (Haring, 2001). To increase steelhead spawning success, recommendations to reduce adult attraction to Sulphur Creek Wasteway have been proposed (Haring, 2001).

While the three agricultural streams selected for this study all have documented steelhead presence, the overall quality of habitat within these drainages ranges from good habitat with excellent spawning gravels, to poor habitat not capable of supporting naturally spawning populations (Romey and Cramer, 2001; and Marnie Tyler, personal communication, WDFW Salmonid Recovery Coordinator). Habitat limiting factors for the lower test drainages are attributed, in part, to velocity refuge, suitable substrate, thermal conditions and migration blockages.

A few examples include:

- Steelhead eggs and fry in the Marion Drain are unlikely to survive due to poor habitat and irrigation spills during the emergence period (Freudenthal et al., 2005).
- The amount of fines and embeddedness within Sulphur Creek would effectively prevent any meaningful production of salmonids in those channels (Romey and Cramer, 2001).
- Summer temperatures in Sulphur Creek Wasteway are near the lethal limit for summer steelhead (see *Results* section).
- Just downstream of the lower Spring Creek sample site (Hess Rd., RM 0.4), a vertical drop is evaluated as a barrier to adult salmonids at most flows (Romey and Cramer, 2001).

NOAA Fisheries has designated the lower reaches of Spring and Sulphur creeks and various segments of Marion Drain as Critical Habitat (www.nwr.noaa.gov/Salmon-Habitat/Critical-Habitat/upload/WA-ESU-MAP.pdf) A more detailed description of site specific habitat may be found in Haring, 2001; Burke et al., 2005; and Freudenthal et al., 2005.

Marion Drain

Marion Drain discharges into the Yakima River 2.2 miles upstream of the mouth of Toppenish Creek at river mile 82.6. Marion Drain is a 19-mile-long drainage ditch with a watershed area of approximately 85,786 acres, collecting water from Harrah Drain, Toppenish Creek, Wanity Slough, and groundwater extrusion, all within the Yakama Nation lands. Approximately 59% of the watershed is in agricultural crops. The majority of this acreage is in apple (9%), hops (9%), and corn (9%) production (Appendix B).

Although a channelized conveyance, the upper Marion Drain provides spawning habitat for fall chinook, summer steelhead, and resident fishes (Freudenthal et al., 2005; Haring, 2001). Coho have been observed in the drain (Haring, 2001). A subset of historical pesticide detections within Marion Drain includes atrazine, simazine, carbaryl, and trifluralin as well as cancelled pesticides (parathion, dieldrin, 4,4'-DDE, and DDT) (Ebbert and Embrey, 2002; Joy and Patterson, 1997).

Sulphur Creek Wasteway

Sulphur Creek wasteway is a highly channelized agricultural conveyance that discharges into the Yakima River at river mile 61.0. Approximately 35% of the 103,010 acre watershed is in agricultural production. The majority of this acreage is in grapes (11%), apples (5%), and corn (5%) (Appendix B).

The fish distribution in Sulphur Creek Wasteway includes spawning coho; however, suitable spawning gravels and low velocity habitat for emerging fry are rare. Salmonids are attracted to Sulphur Creek Wasteway by the high volume of irrigation return flows. The Yakama Nation, Irrigation Districts, and WDFW are working to secure funding to prevent adult salmonids from entering Sulphur Creek Wasteway. Summer steelhead, fall chinook, and spring chinook have been documented as present in Sulphur Creek Wasteway (Haring, 2001).

Prior pesticide detections in the Sulphur Creek Wasteway include azinphos methyl, diazinon, atrazine, carbaryl, and endosulfan as well as cancelled pesticides (dieldrin and DDT and its degradates) (Ebbert and Embrey, 2002).

Spring Creek

Spring Creek terminates at its confluence with the Lower Yakima River at RM 41.8. The Spring Creek drainage is 27,372 acres with 51% of the area cropped. The dominant crops in the Spring Creek watershed are grapes (13%), wheat (12%), and apples (4%); an additional 13% of the cropland is enrolled in the Conservation Reserve Program.

The fish distribution in the lower reach includes spawning coho and rearing spring chinook. The presence of coho, spring chinook, fall chinook, and summer steelhead has been documented in the lower reach (Haring, 2001).

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) (Ebbert and Embrey, 2002)).

Study Design and Methods

Sampling was designed to address pesticide presence in Endangered Species Act (ESA)-listed, salmonid-bearing streams during typical pesticide-use periods. To understand factors affecting pesticide fate, transport, and toxicity to non-target organisms, conventional parameters are analyzed during each sample event. These parameters include discharge, temperature, pH, conductivity, and total suspended solids (TSS). Sampling frequency, field procedures, and laboratory procedures are described below. Additional information about the study design and methods are described in the quality assurance project plan for this study (Johnson and Cowles, 2003).

Sampling Frequency

Using an adaptive management approach, monitoring subsequent to 2003 was adjusted to focus on periods with the maximum probability of detecting pesticide residues. Key design components included:

- 2003 – Exploratory
  - Nine sample sites distributed across Thornton Creek, Marion Drain, Sulphur Creek Wasteway, and Spring Creek.
  - Wide spectrum laboratory analysis which includes semivolatile organic compounds (SVOCs).
  - Distributed sample frequency. Emphasis placed on spring pesticide-use season and fall storm events.
- 2004 – Emphasis on sample frequency within integrator sites
  - Reduced sample sites to six. Emphasis on downstream sites which integrate contributions of entire watershed.
  - Focused analytical resources on pesticides most likely to occur in selected reaches. SVOCs eliminated as non-pesticide product.
  - Sample frequency increased. Specific storm-event sampling eliminated.
- 2005 – Continued frequency emphasis, revision of analytical methodology
  - Six sample sites maintained.
  - Laboratory methods modified to include several pyrethroid insecticides and additional degradate compounds.
  - Sample frequency maintained

Minor site location adjustments were necessary due to hydraulic modifications within specific stream segments. Reasoning behind specific site location and analytical adjustments are described in Burke et al. (2005) and Anderson et al. (2004). Historical site development may be found in Johnson and Cowles (2003). Design frequency and analytical components are summarized in Table 1.

Table 1. Sampling frequency and analyses.

Watershed/Site	Designation	[1]Sample Frequency and Analytical Request									
		2003			2004			2005			Sample event total
		Frequency		Lab Req.	Frequency		Lab Req.	Frequency		Lab Req.	
		Type	No.		Type	No.		Type	No.		
Urban: Cedar-Sammamish											
Thornton Creek 3	Mainstem	A,S	18	P2,SV	A	31	P1	A	29	P4	78
Thornton Creek 2	South Fork	A,S	18	P2,SV							18
Thornton Creek 1	North Fork	A,S	18	P2,SV	B	16	P1	B	15	P4	49
Agricultural: Lower Yakima											
Marion Drain 2	Downstream	A,B	21	P2	A	30	P3	A	29[2]	P4	80
Marion Drain 1	Upstream	A	12	P2							12
Sulphur Creek Wasteway	Mainstem	A,B	21	P2	A	31	P3	A	29	P4	81
Spring Creek 3	Upstream	A,B	21	P2	A	31	P3	A	29	P4	81
Spring Creek 2	Midstream	A	12	P2				B	15	P4	27
Spring Creek 1	Downstream	A	12	P2	B	15	P3				27
Total Events			153			154			146		453

A = Weekly sampling. April through June 2003, late March through October 2004, March through mid-Sept 2005
B = Biweekly sampling. July through September 2003, late March through October 2004, March through mid-Sept 2005
S = Storm-event sampling on October 15, November 15-16, and December 10, 2003
P1 = Organophosphorus and nitrogen containing pesticides, herbicides
P2 = P1 plus organochlorine and carbamate pesticides
P3 = P2 through June, organochlorine pesticides discontinued thereafter (n=14 weekly chlorinated, n=7 biweekly)
P4 = P2 and pyrethroid pesticides
SV = Semivolatile organic carbon compounds, not sampled during storm events
[1]Minor variations in sample/analyte determination due to shipping or analytical difficulties.
[2]Additional four weeks of organophosphorus pesticide sampling (Sept-Oct) not included in total

Field Procedures

Field procedures are defined in the quality assurance (QA) project plans (Johnson and Cowles, 2003; Burke et al., 2006). Any changes in methodology specified in the original QA project plan are documented in the yearly monitoring reports (Anderson et al., 2004; Burke et al., 2005). Field methods are a direct application or modification of USGS or EPA procedures.

Pesticides were collected by hand-compositing grab samples from quarter-point transects across each stream. A one-liter transfer container was used to dip into the stream and pour water into the sample containers. Sample/transfer containers were delivered pre-cleaned by the manufacturer to EPA specifications (EPA, 1990). After collection, all samples were labeled and preserved according to the QA project plan (Johnson and Cowles, 2003).

Temperature, pH, and conductivity were measured in the field using Environmental Assessment Program sampling protocols (Cusimano, 1993; Ward, 2001; Bilhimer and LeMoine, 2004), USGS (USGS, 2006a), and EPA methods (EPA, 2004). Temperature instruments were calibrated against a National Institute of Standards and Technology (NIST) primary reference (Wagner et al., 2000; USGS, 2006a).

Discharge for all sites except Sulphur Creek Wasteway was measured using a Marsh-McBirney flow meter and top-setting wading rod, as described in the USGS method for "Measurement of Discharge by Conventional Current-Meter Method" (Rantz et al., 1983). Discharge data for Sulphur Creek Wasteway was obtained from an adjacent U.S. Bureau of Reclamation gaging station, "SUCW – Sulphur Creek Wasteway at Holaday Road Near Sunnyside". Fifteen-minute discharges were available during the sampling period. The record closest to the actual sampling time was used in lieu of field measurements.

Laboratory Analyses, Quality Assurance, and Quality Control

Laboratory methods are presented in Table 2 and have been discussed in the QA project plans (Johnson and Cowles, 2003; amended in Burke et al., 2006), and monitoring reports (Anderson et al., 2004; Burke et al., 2005).

Table 2. Summary of laboratory methods.

Analyte	[1]Analytical Methods		
	Extraction	Analysis	Reference
TSS	n/a	Gravimetric	EPA 160.2
[2]Pesticides: 2003, 2004	3510	GC/AED	8085
[2]Pesticides: 2005	3510	GC/MS	8270
Herbicides	8151	GC/MS	8270
Carbamates: 2003	8318	HPLC	8318
Carbamates: 2004, 2005	n/a	HPLC	531.1M
Semivolatiles	3510	GC/MS	8270

[1]All analytical methods refer to EPA SW 846, or variation thereof, unless otherwise noted.
[2]Pesticides refers to all forms tested unless indicated otherwise.
AED = Atomic emission detection
GC = gas chromatograph
HPLC = high performance liquid chromatography
MS = mass spectrometry
n/a = not applicable

Over the course of this study, Ecology's Manchester Laboratory migrated from a gas chromatography (GC)/atomic emission detector (AED) to a GC/mass spectrometry (MS) method. Similarly, the extraction and analysis of carbamate insecticides changed during a switch of analysts from Phillip Services Corporation (Vancouver, BC) to Manchester Laboratory.

In general, implementation of revised pesticide and carbamate procedures resulted in an improvement of detection limits and/or pesticide residue identification. Reduced detection limits may increase the frequency of detection of certain residues. Performance detection limits and residue identification are presented in Appendix C. Herbicide and total suspended solids (TSS) analyses remain unchanged.

Performance of laboratory analyses is governed by quality assurance and quality control (QA/QC) protocols. The QA/QC protocol employs diverse application of blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSD). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. A detailed evaluation of QA/QC is presented in Appendix C.

No pesticides were detected and confirmed in blanks, indicating both field and laboratory actions were free from contamination. Replicate results show pesticide measurements were reproducible with a desired degree of precision, and met or improved upon typical results obtained by federal agencies (Martin, 2002). Surrogate and laboratory control sample results indicate pesticide residues were accurately recovered. The relative percent difference of MS/MSD results was consistently less than 15%, indicating the overall field and laboratory process were accurate, precise, and reproducible. See Appendix C for details.

Results

This study investigated pesticide occurrence in selected salmonid-bearing surface waters. Watersheds and monitoring locations with a likely combination of off-site pesticide transport and salmonid utilization were chosen. From 2003 through 2005, the majority of pesticide detections were below assessment criteria. Of the 157 compounds included in the analytical methodology, eight currently registered insecticides or degradates (azinphos methyl, carbaryl, chlorpyrifos, diazinon, disulfoton, endosulfan sulfate, malathion, and oxyfluorfen), and one legacy compound (DDT) and its degradate (DDE), exceeded an assessment criteria.

Assessment Criteria

Assessment of effects to endangered species is evaluated through three mechanisms:

- Pesticide registration toxicity and risk assessment criteria.
- Washington State water quality standards for the protection of aquatic life (WAC 173-201A).
- EPA National Recommended Water Quality Criteria (NRWQC).

Pesticide Registration Toxicity Criteria

The EPA uses risk quotients (RQ) to assess the potential risk of a pesticide to non-target organisms. A RQ is calculated by dividing the environmental concentration by either an acute or chronic toxicity value, which gives an evaluation of exposure over toxicity. The resulting RQ is a unitless value that is compared to levels of concern (LOC). The LOCs set by EPA are presented in Table 3 and are used to assess the potential risk of a pesticide to non-target organisms.

Table 3. Risk quotient criteria for direct and indirect effects on threatened and endangered fish.

Test Data	Risk Quotient	Presumption
Acute LC50	>0.5	Potentially high acute risk
Acute LC50	>0.1	Risk that may be mitigated through restricted use classification
Acute LC50	>0.05	Endangered species may be affected acutely, including sublethal effects
Chronic NOEC	>1	Chronic risk; endangered species may be affected chronically, including reproduction and effects on progeny
Acute invertebrate LC50	>0.5	May be indirect effects on T&E fish through food supply reduction
Aquatic plant acute LC50	>1	May be indirect effects on aquatic vegetative cover for T&E fish

(Turner, 2003)
T&E – Threatened and endangered

The endangered species LOC (0.05 for aquatic species) is used as a comparative value to assess potential risk to threatened or endangered salmonids. The endangered species RQ can also be expressed as 1/20th of the acute LC50 for aquatic organisms. To assess the potential risk of a pesticide to salmonids, the LC50 for rainbow trout is commonly used as a surrogate species. Thus the endangered species LOCs presented in subsequent tables are 1/20th of the rainbow trout LC50. When available, the endangered species LOC for specific salmonids is also presented.

The EPA traditionally determines RQs based on edge of field runoff into a pond, thus representing a worst-case exposure scenario. The RQs calculated for this report are for streams and therefore are expected to be lower.

Acute toxicity is calculated by standardized toxicity tests using lethality as the criteria. A properly conducted test will use a sensitive (but representative) species, at a susceptible life stage (usually young, though not immature), and will subject the test species to a pesticide under range of concentrations (minimum: no effect, 50% and 100% mortality). The dose response curve may be calculated, and the LC_{50}, lethal concentration to cause mortality in 50% of test species will be derived. For fish, the lethality test is conducted over 96 hours at a constant concentration. Acute invertebrate toxicity is normally calculated over 48 hours, with the criteria being mortality or immobility (LC_{50}, or effective concentration - EC_{50} for immobility). Acute toxicity testing for aquatic plants is conducted over 96 hours, and the criterion is reduction in growth (EC_{50}).

Chronic tests normally use reproductive effects, or effect to offspring, as the criteria. The dose response curve is evaluated to determine no observable effect concentration (NOEC). The chronic toxicity test is longer than 96 hours (21 days for fish, 14 days for invertebrate, 5 to 60 days for plants) to simulate exposure resulting from a persistent chemical, or effect of repeated applications.

Water Quality Criterion and Standards

The National Recommended Water Quality Criteria (NRWQC) are established by the EPA Office of Water for the protection of aquatic life, as established under the federal Clean Water Act (33 United States Code 1251 et. seq.). The pesticide criteria established under the CWA are closely aligned with invertebrate acute and chronic toxicological criteria. States often adopt the NRWQC as their promulgated (legal) standards. The NRWQC was updated in 2006, and those criteria are used in this report (EPA, 2006). Washington State water quality standards are established in the Washington Administrative Code (WAC), Chapter 173-201A.

Aquatic life standards, criterion, pesticide regulatory criteria, and toxicity (acute and chronic) results for fish, invertebrates, and aquatic plants are presented in Appendix D, and will hereafter be referred to as assessment criteria. Chemicals numerically above (exceeding) assessment criteria are presented in Table 4.

Numeric exeedances of values in Table 4 do not necessarily indicate that the water quality criteria have been exceeded. There is typically a temporal duration of exposure criteria in addition to numeric criteria for a water quality standard. For example, the proposed acute aquatic life criteria for diazinon reads *"…freshwater aquatic life and their uses should not be* *affected unacceptably if the one-hour average concentration of diazinon does not exceed 0.17 µg/L more than once every three years on the average.”* (EPA, 2003).

Table 4. Assessment criteria for selected pesticides. Values in ug/L.

Chemical	Subject	Species	Toxicology		[1]Risk Quotient		[2]Standard/Criterion	
			Acute LC50	Chronic NOEC	ESLOC	Acute invert.	WAC	NRWQC
[3]4,4-DDT							0.001	0.001
[3]4,4-DDE							0.001	0.001
Azinphos methyl	Fish	Rain. T.	2.9	0.23	0.145			
	Fish	Coho	3.2		0.16			
	Invert	*Daph. M.*	1.1	0.25		0.55		0.01
Carbaryl	Fish	Rain. T.	1200	600	60			
	Fish	Chinook	2400		120			
	Invert	*Daph. M.*	5.6	1.5		2.8		
Chlorpyrifos	Fish	RT/FM	3	0.57	0.15			
	Invert	*Daph. M.*	0.1	0.04		0.05	0.041	0.041
[4]Diazinon	Fish	RT/BT	90	0.8	4.5			
	Invert	*Daph. M.*	0.8	0.17		0.4		0.17
Disulfoton	Fish	Rain. T.	1850	220	92.5			
	Invert	*Daph. M.*	13	0.04		6.5		
Endosulfan sulfate	Fish	Rain. T.	2.2		0.11			
	Invert	*Daph. M.*	580			290	0.056	
Malathion	Fish	Rain. T.	4.1	2	0.205			
	Fish	Coho	170		8.5			
	Invert	*Daph. M.*	1	0.06		0.5		0.1
Oxyfluorfen	Plant	*Sel. Cap.*	0.29	0.1				

[1]ESLOC is Endangered Species Level of Concern. Acute invertebrate is 0.5 the LC50 for invertebrates and represents a reduction in food available to endangered species.
[2]Lowest standard or criterion. Chronic, used if available. Otherwise acute standard applied.
[3]Value is representative of the sum of DDT and its metabolites (DDD, and DDE).
[4]Diazinon standards have been finalized, 0.17 µg/L in 2005 (71FR9336).
References presented in Appendix D.
RT = Rainbow Trout, FM = Fathead Minnow, BT = Brook Trout,
Daph. m. = *Daphnia magna*, *Sel. cap.* = *selenastrum capricornutum*

Also, toxicity values such as those used for pesticide registration are determined from continuous exposure over time (e.g., LC_{50} freshwater fish acute toxicity tests are run for 96 hours at a constant concentration). Therefore, when comparing the monitoring data either to the aquatic life criteria or directly to a toxicity criterion, one must consider the duration of exposure as well as the numeric toxicity value. It is not possible to determine if an aquatic life criterion has been exceeded based solely on an individual sample because the sampling frequency is, at best, weekly which does not allow for assessment of the temporal component of the standard.

Conventional Parameters

Conventional parameters were collected to better understand the fate and transport of pesticides. Additionally, fisheries occupation and habitat utilization may be estimated from conventional results. Discharge provides an indication of rainfall response and operational influences of irrigation systems on the monitoring locations in the Lower Yakima watershed. Also, the load or source contribution of pesticides to receiving waterbodies is a function of chemical concentration and discharge quantity. Temperature results indicate potential habitat utilization by threatened and endangered species, and directly relate to pesticide degradation and toxicity. Conductivity measures the dissolved ions in solution and may be indicative of groundwater contributions to discharge. The stream pH has a direct bearing on the degradation of select pesticide compounds. A summary of conventional water quality results are presented in Table 5.

Table 5. Summary conventional parameter results.

Site	Discharge (cfs)			Temperature (°C)			TSS (mg/L)			Conductivity (µS/cm)			pH		
	Min	Med	Max	Min	Med	Max	Min	Med	Max	Min	Med	Max	Min	Med	Max
Thornton Cr.	2.6	4.3	37.8	6.7	14.7	21.9	1	6	257	120	223	291	6.9	7.8	8.6
Marion Dr.	1.7	49	316.5	7.9	16.2	24	1	9	62	159	254	375	7.1	8.3	9.3
Sulphur CW	51.4	173.3	509	7.8	16.9	25	7	27	722	164	308	700	7.6	8.3	8.9
Spring Cr.	0.04	36.5	88.6	2.7	17.1	30.3	1	28	94	120	219	652	7	8.3	9.5

TSS – Total suspended solids

Maximum conductivity values in Spring Creek occurred when TSS were low, indicating groundwater extrusion may be present.

Temperature influences the likelihood of steelhead presence and increased susceptibility to pesticide toxicity. Most anadromous (sea-run) steelhead stocks have evolved with the temperature regime of streams they use for spawning and migration, and alteration of the normal temperature pattern can result in reduced fitness (McCullough et al., 2001). Salmonids exhibit considerable variation in thermal preferences, yet generalized thresholds illustrate potential temperature influence on steelhead occupation and associated toxicity. For example the upper optimum temperature regime for steelhead spawning is 11-12°C based on constant or acclimation temperatures (McCullough et al., 2001; derived from laboratory testing and hatchery review).

Steelhead smoltification may be impaired above 12-14°C (Zaugg, 1981; Hoar, 1988). The preferred daily average maximum temperature of yearling juveniles in the South Umpqua River, Oregon is 18°C (Roper et al., 1994). Migration of summer steelhead may be blocked at sustained temperatures in excess of 21°C (Strickland, 1967, as cited by Stabler, 1981; Snake River analysis of average temperature). Additionally, Columbia River Steelhead, acclimated to a river temperature of 19°C, had a lethal threshold of 21°C (Coutant, 1970, one week constant temperature; Coutant, 1999).

Further the susceptibility of salmonids to pesticide toxicity may increase at greater temperatures. For example, the acute toxicity of chlorpyrifos to rainbow trout increases with temperature (i.e., the LC50 at 2°C is 51 µg/L and < 1 µg/L at 18°C)(Mayer and Ellersick, 1986).

Temperature profiles for Marion Drain and Sulphur Creek Wasteway are similar; year 2005 data for the Sulphur Creek Wasteway is presented in Figure 3. Spring Creek temperature results are presented in Figure 4. Generalized upper thresholds of select summer steelhead life stages are presented with the figures. Results for all sites are presented in Appendix G.

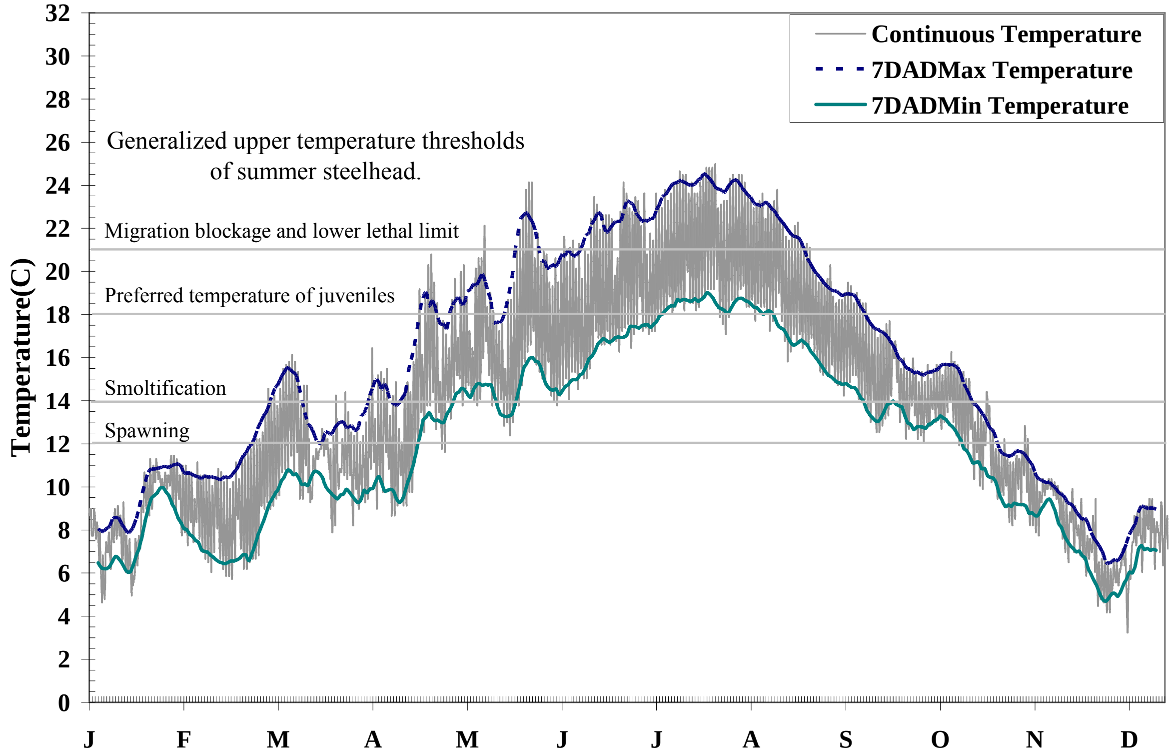

Figure 3. Temperature profile for the Sulphur Creek Wasteway.

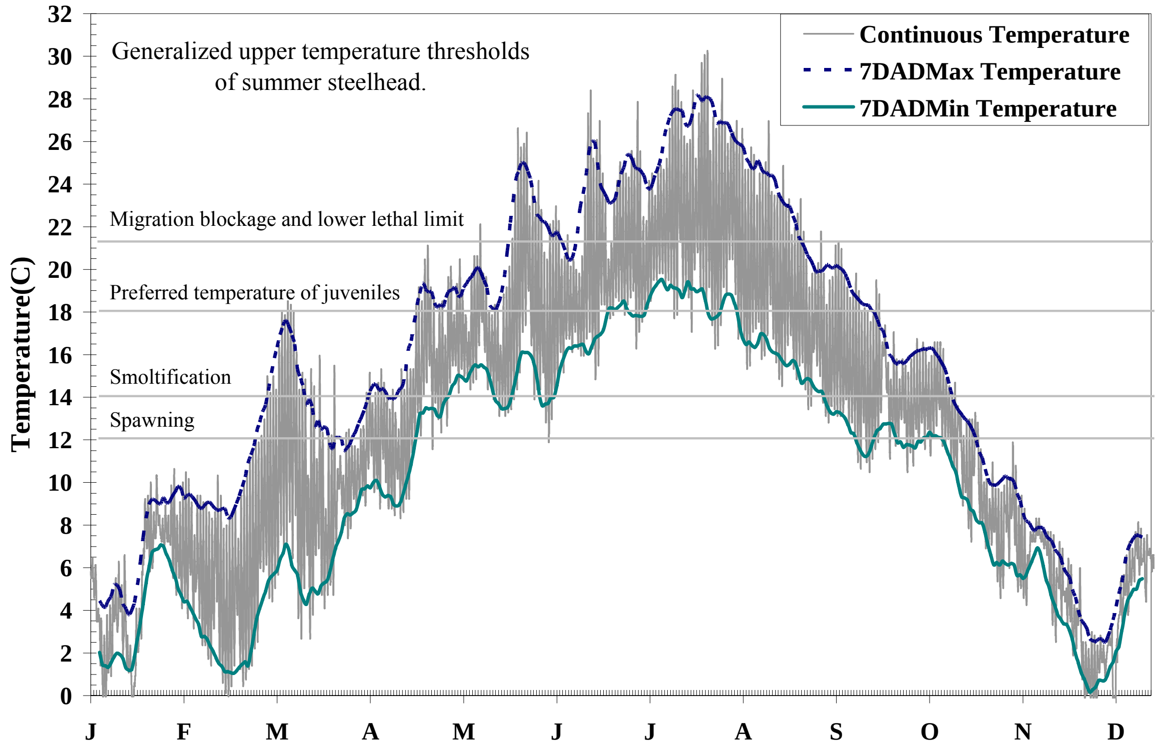

Figure 4. Temperature profile for Spring Creek.

Pesticide Distribution

From 2003 through 2005, 453 samples were collected from urban and agricultural sites. The pesticides detected are grouped into types (e.g., insecticide, herbicide) to determine the general distribution of pesticides found. In both the urban and agricultural watersheds, herbicides were the most frequently detected pesticide. However, there were two general differences between the urban and agricultural drainages. Pentachlorophenol, a wood preservative having herbicidal properties, was frequently detected in the urban watershed (Figure 5) while insecticides were more frequently detected in the agricultural watershed (Figure 6).

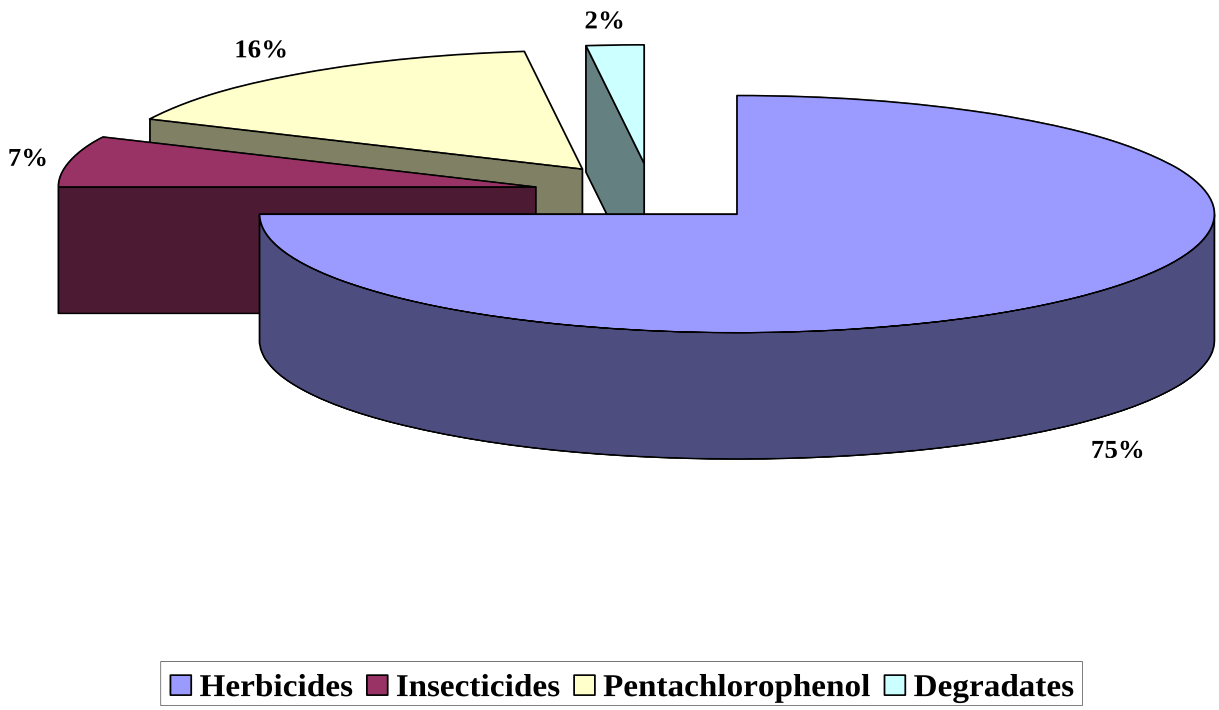

Figure 5. Distribution of pesticides detected in Thornton Creek.

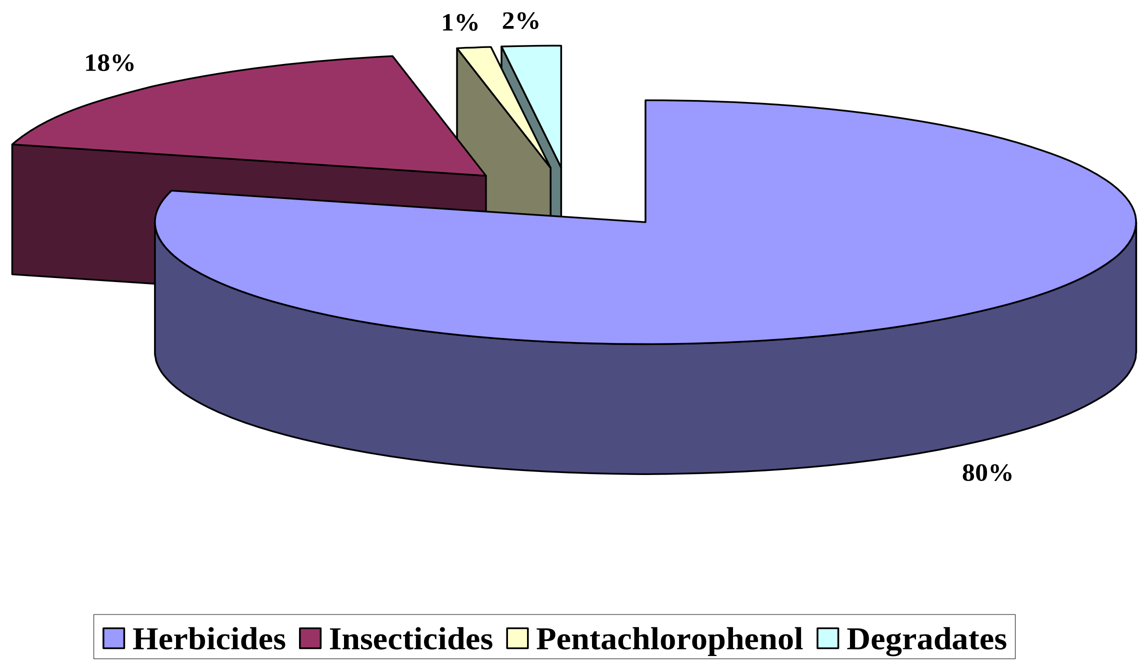

Figure 6. Distribution of pesticides detected in the Lower Yakima watershed.

Pesticide Detections by Basin

Monitoring results are presented for downstream reaches terminating at the confluence with the major waterbodies, Lake Washington and Yakima River. Monitoring was conducted at (1) Thornton Creek prior to its confluence with Lake Washington and (2) Marion Drain, Sulphur Creek Wasteway, and Spring Creek prior to their confluence with the Lower Yakima River.

Upstream water monitoring was also conducted at Thornton Creek, Marion Drain, and Spring Creek. Monitoring results for upstream sites are presented in Appendix F, and all results are available through Ecology's Environmental Information Management (EIM) system www.ecy.wa.gov/eim/. In general, pesticides are detected less frequently, yet often at higher magnitudes, in the upstream reaches.

In the summary tables for each drainage, the 2003 results are shaded to indicate the sampling frequency and duration are substantially different than subsequent years. Thus, a direct comparison of detection frequency from 2003 to 2004 and 2005 may be misleading. The summary tables also include the lower practical quantitation limit (LPQL) which is a statistically derived value indicating the lowest concentration that can be accurately measured. Compounds detected below this level are qualified as estimates.

Thornton Creek

From 2003 through 2005, 78 sample events were conducted in Thornton Creek; these are summarized in Table 6. The most frequently detected compounds include pentachlorophenol, and the herbicides triclopyr, dichlobenil, and MCPP. Diazinon was the most frequently detected insecticide. Although pentachlorophenol was detected less frequently in 2005 than preceding years, this seems to be an artifact of an updated analytical methodology that appears to be more susceptible to constituent interference in the water samples.

Maximum diazinon concentrations were usually observed during May of 2003-2005. However, only one detection for diazinon (0.21 µg/L on May 14, 2003) in the South Fork Thornton Creek was numerically above the chronic invertebrate assessment criterion and NRWQC acute standard. It is important to note the rapid decline and magnitude of diazinon detections after commercially banning this substance in December 2004 for homeowner use in the United States. The detection frequency declined from 39% in 2003, to 13% in 2004, and to 3% in 2005.

The acute risk quotient (RQ) for rainbow trout was calculated for all pesticides detected at the mouth of Thornton Creek (Figure 7). No RQs exceed the ESLOC of 0.05. Similarly, no detections were observed to be numerically above the water quality criterion, or invertebrate toxicological or risk criteria, in the downstream or North Fork Thornton Creek stations. Risk quotient results for all sites are available in Appendix E. Summary results for all parameters are presented in Appendix F.

Table 6. Summary of pesticide detections in Thornton Creek. Concentrations reported as µg/L.

Chemical	Common Name	[1]Type	LPQL	2003, n=18			2004, n=31			2005, n=29			Criteria	
				Freq	Median	Max	Freq	Median	Max	Freq	Median	Max	ESLOC	NRWQC
Pentachlorophenol	Penta	WP	0.08	78%	0.015	0.083	42%	0.016	0.078	21%	0.0081	0.03	0.75	[2]6 to 83
Triclopyr	(several)	H	0.097	78%	0.0375	0.093	42%	0.034	0.085	14%	0.026	0.067	32.5	
Dichlobenil	Casoron	H	0.064	67%	0.017	0.052	77%	0.012	0.1	83%	0.0175	0.098	246.5	
MCPP	Mecoprop	H	0.158	50%	0.03	0.15	39%	0.023	0.1	34%	0.016	0.15		
2,4-D	(several)	H	0.107	44%	0.043	0.14	42%	0.035	0.21	17%	0.023	0.16	29	
Diuron	Karmex	H	0.193	44%	0.1135	0.21	23%	0.0075	0.17	28%	0.0205	0.023	97.5	
Diazinon	(several)	I-OP	0.026	39%	0.025	0.09	13%	0.0145	0.095	3%	0.023	0.023	4.5	0.17
Prometon	Pramitol 5PS	H	0.032	22%	0.018	0.027	23%	0.0056	0.025	38%	0.016	0.036	600	
Benzamide, 2,6-dichloro-		D	0.22	17%	0.05	0.058	--			--				
Simazine	Simazine	H	0.032	17%	0.014	0.025	--			--			3525	
4-Nitrophenol		D	0.15	6%	0.011	0.011	--			--			190	
Ethoprop	Mocap	I-OP	0.026	--			3%	0.036	0.036	--			51	
Trifluralin	Treflan	H	0.049	--			--			34%	0.0175	0.025	2.05	
MCPA	(several)	H	0.158	--			--			10%	0.028	0.072	57.5	

Results as reported by Manchester Environmental Laboratory
--Test for pesticide yielded no detections.
[1]Use type descriptors: H = herbicide, I-OP = organophosphorus insecticide, WP = wood preservative.
[2]Pentachlorophenol criteria range presented as a function of pH-based chronic standard, $\leq e^{[1.005(pH) - 5.134]}$. pH range of 6.9 to 9.5 applied.
Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as 'several'.

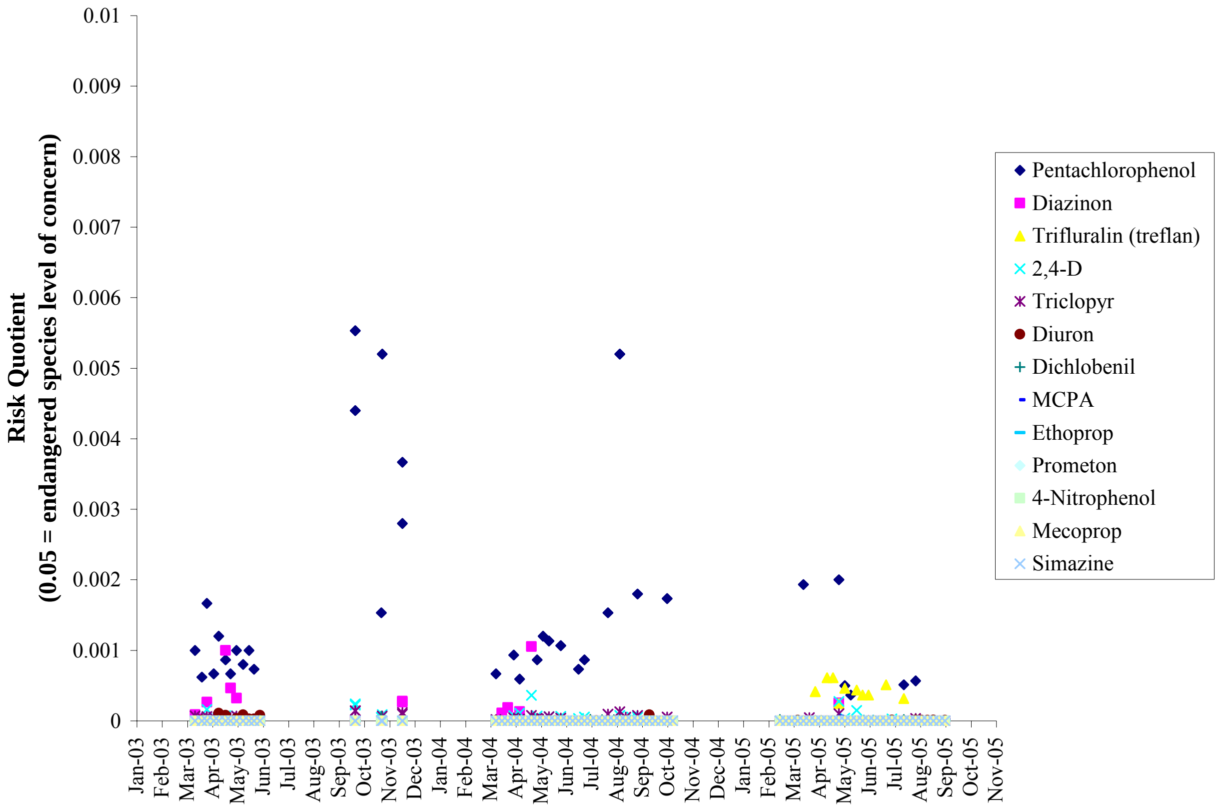

Figure 7. Acute rainbow trout risk quotients for pesticide detections at the mouth of Thornton Creek, 2003-2005. Legend sorted from highest (pentachlorophenol) to lowest risk quotient.

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Lower Yakima Watershed

In the Lower Yakima watershed (WRIA 37), Marion Drain, Sulphur Creek Wasteway, and Spring Creek were monitored. Forty different pesticides or degradate products were detected in the drainages of the Lower Yakima watershed. While each waterbody is distinct, a few detection characteristics are common among Marion Drain, Sulphur Creek Wasteway, and Spring Creek.

- 2,4-D, bromacil (terbacil in Marion Drain), atrazine, and diuron were the most frequently detected herbicides.
- Chlorpyrifos was the most frequently detected insecticide.
  - Malathion and azinphos methyl were detected at all sites.
  - Malathion was detected at all sites in all years (except at mid- Spring Creek).

The life stage of Mid-Columbia summer steelhead is described with respect to pesticide detections in Marion Drain, Sulphur Creek Wasteway, and Spring Creek. The lifecycle illustration in Figures 8-10 are general representations of the complex steelhead lifecycle in the Yakima basin (Haring, 2001) and are not intended to determine fish presence or absence. Additionally, the greatest toxicological concern is presented for a given date (i.e., fish > invertebrates > regulatory standards/criteria).

Marion Drain

In Marion Drain, 18 herbicides, nine insecticides, one degradate, and one wood preservative were detected (Table 7 and Figure 8). Over the 2003-05 study period, chlorpyrifos was the most frequently detected insecticide, followed by malathion, ethoprop, and dimethoate. Malathion was detected in 10%, 20%, and 30% of samples during 2003, 2004, and 2005, respectively.

Chlorpyrifos was consistently detected during the spring and fall over the study period. Late season detections of chlorpyrifos coincide with summer steelhead spawning runs, summer rearing, and winter migration (Figure 8). Early season detections of chlorpyrifos coincide with spawning, incubation, emergence, fry colonization, and smolt out-migration of summer steelhead. Several chlorpyrifos detections were observed to be numerically above the Washington State chronic values of 0.041 µg/L and exceeded the acute invertebrate risk quotient of 0.5. On September 21, 2005, one detection exceeded the EPA Endangered Species Level of Concern (ESLOC). Fall detection magnitudes were consistently observed above regulatory criteria, and elevated spring magnitudes were more episodic in nature.

Malathion was detected with increasing frequency from 2003-2005. A single detection of malathion observed in 2004 and in 2005 exceeded the ESLOC. The 2004 detection of malathion (3.05 µg/L) approached the LC50 for rainbow trout (4 µg/L). Additional single detections in 2004 and 2005 were numerically above the chronic invertebrate criteria and/or NRWQC chronic standard. Summer detections of malathion coincide with spawning, incubation, emergence, fry colonization, smolt outmigration, and rearing of summer steelhead.

A single detection of endosulfan sulfate (0.36 µg/L) exceeded the ESLOC and the Washington acute water quality standard of 0.22 µg/L.

Table 7. Summary of pesticide detections in Marion Drain. Concentrations reported as µg/L.

Chemical	Common Name	[1]Type	LPQL	2003, n=18			2004, n=31			2005, n=29			Criteria	
				Freq	Median	Max	Freq	Median	Max	Freq	Median	Max	ESLOC	NRWQC
2,4-D	(several)	H	0.107	76%	0.061	0.29	77%	0.045	0.22	38%	0.056	0.17	29	
Terbacil	Sinbar	H	0.097	76%	0.0785	0.26	67%	0.088	0.37	86%	0.12	0.46	2310	
Atrazine	Aatrex	H	0.035	62%	0.0059	0.017	60%	0.014	0.142	72%	0.019	0.035	265	
Chlorpyrifos	Dursban	I-OP	0.026	43%	0.023	0.085	37%	0.02	0.1	24%	0.02	0.4	0.15	0.041
Pendimethalin	Prowl	H	0.048	43%	0.044	0.1	13%	0.046	0.126	28%	0.028	0.065	6.9	
Bromoxynil	Buctril	H	0.107	38%	0.0285	0.052	23%	0.034	0.081	3%	0.04	0.04	5	
MCPA	(several)	H	0.158	33%	0.044	0.068	23%	0.032	0.297	10%	0.052	0.075	57.5	
Diuron	Karmex	H	0.193	24%	0.015	0.041	53%	0.0255	0.16	21%	0.0165	0.092	97.5	
Dimethoate	Dimethoate	I-OP	0.026	19%	0.00625	0.13	13%	0.0305	0.14	--			310	
Trifluralin	Treflan	H	0.049	19%	0.0096	0.016	7%	0.0153	0.023	24%	0.02	0.025	2.05	
Dicamba I	Banvel	H	0.107	19%	0.0105	0.012	--			--			1400	
Bentazon	Basagran	H	0.132	14%	0.053	0.063	53%	0.125	2.5	14%	0.0755	0.15	>5000	
Bromacil	Hyvar	H	0.13	14%	0.01	0.013	23%	0.0072	0.052	--			1800	
Malathion	(several)	I-OP	0.026	10%	0.01355	0.024	20%	0.0275	3.05	30%	0.0215	0.23	0.205	0.1
Alachlor	Lasso	H	0.189	10%	0.00405	0.0061	10%	0.005	0.04	14%	0.021	0.058	105	
Azinphos methyl	Guthion	I-OP	0.052	10%	0.00475	0.0064	--			--			0.145	0.01
EPTC	Eptam	H	0.065	5%	0.038	0.038	27%	0.008	0.027	7%	0.025	0.032	700	
Ethoprop	Mocap	I-OP	0.026	5%	0.046	0.046	20%	0.0485	0.18	15%	0.03	0.27	51	
Simazine	Simazine	H	0.032	5%	0.002	0.002	17%	0.022	0.031	45%	0.021	0.033	3525	
Propartige	Omite	I-SE	0.065	5%	0.015	0.015	3%	2.144	2.144	3%	0.092	0.092	5900	
Carbaryl	Sevin	I-C	0.14	5%	0.14	0.14	--			--			60	
Diazinon	(several)	I-OP	0.026	5%	0.007	0.007	--			--			4.5	0.17
Diphenamid		H	0.097	5%	0.093	0.093	--			--			1250	
Endosulfan II	Thionex	I-OC	0.06	5%	0.004	0.004	--			--			0.04	0.056
Endosulfan sulfate		D	0.06	5%	0.36	0.36	--			--			0.11	
Pentachlorophenol	Penta	WP	0.08	5%	0.01	0.01	--			--			0.75	[2]6 to 83
Hexazinone	Velpar	H	0.049	--			10%	0.009	0.036	--			9000	
Metolachlor	Stalwart	H	0.13	--			7%	0.00235	0.0038	28%	0.011	0.012	195	
Prometon	Pramitol 5PS	H	0.032	--			7%	0.0218	0.036	--			600	
Disulfoton	Di-Syston	I-OP	0.02	--			3%	0.023	0.023	--			92.5	

[1]Use type descriptors: D = degradate compound, H = herbicide, I-OC organochlorine insecticide, I-OP = organophosphorus insecticide, I-SE = sulfite ester insecticide, WP = wood preservative.

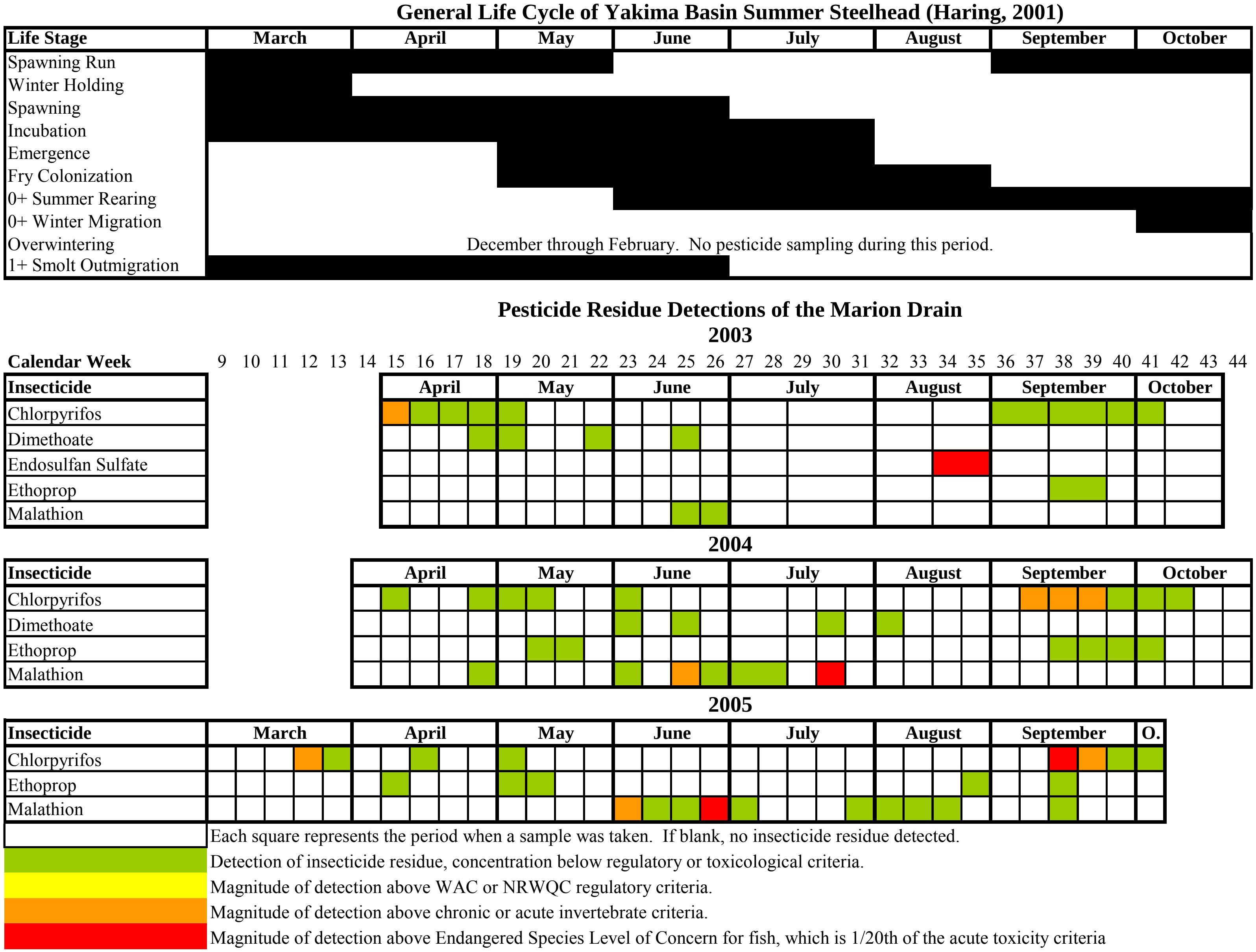

Figure 8. Summer steelhead life stage and pesticide residue detection analysis for the Marion Drain. Successive life stages not shown.

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Sulphur Creek Wasteway

A total of 34 pesticide and degradate compounds were detected in the Sulphur Creek Wasteway: 20 herbicides, 9 insecticides, 4 degradate compounds, and the wood preservative pentachlorophenol (Table 8). The most frequently detected insecticides included chlorpyrifos, azinphos methyl, and malathion.

Degradate compounds for DDT and aldicarb, 4,4-DDE and aldicarb sulfone, respectively were occasionally detected. The rate of detection for 4,4-DDE declined from 21% in 2004 to 10% in 2005.

Pesticide residue results for the Sulphur Creek Wasteway are presented in Figure 9. Azinphos methyl was detected with increasing frequency from 2003-2005, primarily during May and June. May and June are a time of overlapping habitat utilization by summer steelhead, including spawning run, spawning, incubation, smolt outmigration, emergence, fry colonization, and summer rearing. All azinphos methyl detections were numerically above the National Recommended Water Quality Criterion (NRWQC) of 0.01 µg/L. Two detections approached the Endangered Species Level of Concern (ESLOC) on May 15 and June 1, 2005. The azinphos methyl water quality criterion is an order of magnitude lower than the ESLOC (0.145 µg/L) and acute invertebrate risk concentration (0.55 µg/L). The EPA has proposed canceling all registered uses of azinphos methyl by 2010 (71FR33448).

Chlorpyrifos was consistently detected during the spring (March-May) from 2003-2005. The early spring chlorpyrifos detections coincided with spawning run, spawning, incubation, and smolt outmigration summer steelhead life stage activities (Figure 9). Over this three-year spring period, two chlorpyrifos detections were numerically above the Washington State chronic and acute invertebrate risk quotient, with an additional detection exceeding the ESLOC. An early season detection (March 31, 2004) also approached the Washington State chronic standard.

Malathion was detected once in 2003, with an increasing number of detections in 2004 (4) and 2005 (3). None of these observed detections exceeded fisheries or regulatory criteria.

A single detection of disulfoton on August 18, 2004 was numerically above the chronic invertebrate toxicity criteria.

Table 8. Summary of pesticide detections in the Sulphur Creek Wasteway (µg/L).

Chemical	Common Name	[1]Type	LPQL	2003, n=18			2004, n=31			2005, n=29			Criteria	
				Freq	Median	Max	Freq	Median	Max	Freq	Median	Max	ESLOC	NRWQC
2,4-D	(several)	H	0.107	90%	0.088	0.25	84%	0.0805	0.41	83%	0.11	2.2	29	
Bromacil	Hyvar	H	0.13	67%	0.0165	0.07	71%	0.036	0.141	14%	0.045	0.087	1800	
Atrazine	Aatrex	H	0.035	48%	0.0054	0.013	48%	0.0088	0.029	62%	0.019	0.046	265	
Diuron	Karmex	H	0.193	29%	0.0345	0.06	61%	0.052	0.171	48%	0.0345	0.27	97.5	
Pendimethalin	Prowl	H	0.048	24%	0.0066	0.016	3%	0.025	0.025	--			6.9	
Terbacil	Sinbar	H	0.097	19%	0.018	0.029	26%	0.0185	0.063	41%	0.028	0.059	2310	
Chlorpyrifos	Dursban	I-OP	0.026	19%	0.0084	0.013	19%	0.011	0.047	21%	0.019	0.37	0.15	0.041
Bentazon	Basagran	H	0.132	14%	0.025	0.025	42%	0.031	0.04	17%	0.038	0.045	>5000	
Azinphos-methyl	Guthion	I-OP	0.052	14%	0.017	0.023	13%	0.0295	0.042	24%	0.035	0.14	0.145	0.01
Norflurazon	Solicam	H	0.065	10%	0.03805	0.073	16%	0.042	0.048	3%	0.044	0.044	405	
Diazinon	(several)	I-OP	0.026	10%	0.00615	0.0066	3%	0.0082	0.0082	10%	0.014	0.023	4.5	0.17
Dimethoate	Dimethoate	I-OP	0.026	10%	0.01415	0.025	3%	0.018	0.018	--			310	
Pentachlorophenol	Penta	WP	0.08	10%	0.00635	0.0078	3%	0.0054	0.0054	--			0.75	[2]6 to 83
2,4,6 Trichlorophenol	(several)	H	0.218	10%	0.00405	0.0048	--			--			36.5	
4,4'-DDE		D	0.06	5%	0.0029	0.0029	21%	0.002	0.0028	10%	0.0023	0.012	1.6	0.001
Malathion	(several)	I-OP	0.026	5%	0.02	0.02	13%	0.0155	0.024	10%	0.026	0.028	0.205	0.1
Trifluralin	Treflan	H	0.049	5%	0.0003	0.0003	10%	0.0079	0.012	52%	0.02	0.026	2.05	
Simazine	Simazine	H	0.032	5%	0.0089	0.0089	6%	0.014	0.015	17%	0.026	0.038	3525	
MCPP	Mecoprop	H	0.158	5%	0.019	0.019	3%	0.021	0.021	3%	0.012	0.012		
Propargite	Omite	I-SE	0.065	5%	0.158	0.158	--			7%	0.051	0.06	5900	
4-Nitrophenol		D	0.15	5%	0.01	0.01	--			--			190	
Bromoxynil	Buctril	H	0.107	5%	0.02	0.02	--			--			5	
Hexazinone	Velpar	H	0.049	--			39%	0.0135	0.15	--			9000	
MCPA	(several)	H	0.158	--			16%	0.011	0.015	7%	0.0315	0.033	57.5	
3,5-Dichlorobenzoic Acid		D	0.107	--			3%	0.0038	0.0038	--				
Carbaryl	Sevin	I-C	0.14	--			3%	0.16	0.16	--			60	
Dicamba I	Banvel	H	0.107	--			3%	0.016	0.016	--			1400	
Dichlobenil	Casoron	H	0.064	--			3%	0.0047	0.0047	--			246.5	
Disulfoton	Di-Syston	I-OP	0.02	--			3%	0.16	0.16	--			92.5	
EPTC	Eptam	H	0.065	--			3%	0.002	0.002	--			700	
Pronamide	Kerb	H	0.142	--			3%	0.154	0.154	--			3800	
Triclopyr	(several)	H	0.097	--			3%	0.032	0.032	--			32.5	
Aldicarb sulfone		D	0.1	--			--			14%	0.25	0.41	2100	
4,4'-DDT	DDT	I-Cl	0.06	--			--			3%	0.0036	0.0036	0.075	0.001

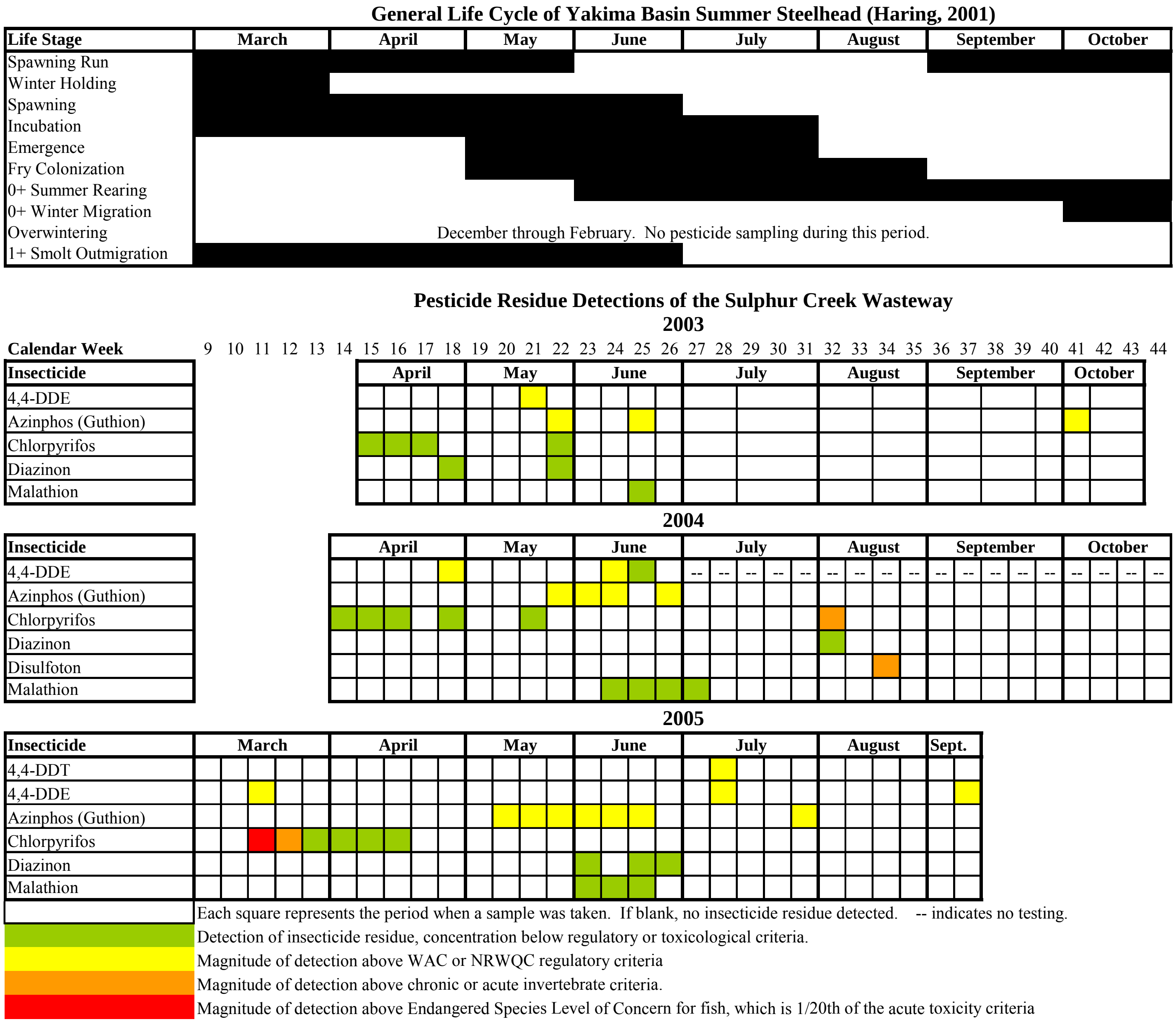

Figure 9. Summer steelhead life stage and pesticide residue detection analysis for Sulphur Creek Wasteway.

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Spring Creek

A total of 29 pesticide or degradate compounds were detected in Spring Creek: 17 herbicides, 7 insecticides, 4 degradates, and the wood preservative pentachlorophenol (Table 9).

Spring Creek pesticide residue results are presented in Figure 10. Azinphos methyl was detected with increasing frequency from 2003-2005, with a sporadic seasonal pattern. While detections occur during several life stages of summer steelhead, no detections occur in succession. All azinphos methyl detections are numerically above the National Recommended Water Quality Criterion (NRWQC) of 0.01 µg/L. One detection on June 8, 2005 approached the Endangered Species Level of Concern (ESLOC).

As observed in Sulphur Creek Wasteway, chlorpyrifos was consistently detected during the spring from 2003-2005. Early spring chlorpyrifos detections also coincided with critical life stages as reported for Sulphur Creek Wasteway. Three chlorpyrifos detections were found to be numerically above the Washington State chronic numeric standard, and one was above the WAC acute numeric standard. All of these three detections exceeded the acute invertebrate risk quotient. No detections exceeded the ESLOC.

Malathion was detected once in 2003, four times in 2004, and once in 2005. The 2004 detections occurred during spawning, incubation, emergence, fry colonization, smolt outmigration, and rearing of summer steelhead.

On June 18, 2003, carbaryl was detected at a concentration of 10 µg/L in the upper Spring Creek station, and 1.7 µg/L at the mid-Spring Creek station. The detections were above the acute and chronic invertebrate criteria of 5.6 and 1.5 µg/L, respectively. The ESLOC for carbaryl is 60 µg/L.

A single detection (0.238 µg/L) of oxyfluorfen on June 18, 2003 at the mid-Spring Creek station approached the aquatic plant LC50 for *Selenastrum capricornutum* (0.29 µg/L) and was greater than the no observable effects concentration (NOEC) criterion of 0.1 µg/L.

4,4-DDE was detected on a few occasions, and all values are numerically above the Washington State chronic standard.

Table 9. Summary of pesticide detections in Spring Creek. Concentrations reported as µg/L.

Chemical	Common Name	[1]Type	LPQL	2003, n=18			2004, n=31			2005, n=29			Criteria	
				Freq	Median	Max	Freq	Median	Max	Freq	Median	Max	ESLOC	NRWQC
2,4-D	several	H	0.107	71%	0.046	0.14	81%	0.061	0.16	62%	0.063	0.14	29	
Bromacil	Hyvar	H	0.13	48%	0.0235	0.04	45%	0.0245	0.086	--			1800	
Atrazine	Aatrex	H	0.035	33%	0.0025	0.012	42%	0.0069	0.024	69%	0.017	0.053	265	
Diuron	Karmex	H	0.193	29%	0.024	0.05	52%	0.0205	0.1	31%	0.022	0.073	97.5	
Chlorpyrifos	Dursban	I-OP	0.026	24%	0.0038	0.0088	19%	0.0115	0.077	24%	0.028	0.089	0.15	0.041
Pendimethalin	Prowl	H	0.048	24%	0.018	0.032	13%	0.064	0.169	--			6.9	
Terbacil	Sinbar	H	0.097	19%	0.0185	0.18	3%	0.055	0.055	3%	0.044	0.044	2310	
Norflurazon	Solicam	H	0.065	14%	0.012	0.027	10%	0.01	0.032	7%	0.079	0.11	405	
Azinphos methyl	Guthion	I-OP	0.052	10%	0.01435	0.022	10%	0.02	0.023	17%	0.035	0.11	0.145	0.01
Simazine	Simazine	H	0.032	10%	0.003	0.0038	6%	0.00965	0.012	14%	0.026	0.042	3525	
Malathion	several	I-OP	0.026	5%	0.013	0.013	16%	0.012	0.03	3%	0.034	0.034	0.205	0.1
4,4'-DDE		D	0.06	5%	0.0029	0.0029	7%	0.0015	0.0015	--			1.6	0.001
Pentachlorophenol	Penta	WP	0.08	5%	0.014	0.014	6%	0.00415	0.0051	--			0.75	[2]6 to 83
4-Nitrophenol		D	0.15	5%	0.0077	0.0077	--			--			190	
Alachlor	Lasso	H	0.189	5%	0.0032	0.0032	--			--			105	
Azinphos ethyl		I-OP	0.052	5%	0.052	0.052	--			--				
Bromoxynil	Buctril	H	0.107	5%	0.0056	0.0056	--			--			5	
Dimethoate	Dimethoate	I-OP	0.026	5%	0.029	0.029	--			--			310	
Endosulfan sulfate		D	0.06	5%	0.016	0.016	--			--			0.11	
Propartige	Omite	I-SE	0.065	5%	0.009	0.009	--			--			5900	
Bentazon	Basagran	H	0.132	--			35%	0.02	0.049	17%	0.052	0.07	>5000	
MCPA	several	H	0.158	--			16%	0.0078	0.016	3%	0.03	0.03	57.5	
Dichlobenil	Casoron	H	0.064	--			3%	0.015	0.015	3%	0.0085	0.0085	246.5	
Dicamba I	Banvel	H	0.107	--			3%	0.021	0.021	--			1400	
Hexazinone	Velpar	H	0.049	--			3%	0.004	0.004	--			0.049	
Diazinon	several	I-OP	0.026	--			--			10%	0.019	0.02	4.5	0.17
Prometon	Pramitol 5PS	H	0.032	--			--			10%	0.021	0.022	600	
Metolachlor	Stalwart	H	0.13	--			--			7%	0.009	0.013	195	
Aldicarb sulfone		D	0.1	--			--			3%	0.1	0.1	2100	

Results as reported by Manchester Environmental Laboratory

--Test for pesticide yielded no detections.

[1]Use type descriptors: D = degradate compound, H = herbicide, I-OC organochlorine insecticide, I-OP = organophosphorus insecticide, I-SE = sulfite ester insecticide, WP = wood preservative.

[2]Pentachlorophenol criteria range presented as a function of pH based chronic standard, $\leq e^{[1.005(pH) - 5.134]}$. pH range of 6.9 to 9.5 applied.

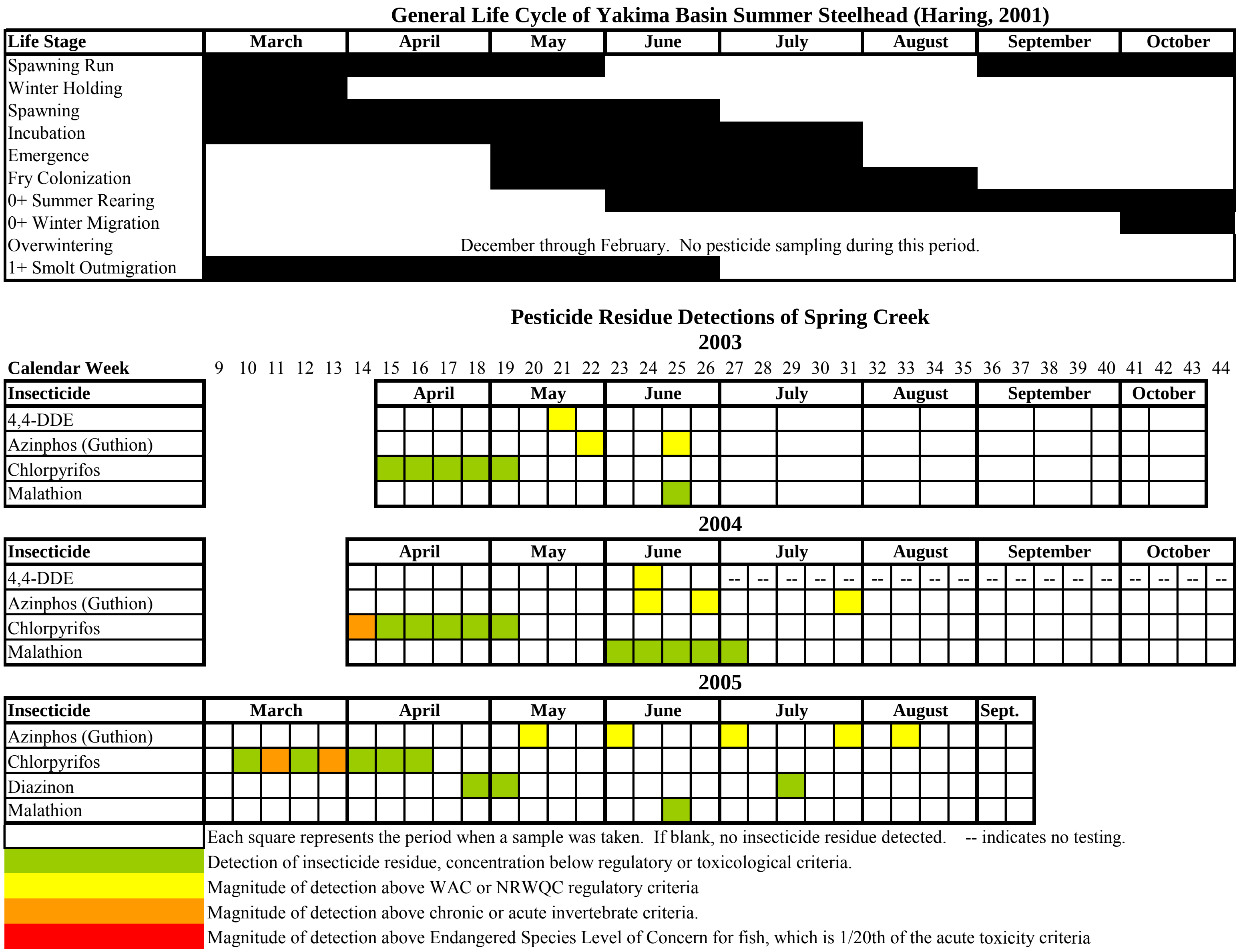

Figure 10. Summer steelhead life stage and pesticide residue detection analysis for Spring Creek.

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Detection in Relation to Use

There is general correlation between the use of a pesticide and detections measured in surface water. Table l0 presents the typical timing and application rates for a pesticide if used in a particular year. Pesticide detections in nearby waterways normally occur within 60 days of application. The notable exception is the malathion detection in Marion Drain during late July of 2004 (3.05 µg/L) which does not correspond to a typical use.

A number of factors may contribute to off-site transport of pesticides such as quantity applied, application method, storm events in relation to application, physical/chemical characteristics of the pesticide, and soil to which it is applied.

Pesticide use information in urban areas is not available, thus it is difficult to associate pesticide detections with a particular use in the Thornton Creek watershed.

Table 10. Use rate of selected chemicals in the Lower Yakima watershed, WRIA 37.

Crop Name[1]	Acres in Prod.	[2]% Crop Acres	[3]lbs. A.I. per Acre	[3]Apps. per Season	[3]% Acres Treated	Approx. Timing for App(s)	Primary Method of Application	Common Application Equipment
				Azinphos methyl				
Apple	54,925	15.7	1.00	2.50	60	June & Aug	Ground	airblast sprayer
Cherry	12,014	3.4	1.00	1.75	90	May & July	Ground	airblast sprayer
Peach[4]	1,685	0.5	0.87	1.75	50	May & July	Ground	airblast sprayer
Pear	6,988	2.0	1.00	1.00	80	April	Ground	airblast sprayer
Potato[4]	2,677	0.8	0.50	1.00	15	May	Air or chemigation	
				Chlorpyrifos				
Apple	54,925	15.7	1.75	1.00	70	April	Ground	Airblast sprayer
Asparagus	4,966	1.4	1.00	1.00	8	April	Ground	Boom sprayer
Cherry	12,014	3.4	2.00	1.00	65	March	Ground	Airblast sprayer
Corn, sweet	1,927	0.6	1.15	1.00	7	May	Ground	Boom sprayer
Pear	6,988	2.0	2.00	1.00	40	April	Ground	Airblast sprayer
Peach	1,685	0.5	0.75	1.00	30	March	Ground	Airblast sprayer
Grapes, concord	26,089	7.5	1.00	1.00	40	March	Ground	Various
Grapes, wine	15,072	4.3	1.00	1.00	40	March	Ground	Various
Mint	8,141	2.3	2.00	1.00	10	Sept	Air or ground	
				Diazinon				
Apple	54,925	15.7	2.00	1.00	< 1	April	Ground	Airblast sprayer
Cherry	12,014	3.4	2.00	1.00	13	March	Ground	Airblast sprayer
Pear	6,988	2.0	2.00	1.00	7	April	Ground	Airblast sprayer
				Endosulfan				
Apple	54,925	15.7	2.00	1.00	10	April	Ground	Airblast sprayer
Cherry	12,014	3.4	2.00	1.00	20	March	Ground	Airblast sprayer
Grapes, wine[5]	15,072	4.3	1.50	2.00	5	May	Ground	Various
Peach	1,685	0.5	2.00	1.00	50	March	Ground	Airblast sprayer
Pear	6,988	2.0	2.00	1.00	45	March	Ground	Airblast sprayer
Potato	2,677	0.8	1.85	1.00	1	Sept	Air or chemigation	
				Malathion				
Alfalfa hay	33,739	9.7	1.00	2.00	1	May	Air	
Apple	54,925	15.7	4.00	2.00	< 1	April	Ground	Airblast sprayer
Asparagus	4,966	1.4	1.00	1.00	15	August	Ground	Boom sprayer
Cherry	12,014	3.4	1.50	2.00	57	June	Ground	Airblast sprayer
Corn, field	18,704	5.4	1.00	1.00	< 5	June	Ground	Boom sprayer
Corn, sweet	1,927	0.6	1.00	1.00	< 5	June	Ground	Boom sprayer
Mint	7,047	2.3	1.00	1.00	3	June	Air or ground	
Wheat	75,068	21.5	1.00	1.00	< 5	June	Air	

[1]The crops named are any of the top 20 crops (determined by acres in production) in WRIA 37 that typically have the listed active ingredient (A.I.) applied.
[2]This column denotes the percent of total acreage that is cropped for agricultural production.
[3]If the pesticide is used in this season, this is the typical use rate.
[4]Azinphos methyl is proposed for cancellation on this crop after Sept 30, 2006.
[5]The end-use of products containing endosulfan on grapes was terminated on Dec 5, 2005.

Historical Review

Over the years, various entities have conducted pesticide investigations in Thornton Creek and the Lower Yakima watershed. The majority of studies have been conducted by the United States Geological Survey (USGS) National Water Quality Assessment Program (NAWQA). USGS data for Thornton Creek covers March 1996 through September 2005. Monitoring data from the Granger Drain (March 1999 through September 2004) are used as a comparison for the three Lower Yakima drainages in this study.

Thornton Creek

Since 1996, the USGS has periodically monitored Thornton Creek. Historical review reflects USGS data through 2002, and USGS/Ecology results for 2003-2005 (Tables 11 and 12).

The insecticide detection profile of Thornton Creek has changed over the years. Urban use (registration) restriction for chlorpyrifos (2000) and cancellation for diazinon (2004) resulted in reduction of frequency and magnitude of detections. Carbamate (carbaryl) and pyrethroid products constitute substitution compounds for the organophosphorus insecticides, including diazinon, malathion, and chlorpyrifos. The detection rate for carbaryl has risen slightly over the years, yet not in proportion to historically applied insecticides. Additionally, the magnitude of carbaryl detections has not approached the Endangered Species Level of Concern (ESLOC) or invertebrate toxicological criteria used for pesticide registration decisions.

The frequency and magnitude of herbicide detections in Thornton Creek have followed a less distinct pattern. Atrazine and simazine have been detected on a less frequent (and lower magnitude) basis from 1996 to 2005. Trifluralin was rarely detected until 2005, when it was detected in 33% of samples. The median detected value of all herbicides in 2005 is less than in 1996 and 1997. The maximum detection of trifluralin in 1997 (1.2 µg/L) was greater than the chronic rainbow trout no observable effects concentration (NOEC) of 1.14 µg/L. No other herbicide detections exceeded assessment criteria.

Table 11. Historical insecticide detection profile for Thornton Creek. Concentrations in µg/L.

USGS	1996, n=25			1997, n=15			2003, n=7			2004, n=9			2005, n=16		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Diazinon	88%	0.033	0.2	80%	0.022	0.501	43%	0.037	0.11	33%	0.042	0.044	--		
Malathion	24%	0.017	0.042	27%	0.027	0.034	14%	0.015	0.015	--			6%	0.0171	0.0171
Carbaryl	12%	0.02	0.044	7%	0.009	0.009	48%	0.0199	0.154	33%	0.2	0.48	31%	0.0096	0.0746
Chlorpyrifos	4%	0.006	0.006	13%	0.045	0.075	--			--			--		
Lindane	--			7%	0.02	0.02	--			--			--		
Ecology							2003, n=18			2004, n=31			2005, n=29		
Chemical							Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Diazinon							39%	0.025	0.09	13%	0.0145	0.095	3%	0.023	0.0023
Malathion							--			--			--		
Carbaryl							--			--			--		
Chlorpyrifos							--			--			--		
Ethoprop							--			3%	0.036	0.036	--		

-- Compound tested and no residues detected
USGS results are through Sept 14, 2005
Ecology results are through Oct 15, 2005
USGS and Ecology results are analyzed for the same suite of compounds. Compounds which were never detected are not listed.

Table 12. Historical herbicide detection profile for Thornton Creek. Concentrations in ug/L.

USGS	1996, n=25			1997, n=15			2003, n=7			2004, n=9			2005, n=16		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Prometon	100%	0.028	0.201	93%	0.08	0.12	86%	0.0175	0.0447	78%	0.015	0.04	69%	0.008	0.0109
Simazine	48%	0.0085	0.37	40%	0.02	0.201	29%	0.025	0.045	33%	0.012	0.027	38%	0.007	0.009
Trifluralin	4%	0.007	0.007	7%	0.042	1.2	14%	0.005	0.005	--			31%	0.005	0.007
Atrazine	20%	0.0036	0.005	67%	0.044	1.2	11%	0.0127	0.0127	--			--		
Dichlobenil	48%	0.04	1.2	27%	0.0375	0.13	--			--			--		
2,4-D	--			--			--			--			26%	0.0738	0.7886
Diuron	12%	0.24	0.45	--			--			--			11%	0.0192	0.0231
Triclopyr	--			7%	0.82	0.82	--			--			--		
Ecology							2003, n=18			2004, n=31			2005, n=29		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Triclopyr							78%	0.0375	0.093	42%	0.034	0.085	14%	0.026	0.067
Dichlobenil							67%	0.017	0.052	77%	0.012	0.1	83%	0.0175	0.098
2,4-D							44%	0.043	0.14	42%	0.035	0.21	17%	0.023	0.16
Diuron							44%	0.1135	0.21	23%	0.0075	0.17	28%	0.0205	0.023
Prometon							22%	0.018	0.027	23%	0.0056	0.025	38%	0.016	0.036
Simazine							17%	0.014	0.025	--			--		
Atrazine							--			--			--		
Trifluralin							--			--			34%	0.0175	0.025

-- Compound tested and no residues detected
USGS results are through Sept 14, 2005
Ecology results are through Oct 15, 2005
USGS and Ecology results are analyzed for the same suite of compounds. Compounds which were never detected are not listed.

Lower Yakima Watershed

Historical analysis (prior to 2005), yielded few results relating to Marion Drain, Sulphur Creek Wasteway, and Spring Creek. USGS results for the Granger Drain (1999-2004) were used to supplement results from the Marion Drain, Sulphur Creek Wasteway, and Spring Creek. Ecology watersheds are analyzed as a sum total of results, by year (Tables 13 and 14).

Interpreting data from several drainages of the Lower Yakima watershed is problematic. Detection frequency and median and maximum values are largely based on the number of sample points in a single year, sample design, and methods of analysis. Occurrence of pesticide residues in the Lower Yakima watershed is specific to intensity of cropping and diversity of crop profile within the drainage. Given the preceding caveats, in general it appears that:

- Chlorpyrifos detection rates are similar from 1999-2004. Azinphos methyl and malathion were consistently detected, yet the detection profile is dominated by the Granger Drain (Granger Drain represents the only data points of 1999 and 2002).
- The 4,4-DDE detection rate and magnitude was reduced following sediment delivery, mitigation efforts of Lower Yakima producers.
- Similar to Thornton Creek, the most notable exception in the detection profile is for the insecticide carbaryl. Carbaryl was frequently detected from 1999-2004 in the Granger Drain. The maximum carbaryl concentration of 4.78 µg/L occurred on July 28, 1999, and the median detected value (n=80) is 0.0137 µg/L. The lowest criterion for comparison is 1.5 µg/L for chronic invertebrate effects. The reduced detection rate in the WSDA/Ecology study is likely due to use patterns and a less sensitive laboratory detection limit.

Table 13. Historical insecticide and degradate detection profile for drainages of the Lower Yakima watershed. Concentrations in µg/L.

USGS	1999, n=13			2002, n=21			2003, n=21			2004, n=19			2005		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Carbaryl	100%	0.0334	4.78	62%	0.023	1.89	43%	0.0192	0.212	74%	0.0079	0.143			
Azinphos methyl	85%	0.0292	0.0756	38%	0.041	0.054	38%	0.02	0.179	47%	0.0144	0.0249			
Chlorpyrifos	15%	0.0016	0.0022	10%	0.0066	0.0101	14%	0.005	0.02	21%	0.0054	0.013			
Malathion	38%	0.0061	0.0369	10%	0.0663	0.125	10%	0.006	0.026	5%	0.0105	0.0105			
Disulfoton	23%	0.04	3.34	5%	0.491	0.491	10%	0.0199	0.0295	--					
Diazinon	23%	0.033	0.085	--			5%	0.0034	0.0034	11%	0.0046	0.0065			
Dimethoate	--			--			5%	0.0055	0.0055	5%	0.0036	0.0036			
Ethoprop	8%	0.017	0.017	--			--			--					
4,4-DDE	92%	0.003	0.0042	19%	0.0035	0.0043	5%	0.0018	0.0018	--					
Ecology	1999			2002			2003, n=63			2004, n=92			2005, n=87[1]		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Chlorpyrifos							29%	0.0049	0.085	25%	0.012	0.1	23%	0.024	0.4
Azinphos methyl							11%	0.017	0.023	8%	0.023	0.042	13%	0.035	0.14
Dimethoate							11%	0.0064	0.13	5%	0.027	0.14	--		
Malathion							6%	0.0165	0.024	16%	0.019	3.05	16%	0.0225	0.23
Diazinon							5%	0.0066	0.007	1%	0.0082	0.0082	7%	0.0165	0.023
Propargite							5%	0.015	0.158	1%	2.144	2.144	4%	0.06	0.092
Endosulfan S.							3%	0.188	0.36	--			--		
Carbaryl							2%	0.14	0.14	1%	0.16	0.16	--		
Ethoprop							2%	0.046	0.046	7%	0.049	0.18	6%	0.03	0.27
Endosulfan II							2%	0.004	0.004	--			--		
Aldicarb sulfone							--			--			6%	0.18	0.41
Disulfoton							--			2%	0.0915	0.16	--		
4,4'-DDE							3%	0.0029	0.0029	4%	0.0018	0.0028	4%	0.0023	0.012

-- Compound tested and no residues detected
[1]n = 91 for organophosphorus compounds
USGS results are through Sept 14, 2004
Ecology results are through Oct 15, 2005
USGS and Ecology results are analyzed for the same suite of compounds. Compounds which were never detected are not listed.

Table 14. Historical herbicide detection profile for the Lower Yakima watershed. Concentrations in ug/L.

USGS	1999, n=13			2002, n=21			2003, n=21			2004, n=19			2005		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
Atrazine	100%	0.0258	0.154	100%	0.0132	0.0934	95%	0.012	0.061	100%	0.0104	0.0306			
Simazine	69%	0.0095	0.226	43%	0.0051	0.0168	38%	0.0039	0.0082	74%	0.0061	0.0311			
Trifluralin	92%	0.0115	0.0822	43%	0.0089	0.0522	38%	0.0065	0.0256	42%	0.0076	0.029			
2,4-D	--			67%	0.1679	1.6748	--			--					
Bromacil	--			61%	0.022	0.029	--			--					
Diuron	--			67%	0.0231	0.3544	--			--					
Pendimethalin	8%	0.0099	0.0099	--			--			--					
Prometon				10%	0.0031	0.0035	--			21%	0.0318	0.040			
Terbacil	--			10%	0.01	0.015	--			--					
Ecology	1999			2002			2003, n=63			2004, n=92			2005, n=87		
Chemical	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max	Freq	Med	Max
2,4-D							81%	0.06	0.29	80%	0.065	0.41	61%	0.07	2.2
Atrazine							51%	0.0047	0.017	50%	0.0087	0.142	68%	0.019	0.053
Bromacil							43%	0.019	0.07	47%	0.03	0.141	5%	0.045	0.087
Terbacil							38%	0.063	0.26	32%	0.063	0.37	44%	0.0775	0.46
Pendamethalin							30%	0.021	0.1	10%	0.028	0.169	9%	0.028	0.065
Diuron							27%	0.023	0.06	55%	0.034	0.171	33%	0.033	0.27
Trifluralin							8%	0.0062	0.016	5%	0.0079	0.023	25%	0.02	0.026
Simazine							6%	0.003	0.0089	10%	0.013	0.031	25%	0.025	0.042
Prometon							--			2%	0.0218	0.036	4%	0.021	0.022

-- Compound tested and no residues detected
USGS results are through Sept 14, 2004
Ecology results are through Oct 15, 2005
USGS and Ecology results are analyzed for the same suite of compounds. Compounds which were never detected are not listed.

Discussion and Conclusions

Three years of monitoring data (2003-2005) have been compiled. Several general conclusions can be drawn from the data in regards to (1) the urban and agricultural drainages and (2) comparison to the EPA risk quotients to assess the potential risk of pesticides.

The majority of the detected pesticides did not exceed a water quality criterion or risk quotient. Of the 51 pesticides or degradates detected, ten were above assessment criteria: 4,4-DDE, 4,4-DDT, azinphos methyl, carbaryl, chlorpyrifos, diazinon, disulfoton, endosulfan sulfate, malathion, and oxyfluorfen.

- Chlorpyrifos, malathion, and endosulfan sulfate exceeded the EPA Endangered Species Level of Concern.
- Azinphos methyl, chlorpyrifos, diazinon, endosulfan sulfate, 4,4-DDE, and 4,4-DDT exceeded either the Washington State Water Quality Standards or the EPA National Recommended Water Quality Criteria.
- Single detections of carbaryl and disulfoton exceeded EPA invertebrate criteria.
- A single detection of oxyfluorfen exceeded the EPA chronic aquatic plant criterion.

Urban

Urban uses were restricted for chlorpyrifos in 2000, and were cancelled for diazinon in 2004. The phase out of these chemicals has resulted in reduced detection frequency and magnitude in Thornton Creek. Carbaryl, a potential replacement for diazinon, was not detected above the method detection limits of this study. The USGS has detected carbaryl at concentrations below effects levels used for pesticide registration decisions (USGS, 2006b). For the Thornton Creek downstream monitoring site, no EPA risk quotients were exceeded for acute or chronic toxicity to fish or aquatic invertebrates.

Agriculture

In the three agricultural drainages – Marion Drain, Sulphur Creek Wasteway, and Spring Creek – several pesticide residues were above assessment criteria, yet few were above criteria on a multi-year basis. These compounds include the currently registered insecticides, azinphos methyl, chlorpyrifos, and malathion. These pesticides were detected in greater frequency with seasonal use:

- Chlorpyrifos was detected in the spring in all drainages, and in the fall in Marion Drain. The detections of chlorpyrifos in September exceeded Washington State Water Quality Standards in 2003-2005 as well as the Endangered Species Level of Concern in 2005.
- Malathion and azinphos methyl were detected during the summer in all three drainages. Malathion exceeded the Endangered Species Level of Concern in Marion Drain in 2004 and 2005. Azinphos methyl exceeded the National Recommended Water Quality Criteria in both Sulphur Creek Wasteway and Spring Creek in 2003-2005.

The presence of Mid-Columbia summer steelhead in the Yakima River basin is influenced by temperature and other habitat conditions of the agricultural drainages. Midsummer (late June through August) temperatures in Marion Drain, Sulphur Creek Wasteway, and Spring Creek may represent a partial thermal blockage to steelhead migration (Strickland, 1967, as cited by Stabler, 1981). The maximum temperatures of these drainages are also near the sustained lethal threshold for adult steelhead (Coutant, 1970). A result of this temperature regime is delayed upstream migration of summer steelhead to the Yakima River (Freudenthal et al., 2005), reducing the probability of steelhead presence in local drains until September.

Elevated spring temperatures in the downstream Lower Yakima River tributaries restrict juvenile rearing habitat (Freudenthal et al., 2005). Yet, these tributaries often have lower maximum temperatures than the mainstem, and struggling juveniles and kelts may use these tributaries as temporary thermal refuge.

Azinphos methyl and malathion detections occurred when summer maximum temperatures may restrict summer steelhead occupation of monitored stream reaches. If summer steelhead are present, elevated temperatures outside of their optimal range may make the steelhead more susceptible to pesticide toxicity. Chlorpyrifos detections exceeded either the Endangered Species Level of Concern or the Washington State Water Quality Standards during a period of expected steelhead occupation (spring and fall).

Chlorpyrifos and malathion detections were above EPA chronic invertebrate risk quotients (RQs). Chlorpyrifos residues in Marion Drain were above the RQ for three consecutive weeks in fall 2004, and two consecutive weeks in fall 2005. Similarly, malathion residues in Marion Drain were above the chronic RQ for two of four weeks in 2005. A similar, but reduced, pattern of malathion and chlorpyrifos concentrations were observed in Sulphur Creek Wasteway and Spring Creek. Repetitive chronic detections of chlorpyrifos and malathion indicate a potential risk to the quantity and quality of macroinvertebrate populations in Marion Drain, Sulphur Creek Wasteway, and Spring Creek.

During this 2003-2005 study, azinphos methyl was frequently detected at a magnitude above the National Recommended Water Quality Criterion, yet no detections exceeded the Endangered Species Level of Concern. All registered uses of azinphos methyl are proposed for cancellation as of 2010.

The frequency and magnitude of 4,4-DDE, and 4,4-DDT detections appear to have declined when compared to historical data of nearby drainages. The reduction is likely due to sediment delivery and mitigation efforts of Lower Yakima agricultural producers.

Co-occurrence and Sub-Lethal Effects

The EPA and Washington State assessment criteria used in this study are based on evaluating the effects of a specific chemical on an organism. The criteria do not take into account the additive or possible synergistic effects of pesticide mixtures or sub-lethal effects, such as the olfactory response of salmonids to certain pesticides.

Table 15 illustrates that, in some cases, multiple detections of pesticides occurred in a single sample.

This study did not conduct analyses for other anthropogenic (human-caused) compounds present in these urban and agricultural drainages. Future studies will need to evaluate the potential effects of multiple stressors and sub-lethal stressors to threatened/endangered salmonids.

Table 15. Number of pesticides detected in a single sample by site[1].

Watershed	Site	2003				2004				2005				2003-2005			
		n	Mn	Av	Mx	n	Mn	Av	Mx	n	Mn	Av	Mx	N	Mn	Av	Mx
Cedar-Sammamish																	
Thornton Creek 3	Main	18	0	5	9	31	0	3	7	29	0	3	8	78	0	3	9
Thornton Creek 2	SF	18	1	3	5									18	1	3	5
Thornton Creek 1	NF	18	0	4	8	16	0	3	6	15	0	3	5	49	0	3	8
Lower Yakima																	
Marion Drain 2	DS	21	0	6	13	30	0	6	11	29[2]	0	4	10	80	0	5	13
Marion Drain 1	US	12	1	5	7									12	1	3	7
Sulphur Creek W.	Main	21	0	4	11	31	1	5	11	29	2	5	9	81	0	5	11
Spring Creek 3	DS	21	0	3	9	31	0	4	10	29	1	3	6	81	0	3	10
Spring Creek 2	MS	12	1	5	9					15	0	3	6	27	0	4	9
Spring Creek 1	US	12	1	6	14	15	0	4	11					27	0	5	14
Total Events		153				154				146				453			

Main = Mainstem of river, representing reach terminating at receiving waterbody (Lake Washington for Thornton Creek, the Lower Yakima River for Sulphur Creek Wasteway).
SF = South Fork Thornton Creek
NF = North Fork Thornton Creek
DS = Downstream, representing reach terminating at receiving waterbody (Lower Yakima River in all cases).
MS = Midstream
US = Upstream
[1]There are minor variations in the number of analyses conducted per sample event due to shipping or analytical difficulties.
[2]Additional four weeks of organophosphorus pesticide sampling (Sept-Oct) is not included in the total.
n = number
Mn = minimum
Av = average
Mx = maximum

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Appendices

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Appendix A. Monitoring Locations

Table A-1. Station locations and descriptions for Thornton Creek, Marion Drain, Spring Creek, and Sulphur Creek Wasteway (Positions shown in decimal fraction).

Site	Years Sampled	Latitude	Longitude	Location Description
Thornton 1	2003-2005	47.7121	122.2886	NE 110th Street upstream of culvert
Thornton 2	2003	47.7069	122.2889	Foot bridge upstream of culvert
Thornton 3	2003-2005	47.7128	122.2747	Downstream of footbridge near Mathews Park
Marion 1	2003	46.325	120.438	Downstream side of bridge at Campbell Rd
Marion 2	2003-2005	46.3306	120.1989	Upstream of bridge at Indian Church Rd
Spring 1	2003, 2004	46.2881	119.7684	Downstream side of culvert below Evans Rd
Spring 2	2003, 2005	46.2583	119.7101	Downstream of the crossing with McCready Rd
Spring 3	2003-2005	46.2344	119.6845	10' downstream of the Chandler Canal overpass
Sulphur 1	2003-2005	46.2513	120.019	Downstream side of bridge at Holaday Rd

Datum = NAD 83

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Appendix B. Crop Area Estimation

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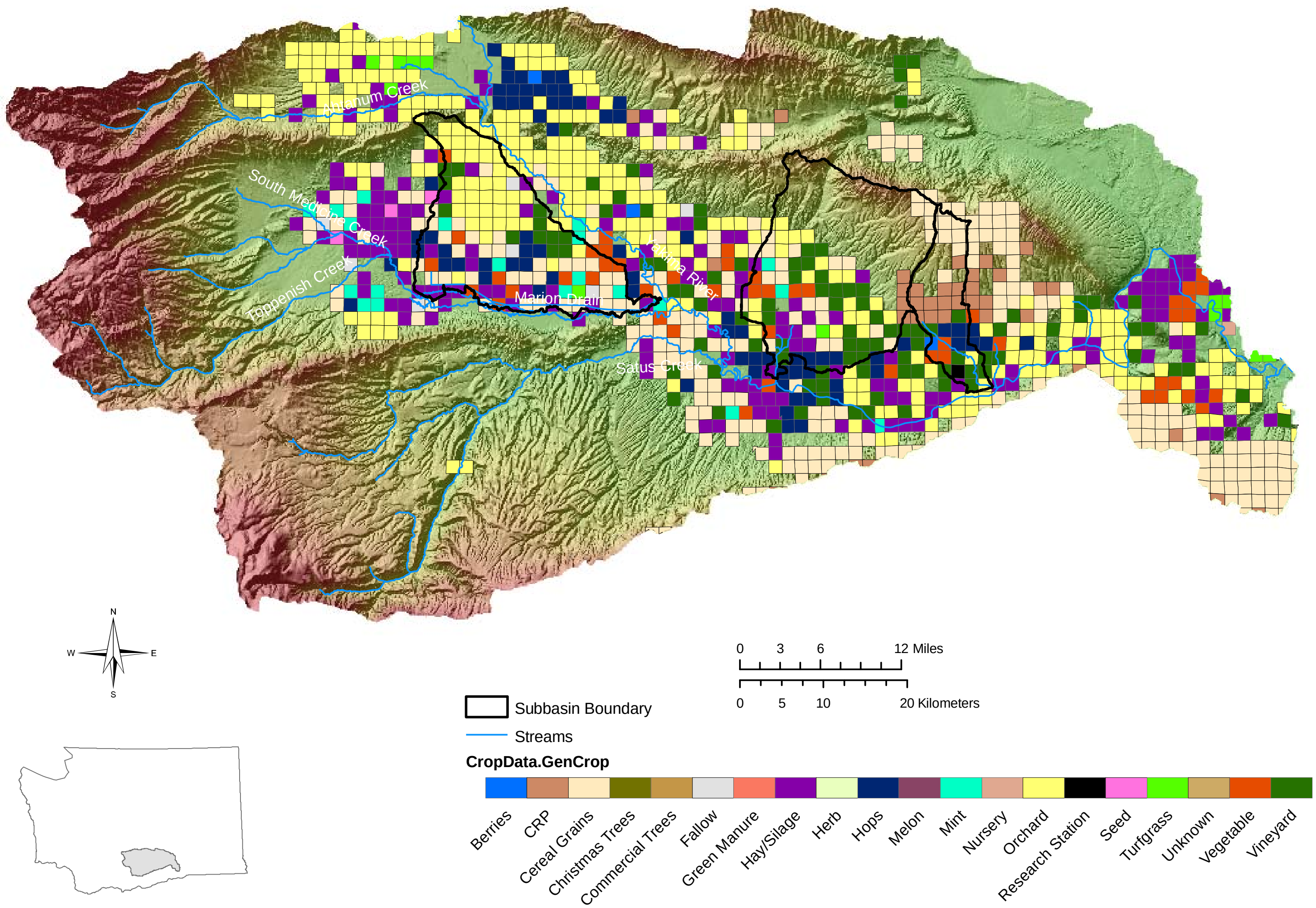

Figure B-1. Crops of the Lower Yakima watershed.

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Table B-1. Marion Drain

Crop	Area (acres)	Watershed Percent Area
Apple	8,076	9.41%
Hops	7,581	8.84%
Corn, Field	7,580	8.84%
Wheat	7,011	8.17%
Alfalfa, Hay	4,793	5.59%
Mint	3,849	4.49%
Grape, Concord	3,500	4.08%
Fallow	2,318	2.70%
Asparagus	995	1.16%
Potato	795	0.93%
Bean, Green	609	0.71%
Grass, Hay	547	0.64%
Pear	500	0.58%
Nectarine/Peach	386	0.45%
Market Crops	363	0.42%
Cherry	281	0.33%
Squash	216	0.25%
Oat	180	0.21%
Dill	145	0.17%
Bean, Dry	133	0.15%
Nursery, Ornamental	121	0.14%
Onion	109	0.13%
Golf Course	99	0.12%
Unknown	80	0.09%
Plum	75	0.09%
Cabbage	69	0.08%
Bluegrass, Seed	51	0.06%
Pea, Green	47	0.06%
Triticale	42	0.05%
Christmas Tree	35	0.04%
Pepper	35	0.04%
Clover, Hay	31	0.04%
Cabbage, Seed	30	0.03%
Barley	14	0.02%
Carrot, Seed	13	0.02%
Apricot	12	0.01%
Pumpkin	11	0.01%
Total Crop Area	50,735	
Watershed Area	85,786	
Percent Agriculture		59%

Table B-2. Sulphur Creek Wasteway

Crop	Area (acres)	Watershed Percent Area
Grape, Concord	7,869	7.64%
Apple	5,342	5.19%
Corn, Field	4,809	4.67%
Alfalfa, Hay	3,610	3.50%
Grape, Wine	3,561	3.46%
Wheat	2,696	2.62%
CRP	1,261	1.22%
Fallow	1,092	1.06%
Asparagus	1,057	1.03%
Cherry	939	0.91%
Hops	903	0.88%
Peppermint	606	0.59%
Sorghum, Hay	546	0.53%
Grass, Hay	226	0.22%
Pear	206	0.20%
Triticale	166	0.16%
Squash	157	0.15%
Nursery	147	0.14%
Nectarine	146	0.14%
Unknown	110	0.11%
Golf Course	108	0.11%
Barley	81	0.08%
Watermelon	75	0.07%
Rye	64	0.06%
Oat	48	0.05%
Plum	43	0.04%
Pasture	34	0.03%
Market Crop	26	0.02%
Pumpkin	19	0.02%
Apricot	17	0.02%
Carrot, Seed	13	0.01%
Bulb, Iris	5	0.00%
Total Crop Area	35,980	
Watershed Area	103,010	
Percent Agriculture		35%

CRP = Conservation Reserve Program

Table B-3. Spring Creek

Crop	Area (acres)	Watershed Percent Area
CRP	3,419	12.49%
Wheat	3,375	12.33%
Grape, Wine	1,919	7.01%
Grape, Concord	1,676	6.12%
Apple	1,043	3.81%
Hops	840	3.07%
Research Station, WSU	521	1.90%
Cherry	401	1.46%
Alfalfa, Hay	113	0.41%
Squash	96	0.35%
Sorghum, Hay	92	0.34%
Pumpkin	68	0.25%
Fallow	65	0.24%
Currant	59	0.22%
Blueberry	58	0.21%
Potato	53	0.19%
Triticale	42	0.15%
Corn, Silage	34	0.13%
Asparagus	27	0.10%
Pasture	24	0.09%
Caneberry	19	0.07%
Nursery, Grape	6	0.02%
Total Crop Area	13,947	
Watershed Area	27,372	
Percent Agriculture		51%

CRP = Conservation Reserve Program
WSU = Washington State University

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Appendix C. Quality Assurance/Control

A rigorous review of sample analysis, quality assurance and quality control (QA/QC), and performance detection limits has been presented in Burke et al. (2005), Anderson et al. (2004), and Johnson and Cowles (2003). A summary of analytical considerations is presented in this section.

Data Qualification

Data may be qualified if one or more analytical factors affect confidence in the prescribed data value. Manchester Environmental Laboratory qualifies data according to the National Functional Guidelines for Organic Data Review (EPA 1999, 2005). Data qualification is presented in Table C-1.

Table C-1. Data qualification.

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

MEL, 2000; EPA, 2005

The multitude of reasons for data qualification are explained in the National Functional Guidelines documents (EPA 1999, 2005). The most frequent reason for a 'J' qualification involves confirmed sample identification which has an estimated value below the practical quantitation limit (PQL). 'NJ' designation is most frequently assigned when confirmation between the AED and GC/MS is not successful.

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 lower PQL (reporting detection limit) for these compounds was very low and often unachievable, thus the samples were frequently rejected. Subsequently, the PQL was raised. The chlorophenoxy herbicides, dinoseb and picloram, typically experience highly variable recoveries and are routinely qualified in samples and method blanks. Demeton-s, oxyfluorfen, norflurazon, fluridone, cyanazine, hexazinone, and dimethoate historically do not perform well because of the uncertainty of the analytical behavior of these compounds, and they are normally qualified as estimates.

Poor performing analytes were normally rejected, UJ or NJ qualified. Except for a specific exception, the preceding qualifications exclude results from analysis in the main body of the report. Data with a higher degree of uncertainty were not compared to promulgated or recommended aquatic life criteria values. The data qualifier, or lack thereof, is available in Ecology's Environmental Information Management database (www.ecy.wa.gov/eim/).

Diuron, an herbicide, is a specific instance for which NJ qualified data are accepted. Diuron and linuron break down to the same product when analyzed by the AED and GC/MS. Propanil also breaks down to similar products, yet may be definitively identified on the GC/MS (Westerlund, personal communication, March 2006). We cannot be sure that what we are observing is diuron, although that is the most frequently used urea pesticide. EPA considered the identification of diuron, linuron, and propanil in the propanil registration eligibility decision (EPA, 2003a). In the review, EPA determined all residues convertible to the diuron and linuron breakdown product would be included in the tolerance expression …'because no validated enforcement method was available for the quantification of individual components from residues of concern' (EPA, 2003a). Identification of diuron, linuron, and propanil was not addressed in the diuron Reregistration Eligibility Decision (RED) (EPA, 2003b).

The identification of diuron and linuron will no longer be an issue in the 2006 sample season. Recent purchase of a liquid chromatography/mass spectrometer (LCMS) by Manchester Laboratory will provide positive identification of diuron and linuron.

Application of 'J' Qualified Values

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

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

Quality Assurance and Quality Control

The quality assurance and quality control protocol (QA/QC) employs blanks, replicates, surrogates, laboratory control samples, and matrix spike/matrix spike duplicates (MS/MSD) (See Burke et al., 2005 and Anderson et al., 2004). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components.

Field and Method Blanks

No target compounds were detected in field blanks. Field blanks and replicates are submitted as 'blind' samples to the laboratory.

Occasionally, 3-hydroxycarbofuran was detected in method blanks. When this occurred, method blanks and samples were re-run to confirm the detection. 3-hydroxycarbofuran was never confirmed in field samples, and this analytical inconsistency of method blanks did not affect sample results.

Surrogate Analysis

Surrogate compounds are selected to evaluate a particular chemical class (Table C-2). Deionized water is fortified with surrogate compounds to assess analyte recovery under laboratory conditions. A given concentration of analyte is added to solution and analyzed under the same conditions as field samples. The difference between the true value and that obtained in analysis is the surrogate recovery. Surrogate criteria were set and modified according to EPA Contract Laboratory Program methodologies (EPA 1999, 2005). Contract Laboratory Program limits for pesticides in general are 30% to 150% (EPA 1999, 2005). When surrogate recoveries violated their respective control limits, the analyst flagged results with a data qualifier or rejected the analysis.

Table C-2. Control limits for pesticide surrogate recoveries.

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

N = nitrogen containing
Cl = chlorinated
OP = organophosphorus

Surrogate performance for 2003-2005 sample analyses is presented in Figure C-1. Surrogate compounds, number of tests, and recovery values comprise the X and Y axes, respectively. The box represents the 25% and 75% frequency distribution. Median value is the triangle contained within the box, and outliers (whiskers) are calculated as ± 2 standard deviations of the mean (σ), or approximately 95% of all values. Thus, each outlier (upper, lower) represents 2.5% of values.

The box plots illustrate the ability of Manchester Environmental Laboratory to accurately analyze standards, and the tendency of organic analysis to underestimate environmental concentration. The median and majority of all values fall within the control limits established by Manchester Laboratory. Outlier values are outside of control limits for nitrogen, phosphorous, and phenol-herbicide surrogates. Data associated with these criteria were qualified as estimates.

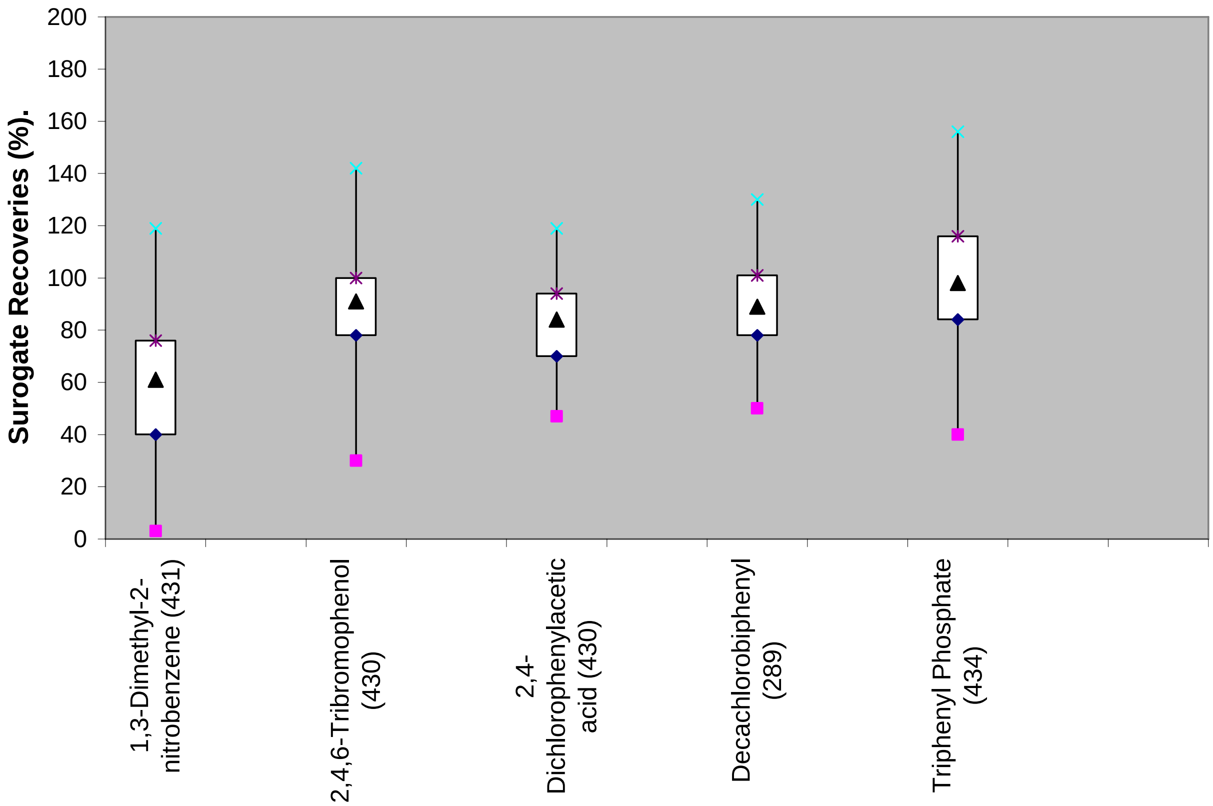

Figure C-1. Surrogate recovery.

Laboratory Control Samples

Laboratory control samples (LCS) estimate the ability to correctly quantify an analyte, without matrix effects. LCS contain deionized water and target analytes. LCS was performed for all compounds of interest at least once, and their concentrations were reported by the laboratory as a percent recovery. While a useful analysis, LCS does not represent actual sample conditions (matrix effects) and compounds are qualified as estimates only if the surrogate or matrix spike/ matrix spike duplicate results are in agreement.

The percent recovery for select LCS are presented in Figure C-2. Due to interference and coelution issues, an LCS for all compounds was not conducted during every analytical run. The median analyte recoveries for azinphos methyl, chlorpyrifos, diazinon, diuron, and malathion were less than 100%. Median recoveries for endosulfan and 4,4'-DDT + 4,4'-DDE were 106 and 109%, respectively. Endosulfan was rarely detected during 2003 to 2005, and no detections occurred simultaneously with outlier LCS values.

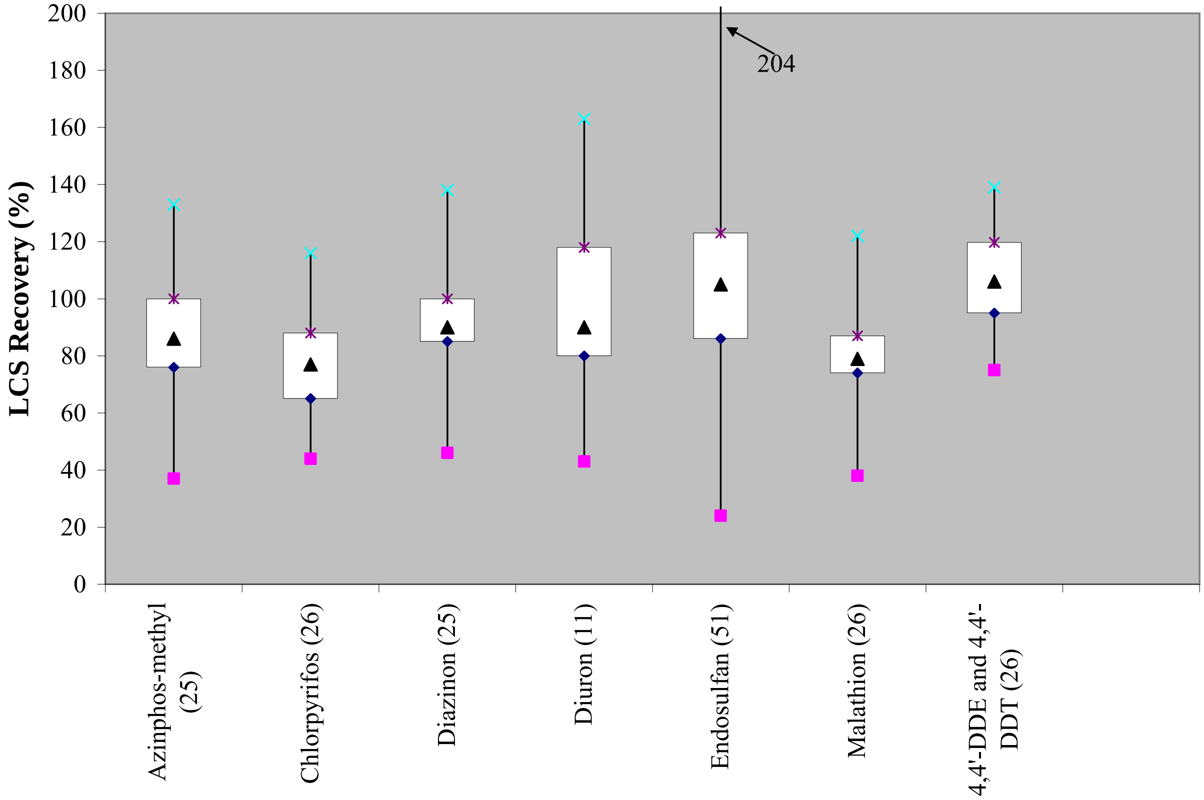

Figure C-2. LCS performance, 2004-2005.

Matrix Spike and Matrix Spike Duplicates

Matrix spike and matrix spike duplicates (MS/MSD) were performed by collecting a volume of water, in duplicate, and spiking with a Manchester Laboratory standard mixture. Pesticide analysis required three spiking mixtures, which were applied on a rotating basis. Only one spiking mixture was required for herbicides. MS/MSDs are an excellent measure of the complete analytical process. Results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency, and analyte recovery. LCS and MS/MSD are best used in combination to evaluate analytical bias. MS/MSD results are presented in Table C-3.

Overall, the average recovery of MS/MSD samples was acceptable, and the relative percent difference (RPD) between samples very low. The average recovery of selected MS/MSD samples was 109%, and the average RPD was 10%.

Table C-3. MS/MSD results, RPD, and mean RPDs for selected pesticides (µg/L).

Chemical	MS	MSD	RPD
4,4'-DDE	79	100	23
	86	83	4
	62	66	6
	80	85	6
	77	95	21
		Mean =	12

Chemical	MS	MSD	RPD
4,4'-DDT	121	120	1
	116	131	12
	83	99	18
	84	122	37
	0	0	0
		Mean =	13

Chemical	MS	MSD	RPD
Azinphos methyl	74	79	7
	91	102	11
	120	101	17
	73	75	3
	108	125	15
	179	192	7
	91	93	2
	98	107	9
		Mean =	9

Chemical	MS	MSD	RPD
Chlorpyrifos	140	117	18
	62	64	3
	111	112	1
	115	137	17
	106	102	4
	73	97	28
	65	69	6
	68	72	6
	64	69	8
		Mean =	10

Chemical	MS	MSD	RPD
Diazinon	88	106	19
	98	100	2
	127	130	2
	108	118	9
	89	95	7
	103	100	3
	145	158	9
	94	103	9
	96	102	6
		Mean =	7

Chemical	MS	MSD	RPD
Diuron	125	131	5
	175	176	1
	108	86	23
	101	99	2
		Mean =	7

Chemical	MS	MSD	RPD
Endosulfan	126	175	33
	266	213	22
	103	140	30
	105	110	5
	151	182	19
	109	126	14
	118	126	7
	130	144	10
	104	120	14
	177	195	10
	103	98	5
	100	103	3
		Mean =	14

Chemical	MS	MSD	RPD
Malathion	182	143	24
	57	57	0
	126	138	9
	133	153	14
	111	102	8
	78	78	0
	106	113	6
	89	91	2
	80	85	6
	110	103	7
		Mean =	8

Replicate Samples

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

Nineteen replicate sets were analyzed. Of those, 15 were consistently identified at the sample qualification level (unqualified; J and NJ qualified estimates) and are presented in Table C-4. One sample, included in Table C-4, is an inconsistent replicate set where the sample was J qualified and the replicate was NJ qualified. Three of 19 replicate sets had inconsistent detections (result/no result) and are presented in Table C-5.

Table C-4. Consistently detected replicate results, RPD, and mean RPDs for selected pesticides (µg/L).

Chemical	Sample		Replicate		RPD
Azinphos methyl	0.034	J	0.042	J	21.05
	0.0064	J	0.0064	J	0.00
	0.017	J	0.017	J	0.00
			Mean =		7.02
Chemical	**Sample**		**Replicate**		**RPD**
Chlorpyrifos	0.056		0.059		5.22
	0.0092	J	0.0089	J	3.31
	0.017	J	0.017	J	0
	0.006	J	0.006	J	0
	0.012	J	0.013	J	8
	0.021	J	0.023	J	9.09
			Mean =		4.3
Chemical	**Sample**		**Replicate**		**RPD**
Malathion	0.02	J	0.02	J	0.00
	0.034	J	0.031	J	9.23
	0.02	J	0.02	J	0.00
			Mean =		3.08
Chemical	**Sample**		**Replicate**		**RPD**
Pentachlorophenol	0.011	J	0.01	J	9.52
	0.018	J	0.012	J	40.00
	0.022	J	0.014	J	44.44
	0.017	J	0.015	NJ	12.50
			Mean =		26.62

Table C-5. Inconsistently detected replicate results, RPD, and mean RPDs for select compounds.

Chemical	Sample		Replicate		RPD
Azinphos methyl	0.032	U	0.0019	J	177.58
Chlorpyrifos	0.0013	J	0.026	U	180.95
Chlorpyrifos	0.0051	J	0.0058	U	12.84
Pentachlorophenol	0.017	J	0.015	NJ	12.50
					95.97

The rate of consistent to inconsistent replicate sets is similar to results of USGS-NAWQA replicate analysis (1992-1997 samples) when the average pesticide concentration was less than 0.1 μg/L (~20%; Martin, 2002). In the USGS study, and this analysis, the associated error of inconsistent replicate sets precludes use in variability analysis. Inconsistent replicate sets had a very high mean RPD, 95.97%.

The RPD of pentachlorophenol (Penta) was higher than other analytes. Penta RPD ranged from 12.5% to 180.95%. This is due to estimation of values at low levels and difficulty of identification due to unidentified organic materials (Bob Carrell, personal communication, 2006). Chemical specific RPDs for other analytes ranged from 0 to 21%.

Overall, the average RPD of consistent replicate sets was very low, 10%. Similarly, the median pooled standard deviation is 14.35%. This value is similar to the NAWQA median pooled relative standard deviation of 15% at concentrations < 0.01μg/L, 13% at concentrations near 0.1 μg/L, and 12% at concentrations near 0.1 μg/L (Martin, 2002)

Method, Estimated, and Practical Quantitation Limits

Method, estimated, and performance practical quantitation limits were determined for this study (Table C-6). Method detection limits (MDLs) were calculated by EPA and Manchester Environmental Laboratory procedures according to 40 CFR Part 136 (see EPA, 1996, 2000, 2005; and MEL, 2000). The target MDL provided by EPA is for illustrative purposes only; actual MDLs will vary by laboratory. The MDL is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom (40 CFR Part 136).

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

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

In some instances, Manchester Laboratory analysts were able to detect pesticides below the EPA method, Manchester method, and Manchester estimated detection limits. This was due to the use of larger volume injections during the 2003-2005 analyses.

Table C-6. Method detection, estimated detection, and practical quantitation limits (μg/L).

Chemical	[1]EPA	[2]Manchester		[3]WSDA		
				2003	2004	2005
	MDL	MDL	EDL	LPQL	LPQL	LPQL
1-Naphthol				0.19	0.13	
2,3,4,5-Tetrachlorophenol	0.022	0.022	0.014	0.087	0.079	0.081
2,3,4,6-Tetrachlorophenol	0.023	0.018	0.014	0.087	0.079	0.081
2,4,5-T	0.033	0.018	0.017	0.125	0.079	0.081
2,4,5-TP (Silvex)	0.033	0.0099	0.022	0.125	0.079	0.081
2,4,5-Trichlorophenol	0.025	0.02	0.017	0.5	0.079	0.081
2,4,6-Trichlorophenol	0.025	0.019	0.017	0.495	0.079	0.081
2,4-D	0.042	0.019	0.028	0.16	0.079	0.0805
2,4-DB	0.05	0.022	0.031	0.19	0.079	0.081
2,4'-DDD	0.02	0.02	0.038	0.018	0.079	0.0825
2,4'-DDE	0.01	0.01	0.037	0.018	0.079	0.0825
2,4'-DDT	0.02	0.02	0.033	0.018	0.079	0.0825
3,5-Dichlorobenzoic Acid	0.042	0.017	0.024	0.16	0.079	0.081
3-Hydroxycarbofuran				0.19	0.13	0.1
4,4'-DDD	0.02	0.02	0.038	0.018	0.079	0.0825
4,4'-DDE	0.02	0.02	0.03	0.018	0.079	0.0825
4,4'-DDT	0.03	0.03	0.033	0.018	0.079	0.0825
4-Nitrophenol	0.073	0.023	0.036	0.29	0.079	0.081
Acephate					1.594	1.6
Acifluorfen (Blazer)	0.15	0.15	0.088	0.64	0.079	0.081
Alachlor	0.1	0.1	0.16	0.335	0.112	0.12
Aldicarb				0.19	0.13	0.1
Aldicarb sulfone+sulfoxide				0.19	0.13	0.25
Aldicarb sulfone						0.1
Aldicarb sulfoxide						0.1
Aldrin	0.006	0.006	0.029	0.018	0.079	0.0825
Alpha-BHC	0.03	0.03	0.023	0.018	0.079	0.0825
Ametryn	0.04	0.04	0.03	0.033	0.031	0.033
Atraton	0.13	0.13	0.03	0.052	0.047	0.049
Atrazine	0.05	0.05	0.03	0.039	0.032	0.033
Azinphos methyl (Guthion)	0.025	0.02	0.01	0.053	0.05	0.052
Azinphos Ethyl	0.02	0.025	0.01	0.053	0.05	0.052
Bendiocarb				0.19	0.13	0.25
Benefin	0.15	0.15	0.07	0.05	0.047	0.049
Bensulide					14.187	1.6
Bentazon	0.006	0.0064	0.038	0.235	0.079	0.081
Benzamide, 2,6-dichloro-				0.22		
Beta-BHC	0.03	0.03	0.023	0.018	0.079	0.0825
Bolstar (Sulprofos)	0.011	0.02	0.01	0.023	0.022	0.023
Bromacil	0.27	0.27	0.08	0.135	0.126	0.13
Bromoxynil	0.042	0.022	0.015	0.16	0.079	0.081
Butachlor	0.16	0.16	0.19	0.199	0.189	0.2

(continued)

Table C-6, continued

Chemical	[1]EPA	[2]Manchester		[3]WSDA		
				2003	2004	2005
	MDL	MDL	EDL	LPQL	LPQL	LPQL
Butylate	0.14	0.14	0.13	0.066	0.063	0.065
Captafol	0.25	0.25	0.041	0.063	0.394	0.415
Captan	0.18	0.18	0.048	0.089	0.213	0.225
Carbaryl				0.19	0.13	0.1
Carbofuran				0.19	0.13	0.1
Carbophenothion	0.009	0.009	0.01	0.033	0.031	0.033
Carboxin	0.41	0.41	0.14	0.199	0.189	0.2
Chlorothalonil (Daconil)	0.18	0.18	0.08	0.079	0.075	0.078
Chlorpropham	0.26	0.26	0.13	0.132	0.127	0.13
Chlorpyrifos	0.004	0.004	0.011	0.026	0.025	0.026
Cis-Chlordane (Alpha-Chlordane)	0.04			0.017	0.079	0.0825
Cis-Nonachlor	0.035			0.018	0.079	0.0825
Coumaphos	0.01	0.01	0.011		1.504	1.6
Cyanazine	0.06	0.06	0.02	0.05	0.047	0.049
Cycloate	0.19	0.19	0.13	0.066	0.063	0.065
Dacthal (DCPA)	0.033	0.008	0.019	0.125	0.079	0.081
Delta-BHC	0.035	0.03	0.023	0.018	0.079	0.0825
Demeton O+S						0.023
Demeton-O	0.021	0.021	0.008	0.033	0.022	0.022
Demeton-S	0.07	0.08	0.008	0.033	0.022	0.022
Di-allate (Avadex)	0.17	0.17	0.16	0.345	0.221	0.23
Diazinon	0.014	0.014	0.009	0.027	0.026	0.026
Dicamba I	0.042	0.022	0.028	0.16	0.079	0.081
Dichlobenil	0.06	0.06	0.1	0.065	0.063	0.063
Dichlorprop	0.046	0.014	0.029	0.17	0.079	0.081
Diclofop-Methyl	0.063	0.013	0.042	0.24	0.079	0.081
Dieldrin	0.02	0.02	0.037	0.018	0.079	0.0825
Dimethoate	0.05	0.05	0.007	0.027	0.025	0.026
Dinoseb	0.063	0.016	0.038	0.24	0.079	0.081
Dioxacarb				0.19	0.13	
Diphenamid	0.13	0.13	0.14	0.099	0.094	0.098
Disulfoton (Di-Syston)	0.016	0.016	0.008	0.02	0.019	0.02
Diuron	0.21	0.21	0.11	0.195	0.189	0.195
Endosulfan I	0	0	0.032	0.018	0.079	0.0825
Endosulfan II	0	0	0.032	0.018	0.079	0.0825
Endosulfan Sulfate	0.03	0.03	0.033	0.018	0.079	0.0825
Endrin	0.03	0.03	0.03	0.018	0.079	0.0825
Endrin Aldehyde	0.02	0.02	0.02	0.018	0.079	0.0825
Endrin Ketone	0.01	0.01	0.03	0.018	0.079	0.0825
EPN	0.008	0.008	0.01	0.033	0.031	0.033
Eptam	0.22	0.22	0.11	0.066	0.063	0.065
Ethalfluralin (Sonalan)	0.08	0.08	0.07	0.05	0.047	0.049

(continued)

Table C-6, continued

Chemical	[1]EPA	[2]Manchester		[3]WSDA		
				2003	2004	2005
	MDL	MDL	EDL	LPQL	LPQL	LPQL
Ethion	0.006	0.006	0.006	0.023	0.022	0.023
Ethoprop	0.012	0.012	0.007	0.027	0.025	0.026
Fenamiphos	0.03		0.009	0.05	0.047	0.049
Fenarimol	0.23	0.23	0.1	0.099	0.094	0.098
Fenitrothion	0.004	0.004	0.008	0.023	0.022	0.023
Fensulfothion	0.08	0.12	0.009	0.033	0.031	0.033
Fenthion	0.011	0.011	0.008	0.023	0.022	0.023
Fenvalerate (2 isomers)						0.066
Fluridone	0.66	0.66	0.2	0.199	0.189	0.2
Fonofos	0.004	0.004	0.007	0.02	0.019	0.02
Gamma-BHC (Lindane)	0.03	0.03	0.023	0.018	0.079	0.081
Heptachlor	0.01	0.01	0.025	0.018	0.079	0.0825
Heptachlor Epoxide	0.008	0.008	0.026	0.018	0.079	0.0825
Hexachlorobenzene	0.04	0.04	0.069	0.018	0.079	0.081
Hexazinone	0.05	0.05	0.04	0.05	0.047	0.049
Imidan	0.007	0.007	0.01	0.036	0.035	0.036
Ioxynil	0.042	0.0063	0.019	0.16	0.079	0.081
Kelthane	0.17			0.051	0.315	0.33
Malathion	0.01	0.01	0.01	0.027	0.025	0.026
MCPA	0.083	0.022	0.05	0.315	0.079	0.081
MCPP (Mecoprop)	0.083	0.029	0.054	0.315	0.079	0.08
Merphos (1 & 2)	0.024	0.06	0.009	0.04	0.038	0.039
Metalaxyl	0.35	0.35	0.17	0.199	0.189	0.2
Methamidophos					1.594	1.6
Methidathion					1.594	1.6
Methiocarb				0.19	0.13	0.1
Methomyl				0.19	0.13	0.1
Methoxychlor	0.03	0.03	0.054	0.088	0.079	0.0825
Methyl Chlorpyrifos	0.008	0.008	0.01	0.027	0.025	0.026
Methyl Parathion	0.005	0.005	0.008	0.023	0.022	0.023
Metolachlor	0.15	0.15	0.17	0.133	0.127	0.13
Metribuzin	0.02	0.02	0.03	0.033	0.031	0.033
MGK264	0.26	0.26	0.16	0.263	0.252	0.26
Mirex	0.04	0.04	0.021	0.018	0.079	0.0825
Molinate	0.17	0.17	0.11	0.066	0.063	0.065
Naled					1.594	1.6
Napropamide	0.11	0.11	0.16	0.099	0.094	0.098
Norflurazon	0.07	0.07	0.06	0.066	0.063	0.065
Oxamyl				0.19	0.13	0.1
Oxychlordane	0.035			0.018	0.079	0.0825
Oxyfluorfen	0.1	0.1	0.22	0.134	0.127	0.13
Parathion	0.009	0.009	0.009	0.027	0.025	0.026
Pebulate	0.11	0.11	0.12	0.066	0.063	0.065

(continued)

Table C-6, continued

Chemical	[1]EPA	[2]Manchester		[3]WSDA		
				2003	2004	2005
	MDL	MDL	EDL	LPQL	LPQL	LPQL
Pendimethalin	0.06	0.06	0.06	0.05	0.046	0.049
Pentachloroanisole	0.035			0.018	0.079	0.08
Pentachlorophenol	0.021	0.007	0.013	0.08	0.079	0.08
Phenothrin						0.066
Phorate	0.006	0.006	0.008	0.023	0.022	0.023
Picloram	0.042	0.004	0.02	0.16	0.079	0.081
Profluralin	0.07	0.07	0.07	0.079	0.075	0.078
Promecarb				0.19	0.13	0.1
Prometon (Pramitol 5p)	0.04	0.04	0.03	0.032	0.031	0.033
Prometryn	0.04	0.04	0.03	0.033	0.031	0.033
Pronamide (Kerb)	0.13	0.13	0.15	0.169	0.127	0.13
Propachlor (Ramrod)	0.12	0.12	0.13	0.079	0.075	0.078
Propargite	0.14	0.14	0.02	0.066	0.063	0.065
Propazine	0.05	0.05	0.03	0.033	0.031	0.033
Propoxur				0.19	0.13	0.1
Resmethrin						0.066
Ronnel	0.005	0.005	0.01	0.023	0.022	0.023
Simazine	0.05	0.05	0.02	0.033	0.031	0.033
Sulfotepp	0.006	0.006	0.005	0.02	0.019	0.02
Tebuthiuron	0.03	0.03	0.03	0.05	0.047	0.049
Terbacil	0.13	0.13	0.06	0.099	0.093	0.098
Terbutryn (Igran)	0.05	0.05	0.03	0.033	0.031	0.033
Trans-Chlordane (Gamma)	0.03			0.018	0.079	0.0825
Trans-Nonachlor	0.035			0.018	0.079	0.0825
Triadimefon	0.13	0.13	0.06	0.086	0.082	0.085
Triallate	0.26	0.26	0.18	0.099	0.094	0.098
Trifluralin (Treflan)	0.09	0.09	0.07	0.05	0.047	0.049
Triclopyr	0.035	0.0091	0.02	0.13	0.079	0.081
Vernolate	0.22	0.22	0.12	0.066	0.063	0.065

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

[2]Manchester Environmental Laboratory.
MDL – Method detection limit is calculated by multiplying the Student's t value appropriate for a 99% confidence level and the standard deviation estimate with n-1 degrees of freedom. (40 CFR Part 136, Appendix B).
EPA 1996, 2000, 2005
EDL – Estimated detection limit is calculated by dividing the approximate amount of primary elements (nitrogen, phosphorus, chlorine) to obtain a detector signal/noise ratio of 3:1 by the fraction of primary elements contained in the analyte, and then extrapolating to the sample concentration (MEL, 2000).

[3]WSDA Pesticides Study, 2003-2005
LPQL: Lower performance practical quantitation limit. Average of lower performance (reporting) values, per analyte for all batches over each study year (14-34 batches per year).

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Appendix D. Assessment Criteria

A review of EPA pesticide assessment documents was conducted to determine the most comparable and up-to-date toxicological guidelines (Table D-1). The 2003-2005 maximum concentration for each chemical is listed on the table, and values in **bold** indicate the result was numerically above toxicity or water quality criteria.

Toxicity Criteria

Rainbow trout are a surrogate for coldwater endangered and threatened species. *Daphnia magna* (invertebrate) and *Selenastrum capricornutum* (green algae also called *pseudokirchneria subcapitata*) represent components of the aquatic food web that may be affected by pesticide use. Alternative species are used only if no data are available for rainbow trout, *Daphnia magna*, or *Selenastrum capricornutum*.

The EPA classifies a laboratory study as 'core' if the study meets guidelines appropriate for inclusion in pesticide registration. Usually a core designation may be made if (1) the study is appropriately designed and monitored, (2) the conditions are controlled, and (3) the duration of exposure is consistent with other studies. Core study criteria are used in the assessment table. In keeping with the pesticide review precedent, the most toxic, acceptable criteria from core studies are used for the species listed above.

Water Quality Criteria

The most recent versions of the Washington State water quality standards and EPA National Recommended Water Quality Criteria (NRWQC) were applied. The toxic standards for Washington State waters remain essentially unchanged following the 1997 rule and 2003 updates (Washington Administrative Code (WAC), Chapter 173-201A). The NRWQC remain largely unchanged from 2004 to 2006, yet the diazinon criteria maximum and continuous concentrations have been finalized at 0.17 µg/L (71FR9336).

Table D-1. Toxicity and regulatory guideline values. All values reported in µg/L.

Chemical	Maximum Detection 2003-2005	[1]Toxicological and Reregistration Criteria													Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
2,4,6-Trichlorophenol	0.0048																	
2,4-D	2.2*	580	79.2	29	RT/FM	1	2200	200	DM	1	7480	340	SC	1				
3,5-Dichlorobenzoic acid	0.0038																	
4,4'-DDE	**0.017**														**1.1[a,b]**	**0.001[a,c]**	**1.1[a]**	**0.001[a]**
4,4'-DDT	**0.0036**														**1.1[a,b]**	**0.001[a,c]**	**1.1[a]**	**0.001[a]**
4-Nitrophenol	0.25																	
Alachlor	0.058	2100	187	105	RT	2	1550	110	DM	2	1.64	0.35	SC	2				
Aldicarb sulfone	0.41*	42000	78	2100	RT/FM	3	280	20	DM	3								
Atrazine	0.142*	5300	65	265	RT/BT	4	6900	140	DM	4	49		SC	4				
Azinphos ethyl	0.052																	
Azinphos methyl	**0.14***	**2.9**	**0.23**	**0.145**	**RT**	**5**	**1.1**	**0.25**	**DM**	**5**								**0.01**
		3.2		**0.16**	**Coho**	**5**												
Bentazon	2.5*	>100000		>5000	RT	6	>100000		DM	6	4500		SC	6				
Benzamide, 2,6-dichloro-	0.091																	
Bromacil	0.17	36000		1800	RT	7	121000		DM	7	6.8		SC	7				
Bromoxynil	0.081*	100	15	5	RT/FM	8	96	2.5	DM	8	80		SC	8				
Carbaryl	**10**	**1200**		**60**	**RT**	**9**	**5.6**	**1.5**	**DM**	**10**	**1100**	**370**	**SC**	**10**				
		2400		**120**	**Chinook**	**10**												
		2400		**120**	**Coho**	**10**												
Chlorpyrifos	**0.4***	**3**	**0.57**	**0.15**	**RT/FM**	**11/12**	**0.1**	**0.04**	**DM**	**11**					**0.083[d]**	**0.041[e]**	**0.083**	**0.041**
Di-allate	0.23																	
Diazinon	**0.21**	**90**	**0.8**	**4.5**	**RT/BT**	**13/14**	**0.8**	**0.17**	**DM**	**13**	**3700**		**SC**	**13**			**0.17**	**0.17**
Dicamba I	0.083	28000		1400	RT	15	34600	16400	DM	15	3700	5	SC/AFA	15				
Dichlobenil	0.12	4930	330	246.5	RT	16/17	6200	560	DM	17	1500	160	SC	17				
Dimethoate	0.14	6200	430	310	RT	18	3320	40	DM	18								
Diphenamid	0.093																	
Disulfoton	**0.16***	**1850**	**220**	**92.5**	**RT**	**19/20**	**13**	**0.04**	**DM**	**20**								
Diuron	0.32	1950	26.4	97.5	RT/FM	21/22	1400	200	DM	22	2.4		SC	22				
Endosulfan I or II	0.016	0.8	0.1	0.04	RT	23	166	2	DM	23					0.22[b,f]	0.056[c,f]	0.22[i]	0.056[i]
Endosulfan sulfate	**0.36**	**2.2**		**0.11**	**ND**	**23**	**580**		**DM**	**23**					**0.22[b,f]**	**0.056[c,f]**		
EPTC - Eptam	0.038*	14000		700	ND	24	6500		ND	24	1360		SC	24				
Ethoprop	0.27*	1020	180	51	RT/FM	25	44	0.8	DM	25								
Hexachlorobenzene	0.16	50000	3.68	2500	Coho/RT	26	16		DM	26	30		SC	26				
Hexazinone	0.15	180000	17000	9000	RT/FM	27/28	151600	20000	DM	27	7	4	SC	27				
		317000		15850	Chinook	27												
		246000		12300	Coho	27												
		317000		15850	Sockeye	27												

Table D-1, continued. Toxicity and regulatory guideline values. All values reported in µg/L.

Chemical	Maximum Detection 2003-2005	[1]Toxicological and Reregistration Criteria													Standards and Criterion			
		Fisheries					Invertebrate				Plant				[2]WAC		[3]NRWQC	
		Acute	Chronic	ESLOC	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	Spp.	Ref	Acute	Chronic	CMC	CCC
Imidan (Phosmet)	0.076	230	3.2	11.5	RT	29	560	0.37	DM	29								
		150		7.5	Chinook	29												
Malathion	**3.05***	**4.1**	**21**	**0.205**	**RT**	**30**	**1**	**0.06**	**DM**	**30**								**0.1**
		170		**8.5**	**Coho**	**31**												
MCPA	0.297*	1150	916	57.5	RT	32	280	77	DM	32	250	32	SC	32				
MCPP - Mecoprop	0.15																	
Metolachlor	0.017	3900	780	195	ND	33	25100		DM	33								
Norflurazon	0.11	8100	770	405	RT	34	15000	1000	DM	34	13	6.23	SC	34				
Oxyflurofen	**0.238**	**410**	**38**	**20.5**	**RT/FM**	**35**	**80**	**13**	**DM**	**35**	**0.29**	**0.1**	**SC**	**36**				
Pendimethalin	0.21	138	6.3	6.9	RT/FM	37	280	14.5	DM	37	5.4	3	SC	37				
Pentachloroanisole	0.021																	
Pentachlorophenol	0.083*	15	11	0.75	RT	38	450	240	DM	38	50		SC	38	8.2-41.0[d,g]	5.2-25.9[e,h]	7.9-107.6[j]	6.1-82.6[k]
Prometon	0.036																	
Pronamide	0.154*	76000		3800	RT	39	7600		DM	39	750		SC	39				
Propargite	2.144	118000	16	5900	RT/FM	40	74	9	DM	40	66.2		SC	40				
Ronnel	0.0089																	
Simazine	0.0071	70500	1200	3525	RT/FM	41	1100		DM	41	100		SC	41				
Tebuthiuron	0.042	143000	9300	7150	RT/FM	42	297000	21800	DM	42	50	13	SC	42				
Terbacil	0.16	46200		2310	RT	43	65000		DM	43	18	4	SC	43				
Triclopyr	0.19	650		32.5	RT	44	12000		DM	44	2300	2	SC/NP	44				
Trifluralin (Treflan)	0.026	41	1.14	2.05	RT	45	560	2.4	DM	45	7.52	5.37	SC	45				

*Values are not analytically qualified. Non-asterisk values have been J-qualified as estimates, normally below the practical quantitation limit.
[1]Criteria identified in EPA reregistration and review documents, or peer reviewed literature. References listed separately.
Time component of standards explained in body of report.
ESLOC refers to Endangered Species Level of Concern
Species abbreviated in table include: RT-Rainbow Trout, FM- Fathead Minnow, BT-Brook Trout, ND-Not Described, DM-*Daphnia magna*, SC-*Selenastrum capricornutum* (also called *pseudokirchneria subcapitata*), *Anabaena flos-aquae*, and *Navicula pellicosa*
[2]WAC: Promulgated standards according to Chapter 173-201A WAC
[3]EPA National Recommended Water Quality Criteria (EPA-822-R-02-047)
CMC: Criteria Maximum Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.
CCC: Criteria Continuous Concentration; estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.
[a]Criteria applies to DDT and its metabolites (ΣDDT). [b]An instantaneous concentration not to be exceeded at any time.
[c]A 24-hour average not to be exceeded. [d]A 1-hour average concentration not to be exceeded more than once every three years on average.
[e]A 4-day average concentration not to be exceeded more than once every three years on average.
[f]Chemical form of Endosulfan is not defined in WAC 173-201A. Endosulfan sulfate may be applied in this instance. [g]$\leq e^{[1.005(pH)-4.830]}$, pH range of 6.9 to 9.5 shown
[h]$\leq e^{[1.005(pH)-5.29]}$, pH range of 6.9 to 9.5 shown [i]Value refers to ∑α and β-endosulfan [j]$\leq e^{[1.005(pH)-4.869]}$, pH range of 6.9 to 9.5 shown
[k]$\leq e^{[1.005(pH)-5.134]}$, pH range of 6.9 to 9.5 shown

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42 - Stavola, A. 2004. Tebuthiuron Analysis of Risks to Endangered and Threatened Salmon and Steelhead. www.epa.gov/espp/effects/tebuthiuron/tebuthiuron_analysis.pdf
43 - Reregistration Eligibility Decision for Terbacil (RED). 1-1998. www.epa.gov/oppsrrd1/REDs/0039red.pdf
44 - Reregistration Eligibility Decision for Triclopyr (RED). 10-1998. www.epa.gov/oppsrrd1/REDs/2710red.pdf
45 - Stavola, A. and M. Patterson. 2004. Trifluralin Analysis of Risks to Endangered and Threatened Salmon and Steelhead. www.epa.gov/espp/effects/triflur-analy.pdf

References: Water Quality Criteria

WAC	Promulgated standards according to Chapter 173-201A WAC
EPA NRWQC	http://epa.gov/waterscience/criteria/wqcriteria.html
4,4'-DDE	65FR66443
4,4'-DDT	65FR31682, 65FR66443
Azinphos methyl	Gold Book: EPA 1986. Quality Criteria for Water. EPA440/5-86-001. www.epa.gov/waterscience/criteria/goldbook.pdf
Chlorpyrifos	Gold Book: EPA 1986. Quality Criteria for Water. EPA440/5-86-001. www.epa.gov/waterscience/criteria/goldbook.pdf
Diazinon	71FR9336
Endosulfan I or II	65FR31682, 65FR66443
Malathion	Gold Book: EPA 1986. Quality Criteria for Water. EPA440/5-86-001.
Pentachlorophenol	65FR31682, 65FR66443

Appendix E. Risk Quotient Results for Fish, Invertebrates, and Plants

This section is designed to present additional exposure and effects information supplemental to the body of the report. Risk quotient graphs are presented for fish, invertebrates, and plants. Chronic aquatic toxicity criteria analysis is presented for invertebrates, which is the most common criteria exceedance. Fifteen chemicals with the greatest risk quotient results are presented on the graphs, and are sorted from top (highest value) to bottom in the legend. All detections are evaluated if toxicity criteria are available for analysis (Appendix D). Toxicity criteria are not available for all pesticides detected. The risk quotient paradigm is presented in Table E-1.

Table E-1. Risk quotient criteria for direct and indirect effects on threatened and endangered fish.

Test Data	Risk Quotient	Presumption
Acute LC50	>0.5	Potentially high acute risk
Acute LC50	>0.1	Risk that may be mitigated through restricted use classification
Acute LC50	>0.05	Endangered species may be affected acutely. Value meant to be protective of acute, chronic and sublethal effects.
Chronic NOEC	>1	Chronic risk; endangered species may be affected chronically, including reproduction and effects on progeny
Acute invertebrate LC50	>0.5	May be indirect effects on T&E fish through food supply reduction
Aquatic plant acute LC50	>1	May be indirect effects on aquatic vegetative cover for T&E fish

Turner, 2003
LC50 Lethal concentration to cause mortality in 50% of test species
NOEC No observable effect concentration
T&E = Threatened and endangered

Figures E1 – E19 are a more detailed presentation of risk quotient data contained in Tables 6-9. Within the figures, the magnitude of the risk quotient may be evaluated.

Figures E1 – E19 are designed to be read in color. If you are reading a black-and-white printed copy, see the online report at www.ecy.wa.gov/biblio/0603036.html

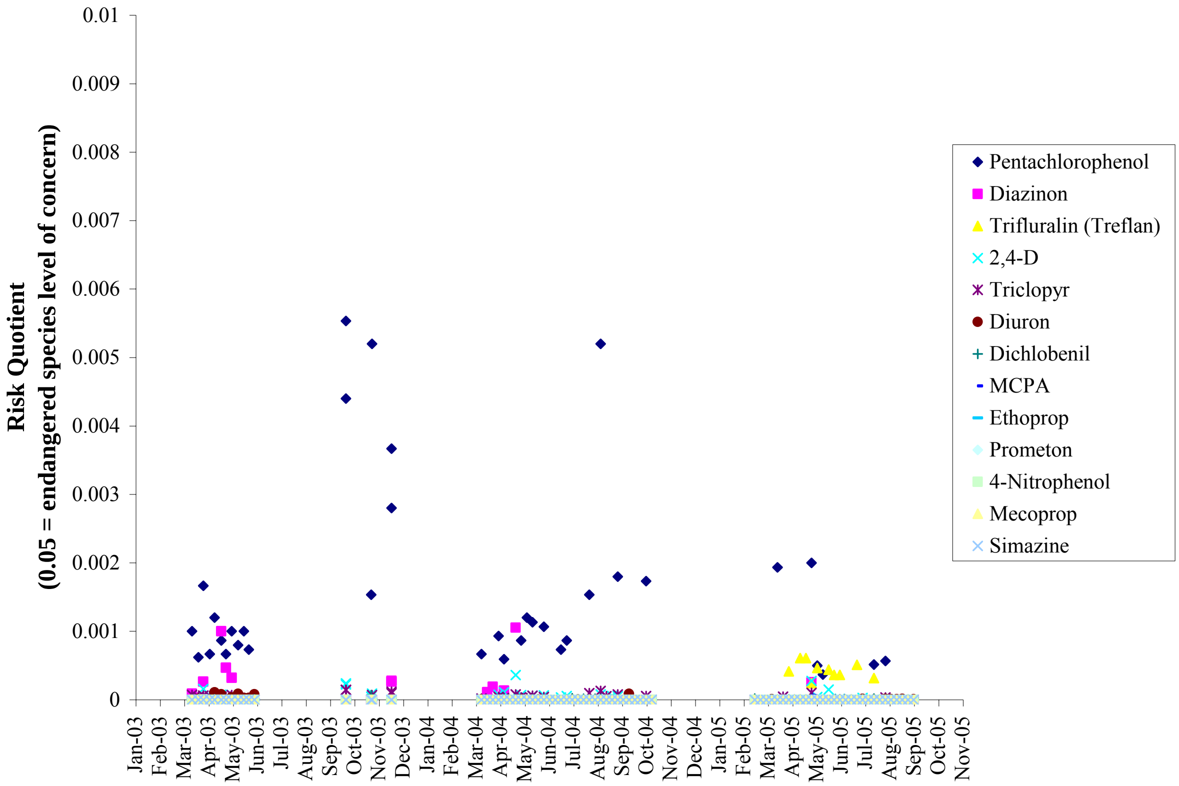

Figure E-1. Fisheries acute risk quotients for the mainstem Thornton Creek.

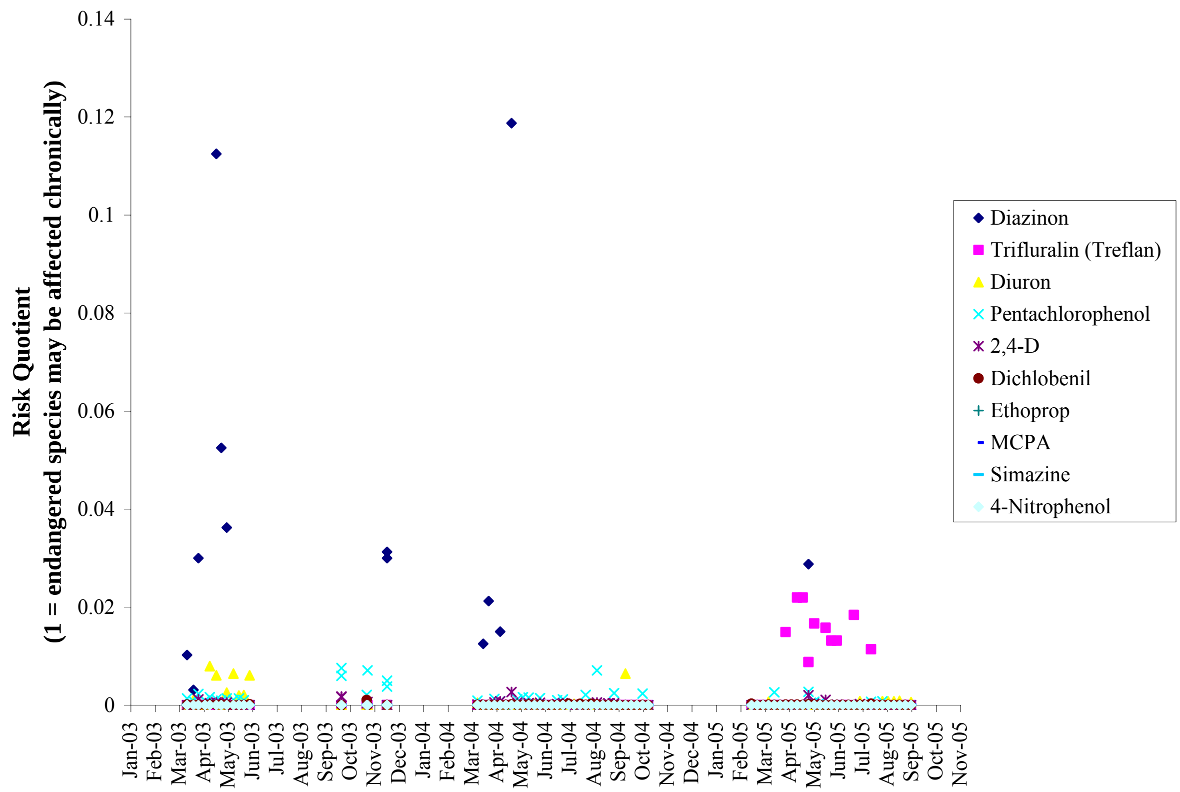

Figure E-2. Fisheries chronic risk quotients for the mainstem Thornton Creek.

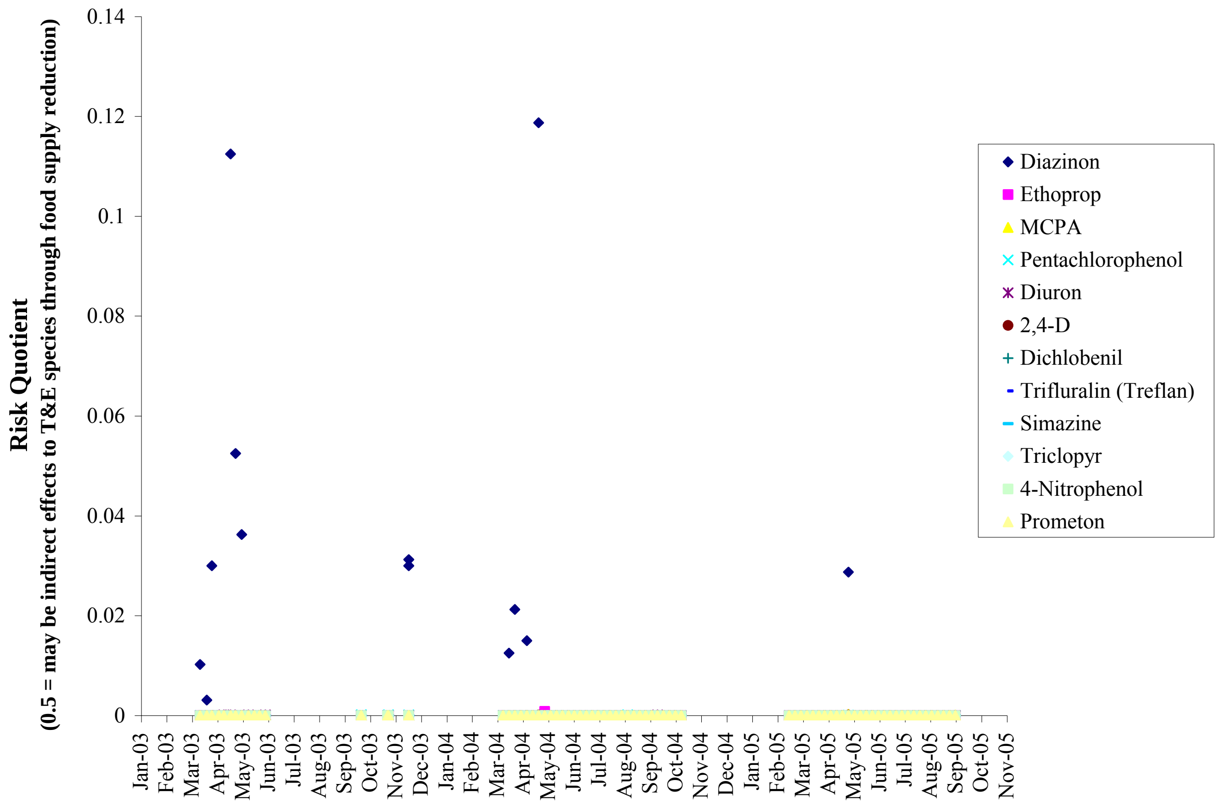

Figure E-3. Acute invertebrate risk quotients for the mainstem Thornton Creek.

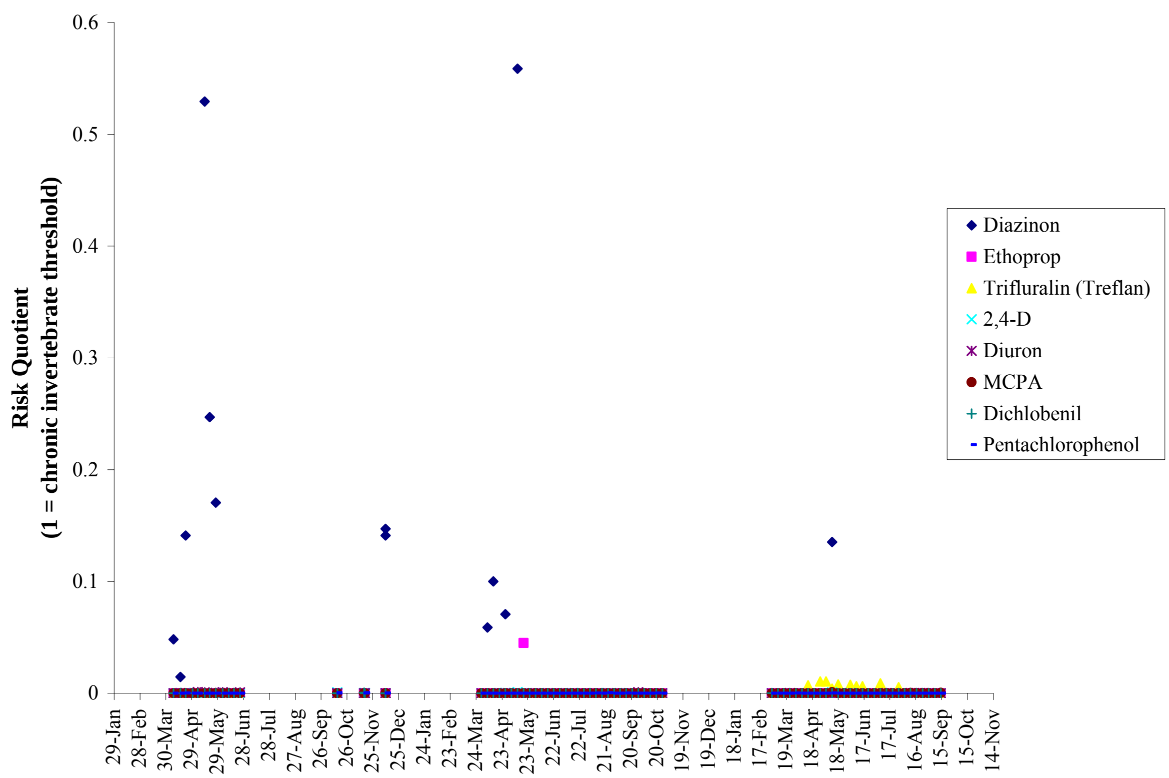

Figure E-4. Chronic invertebrate risk quotients for the mainstem Thornton Creek.

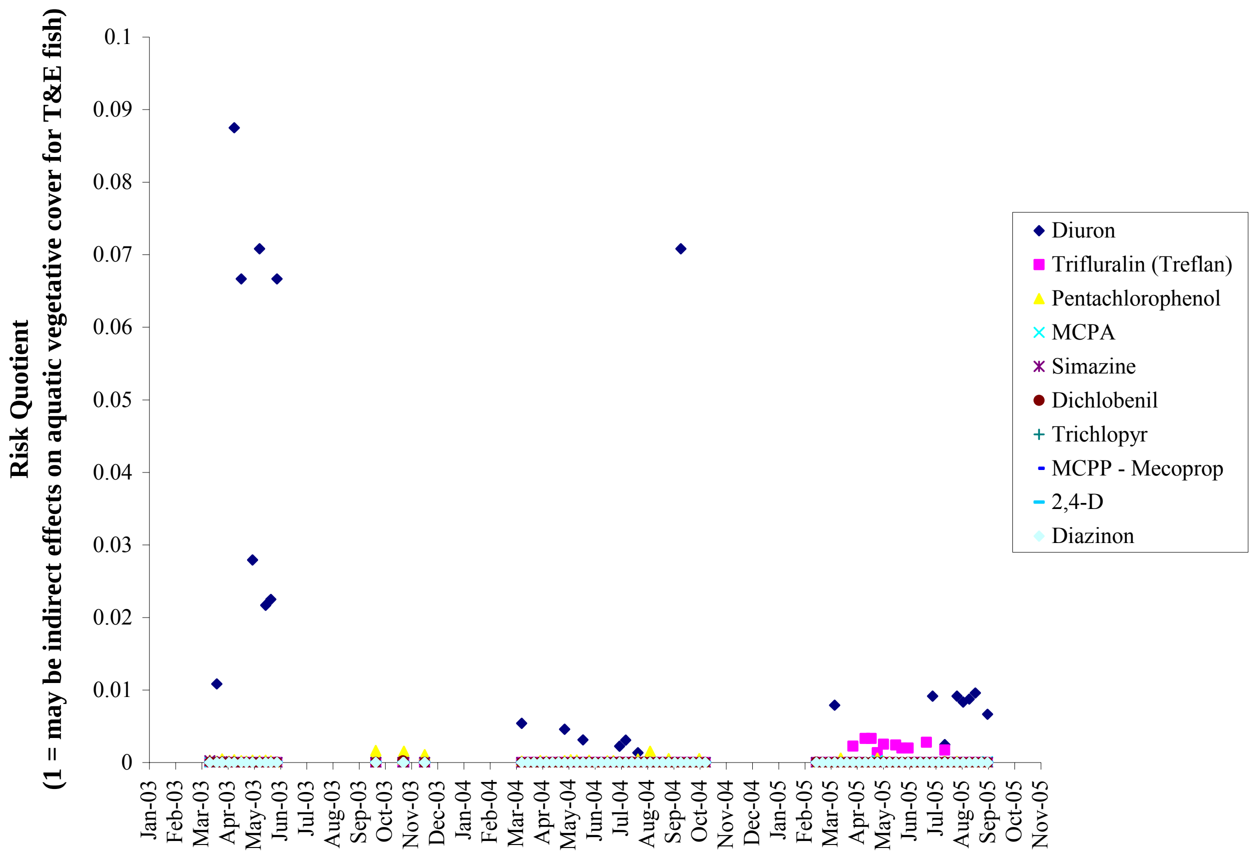

Figure E-5. Acute aquatic plant risk quotients for the mainstem Thornton Creek.

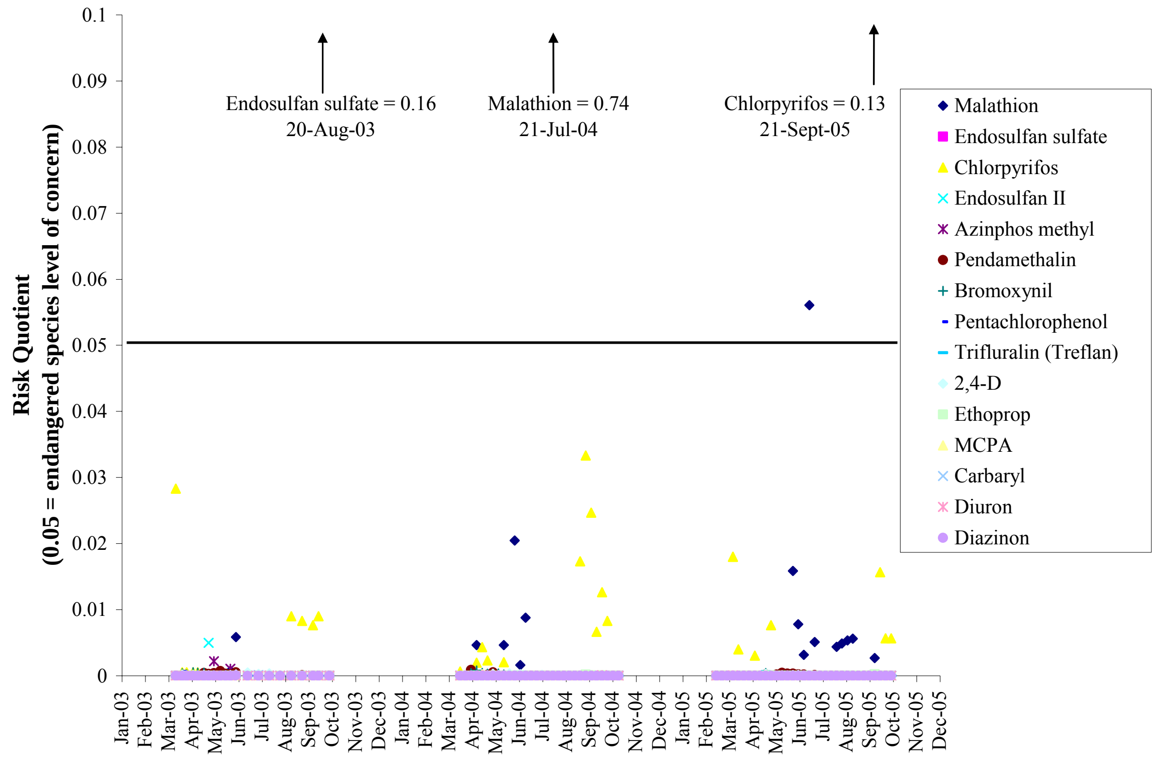

Figure E-6. Fisheries acute risk quotients for the lower Marion Drain.

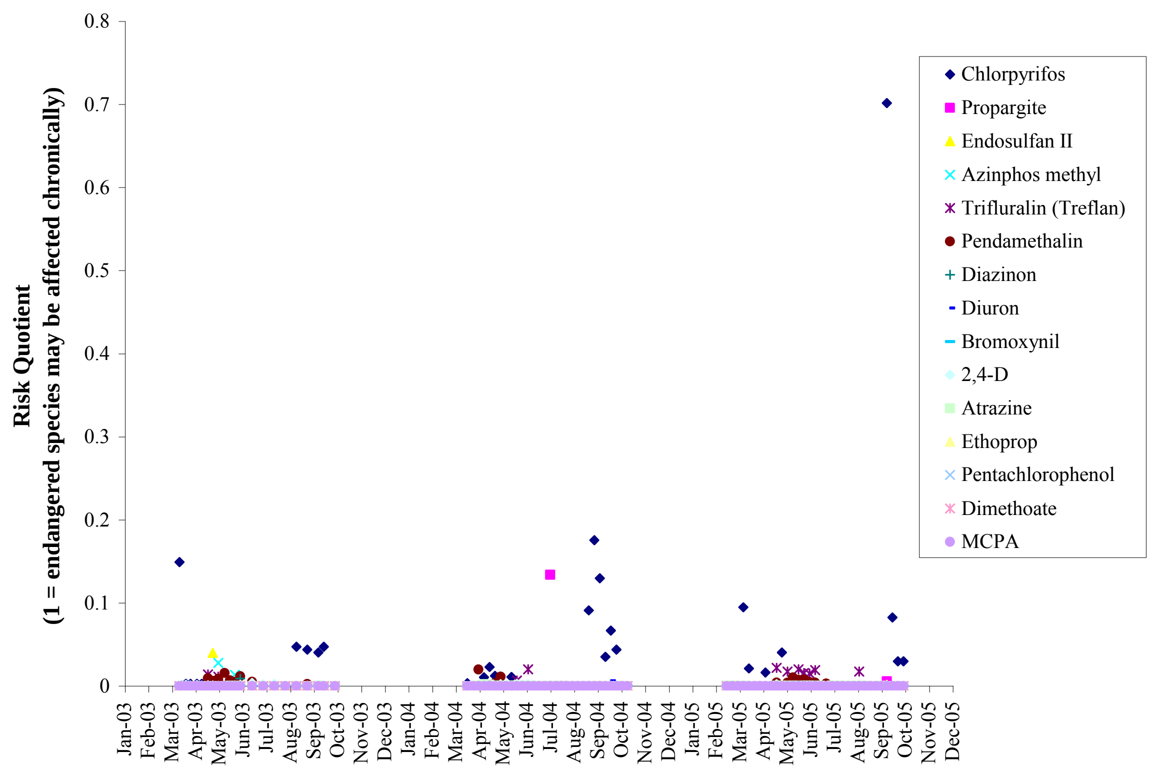

Figure E-7. Fisheries chronic risk quotients for the lower Marion Drain.
Note: no chronic criteria are available for endosulfan sulfate or malathion.

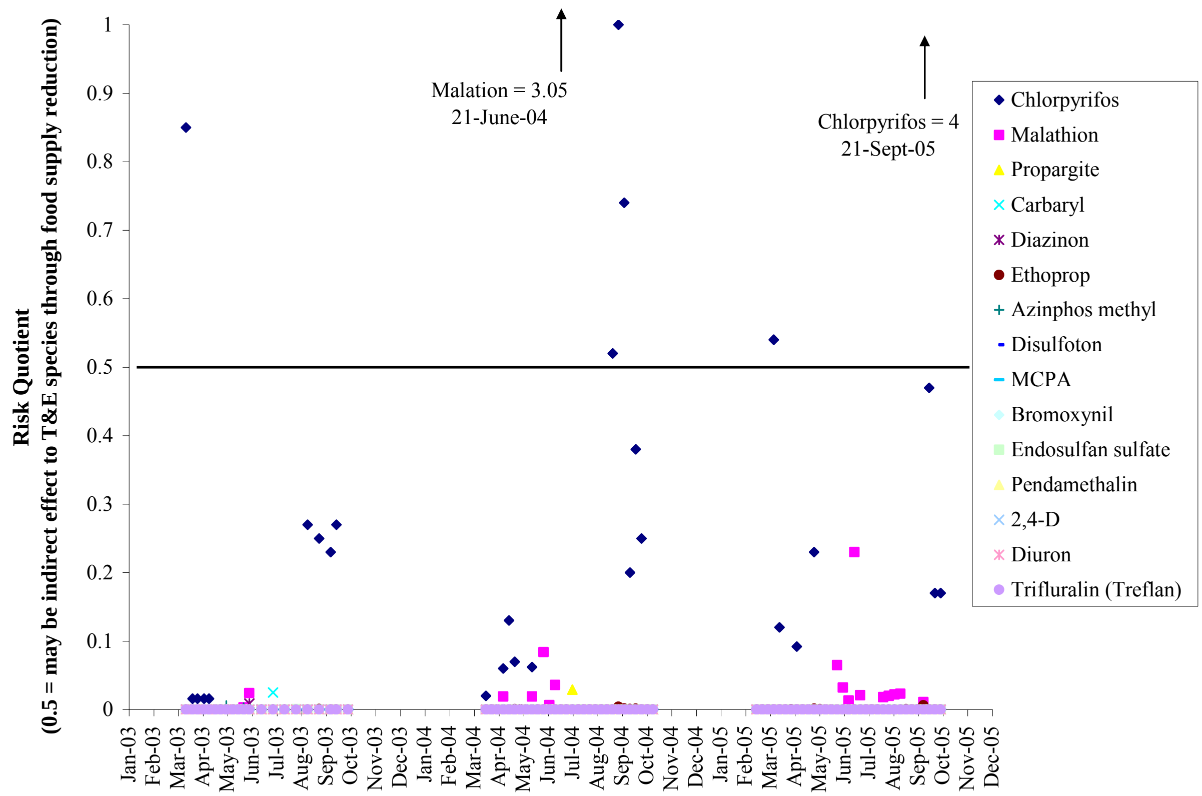

Figure E-8. Acute invertebrate risk quotients for the lower Marion Drain.

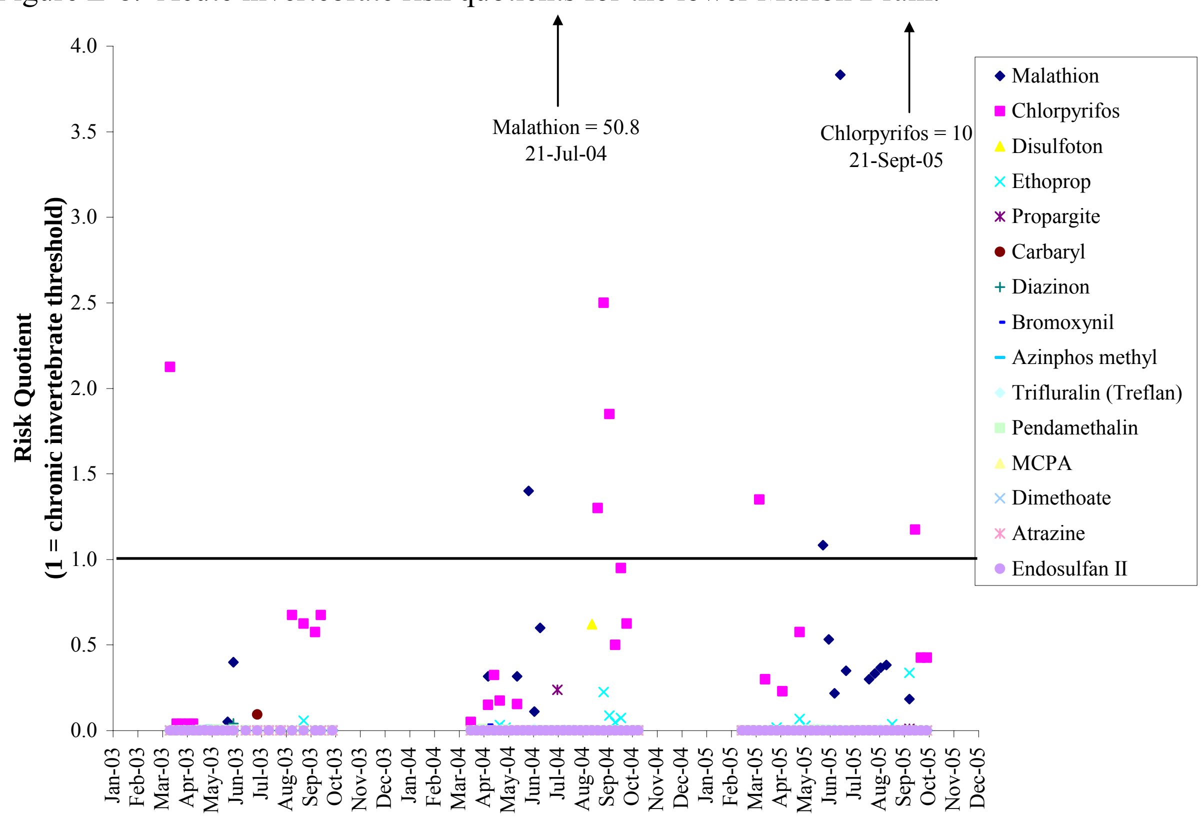

Figure E-9. Chronic invertebrate risk quotients for the lower Marion Drain.

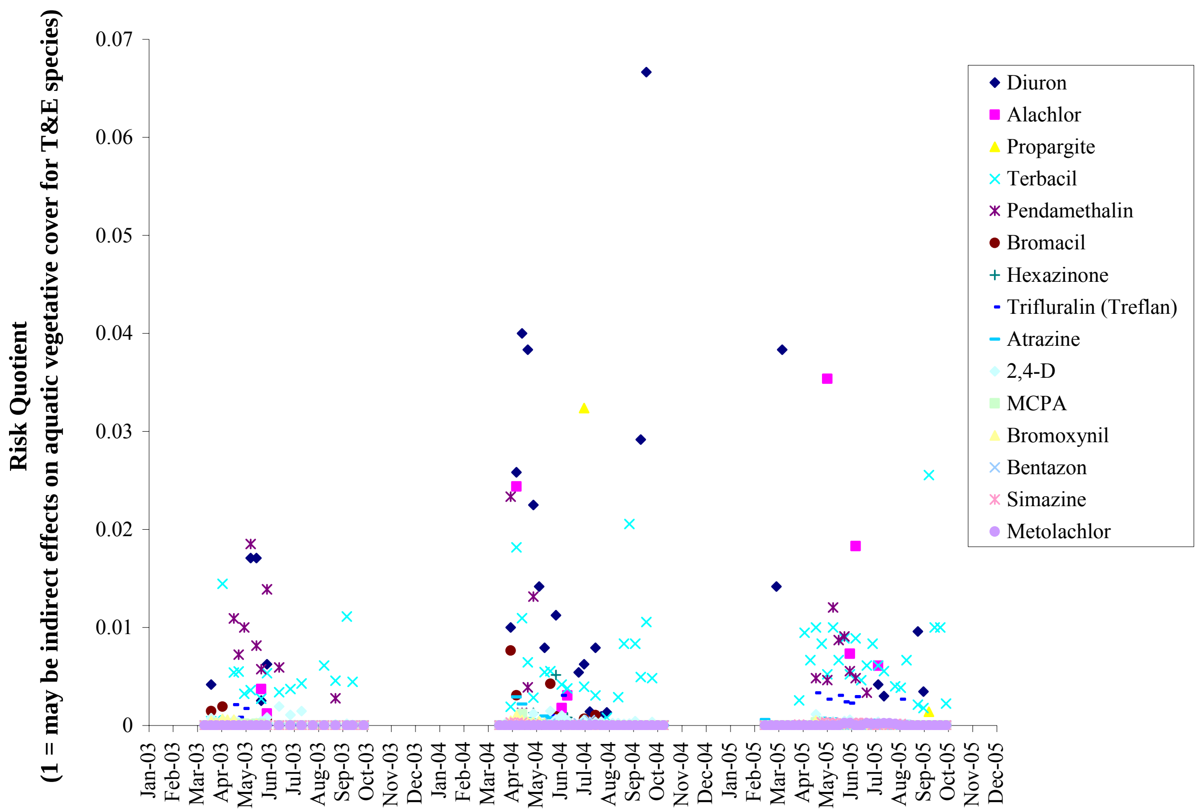

Figure E-10. Acute aquatic plant risk quotients for the lower Marion Drain.

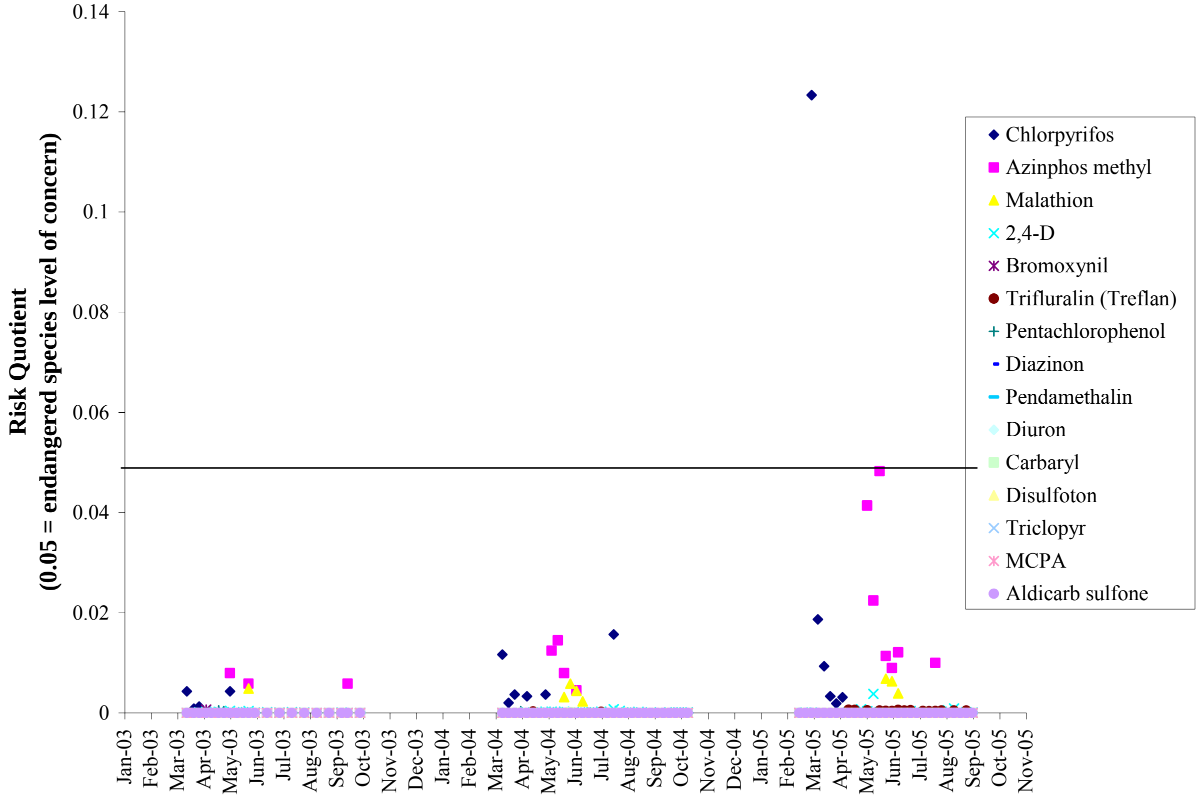

Figure E-11. Fisheries acute risk quotients for Sulphur Creek Wasteway.

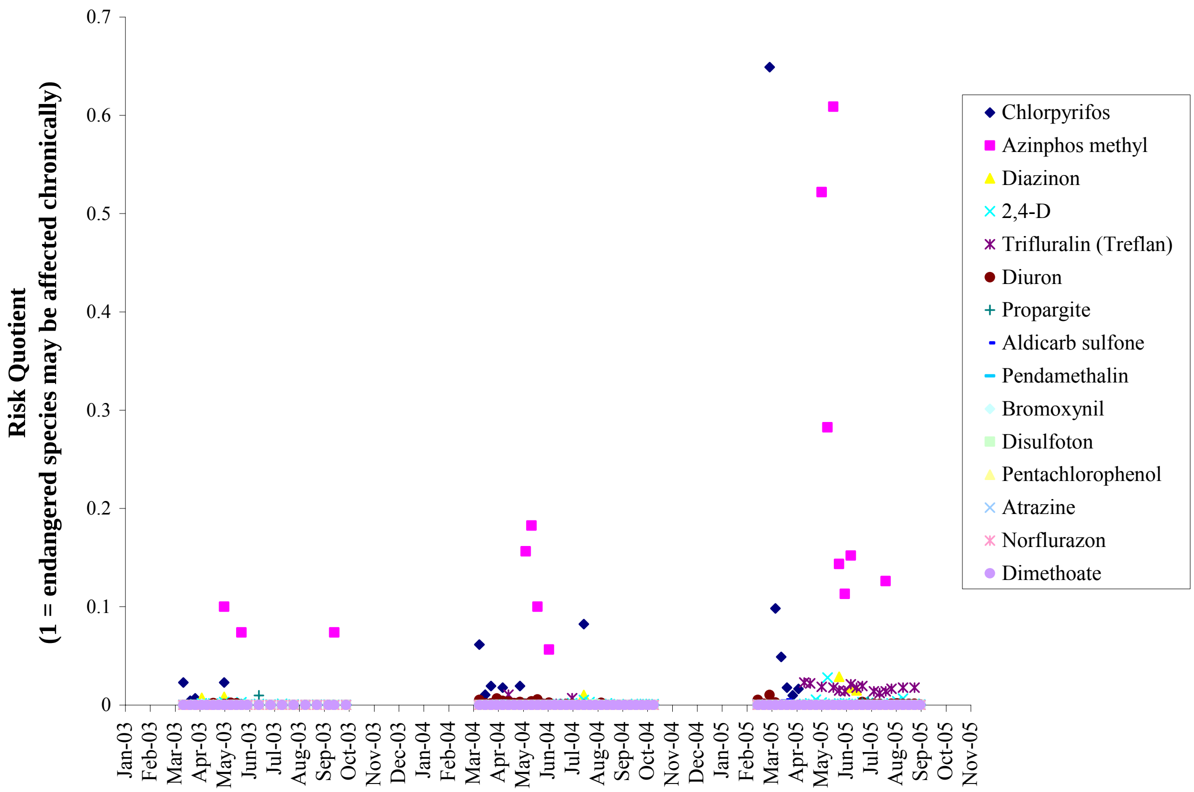

Figure E-12. Fisheries chronic risk quotients for Sulphur Creek Wasteway.

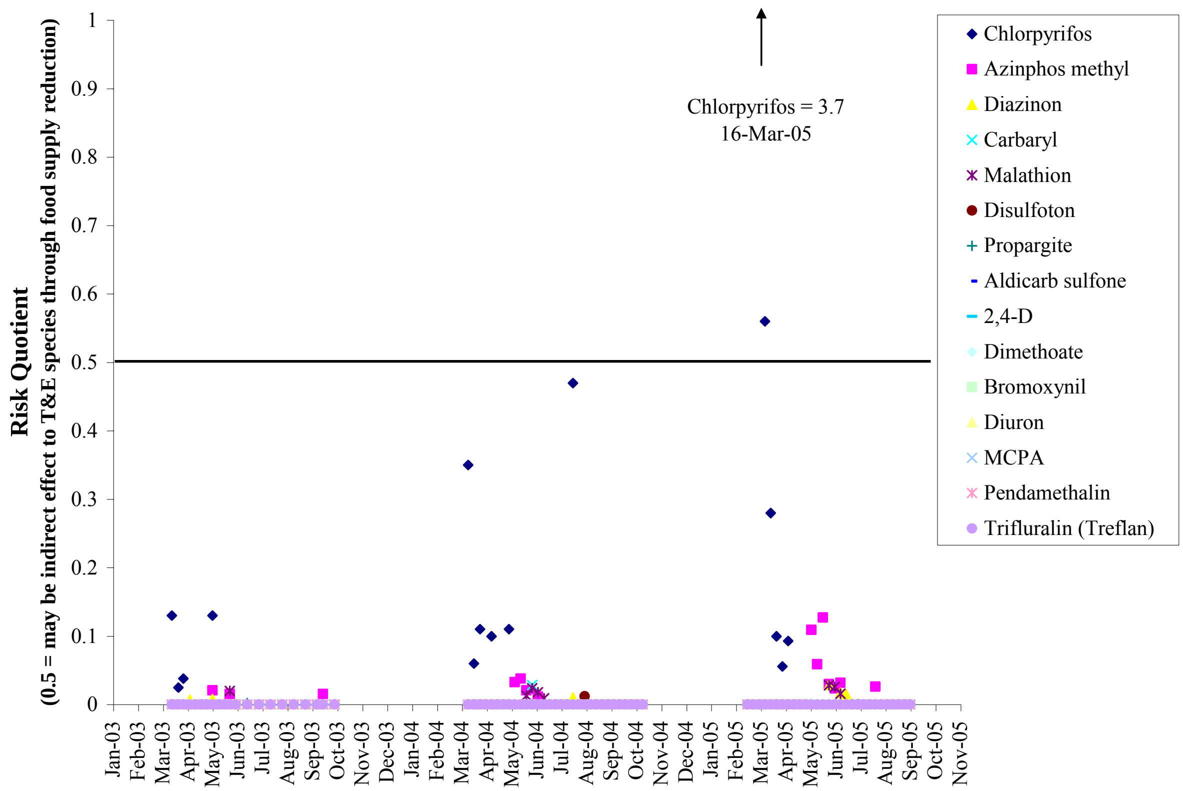

Figure E-13. Acute invertebrate risk quotients for Sulphur Creek Wasteway.

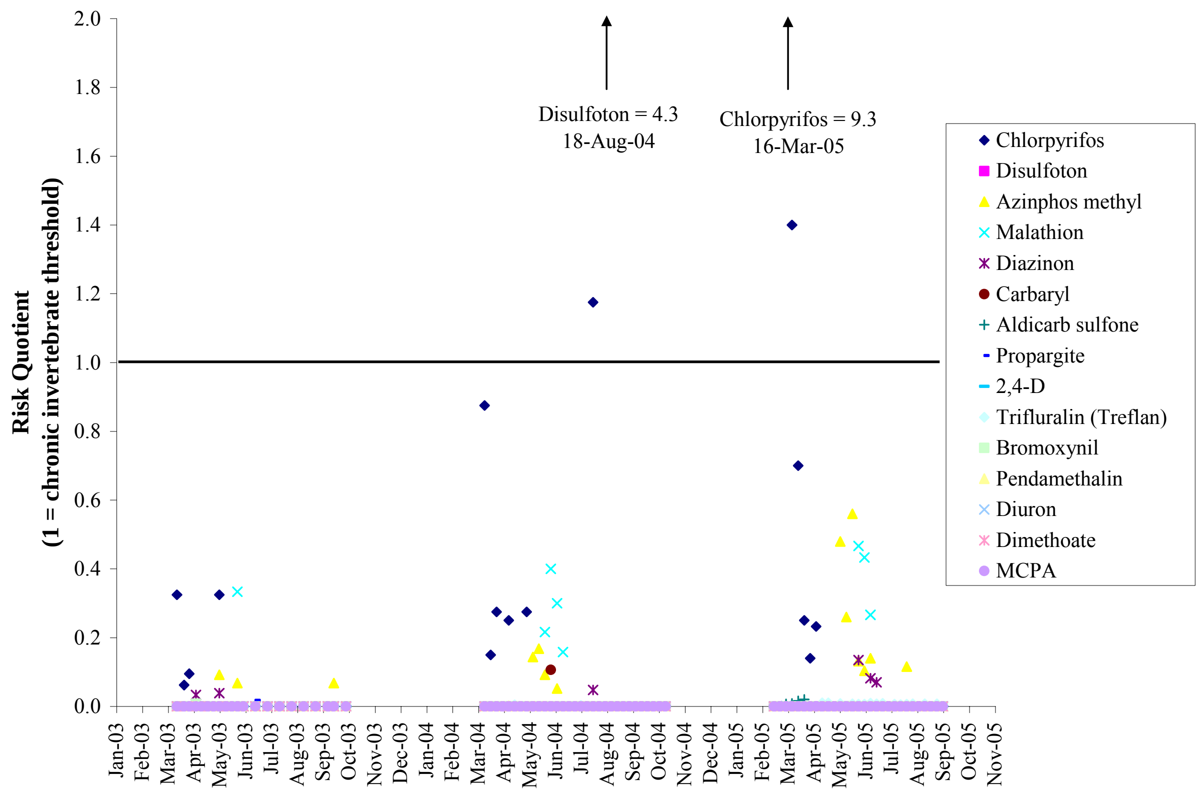

Figure E-14. Chronic invertebrate risk quotients for Sulphur Creek Wasteway.

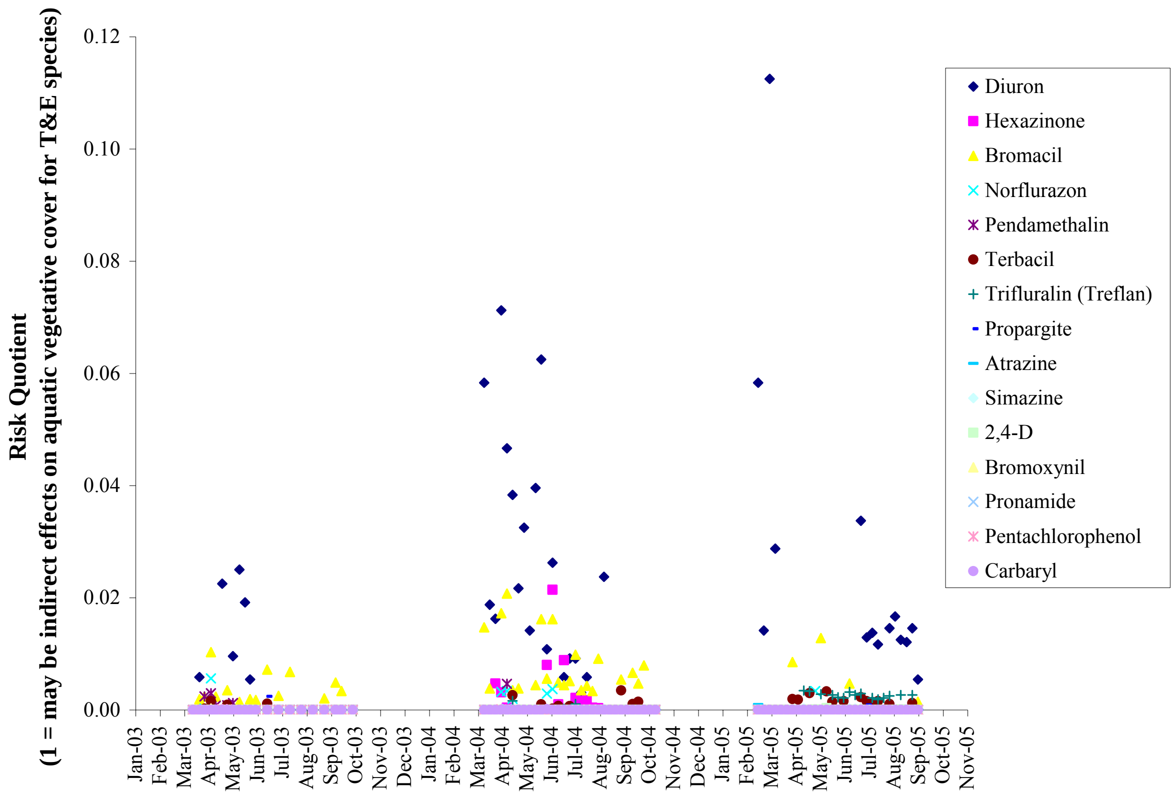

Figure E-15. Acute aquatic plant risk quotients for Sulphur Creek Wasteway.

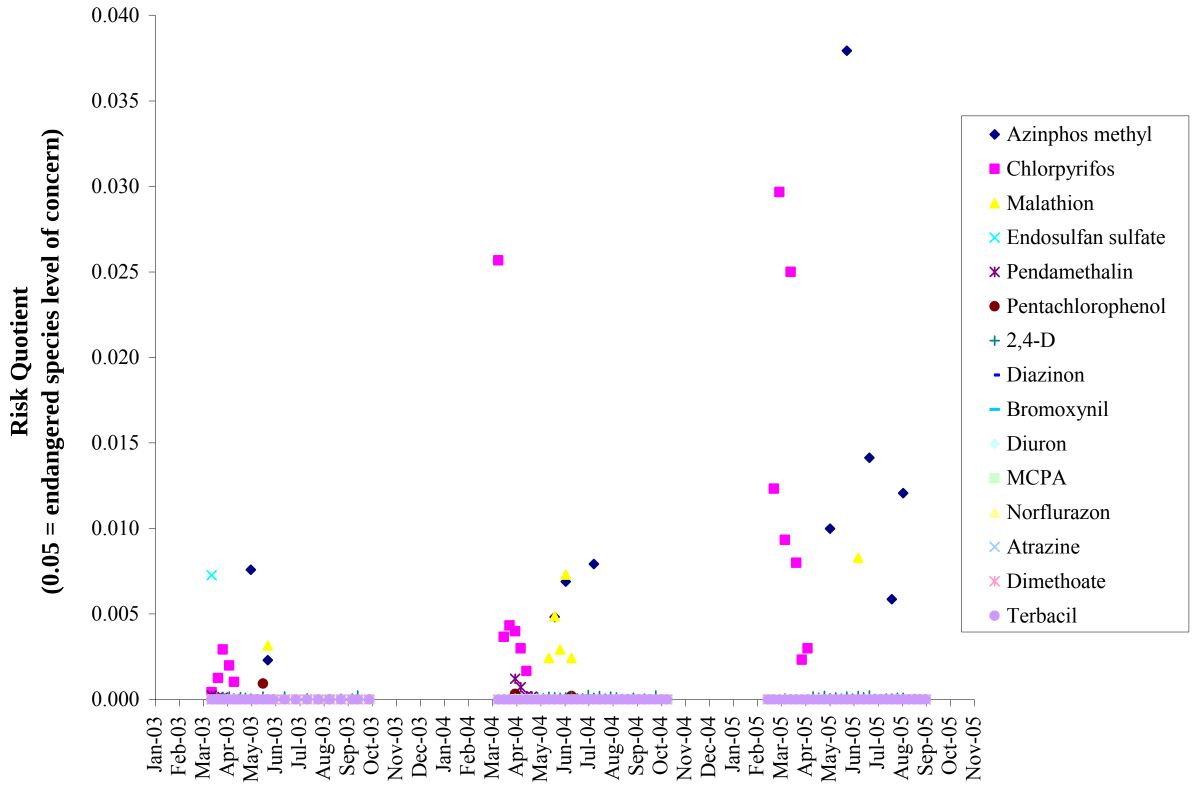

Figure E-16. Fisheries acute risk quotients for lower Spring Creek.

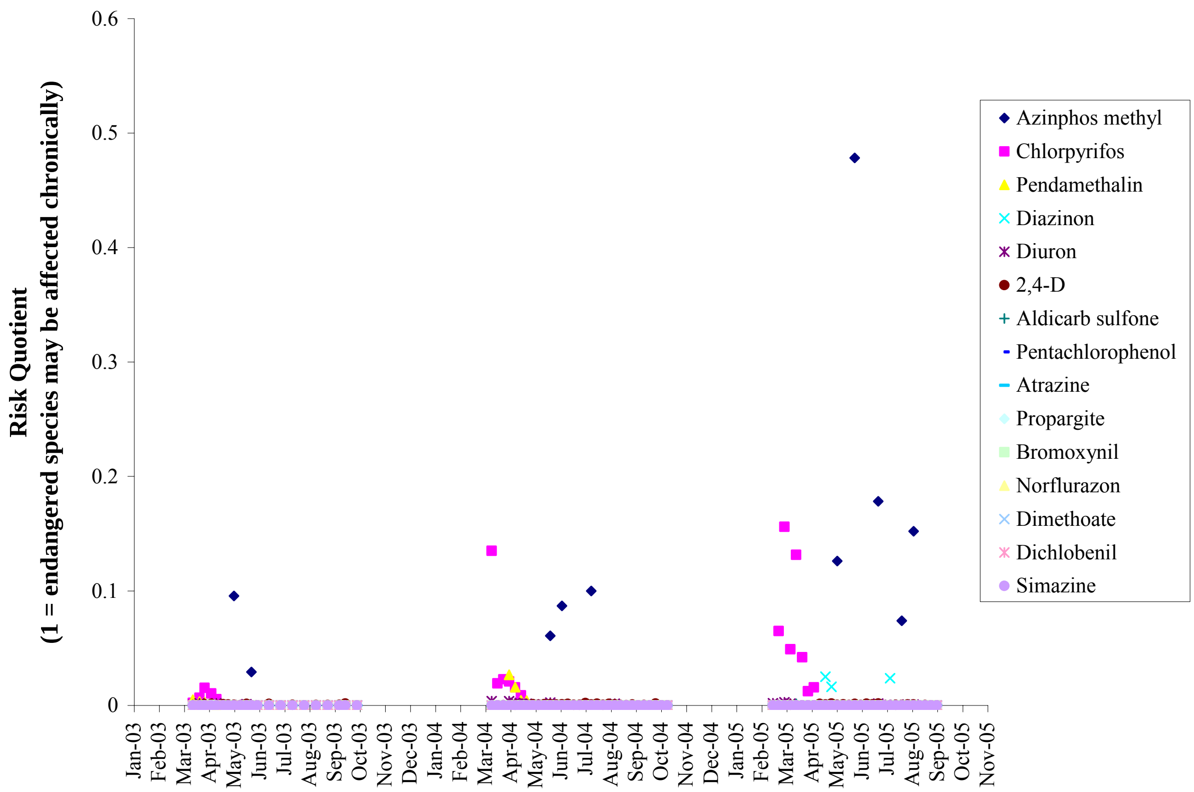

Figure E-17. Fisheries chronic risk quotients for lower Spring Creek.

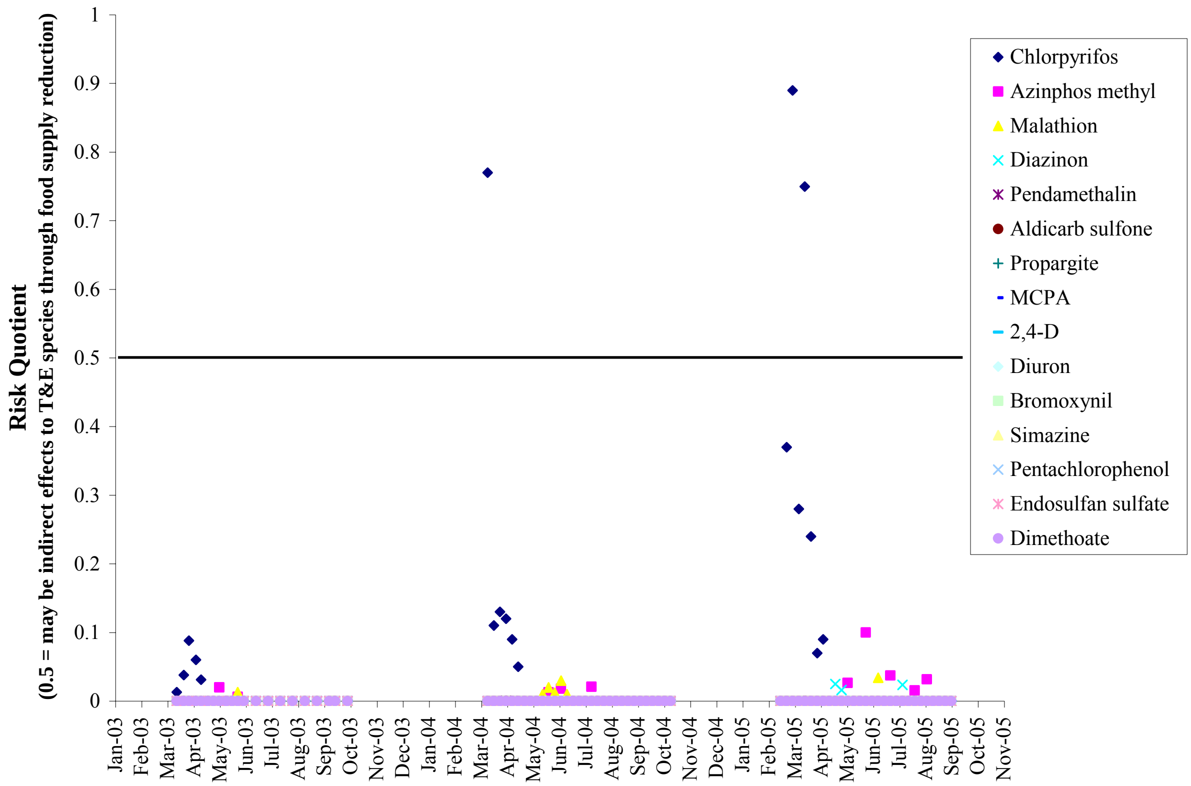

Figure E-18. Acute invertebrate risk quotients for lower Spring Creek.

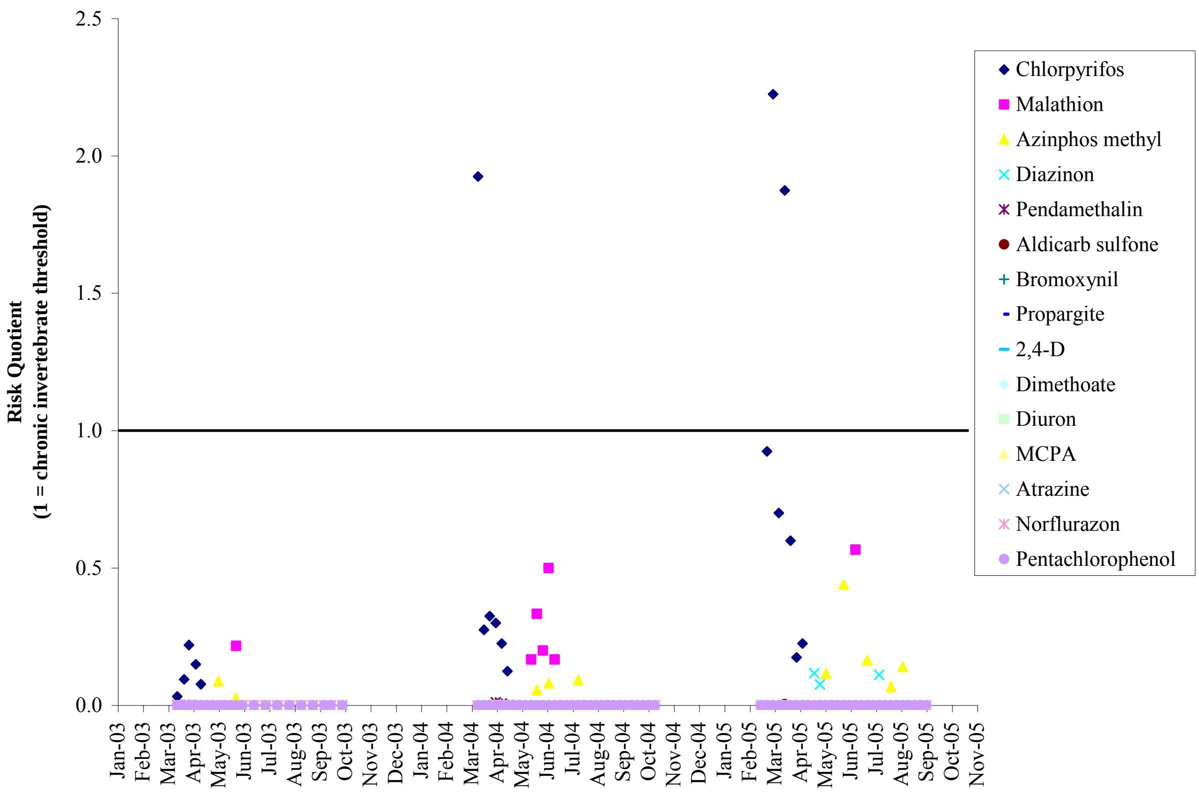

Figure E-19. Chronic invertebrate risk quotients for lower Spring Creek.

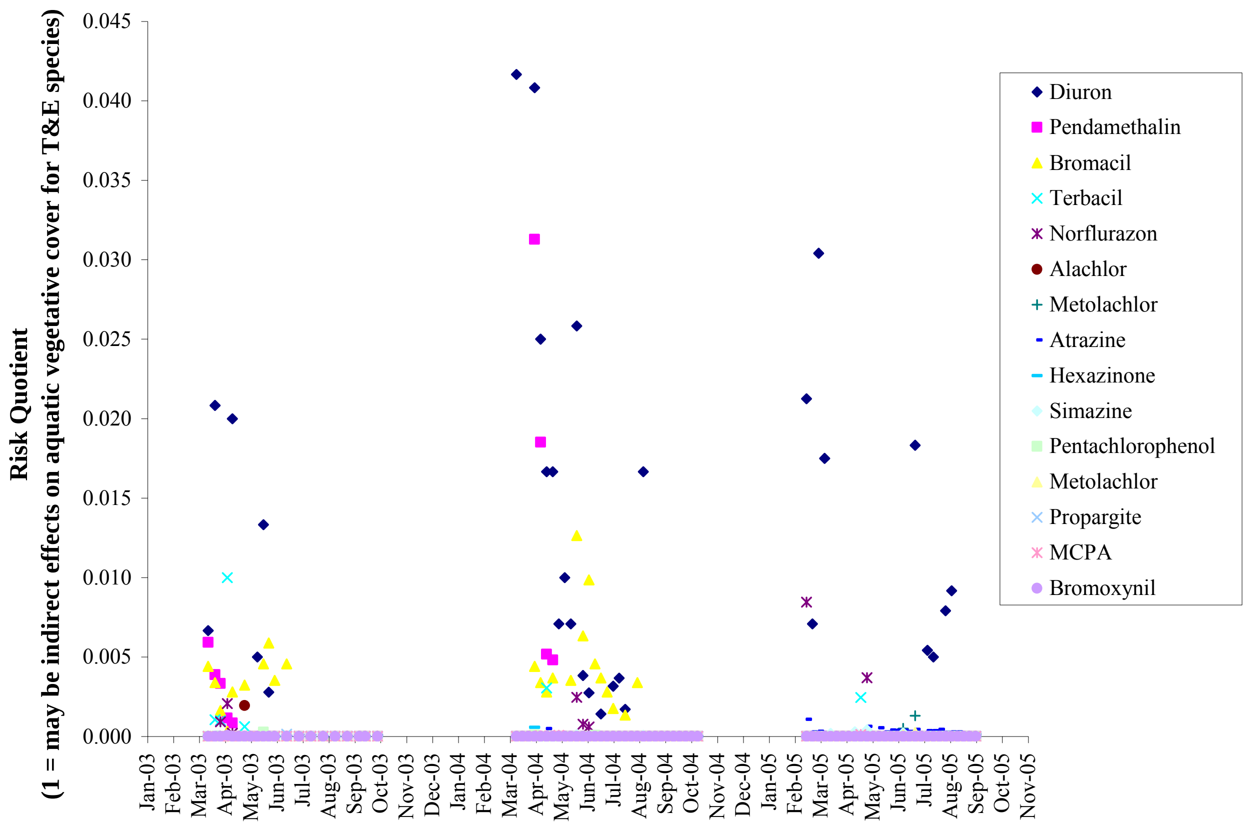

Figure E-20. Acute aquatic plant risk quotients for lower Spring Creek.

Reference

Turner, L. 2003. Chlorpyrifos: Analysis of Risks to Endangered and Threatened Salmon and Steelhead. Environmental Protection Agency, Office of Pesticide Programs. www.epa.gov/oppfead1/endanger/effects/chlorpyrifos-analysis.pdf

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Appendix F. Conventional and Pesticide Results

All sample results are available for download as a comma-delimited file from Ecology's Environmental Information Management website, www.ecy.wa.gov/eim/ Search using the study name "pesticides in salmonid-bearing."

Table F-1. Thornton Creek conventional result summaries, 2003-2005.

Parameter	n	Minimum	Median	Maximum
Thornton 1 (North Fork)				
TSS (mg/L)	46	1	3	123
Temperature (°C)	20,553	6.6	14.2	20.2
pH	45	6.6	7.7	8.3
Conductivity (µmhos/cm)	44	73	228	265
Discharge (cfs)	36	0.1	2	11.1
Thornton 2 (South Fork)				
TSS (mg/L)	12	1	4	211
Temperature (°C)	14	10.6	11.8	14.9
pH	14	7.1	7.8	8.2
Conductivity (µmhos/cm)	13	71	250	270
Discharge (cfs)	14	1.4	2	26.7
Thornton 3 (Mainstem)				
TSS (mg/L)	78	1	6	257
Temperature (°C)	20,551	6.7	14.7	21.9
pH	74	6.9	7.8	8.6
Conductivity (µmhos/cm)	73	120	223	291
Discharge (cfs)	72	2.6	4.3	37.8

Table F-2. Lower Yakima conventional result summaries, 2003-2005.

Parameter	n	Minimum	Median	Maximum
Marion 1				
TSS (mg/L)	12	10	13	22
Temperature (°C)	12	13.0	16.0	19.5
pH	12	7.3	8.1	8.5
Conductivity (µmhos/cm)	11	212	240	288
Discharge (cfs)	12	129.9	183.2	230.9
Marion 2				
TSS (mg/L)	84	1	9	62
Temperature (°C)	20,509	7.9	16.2	24.0
pH	84	7.1	8.3	9.3
Conductivity (µmhos/cm)	83	159	254	375
Discharge (cfs)	81	1.7	49.0	316.5
Sulphur 1				
TSS (mg/L)	81	7	27	722
Temperature (°C)	20,507	7.8	16.9	25.0
pH	81	7.6	8.3	8.9
Conductivity (µmhos/cm)	79	164	308	700
Discharge (cfs)	81	51.4	173.3	509.0
Spring 1				
TSS (mg/L)	35	1	7	24
Temperature (°C)	9,514	9.5	18.2	27.5
pH	35	7.0	7.7	8.9
Conductivity (µmhos/cm)	34	95	172	480
Discharge (cfs)	35	0.3	1.5	6.3
Spring 2				
TSS (mg/L)	27	1	7	80
Temperature (°C)	9,750	6.5	14.7	20.3
pH	27	7.7	8.1	8.5
Conductivity (µmhos/cm)	26	268	420	710
Discharge (cfs)	26	0.3	4.6	15.5
Spring 3				
TSS (mg/L)	81	1	28	94
Temperature (°C)	20,507	2.7	17.1	30.3
pH	81	7.0	8.3	9.5
Conductivity (µmhos/cm)	79	120	219	652
Discharge (cfs)	79	0.04	36.5	88.6

Table F-3. Pesticide residue results for the North Fork of Thornton Creek, 2003-2005. Concentrations reported as µg/L.

Chemical	[1]Use	Common Name	2003, n=18			2004, n=16			2005, n=15		
			Freq	Median	Max	Freq	Median	Max	Freq	Median	Max
Dichlobenil	H	Casoron	67%	0.0265	0.11	75%	0.0115	0.12	80%	0.019	0.11
Triclopyr	H	several	61%	0.037	0.19	38%	0.0275	0.064			
Pentachlorophenol	WP	Penta	61%	0.015	0.08	25%	0.0105	0.026	27%	0.027	0.028
MCPP	H	Mecoprop	56%	0.0425	0.15	38%	0.0255	0.041	33%	0.023	0.04
Prometon	H	Pramitol 5PS	39%	0.013	0.02	38%	0.0068	0.022	27%	0.015	0.025
Diazinon	I-OP	(several)	39%	0.042	0.063	13%	0.0625	0.101	7%	0.017	0.017
2,4-D	H	(several)	33%	0.074	0.16	38%	0.027	0.053	20%	0.051	0.087
Benzamide, 2,6-dichloro-	D		11%	0.0765	0.091						
Diuron	H	Karmex	6%	0.098	0.098	50%	0.0098	0.13	27%	0.0215	0.024
Bromacil	H	Hyvar	6%	0.008	0.008						
Dicamba I	H	Banvel	6%	0.083	0.083						
Pentachloroanisole	D		6%	0.021	0.021						
Tebuthiuron	H	Spike	6%	0.16	0.16						
Trifluralin	H	Treflan							20%	0.017	0.026
MCPA	H	(several)							7%	0.013	0.013

Use Descriptors: H = herbicide, D = degradate compound, I-OP = organophosphorus insecticide, I-C = carbamate insecticide, WP = Wood Preservative.

Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as 'several'.

Table F-4. Pesticide residue results for the South Fork of Thornton Creek, 2003-2005. Concentrations reported as µg/L.

Chemical	[1]Use	Common Name	2003, n=18		
			Freq	Median	Max
Pentachlorophenol	WP	Penta	78%	0.0125	0.075
Dichlobenil	H	Casoron	56%	0.011	0.032
Diuron	H	Karmex	50%	0.07	0.23
Diazinon	I-OP	(several)	44%	0.0295	0.21
2,4-D	H	(several)	11%	0.014	0.017
Triclopyr	H	(several)	11%	0.0125	0.013
4-Nitrophenol	D		6%	0.25	0.25
Benzamide, 2,6-dichloro-	D		6%	0.063	0.063
Prometon	H	Pramitol 5PS	6%	0.005	0.005
Tebuthiuron	H	Spike	6%	0.014	0.014

Use Descriptors: H = herbicide, D = degradate compound, I-OP = organophosphorus insecticide, WP = Wood Preservative.

Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as 'several'.

Table F-5. Pesticide residue results for the upper reach of Marion Drain, 2003-2005. Concentrations reported as µg/L.

Chemical	[1]Use	Common Name	2003, n=12		
			Freq	Median	Max
Atrazine	H	Aatrex	67%	0.004	0.01
Terbacil	H	Sinbar	67%	0.023	0.41
2,4-D	H	(several)	58%	0.027	1.9
MCPA	H	(several)	42%	0.038	0.076
Pendimethalin	H	Prowl	42%	0.010	0.097
Bromoxynil	H	Buctril	33%	0.006	0.012
Dimethoate	I-OP	Dimethoate	33%	0.020	0.024
Chlorpyrifos	I-OP	Dursban	25%	0.006	0.0089
Bromacil	H	Hyvar	17%	0.005	0.007
Dicamba I	H	Banvel	17%	0.042	0.079
Azinphos methyl	I-OP	Guthion	8%	0.0003	0.0003
Malathion	I-OP	(several)	8%	0.015	0.015
Simazine	H	Simazine	8%	0.0016	0.0016
Trifluralin	H	Treflan	8%	0.006	0.006

Use Descriptors: H = herbicide, I-OP = organophosphorus insecticide.
Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as 'several'.

Table F-6. Pesticide residue results for the upper reach of Spring Creek, 2003-2005. Concentrations reported as µg/L.

Chemical	[1]Use	Common Name	2003, n=12			2004, n=15		
			Freq	Median	Max	Freq	Median	Max
2,4-D	H	(several)	75%	0.051	0.31	69%	0.06	0.73
Bromacil	H	Hyvar	58%	0.026	0.12	19%	0.015	0.02
Atrazine	H	Aatrex	50%	0.0027	0.0056	44%	0.0076	0.011
Pendimethalin	H	Prowl	42%	0.026	0.088	38%	0.0535	0.21
Chlorpyrifos	I-OP	Dursban	42%	0.018	0.05	25%	0.0155	0.02
Norflurazon	H	Solicam	33%	0.0135	0.065	13%	0.0495	0.058
Terbacil	H	Sinbar	33%	0.0555	0.21	13%	0.0207	0.032
Diuron	H	Karmex	25%	0.031	0.32	50%	0.046	0.22
MCPA	H	(several)	17%	0.0275	0.037	19%	0.022	0.024
Simazine	H	Simazine	17%	0.00215	0.0031	13%	0.0205	0.032
Azinphos methyl	I-OP	Guthion	17%	0.0141	0.025	6%	0.018	0.018
Dicamba I	H	Banvel	17%	0.0076	0.011	6%	0.044	0.044
4,4'-DDE	D		17%	0.01025	0.017			
Dichlobenil	H	Casoron	17%	0.0027	0.0041			
Hexazinone	H	Velpar	17%	0.0237	0.043			
Malathion	I-OP	(several)	8%	0.0032	0.0032	13%	0.0175	0.021
4-Nitrophenol	D		8%	0.0054	0.0054	6%	0.014	0.014
Carbaryl	I-C	Sevin	8%	10	10			
Di-allate	H		8%	0.23	0.23			
Dimethoate	I-OP	Dimethoate	8%	0.0028	0.0028			
Diphenamid	H		8%	0.048	0.048			
Endosulfan I	I-OC	Thionex	8%	0.016	0.016			
Hexachlorobenzene	F		8%	0.16	0.16			
Phosmet	I-OP	Imidan	8%	0.076	0.076			
Metolachlor	H	Stalwart	8%	0.017	0.017			
Pronamide	H	Kerb	8%	0.0031	0.0031			
Ronnel	I-OP		8%	0.0071	0.0071			
Trifluralin	H	Treflan	8%	0.0019	0.0019			
Oxyfluorfen	H	Goal				13%	0.031	0.041
Bentazon	H	Basagran				6%	0.039	0.039

Use Descriptors: H = herbicide, D = degradate compound, I-OP = organophosphorus insecticide, I-OC = organochlorine insecticide, I-C = carbamate insecticide.

Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as 'several'.

Table F-7. Pesticide residue results for the middle reach of Spring Creek, 2003-2005. Concentrations reported as µg/L.

Chemical	[1]Use	Common Name	2003, n=12			2005, n=15		
			Freq	Median	Max	Freq	Median	Max
Bromacil	H	Hyvar	92%	0.031	0.17			
2,4-D	H	(several)	75%	0.046	0.17			
Atrazine	H	Aatrex	50%	0.00335	0.0098	93%	0.0195	0.048
Diuron	H	Karmex	42%	0.031	0.27	7%	0.053	0.053
Pendimethalin	H	Prowl	42%	0.0072	0.02			
Terbacil	H	Sinbar	42%	0.086	0.21			
Chlorpyrifos	I-OP	Dursban	33%	0.004	0.0072	20%	0.029	0.059
Norflurazon	H	Solicam	33%	0.029	0.062	13%	0.026	0.034
Simazine	H	Simazine	25%	0.0044	0.017			
Bentazon	H	Basagran	8%	0.022	0.022	60%	0.075	0.093
Azinphos methyl	I-OP	Guthion	8%	0.01	0.01	7%	0.028	0.028
Pentachlorophenol	WP	Penta	8%	0.018	0.018	7%	0.043	0.043
Bromoxynil	H	Buctril	8%	0.029	0.029			
Carbaryl	I-C	Sevin	8%	1.7	1.7			
Endosulfan Sulfate	D		8%	0.019	0.019			
Malathion	I-OP	(several)	8%	0.076	0.076			
Oxyfluorfen	H	Goal	8%	0.238	0.238			
4,4'-DDE	D					7%	0.0026	0.0026
Phosmet	I-OP	Imidan				7%	0.022	0.022
Propazine	H	Propazine				7%	0.0089	0.0089

Use Descriptors: H = herbicide, D = degradate compound, I-OP = organophosphorus insecticide, I-C = carbamate insecticide, WP = Wood Preservative.

Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Others with multiple, competing labels, are listed as ‘several’.

Appendix G. Temperature Profiles

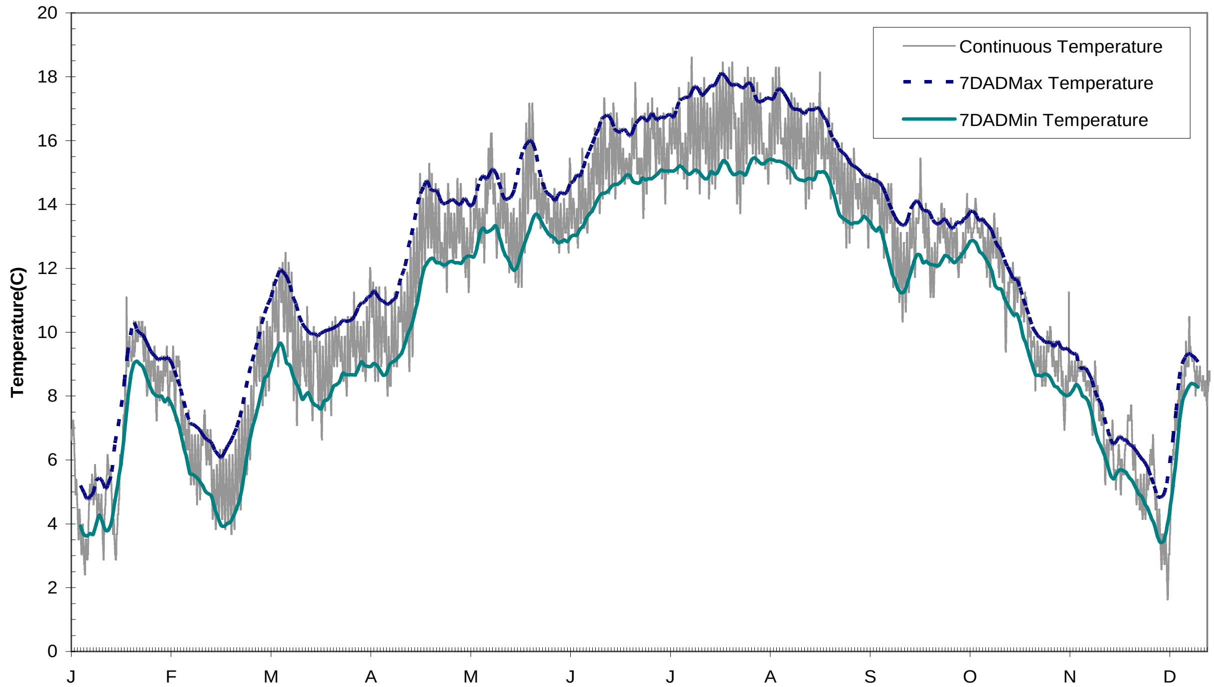

Figure G-1. Year 2005 temperature profile for the North Fork of Thornton Creek.

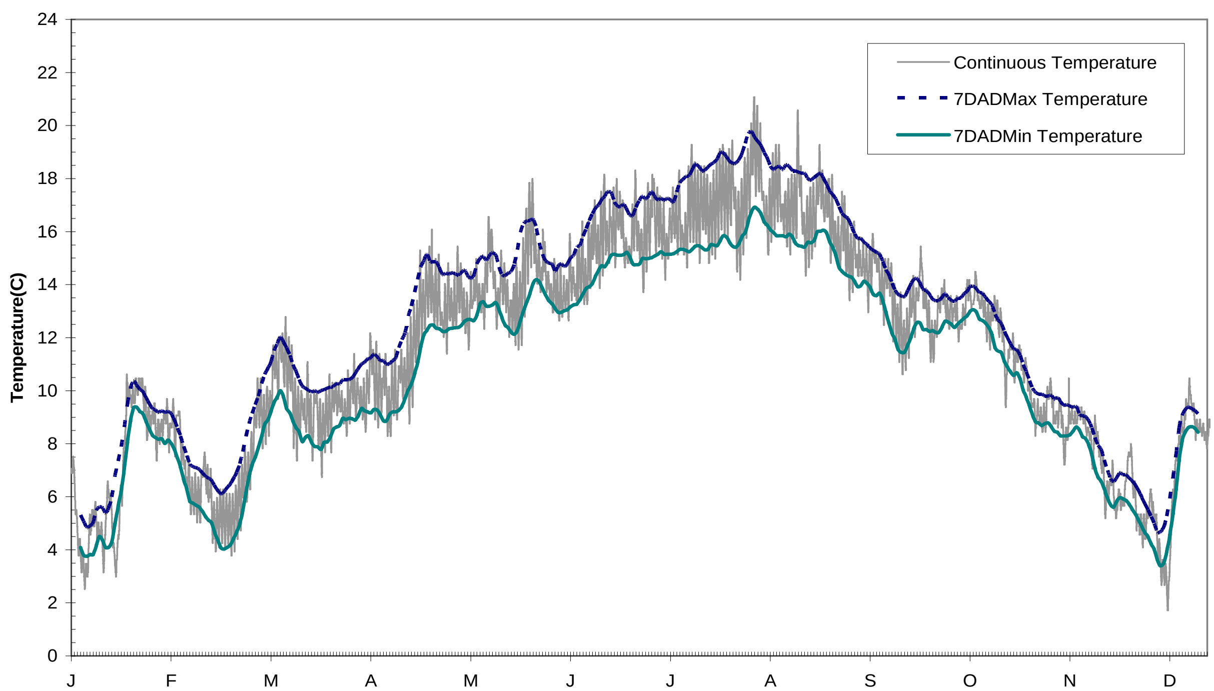

Figure G-2. Year 2005 temperature profile for the mainstem of Thornton Creek.

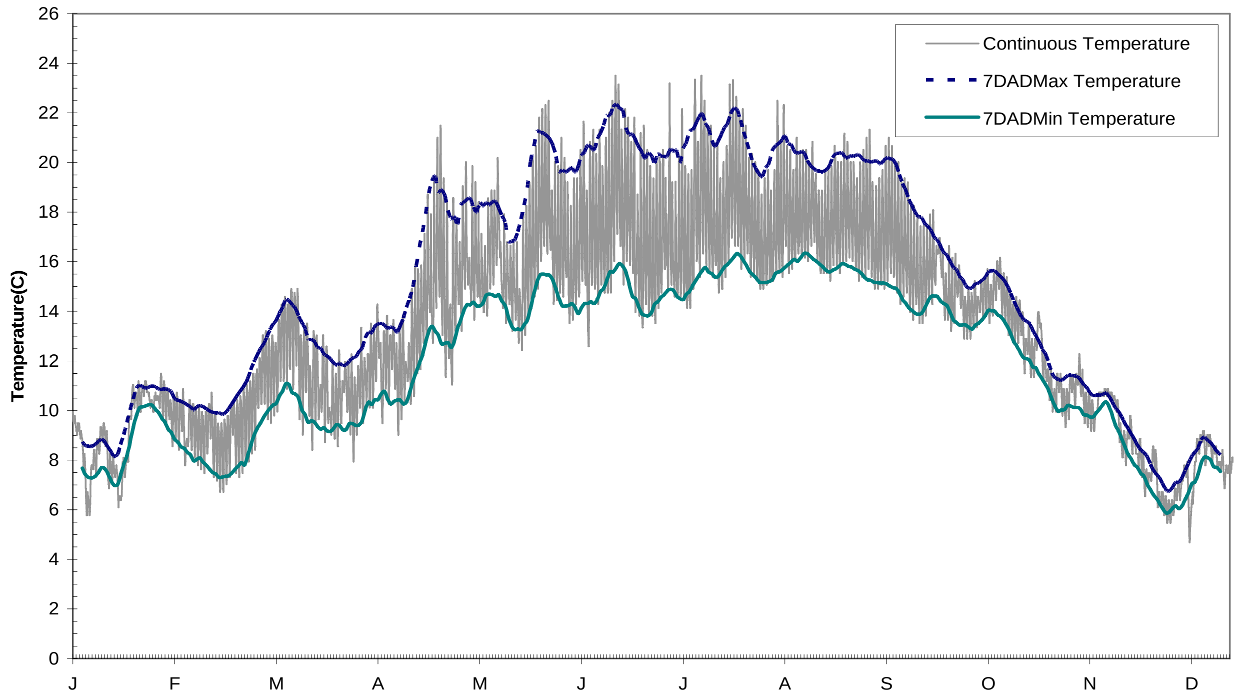

Figure G-3. Year 2005 temperature profile for the mainstem of Marion Drain.

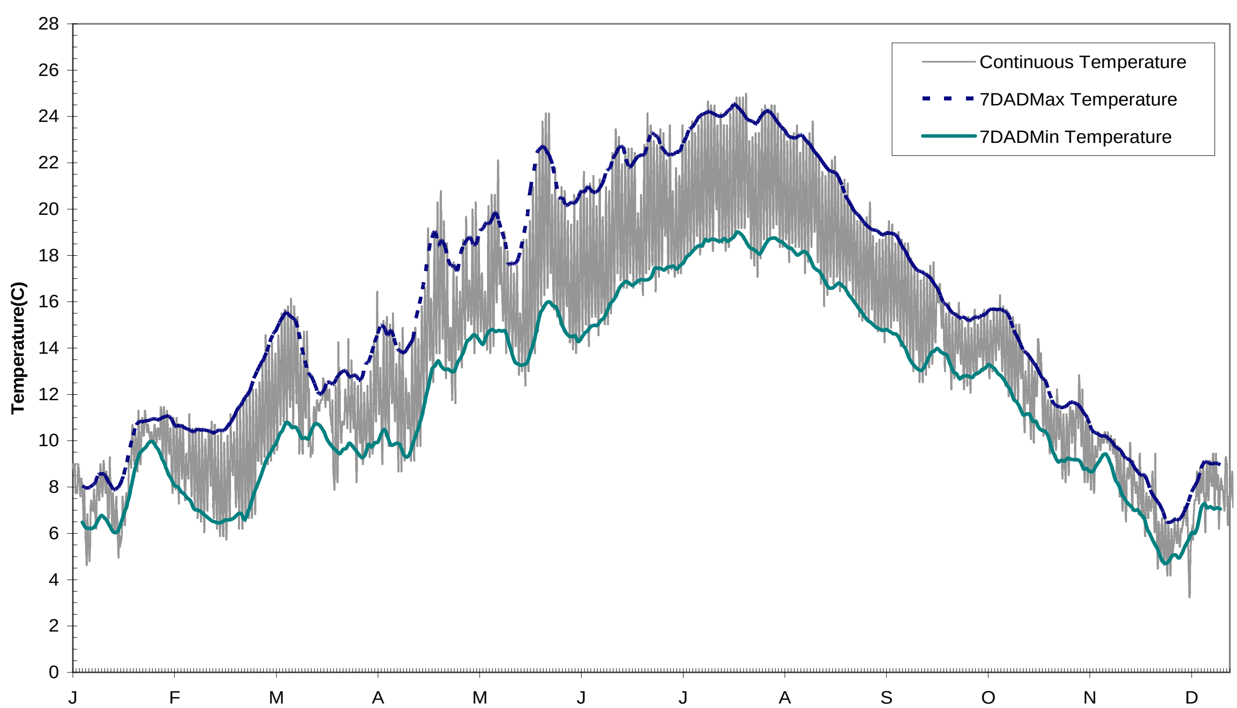

Figure G-4. Year 2005 temperature profile for the mainstem of Sulphur Creek Wasteway.

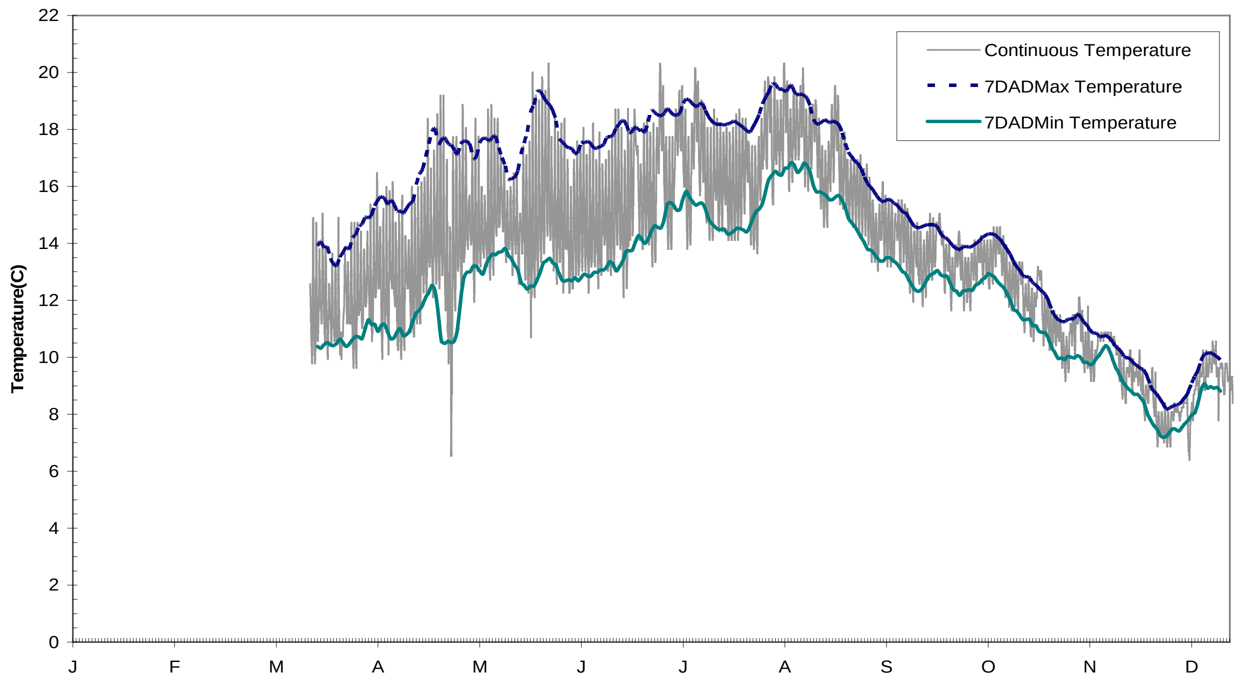

Figure G-5. Year 2005 temperature profile for the midstream Spring Creek station.

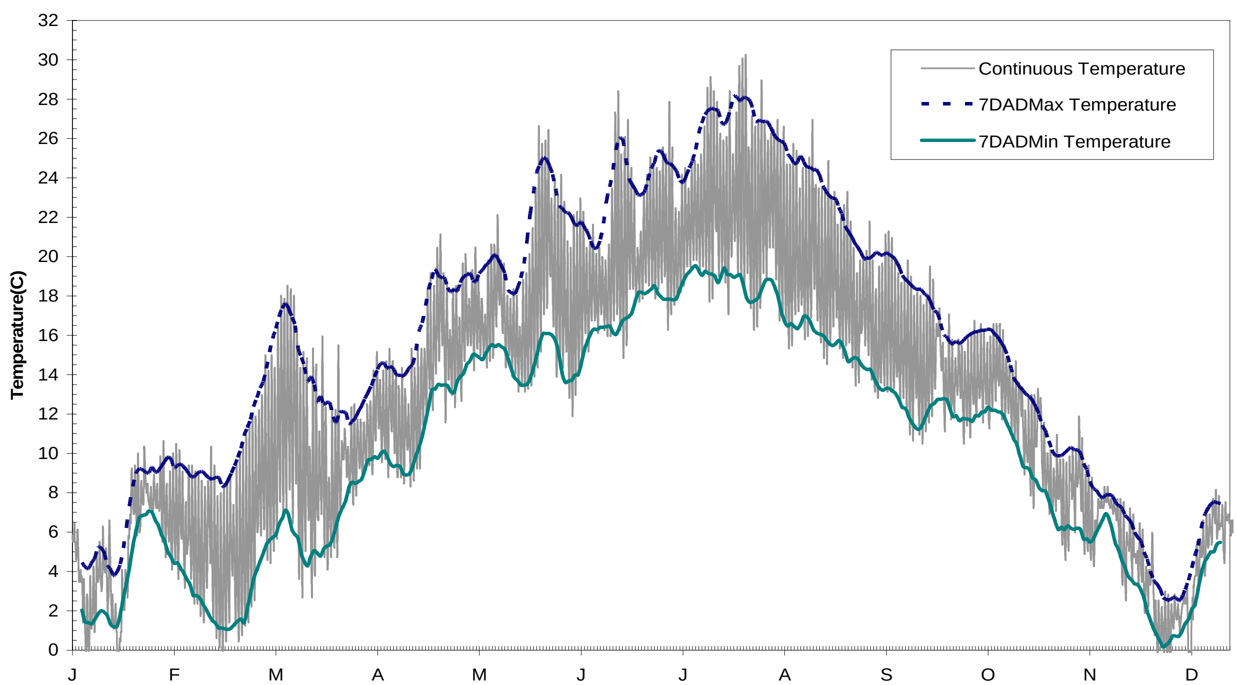

Figure G-6. Year 2005 temperature profile for the mainstem of Spring Creek.