WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Washington State Pesticide Monitoring Program

1995 Surface Water Sampling Report

January 1998

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Washington State Pesticide Monitoring Program

1995 Surface Water Sampling Report

by
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Environmental Investigations and Laboratory Services Program
Olympia, Washington 98504-7710

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Water Body No. (see Abstract)

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Table of Contents

List of Figures and Tables

Page

Figures

Tables

Abstract

Initiated in 1991 by the Department of Ecology, the Washington State Pesticide Monitoring Program (WSPMP) analyzes ground water, surface water, fish tissue, and sediments for pesticide residues. The results of these analyses are used to provide information on how these residues are distributed in the environment and how these patterns are changing over time.

WSPMP surface water samples were collected at seven sites in April, June, August, and September of 1995. Samples were collected monthly at four additional sites from March through September in conjunction with the Yakima River total maximum daily load (TMDL) study performed in 1995 by Ecology's Watersheds Assessments Section. Sites were selected to represent various pesticide uses, including use (1) by irrigated agriculture in the Columbia Basin and Yakima Valley, (2) on cranberry farms on the Washington coast, (3) in urban and suburban areas, and (4) by forest practices (Christmas tree farms).

Samples were analyzed for 161 pesticides and breakdown products in the following chemical groups: chlorinated pesticides, organo-phosphorus pesticides, nitrogen-containing pesticides, pyrethroid pesticides, chlorinated herbicides, and carbamates. Conventional parameters measured included total suspended solids, total organic carbon, conductivity, nitrate+nitrite, temperature, pH, and flow.

Thirty-nine pesticides and breakdown products were detected in WSPMP samples. Seven additional compounds were found in samples for the Yakima River TMDL. The most frequently detected pesticides were 4,4'-DDE, azinphos-methyl, chlorpyrifos, 2,4-D, atrazine, simazine and terbacil. Washington State and/or USEPA aquatic life criteria were exceeded at four WSPMP sites, and all four of the Yakima River TMDL sites. Pesticides above criteria were total DDT, azinphos-methyl (Guthion), chlorpyrifos (Dursban, Lorsban), and malathion. Levels of carbaryl, diazinon, and endosulfan exceeded National Academy of Sciences (NAS) recommended maximum concentrations to protect aquatic life and wildlife.

Pesticide use on cranberries in the Grayland area resulted in a high number and frequency of detections in Grays Harbor County Drainage Ditch No.1 (GHCDD-1). Five insecticides and five herbicides were found in all four sample periods. Five insecticides were detected at concentrations exceeding water quality criteria, three of these at the highest levels ever recorded in the state. These results prompted an intensive survey in 1996 to assess pesticide contamination from cranberry bog drainage in the Grayland area.

A large number of pesticides were also detected in Crab Creek Lateral and EL68D (Figure 1), 16 and 19 respectively. These streams are irrigation returns in the Mid-Columbia Basin. Concentrations of three insecticides from Crab Creek Lateral and two from EL68D were above water quality criteria. Effects from the combination of all these pesticides are unknown, but are likely to be greater than individual effects.

Azinphos-methyl and chlorpyrifos were found at concentrations above water quality criteria in samples from Cowiche Creek, which drains orchards northwest of Yakima. Similar levels of these two pesticides have been found in other streams in Washington adjacent to orchards, indicating that label requirements and/or application techniques for tree fruit are not adequate to keep these pesticides out of surface waters.

High concentrations of total DDT and azinphos-methyl were detected in a majority of the samples collected from the Yakima River and three of its tributaries. Other insecticides found included carbaryl, chlorpyrifos, diazinon, and malathion. Guidelines outlined in the report for the Yakima River TMDL should reduce levels of total DDT in the water column below state standards by reducing suspended sediment to which DDT binds. However, azinphos-methyl and the other currently used insecticides are probably not bound to sediment particles and may continue to be a problem after sediment controls are in place.

Recommendations include:

- An assessment of irrigation returns in the Mid-Columbia Basin to determine how pesticides are affecting aquatic life and wildlife in the basin.
- Changes to pesticide application techniques for tree fruit to keep insecticides out of surface waters and subsequent monitoring to evaluate the effectiveness of new techniques.
- Periodic monitoring of streams in the Yakima Valley to determine if BMPs developed to reduce suspended sediment are helping to reduce concentrations of currently used pesticides.

Water Body Numbers:

WA-15-5000
WA-24-1030
WA-26-1092
WA-36-9110
WA-37-1010
WA-37-1014
WA-37-1024
WA-37-1030
WA-38-1015
WA-39-1032
WA-41-1016

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- ◊ Dickey Huntamer, Norm Olson, and Stuart Magoon of Ecology's Manchester Environmental Laboratory for their extra efforts to provide exceptional analytical services and for their valuable technical advice.
- ◊ The U.S. Bureau of Reclamation and the U.S. Geological Survey for providing stream flow data.
- ◊ Joe Joy and Barbara Patterson for sample collection and supplying data from the Yakima River sites.
- ◊ Glenn Merritt for providing valuable review comments for the draft report.
- ◊ Joan LeTourneau for formatting the final report.

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Summary

A total of 39 pesticides and breakdown products were detected in 32 surface water samples collected for the WSPMP from eight sites in April, June, August, and September of 1995. Seven additional compounds were found in 24 samples collected monthly from four sites in conjunction with the Yakima River total maximum daily load (TMDL) (Joy and Patterson, 1997).

The herbicide 2,4-D was the most frequently detected pesticide and was found in 25 samples from eight sites. Other commonly detected herbicides were atrazine, simazine, and terbacil. Azinphos-methyl (Guthion) and chlorpyrifos (Dursban, Lorsban) were the insecticides found most often.

Four pesticides were detected at concentrations exceeding Washington State and/or U.S. Environmental Protection Agency (USEPA) aquatic life criteria (Table 1). In other samples, concentrations of carbaryl, diazinon, and malathion were above National Academy of Sciences (NAS, 1973) recommended maximum concentrations to protect aquatic life and wildlife. In one sample from Grays Harbor County Drainage Ditch No.1 (GHCDD-1), carbofuran exceeded Canadian water quality guidelines (CCREM, 1987).

Numerous pesticides are present consistently in water draining from cranberry bogs in Grayland. In GHCDD-1, 19 compounds were detected in water samples collected in 1995. Concentrations of azinphos-methyl and total DDT exceeded the USEPA (1986) water quality criterion, and chlorpyrifos was above Washington State water quality standards. All detected levels of diazinon easily exceeded the NAS recommendation, and one detection of carbofuran was above the Canadian guideline. Carbofuran, chlorpyrifos, and diazinon were found at the highest levels ever recorded in state surface waters. Ten of the 19 pesticides were detected in all four sample periods and another two were found in three periods, which is the highest number of multiple detections at WSPMP sample sites. This indicates that a high proportion of the compounds found in GHCDD-1 are in the water for extended periods of time, and resident flora and fauna may be experiencing adverse effects that would not be expected for short duration exposures. Concentrations of some insecticides are high enough to be acutely toxic to some invertebrates. If the effects are additive or synergistic, mixtures of these insecticides may result in impacts to aquatic fauna that are more damaging than would be expected from the individual pesticides.

These results from GHCDD-1 prompted meetings between Ecology, the USEPA, the cranberry industry, and other interested groups in the fall of 1995 and spring of 1996. These meetings resulted in several studies in 1996 to assess pesticide contamination associated with cranberry farming in the Grayland area. A report by Ecology (Davis *et al.*, 1997) evaluates the extent and severity of contamination in water, sediment, and fish and shellfish. Related studies are discussed and referenced in the Ecology report.

Table 1. Pesticides Exceeding Water Quality Criteria in 1995 (µg/L, ppb)

Water Body	Pesticide	Date	Concentration	Criteria (chronic)	Reference
GHCDD-1	total DDT	April 17	0.019	0.001	WAC 173-201A
		June 19	0.014		
		August 8	0.02		
		October 2	0.017		
	azinphos-methyl	June 19	0.21	0.01	USEPA, 1986
		August 8	0.48		
		October 2	0.018		
	chlorpyrifos	April 17	0.045	0.041	WAC 173-201A
		August 8	0.13		
Crab Creek Lateral	azinphos-methyl	June 26	0.08	0.01	USEPA, 1986
		July 31	0.025		
EL68D	chlorpyrifos	Sept. 25	0.39	0.041	WAC 173-201A
	malathion	June 26	0.13	0.1	USEPA, 1986
Cowiche Creek	azinphos-methyl	June 26	0.12	0.01	USEPA, 1986
		July 31	0.049		
		Sept. 25	0.079		
Yakima River	total DDT	June 19	0.004	0.001	WAC 173-201A
		August 1	0.004		
		Sept. 26	0.002		
	azinphos-methyl	May 22	0.028	0.01	USEPA, 1986
		June 19	0.036		
		July 17	0.028		
		August 1	0.021		
	chlorpyrifos	June 19	0.12	0.041	WAC 173-201A

Table 1 (cont.). Pesticides Exceeding Water Quality Criteria in 1995 (µg/L, ppb)

Water Body	Pesticide	Date	Concentration	Criteria (chronic)	Reference
Granger Drain	total DDT	April 25	0.009	0.001	WAC 173-201A
		May 22	0.024		
		June 19	0.36		
		July 17	0.085		
		August 1	0.094		
		Sept. 26	0.025		
Granger Drain	azinphos-methyl	May 22	0.063	0.01	USEPA, 1986
		June 19	0.1		
		July 17	0.038		
		August 1	0.04		
Sulfur Creek Wstwy	total DDT	April 25	0.005	0.001	WAC 173-201A
		May 22	0.009		
		June 19	0.012		
		July 17	0.012		
		August 1	0.038		
		Sept. 26	0.007		
	azinphos-methyl	May 22	0.1	0.01	USEPA, 1986
		June 19	0.14		
		July 17	0.048		
		Sept.26	0.026		
Spring Creek	total DDT	May 22	0.005	0.001	WAC 173-201A
		June 19	0.01		
		July 17	0.007		
		August 1	0.022		
		Sept. 26	0.005		
	azinphos-methyl	May 22	0.13	0.01	USEPA, 1986
		June 19	0.074		
		July 17	0.041		
		Sept. 26	0.014		
	chlorpyrifos	March 20	0.48	0.041	WAC 173-201A

A high number of different pesticides were also detected in samples from two irrigation returns in the Mid-Columbia Basin: Crab Creek Lateral (16) and EL68D (19). Most of these compounds were herbicides, found at low levels. Azinphos-methyl from Crab Creek Lateral, and chlorpyrifos and malathion from EL68D exceeded USEPA or Washington State water quality criteria.

Chlorpyrifos and endosulfan from Crab Creek Lateral were above NAS recommended maximum levels. Although most of the concentrations were relatively low, the high number of different compounds present at the same time could be resulting in unexpected negative impacts.

Azinphos-methyl and chlorpyrifos, insecticides commonly used on orchards, were found at concentrations above water quality criteria in samples from Cowiche Creek northwest of Yakima. Similar levels of these two pesticides have been found in other streams in Washington adjacent to orchards (Davis, 1996), indicating that label requirements and/or application techniques for tree fruit are not adequate to keep these pesticides out of surface waters.

Concentrations of total DDT and azinphos-methyl exceeding Washington State and USEPA criteria were detected in a majority of the samples collected from the Yakima River and three of its tributaries. Other insecticides found above Washington State standards or NAS recommendations included carbaryl, chlorpyrifos, diazinon, and malathion. Guidelines outlined in the report for the Yakima River TMDL should reduce levels of total DDT in the water column below state standards by reducing suspended sediment that DDT binds to. However, azinphos-methyl and the other currently used insecticides are probably not bound to sediment particles and may continue to be a problem after sediment controls are in place.

Recommendations

Additional Sampling for the WSPMP

- Periodically monitor streams in the Yakima Valley to determine if suspended sediment reduction guidelines outlined in the Yakima River TMDL report have also reduced concentrations of currently used pesticides in surface waters.

Intensive Surveys

- Perform an intensive survey to determine the impacts of pesticide contamination on aquatic life and wildlife in streams within the Mid-Columbia Basin.

(Intensive surveys are not an objective of the WSPMP and would require separate funding and implementation)

Additional Recommendations

- Revise label requirements and/or application techniques for azinphos-methyl and chlorpyrifos when used to control pests on tree fruit so that concentrations in streams adjacent to orchards are reduced to acceptable levels.

- Develop Washington State Water Quality Standards for the following insecticides that are frequently detected in surface waters of the state at concentrations potentially harmful to aquatic life: azinphos-methyl (Guthion), carbofuran, diazinon, and malathion.

- Develop Washington State Water Quality Standards for the following herbicides that are the most frequently detected pesticides in the state: (in order of frequency of detection) 2,4-D, DCPA (Dacthal), simazine, atrazine, dichlobenil, and bromacil.

- Develop guidelines for Washington State Water Quality Standards that address additivity for cases where multiple pesticides are detected in the same sample.

Interagency Coordination

- Present findings of this study to the Washington State Department of Agriculture and the Washington State University Cooperative Extension.

- Collaborate with these agencies to develop alternative substances, application rates, integrated pest management, or other best management practices (BMPs) to mitigate potential adverse effects from continued use of target compounds.

- Collaborate with agencies and growers to design studies to evaluate effectiveness of BMP implementation.

Introduction

The Washington State Pesticide Monitoring Program (WSPMP) was initiated in 1991 by the Department of Ecology (Ecology) to monitor pesticide residues in ground water and surface water, including associated biota such as fish, shellfish, and waterfowl and bed sediments. Ground water and surface water monitoring are being implemented as separate tasks; this report addresses surface water sampling for 1995. Fish samples were collected in September 1995 and will be covered in a separate report. The goal and objectives of the WSPMP are as follows:

Goal

To characterize pesticide residues geographically and over time in ground water and surface water (including sediments and biota) throughout Washington.

Objectives

- Identify and prioritize aquifers, lakes, and streams with known or potential pesticide contamination.
- Quantify pesticide concentrations in high priority areas.
- Document temporal trends in pesticide types and concentrations at selected sites.
- Provide data to the State Department of Health for assessment of potential adverse effects on human health.
- Assess the potential for adverse effects of pesticides on aquatic biota.
- Construct and maintain a pesticide database for ground water and surface water in Washington.
- Provide information for the improvement of pesticide management in Washington State.

The WSPMP is an ongoing screening survey to identify potential pesticide contamination problems. Most sites are sampled for one year only, unless high concentrations or numbers of pesticides are found. When a potential problem is identified, a site may be sampled again the following year to verify and better define the problem, but intensive sampling is beyond the scope of the WSPMP. True trend monitoring to document statistically significant changes over time is also beyond the scope of this program. Trend monitoring for the WSPMP is limited to simple observations of the types and concentrations of pesticides found at a site over a period of two or three years.

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Methods

Sampling Design

Samples were collected at eight sites (Figure 1) in April, June, July/August, and September/October of 1995. July/August and September/October samples were collected in the last week of one month and the first week of the next month, and each pair represents one sample period. April and June are intended to represent the peak pesticide application period (late-March to early-July). July/August represents summer pesticide applications. Sampling in September/October was conducted to represent previously applied pesticide residues transported to streams in fall storm-water runoff.

The number of sample sites and the frequency of sampling were determined primarily by available funding. Within a particular watershed, streams were selected based on their probability of being contaminated with pesticides and potential impacts to the environment. Sources of this information for each site are different and often numerous, so listing them here is not practical. Typically, representatives from other government agencies, such as the Conservation District, Cooperative Extension Service, and the U.S. Geological Survey are contacted for their input. Information from the private sector is also used.

Sampling for the WSPMP is integrated into Ecology's five-year watershed planning cycle. Sites are selected for pesticide sampling within watersheds scheduled for Needs Assessments the following year. Results from the WSPMP are used to identify areas with potential pesticide-related problems. These results are presented during Needs Assessments for the watersheds so potential problems can be evaluated more effectively using recent, pertinent data.

The sampling emphasis for the 1995 WSPMP was within the Kitsap, Lower and Mid Columbia River, and Upper and Lower Yakima River watersheds. The Lower Yakima River watershed was due to come up in 1996 in the watershed cycle, but was combined with the Upper Yakima for convenience and continuity.

Washington State Pesticide Monitoring Program

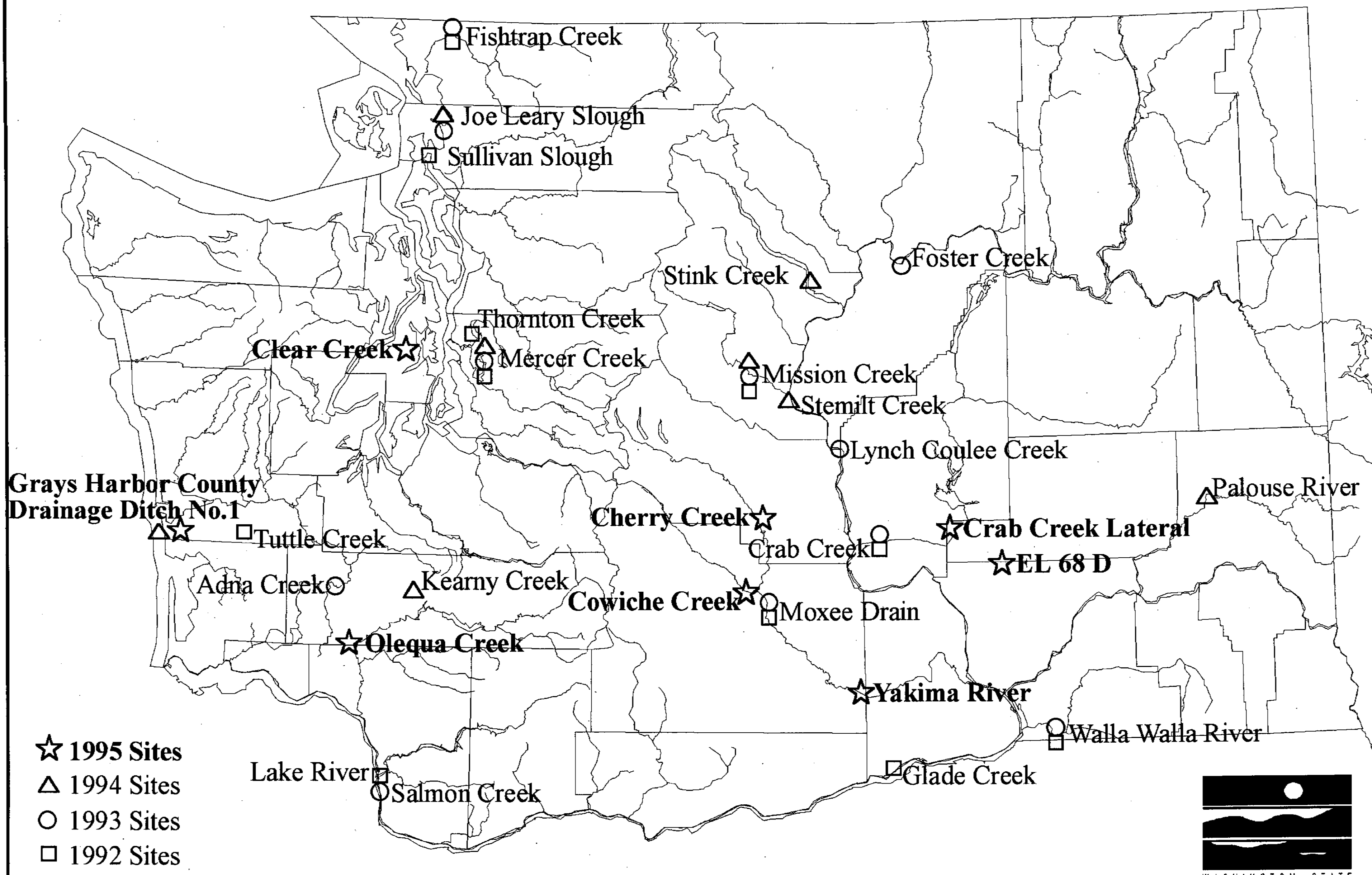

Figure 1. 1992, 1993, 1994, and 1995 WSPMP Surface Water Sampling Sites

Grays Harbor County Drainage Ditch No.1 (GHCDD-1) was sampled for the second year to verify detections. Verification (trend) sampling does not necessarily follow the watershed approach cycle. GHCDD-1 was first sampled in 1994 for the Western Olympic watershed needs assessment.

Three sites, Granger Drain, Sulfur Creek Wasteway, and Spring Creek, were sampled in coordination with the Yakima River TMDL (Joy and Patterson, 1997). These sites were selected because they contributed some of the highest suspended sediment loads to the river, and because there was sufficient historical pesticide data to make comparisons over time. Funding for the TMDL would have limited pesticide analyses to chlorinated insecticides only, but by pooling resources with the WSPMP it was possible to analyze samples for organophosphorus and nitrogen-containing pesticides as well, to the benefit of both projects. These three sites are near the Yakima River mainstem site, which was also part of the TMDL. Each of these sites was sampled monthly from March to September, encompassing the irrigation season for the Yakima Valley. Latitude, longitude, and state plane coordinates are listed for each site in Appendix A.

WSPMP samples were analyzed for 161 pesticides and breakdown products (Appendix B). Samples were also collected for total suspended solids (TSS), total organic carbon (TOC), conductivity, and nitrate+nitrite. Field measurements were taken for temperature, pH, and flow.

Sampling Sites

Table 2. List of Sample Sites, Locations, and Pesticide Uses Typical of the Site

Sample Site	Location	Represented Pesticide Use
Clear Creek	at Silverdale, Kitsap Co.	suburban, rural
GHCDD-1	at Grayland, Grays Harbor Co.	cranberries
Olequa Creek	at Vader, Lewis Co.	Christmas tree farms
Cherry Creek	at Thrall, Kittitas Co.	various row crops, orchards
Crab Creek Lateral	at Royal Lake, Adams Co.	orchards, row crops
EL68D	at Hwy. 17, Franklin Co.	various row crops
Cowiche Creek	near Hwy. 12, Yakima Co.	orchards
Yakima River	at Euclid Rd bridge, Yakima Co.	hops, orchards, row crops, urban

Sampling Procedures, Analytical Methods, and QA/QC

Details of sampling procedures are outlined by Davis (1993). Procedures essentially followed those described in the Illinois EPA (1987) field methods manual. A report by Ecology's Manchester Environmental Laboratory (Huntamer, *et al.*, 1992) gives the details of the analytical methods used for the WSPMP and modifications to the methods necessary to incorporate the expanded target analyte list. A brief discussion of sampling procedures, analytical methods, and quality assurance/quality control is in Appendix C. A data quality review is presented in Appendix D.

Results and Discussion

Pesticides Detected

A total of 39 pesticides and breakdown products were detected in water samples collected for the 1995 WSPMP (Table 3). Seven additional compounds were found in samples for the Yakima River TMDL (Table 4). The concentrations of most compounds were in the parts per trillion range. Only MCPA from Clear Creek; carbofuran, dichlobenil, and napropamide from GHCDD-1; and propargite from EL68D were detected in the parts per billion range.

Pesticides that exceeded water quality criteria for the protection of aquatic life are highlighted with bold type in Tables 3 and 4. Nine insecticides were detected at concentrations above criteria; no herbicides were found above criteria. For reference, pesticides detected in the 1992, 1993, and 1994 WSPMP have been included in Appendices E-1, E-2, and E-3.

Breakdown Products

Four breakdown products of target pesticides were detected. DDE and DDD are metabolites of DDT and are more persistent in the environment than DDT, but less toxic. Since the ban of DDT in 1972, it would be expected that the proportion of metabolites would increase as the limited supply of the parent compound slowly degrades. DDE and DDD were detected in all four samples from GHCDD-1, but not DDT. DDE, DDD, and DDT were detected in all three tributaries to the Yakima River, but only DDE was found in samples from the mainstem site. In most cases, the concentration of DDT was lower than DDE, but in the sample from Granger Drain in June, the level of DDT was an order of magnitude higher than DDE or DDD, possibly indicating recent use. However, it is more likely that the DDT was from recently disturbed soils where undegraded DDT from historical use was buried (Risebrough and Jarman, 1984; Agee, 1986).

Disulfoton sulfone, the major degradation product of disulfoton, was detected at six of the sites, while disulfoton was found at only three sites. Information regarding the toxicity and persistence of disulfoton sulfone was not found, although, judging from its detection frequency, it appears to be more persistent than the parent compound.

A metabolite of dichlobenil, 2,6-dichlorobenzamide, was detected in all four of the samples from GHCDD-1. Dichlobenil was also found in these samples, and at relatively high concentrations. Information about this breakdown product could not be found either.

Table 3. Pesticides Detected in Water Samples Collected for the 1995 WSPMP (µg/L, ppb)

	Clear Creek				GHCDD-1[1]				Olequa Creek				Cherry Creek			
	18-Apr	20-Jun	7-Aug	2-Oct	17-Apr	19-Jun	8-Aug	2-Oct[2]	17-Apr	19-Jun	8-Aug	2-Oct	24-Apr	26-Jun	31-Jul	25-Sep
Insecticides																
4,4'-DDE					0.0081	0.0059	0.0067	0.005								
4,4'-DDD					0.011	0.008	0.013	0.012								
total DDT					**[3]0.019**	**[3]0.014**	**[3]0.02**	**[3]0.017**								
azinphos-methyl (Guthion)						**[4]0.21**	**[4]0.48**	**[4]0.018 J**								
carbofuran					0.4	0.785 J	**[5]2.3**	0.25								
chlorpyrifos (Lorsban)					**[3]0.045 J**	**[6]0.012 J**	**[3]0.13 J**	**[6]0.016 J**								
diazinon	**[6]0.012 J**			0.004 J	**[6]0.014 J**	**[6]0.22**	**[7]0.68**	**[6]0.03 J**						**[6]0.024 J**		
disulfoton sulfone														0.011 J		
malathion			**[6]0.051 J**													
Herbicides																
2,4-D	0.022 J	0.014 J	0.11	0.023 J	0.93	0.75	0.55	0.14				0.003 NJ	0.022 J	0.079	0.089	0.037
atrazine									0.025 J	0.30		0.010J			0.035 J	0.008 J
bromacil	0.013 NJ			0.032 J										0.069 J		
bromoxynil														0.011 NJ		
DCPA (Dacthal)													0.010 J			
dicamba		0.032 J	0.20	0.007 NJ	0.013 NJ							0.004 NJ			0.021 J	0.0098 J
dichlobenil				0.0098 J	3.1	7.5	2.0	0.92								
2,6-dichlorobenzamide					0.43 J	0.54 J	0.50 J	0.71 J								
dichlorprop					0.081		0.035 J	0.033 J								
diuron				0.036 NJ								0.017 NJ				
MCPA			1.2		0.020 NJ								0.066 J	0.010 NJ		0.015 J
MCPP	0.034 J		0.10	0.009 NJ									0.025 NJ			
metribuzin								0.01 NJ								
napropamide					1.5	0.38	0.34	0.26								
norflurazon					0.59	0.44 J	0.36 J	0.49 J								
simazine					0.058 J											
tebuthiuron												0.013 J				
terbacil								0.017 J								
triclopyr	0.015 J	0.006 J	0.23	0.014 J	0.033			0.045				0.006 NJ				
Fungicide																
pentachlorophenol					0.034		0.016 J				0.028					

Values in bold exceed water quality criteria

[1] - GHCDD-1 = Grays Harbor County Drainage Ditch No. 1

[2] - Values are means of duplicate analyses

[3] - Exceeds Washington State Water Quality Standards, WAC 173-201A

[4] - Exceeds USEPA (1986) Quality Criteria for Water

[5] - Exceeds Canadian Water Quality Guidelines (CCREM, 1987)

[6] - Exceeds National Academy of Sciences (1973) Recommended Maximum Concentration

[7] - Exceeds USEPA Lifetime Health Advisory for drinking water

J = The analyte was positively identified. The numerical value is an estimate.

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

Table 3 (cont.). Pesticides Detected in Water Samples Collected for the 1995 WSPMP (µg/L, ppb)

	Crab Creek Lateral				EL 68 D				Cowiche Creek				Yakima River			
	24-Apr	26-Jun[1]	31-Jul	25-Sep	24-Apr	26-Jun	31-Jul	25-Sep	24-Apr	26-Jun	31-Jul	25-Sep	24-Apr[1]	19-Jun	1-Aug[1]	26-Sep
Insecticides																
4,4'-DDE														**[2]0.004 J**	**[2]0.0039**	**[2]0.002 J**
azinphos-methyl (Guthion)		**[3]0.08 J**	**[3]0.025 J**							**[3]0.12**	**[3]0.049 J**	**[3]0.079 J**		**[3]0.036 J**	**[3]0.021 J**	**[4]0.008 NJ**
chlorpyrifos (Lorsban)	**[4]0.036 J**	**[4]0.009 NJ**			**[4]0.028 J**			**[2]0.39 J**	**[4]0.031 J**	**[4]0.004 NJ**				**[2]0.12**		
dimethoate			0.090 J				0.13 J				0.003 NJ				0.003 NJ	
disulfoton															0.027 J	
disulfoton sulfone						0.015 J		0.007 J							0.012 J	0.012 J
endosulfan I			**[4]0.011 J**													
endosulfan II			**[4]0.014 J**													
ethoprop																0.029 J
malathion			0.007 J			**[3]0.13**	**[4]0.011 J**			0.005 NJ					**[4]0.01 J**	
propargite						0.19 J	1.5	0.12 J							0.016 J	
Herbicides																
2,4-D	0.029 J	0.11	0.60	0.008 J	0.051	0.019	0.066	0.013 J			0.001 J			0.029 J	0.065	0.015 J
alachlor	0.019 J	0.02 J			0.008 NJ	0.044 J										
atrazine		0.013 J		0.008 J				0.01 J						0.034 J	0.014 J	0.01 J
bentazon	0.15	0.12		0.15	0.014 J	0.094	0.15	0.13							0.026 J	0.024 J
bromacil					0.016 J	0.049 J	0.024 J	0.037 J								
bromoxynil	0.089				0.063	0.008 J	0.0053 J									
chlorpropham								0.27								
DCPA (Dacthal)	0.83	0.010 J	0.002 NJ		0.098	0.023 J	0.007 J	0.008 J								
dicamba		0.006 NJ	0.002 NJ					0.005 J								
EPTC (Eptam)		0.36				0.068 J										
MCPA					0.042 J		0.007 J									
MCPP							0.011 NJ									
metolachlor		0.033 J														
metribuzin					0.036 J		0.010 J	0.005 NJ								
simazine		0.03 J							0.008 J					0.023 J		0.01 J
terbacil	0.34	0.14 J	0.053 J	0.14 J	0.18 J	0.12 J	0.067 J	0.13 J							0.038 J	0.12 J

Values in bold exceed water quality criteria

[1] - Values are means of duplicate analyses

[2] - Exceeds Washington State Water Quality Standards, WAC 173-201A

[3] - Exceeds USEPA (1986) Quality Criteria for Water

[4] - Exceeds National Academy of Sciences (1973) Recommended Maximum Concentration

J = The analyte was positively identified. The numerical value is an estimate.

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

Table 4. Pesticides Detected in Water Samples Collected as a Part of the 1995 Yakima River TMDL (µg/L, ppb)

	Granger Drain							Sulfur Creek Wasteway						
Sample Date	20-Mar	25-Apr	22-May	19-Jun	17-Jul	1-Aug	26-Sep	20-Mar	25-Apr	22-May	19-Jun	17-Jul	1-Aug	26-Sep
Insecticides														
4,4'-DDE		0.0086	0.016	0.03	0.037	0.045	0.013		0.0052	0.006	0.008 J	0.012	0.022	0.0068
4,4'-DDT			0.008	0.31	0.031	0.037	0.0084			0.003	0.004 J		0.01	
4,4'-DDD				0.017 J	0.017 J	0.012 J	0.004						0.0055	
total DDT		**[1]0.0086**	**[1]0.024**	**[1]0.36**	**[1]0.085**	**[1]0.094**	**[1]0.0254**		**[1]0.0052**	**[1]0.009**	**[1]0.012**	**[1]0.012**	**[1]0.0375**	**[1]0.0068**
azinphos-methyl			**[2]0.063 NJ**	**[2]0.1 J**	**[2]0.038 J**	**[2]0.04 J**				**[2]0.1 J**	**[2]0.14 J**	**[2]0.048 J**	**[3]0.008 J**	**[2]0.026 J**
carbaryl						**[3]0.54 J**								
chlorpyrifos									**[3]0.016 J**					
diazinon										0.009 J			0.004 J	
dimethoate											0.15			
disulfoton						0.022 J							0.019 J	
disulfoton sulfone					0.011 J	0.28 J	0.071 J						0.04 J	
malathion						**[3]0.051 J**								
methoxychlor							0.049 J							
propargite					0.21	0.15						0.067 NJ		
Herbicides														
atrazine		0.12		0.058 J	0.032 J	0.026 J					0.013 J	0.014 J		
alachlor					0.062 J									
bromacil		0.046 J				0.021 J			0.015 J			0.035 J		
cyanazine						0.026 J								
ethalfluralin						0.035 J								
hexazinone		0.094 J												
simazine		0.22	0.094 J	0.023 J	0.029 J	0.046 J				0.096		0.006 J		
terbacil							0.058 J					0.009 J	0.006 J	0.077 J
trifluralin					0.037 J	0.045 J								

Values in bold exceed water quality criteria for the protection of aquatic life

[1] - Exceeds Washington State Water Quality Standards, WAC 173-201A

[2] - Exceeds USEPA (1986) Quality Criteria for Water

[3] - Exceeds National Academy of Sciences (1973) Recommended Maximum Concentration

J = The analyte was positively identified. The numerical value is an estimate.

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

Table 4 (cont.). Pesticides Detected in Water Samples Collected as a Part of the 1995 Yakima River TMDL (µg/L, ppb)

	Spring Creek							Yakima River[4]		
Sample Date	20-Mar	25-Apr	22-May	19-Jun	17-Jul	1-Aug	26-Sep	20-Mar	22-May	17-Jul
Insecticides										
4,4'-DDE			0.0046	0.007	0.007	0.012	0.0049			
4,4'-DDT				0.003 J		0.0067				
4,4'-DDD						0.0033				
total DDT			**[1]0.0046**	**[1]0.010**	**[1]0.007**	**[1]0.022**	**[1]0.0049**			
azinphos-methyl			**[2]0.13**	**[2]0.074 J**	**[2]0.041 J**	**[3]0.004 J**	**[2]0.014 J**		**[2]0.028 NJ**	**[2]0.028 J**
chlorpyrifos	**[1]0.48**	**[3]0.024 J**								
diazinon					**[3]0.013 J**	0.003 J				
disulfoton sulfone					0.004 NJ					0.02 NJ
malathion				0.007 J						
propargite										0.032 J
Herbicides										
atrazine										0.035 J
bromacil		0.021 J			0.034 J					
norflurazon					0.046 J					
simazine		0.047 J								0.025 J
terbacil							0.049 J			0.052 J

Values in bold exceed water quality criteria for the protection of aquatic life

[1] - Exceeds Washington State Water Quality Standards, WAC 173-201A

[2] - Exceeds USEPA (1986) Quality Criteria for Water

[3] - Exceeds National Academy of Sciences (1973) Recommended Maximum Concentration

[4] - See Table 3 for Yakima River results for April, June, August, and September

J = The analyte was positively identified. The numerical value is an estimate.

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

Conventional Parameters

Results of conventional parameter analyses and field measurements are presented in Table 5. Cowiche Creek and EL68D are classified as Class A surface waters, and as such the state temperature standard is 18.0°C. Water temperature in these two streams was higher than the standard in June and August of 1995. It is unknown if these high temperatures were the result of human activities. Other parameters were within acceptable values.

Site Evaluations

Clear Creek

Clear Creek is a small stream that originates and runs through the length of Clear Creek Valley near Silverdale on the Kitsap peninsula, and discharges into Dyes Inlet. Land use in the Clear Creek Valley is exclusively suburban/rural residential, with a few small hobby farms, but no agriculture. Drainage for the commercial section of Silverdale and its roads and parking lots, including the Silverdale Mall, is separate and discharges directly into Dyes Inlet. The section of the creek that flows through Silverdale has been nearly undisturbed by commercial and residential development, and a wide riparian zone has been left intact. The sampling site was about one-half mile upstream from the mouth at Ridgetop Road in Silverdale.

Ten pesticides were detected in Clear Creek; eight were herbicides and three insecticides. Diazinon, a commonly used organophosphorus insecticide, was found in April at a concentration of 0.012 µg/L, which exceeds the National Academy of Sciences (NAS) recommended maximum concentration for protection of aquatic life of 0.009 µg/L (NAS, 1973). Malathion, another organophosphorus insecticide, was detected in August at 0.051 µg/L, which is above the NAS recommended maximum of 0.008 µg/L. The detected level of malathion does not exceed the U.S. Environmental Protection Agency (USEPA) water quality criterion of 0.1 µg/L (USEPA, 1986). Most of the eight herbicides were found at low concentrations, well below any available criteria. MCPA was the exception. It was detected at 1.2 µg/L, which is higher than any other detections of this compound by the WSPMP, but still below the only available criterion of 2.6 µg/L (CCREM, 1987).

Triclopyr and 2,4-D were found in all four samples from Clear Creek, and dicamba and MCPP were detected in three of the four samples. None of these four herbicides was detected at levels that would be expected to cause adverse impacts, but chronic and/or cumulative effects may be significant, especially with the addition of high concentrations of other compounds like MCPA for short periods.

Table 5. Results of Conventional Parameters for the 1995 WSPMP

	TOC (mg/L)				TSS (mg/L)				Nitrate+Nitrite (mg/L-N)				Conductivity (µmho/cm)			
	April	June	August	October	April	June	August	October	April	June	August	October	April	June	August	October
Clear Creek	7.4	3.2	11.2	5.0	3	2	7	4	0.377	0.536	0.569	0.393	54.3	159	119	157
GHCDD-1	13.6	11.4	13.2	12.4	17	9	2	5	0.157	0.144	1.69	0.133	119	191	191	200
Olequa Creek	2.8	3.4	2.9	4.0	2	2	3	2	0.397	0.225	0.117	0.223	188	88	103	106
Cherry Creek	5.0	3.9	5.3	3.1	129	52	77	27	0.628	0.808	1.77	0.707	232	248	370	245
Crab Creek Lateral	2.6	2.3	2.8	3.6	22	20	30	3	2.84	3.34	3.24	3.28	371	379	360	390
EL 68 D	3.8	2.8	3.1	2.8	104	90	100	17	2.55	5.36	4.81	3.20	313	355	328	348
Cowiche Creek	4.1	3.2	2.8	2.4	13	41	12	11	0.106	0.174	0.290	0.951	149	122	180	281
Yakima River	2.8	2.6	2.2	3.2	12	29	25	19	0.379	1.05	1.46	1.55	176	212	235	255

	Temperature (°C)				pH				Flow (CFS)			
	April	June	August	October	April	June	August	October	April	June	August	October
Clear Creek	5.8	11.9	14.2	11.9	7.2	7.6	7.3	7.4	11.1	3.0	11.7	7.7
GHCDD-1	8.3	13.6	14.7	14.1	7.2	6.6	6.7	6.4	8.9	6.2	7.2	5.1
Olequa Creek	5.8	13.9	17.1	13.7	8.1	7.7	7.6	7.2	63.8	13.7	7.7	5.3
Cherry Creek	10.6	14.7	13.8	13.9	7.9	8.1	7.9	7.8	125	71	145	349
Crab Creek Lateral	15.0	19.4	18.4	16.3	8.1	8.5	8.1	8.3	35	52	70	65
EL 68 D	15.0	[1] **20.3**	[1] **18.5**	16.9	8.0	8.1	8.0	8.3	125	209	270	340
Cowiche Creek	13.5	[1] **18.6**	[1] **19.2**	15.0	8.7	8.0	8.5	8.1	77	52	25	23
Yakima River	14.4	18.1	21.3	16.6	8.4	8.1	8.3	8.4	3134	2521	1454	1974

[1] - Exceeds Washington State Water Quality Temperature Standard for Class A streams.

Grays Harbor County Drainage Ditch No.1 (GHCDD-1)

GHCDD-1 drains cranberry bogs in the northern portion of the Grayland area and flows north through tide gates into South Bay near Bay City in Grays Harbor. This is a natural drainage of an area that was probably once a wetland, but it has been channeled to drain the cranberry bogs and surrounding residential property more efficiently. The sample site was at the bridge on Schmid Road in Grayland.

This site was sampled in 1994 for the WSPMP, and was recommended for continued sampling due to the high number and frequency of pesticide detections. None of the pesticides detected in 1994 was found at excessively high levels, but three of four insecticides detected exceeded criteria. In addition, three of the seven herbicides identified were found in all three of the samples collected that year.

In 1995 samples from GHCDD-1, six insecticides were detected. The same four insecticides seen in 1994 were detected again in 1995. Five insecticides were found in all four 1995 samples, and all six exceeded water quality criteria in at least one sample. Total DDT, chlorpyrifos, and diazinon exceeded criteria in all four samples. In the August sample, concentrations of carbofuran, chlorpyrifos, and diazinon were the highest ever recorded in state waters, and the level of azinphos-methyl equals the state high as recorded by the U.S. Geological Survey (USGS) (Wagner *et al.*, 1996). Any one of these insecticides at these concentrations is likely to be toxic to at least some of the aquatic life, and in combination their toxicity is probably additive. Animals that are not immediately impacted may succumb to chronic contamination by multiple toxic chemicals as seen here that are present from April to October.

As in 1994, none of the herbicides exceeded water quality criteria, but four of them – 2,4-D, dichlobenil, napropamide, and norflurazon – were detected in all four samples. Of these four, a water quality criterion is available for 2,4-D only. Concentrations of these four compounds were very high as compared to other detections by the WSPMP. Levels of dichlobenil and napropamide are the highest seen in state waters.

Olequa Creek

Olequa Creek originates two or three miles north of Winlock in Lewis County, and flows south through Winlock to Vader where it joins with Stillwater Creek just before flowing into the Cowlitz River near the Lewis/Cowlitz County line. Olequa Creek and several small tributaries flow through or near numerous Christmas tree farms, which is the primary commercially grown crop in the area and the most likely source of pesticide contamination. Samples were collected at the bridge on highway 506 in Vader before the confluence with Stillwater Creek.

Only one pesticide was detected in each of the samples collected in April, June, and August, but six were found in the October sample. Concentrations of all detections were low except atrazine in June, and all detected pesticides were herbicides except pentachlorophenol in August. The level of atrazine found in June did not exceed water quality criteria, but at 0.30 µg/L was the highest concentration yet recorded by the WSPMP in surface water. Four of the herbicides detected are commonly used for forest management (Norris and Dost, 1991), but atrazine is the only one that is registered for use on Christmas trees in Washington. Atrazine was found in samples collected in April, June, and October, and was the only pesticide detected more than once.

Cherry Creek

Cherry Creek drains an agricultural area southeast of Ellensburg that produces a variety of crops including corn, potatoes, apples, pears, grains, and hay. Many of the crops are irrigated from canals using furrow irrigation that results in substantial runoff into creeks and drainage ditches that discharge into Cherry Creek, which then flows into the Yakima River. Cherry Creek was sampled at Thrall at the U.S Bureau of Reclamation (USBR) stream gauge. This site is at a point just downstream from the confluence with Badger Creek, but upstream from the confluence with Wilson Creek. Stream flow data were obtained from the USBR.

Nine pesticides were detected in the four samples collected from Cherry Creek. Diazinon, the only insecticide found, was detected at a concentration of 0.024 µg/L in June, which exceeds the NAS recommended maximum of 0.009 µg/L. Disulfoton sulfone is the breakdown product of the insecticide disulfoton, and was also detected in June. The remaining eight compounds found in Cherry Creek were herbicides; 2,4-D was detected in all four samples, MCPA in three, and atrazine and dicamba in two. Herbicide concentrations were all well below any applicable criteria.

The USGS (Rinella *et al.*, 1992) sampled and analyzed water from Cherry Creek for pesticides in 1988-89 as a component of the Yakima River Basin National Water Quality Assessment Program (NAWQA). The USGS target pesticide list and detection limits were similar to those for the WSPMP. Herbicides detected by both sampling programs were similar, but concentrations reported by the USGS tended to be higher than for the WSPMP. Insecticide detections were very different. The USGS found four organochlorine insecticides in multiple samples, and a carbamate insecticide in one sample, but did not detect any organophosphorus insecticides. One organophosphorus insecticide was found in samples collected for the WSPMP, but no organochlorine or carbamate insecticides were detected.

One possible explanation for these differences is the increased use of mulching in the irrigation furrows (Burghart, 1992). Organochlorine pesticides are typically bound to sediment particles, so reduction of erosion and sediment transport by furrow mulching would likely result in reduced concentrations of pesticides in the creek. However, the average suspended sediment load has remained the same at about 70 mg/L, which suggests that furrow mulching has not reduced the sediment load.

Crab Creek Lateral and EL68D

Crab Creek Lateral and EL68D are irrigation return ditches near Othello in the Columbia Basin Irrigation Project (CBIP). Irrigation water originating from the West Canal collects in Crab Creek Lateral from the Royal Slope area west of Othello and north of highway 26 in Grant

County, and discharges through Royal Lake to Lower Crab Creek. Irrigation water supplied by the East Low Canal drains into EL68D from the Paradise Flats area east of Othello in Adams County, and discharges into the Potholes Canal at Highway 17 near Scooteney Reservoir.

Water samples were collected from Crab Creek Lateral at the flow gauge, and flow measurements were obtained from the USGS that monitors the gauge. Samples were collected from EL68D where it crosses under Highway 17, and flow was obtained from a staff gauge and rating table maintained by the USBR.

Numerous crops are grown in both areas, and alfalfa, wheat, dry beans, and corn are major crops that are grown on similar acreage in both areas (Wagner *et al.*, 1996). Differences include more acres of apples in the Crab Creek Lateral drainage, as well as more acres of potatoes, mint, and pea seed in the EL68D drainage area.

Sixteen pesticides were detected in samples from Crab Creek Lateral, five insecticides and 11 herbicides. Three of the insecticides – azinphos-methyl, chlorpyrifos, and endosulfan – were found at concentrations above water quality criteria. Chlorpyrifos was detected in April and June, azinphos-methyl in June and July, and endosulfan in July only. None of the herbicides exceeded criteria. Terbacil and 2,4-D were found in all four samples, bentazon and DCPA in three, and alachlor, atrazine, and dicamba in two.

A similar list of pesticides was detected in EL68D, a total of 19, with five insecticides and 14 herbicides. Three insecticides and nine herbicides were common to both sites. No herbicides exceeded water quality criteria in samples from EL68D, but two insecticides did, chlorpyrifos and malathion. Chlorpyrifos was found in April and September, and malathion in June and July. Five herbicides were found in all four samples: 2,4-D, bentazon, bromacil, DCPA, and terbacil. Bromoxynil and metribuzin were found in three samples, alachlor and MCPA in two.

Crab Creek Lateral and EL68D were each sampled 29 times in 1993 and 1994 by the USGS as a part of the Central Columbia Plateau NAWQA (Wagner *et al.*, 1996). The USGS found 36 pesticides, 11 insecticides, and 25 herbicides in Crab Creek Lateral, as well as 33 pesticides, 12 insecticides, and 21 herbicides in EL68D. Nearly all of the compounds detected in WSPMP samples were also found by the USGS. One notable exception was endosulfan, which was found above water quality criteria in one WSPMP sample, but was not detected by the USGS. The USGS detected more pesticides at both sites primarily because they collected more samples, but also because some of their detection limits were lower. Azinphos-methyl and chlorpyrifos exceeded criteria in USGS and WSPMP samples. Carbaryl and diazinon were also detected above criteria by the USGS, but these two insecticides were not found in WSPMP samples. None of the herbicides detected by the USGS in Crab Creek Lateral or EL68D exceeded water quality criteria.

Samples were collected from Crab Creek Lateral on June 26, 1995 by the USGS and for the WSPMP as an inter-laboratory comparison. Samples were collected separately by each agency, but within five minutes of each other. Not all of the same compounds were analyzed for by both agencies, and different analytical methods were used. Detected pesticides that were common to both target lists are compared in Appendix D-4. Concentrations for most compounds were similar, but five were detected by the USGS below the detection limit for the WSPMP. Reported concentrations for the WSPMP tended to be higher than USGS values.

Cowiche Creek

Cowiche Creek drains a large area northwest of Yakima, and flows into the Naches River about three miles upstream from its confluence with the Yakima River. The north fork of Cowiche Creek runs through an agricultural area consisting primarily of orchards, and land along the south fork is sparsely populated until it approaches the confluence with the north fork. Water was collected near the creek mouth at the bridge on Powerhouse Road. Stream flow was obtained from a staff gauge at the bridge and a rating table maintained by the USBR.

Only six pesticides were detected in samples from Cowiche Creek, four insecticides and two herbicides. Azinphos-methyl was found in three of the samples, and chlorpyrifos in two at levels exceeding water quality criteria. The three azinphos-methyl detections were above the USEPA criterion of 0.01 µg/L. Levels of chlorpyrifos exceeded the NAS recommended maximum concentration of 0.001 µg/L, but not the Washington State chronic criterion of 0.041 µg/L. Azinphos-methyl and chlorpyrifos are commonly used to control pests on tree fruit crops, and are often found in streams adjacent to orchards (Davis, 1996), indicating that label requirements and/or application techniques may need to be changed to keep these insecticides out of surface waters. The other four pesticides were each detected once at a low concentration.

Yakima River and Tributaries

The Yakima River is one of the largest rivers in the state. The river originates in Kittitas County from Keechelus and Kachess Lakes on the east side of the Cascade Mountains near Snoqualmie Pass. The Yakima River flows southeast through the Kittitas and Yakima Valleys ultimately discharging into the Columbia River near Richland. Tributaries include the Cle Elum, Teanaway, and Naches Rivers, as well as numerous creeks and irrigation returns. Much of the water is diverted for irrigation in the Yakima Valley, but some is recovered through surface and subsurface routes (Joy and Patterson, 1997).

Water samples were collected from the bridge on Euclid Road near Grandview. Samples collected in April, June, August, and September were analyzed for all 161 target pesticides as a part of the WSPMP. Three additional samples were collected in March, May, and July as a part of the Yakima River TMDL, and analyses for these samples did not include carbamates and chlorinated herbicides.

No pesticides were detected in samples collected from the Yakima River in March or April. Nine insecticides and five herbicides were found in the other five samples. Four of the insecticides – 4,4'-DDE, azinphos-methyl, chlorpyrifos, and malathion – exceeded water quality criteria. All three detections of 4,4'-DDE in June, August, and September were above the Washington State chronic criterion of 0.001 µg/L. Concentrations of azinphos-methyl found in samples collected in May, June, July, and August exceeded the USEPA criterion of 0.01 µg/L, and the level detected in September was above the NAS recommendation of 0.001 µg/L. Chlorpyrifos was detected in the June sample only, but at a concentration of 0.12 µg/L that exceeded the Washington State acute standard of 0.083 µg/L. Malathion was also detected just once, at 0.01 µg/L in August above the NAS recommended maximum level of 0.008 µg/L, but below the USEPA (1986) criterion of 0.1 µg/L. None of the herbicides exceeded water quality criteria. Only two chlorinated herbicides were detected in the four samples analyzed for them: 2,4-D and bentazon. The other three herbicides were nitrogen-containing compounds.

The three tributaries sampled for pesticides as part of the Yakima River TMDL – Granger Drain, Sulfur Creek Wasteway, and Spring Creek – drain areas where the land use is primarily agriculture and pasture. A wide variety of crops are grown in these areas, and there is a different mixture of crop types in each of the drainages. Crops grown on land draining into Granger Drain and Sulfur Creek Wasteway are primarily row crops, and the type can vary from year to year. Hops, orchards, and vineyards are also important in the Granger Drain area, but less than two percent of the land around Sulfur Creek Wasteway is used for these three crops. Very little land around Spring Creek is used for row crops. Instead, the dominant crops are hops, tree fruits, and grapes.

All three sites were sampled at the USGS flow gauges, which are located at the first access point upstream from the stream's confluence with the Yakima River. The site at Granger Drain was upstream of the town of Granger, and the site at Spring Creek was upstream of the confluence with Snipes Creek.

Twenty-three pesticides were detected in the three tributaries: 13 insecticides and 10 herbicides. DDT and its breakdown products, DDE and DDD, and azinphos-methyl were found in at least four samples from all three sites. All concentrations of total DDT (DDT+DDD+DDE) exceeded state water quality standards, and most detections of azinphos-methyl were above the USEPA (1986) criterion. The level of DDT in the June sample from Granger Drain of 0.31 µg/L was unusually high, and may indicate recent use. However, it is more likely that the DDT was from recently disturbed soils where undegraded DDT from historical use was buried (Agee, 1986).

Other insecticides were found in only one or two samples per site. Chlorpyrifos was detected at 0.48 µg/L in the March sample from Spring Creek, which is well above the state acute criterion of 0.083 µg/L, and was the only pesticide found in samples from the three sites in March. Other insecticides found above water quality standards include carbaryl and malathion in the August sample from Granger Drain, and diazinon in the July sample from Spring Creek. No herbicides exceeded water quality criteria, but atrazine, bromacil, simazine, and terbacil were detected frequently.

The Yakima River at Euclid Road bridge and the three tributaries were sites sampled by the USGS in 1988-89 for the Yakima River Basin NAWQA (Rinella *et al.*, 1992). The sites at Euclid Road bridge and Spring Creek were only sampled once in July of 1988 by the USGS. A better USGS mainstem site for comparisons was located downstream at Kiona, which was sampled 10 times.

Concentrations of total DDT at all four sites were similar between data sets. However, no other chlorinated pesticides were common to both data sets. Methoxychlor was detected in a sample from Granger Drain collected in September 1995, but was not found in any of the USGS samples. Dieldrin and endosulfan were detected in many of the USGS samples, but not in any of the samples collected in 1995.

Detections of organophosphorus pesticides were also dissimilar between data sets. Diazinon, disulfoton, and malathion were the only compounds common to both data sets, but not necessarily from the same sites or at similar concentrations. Parathion was detected at three of the USGS sites, but none of the sites sampled in 1995. Azinphos-methyl was found in most of the samples from each site in 1995, but was not included as a target pesticide by the USGS. These differences are probably the result of some parathion uses being canceled by the state, and replaced in many cases by azinphos-methyl. Some uses of parathion were replaced by chlorpyrifos, which was picked up in 1995, but not by the USGS.

The most frequently detected herbicides in both studies were atrazine and simazine. 2,4-D was also found in many USGS samples, and in three of the four WSPMP Yakima River samples analyzed for chlorinated herbicides.

The report for the Yakima River TMDL outlines a phased approach to reduce suspended sediment loads entering the Yakima River over a 20-year period, with the final goal of compliance with DDT water quality criteria (Joy and Patterson, 1997). This plan is based on the correlation of suspended sediment concentration with the level of DDT, which is the result of the DDT binding to the suspended sediment. When the suspended sediment load is reduced, then the level of DDT will also be reduced. However, this association does not apply to many of the currently used pesticides that do not have a strong affinity for sediment particles as DDT does. Farming practices implemented to reduce erosion and suspended sediment loading to the Yakima River will probably help reduce all pesticides, but it is not clear how effective this will be for currently used pesticides. Some of these compounds may continue to be a problem after sediment controls are in place.

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Appendices

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Appendix A. Surface Water Sampling Site Positions for the 1995 WSPMP

Site Name	Latitude			Longitude			State Plane	
	deg	min	sec	deg	min	sec	X	Y
Clear Creek at Silverdale	47	39	15	122	41	08	1461398	853698
GHCDD-1 at Schmid Road	46	48	58	124	05	25	1101412	561171
Olequa Creek at Vader	46	24	50	122	57	46	1378899	403724
Cherry Creek at Thrall	46	55	33	120	30	02	1999851	577907
Crab Creek Lateral at Royal Lake	46	52	32	119	20	54	2288035	564529
EL68D at Hwy. 17	46	43	43	119	02	58	2363718	512383
Cowiche Creek near Hwy. 12	46	37	38	120	34	53	1979524	471788
Yakima River at Euclid Rd. Bridge	46	13	01	119	54	58	2147785	323052
Granger Drain at gauge	46	20	39	120	11	11	2079203	368768
Sulfur Creek Wasteway at gauge	46	15	04	120	01	08	2121712	335049
Spring Creek at gauge	46	14	02	119	41	02	2206523	329466

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Appendix B. Target Pesticides List for Water Analyses

Chlorinated Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
4,4'-DDT	0.035	cis-nonachlor	0.035
4,4'-DDE	0.035	trans-nonachlor	0.035
4,4'-DDD	0.035	oxychlordane	0.035
2,4'-DDT	0.035	dicofol (kelthane)	0.17
2,4'-DDE	0.035	dieldrin	0.035
2,4'-DDD	0.035	endosulfan I	0.035
DDMU	0.035	endosulfan II	0.035
aldrin	0.035	endosulfan sulfate	0.035
alpha-BHC	0.035	endrin	0.035
beta-BHC	0.035	endrin aldehyde	0.035
delta-BHC	0.035	endrin ketone	0.035
gamma-BHC (Lindane)	0.035	heptachlor	0.035
captan	0.14	heptachlor epoxide	0.035
captafol	0.21	methoxychlor	0.035
cis-chlordane	0.035	mirex	0.035
trans-chlordane	0.035	pentachloroanisole	0.035
alpha-chlordene	0.043	toxaphene	0.85
gamma-chlordene	0.035		

Pyrethroid Pesticides

fenvalerate	0.14	phenothrin	0.14
cis-permethrin	0.14	resmethrin	0.14

Sulfur-Containing Pesticides

propargite	0.28

[1] - Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

Appendix B (cont.). Target Pesticides List for Water Analyses

Organophosphorus Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
acephate	0.30	fensulfothion	0.075
azinphos-ethyl	0.12	fenthion	0.055
azinphos-methyl	0.12	fonophos	0.045
carbophenothion	0.80	imidan	0.080
chlorpyrifos	0.055	malathion	0.060
chlorpyrifos-methyl	0.050	merphos	0.12
coumaphos	0.090	methamidophos	0.30
DEF	0.11	mevinphos	0.075
demeton-O	0.055	paraoxon-methyl	0.15
demeton-S	0.060	parathion	0.060
diazinon	0.060	parathion-methyl	0.055
dichlorvos	0.060	phorate	0.055
dimethoate	0.060	phosphamidan	0.18
dioxathion	0.12	propetamphos	0.15
disulfoton	0.045	ronnel	0.055
EPN	0.075	sulfotepp	0.045
ethion	0.055	sulprofos	0.055
ethoprop	0.060	temephos	0.70
fenamiphos	0.12	tetrachlorvinphos	0.15
fenitrothion	0.055		

Chlorinated Herbicides

2,4-D	0.042	bromoxynil	0.042
2,4-DB	0.050	DCPA (Dacthal)	0.033
2,4,5-T	0.033	dicamba	0.042
2,4,5-TB	0.038	dichlorprop	0.046
2,4,5-TP (Silvex)	0.033	diclofop-methyl	0.063
2,3,4,5-tetrachlorophenol	0.023	dinoseb	0.063
2,3,4,6-tetrachlorophenol	0.023	ioxynil	0.042
2,4,5-trichlorophenol	0.025	MCPA	0.083
2,4,6-trichlorophenol	0.025	MCPP	0.083
3,5-dichlorobenzoic acid	0.042	pentachlorophenol	0.021
4-nitrophenol	0.073	picloram	0.042
acifluorfen	0.17	trichlopyr	0.035
bentazon	0.063		

[1] - Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

Appendix B (cont.). Target Pesticides List for Water Analyses

Nitrogen-Containing Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
alachlor	0.26	metolachlor	0.28
ametryn	0.071	metribuzin	0.071
atraton	0.21	MGK-264	0.50
atrazine	0.071	molinate	0.14
benefin	0.11	napropamide	0.21
bromacil	0.28	norflurazon	0.14
butachlor	0.25	oxyfluorfen	0.28
butylate	0.14	pebulate	0.14
carboxin	0.78	pendimethalin	0.11
chlorothalonil	0.17	profluralin	0.17
chlorpropham	0.28	prometon	0.071
cyanazine	0.11	prometryn	0.071
cycloate	0.14	pronamide	0.28
diallate	0.27	propachlor	0.17
dichlobenil	0.16	propazine	0.071
diphenamid	0.21	simazine	0.072
diuron	0.48	tebuthiuron	0.11
eptam	0.14	terbacil	0.21
ethalfluralin	0.11	terbutryn	0.071
fenarimol	0.21	triadimefon	0.18
fluridone	0.43	triallate	0.18
hexazinone	0.11	trifluralin	0.11
metalaxyl	0.48	vernolate	0.14

Carbamates

1-naphthol	NAF[2]	carbofuran	0.28
3-hydroxycarbofuran	NAF	methiocarb	NAF
aldicarb	NAF	methomyl	NAF
aldicarb sulfone	NAF	oxamyl	NAF
aldicarb sulfoxide	NAF	propoxur	NAF
carbaryl	0.28		

[1] - Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample

[2] - NAF = Not Analyzed For

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Appendix C.

Sampling Procedures

Samples were collected using U.S. Geological Survey (USGS) depth integrating samplers modified so that the water sample contacts only teflon or glass. Samples were hand composited, filling containers one-third full from each point in a quarter point transect across the streams. Samples were held on ice during transportation to the laboratory.

Analytical Methods

Analytes in Appendix B are grouped by analytical method. Chlorinated pesticides, organophosphates, nitrogen-containing pesticides, pyrethroids, and sulfur-containing pesticides were all analyzed with EPA Method 1618 (modified), which uses capillary column GC analysis with an atomic emission detector (AED) and ion-trap GC/MS confirmation. Chlorinated herbicides were analyzed using Manchester Laboratory modified EPA Method 1658, which also uses capillary column GC analysis with an AED and ion-trap GC/MS confirmation. Carbamates were analyzed with EPA Method 531.1 (modified).

Quality Assurance/Quality Control

Matrix spike and matrix spike duplicate (MS/MSD) and field duplicate (split) samples were collected from a different site for each collection period. In April, the MS/MSD and field duplicate samples were collected from the Yakima River site, from Crab Creek Lateral in June, from the Yakima River again in August, and from GHCDD-1 in October. MS/MSD samples were used to estimate analytical precision and accuracy. Field duplicates were also used to assess analytical precision.

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Appendix D.

Data Review

Data packages and quality control results from samples analyzed by Ecology's Manchester Environmental Laboratory were reviewed and assessed by Dickey Huntamer, Norman Olson, and Karin Feddersen.

No significant problems were encountered for most of the analyses. Due to significant baseline noise in chromatograms for the April and June carbamate analyses, quantitation limits for these results were raised to two-and-a-half times the noise level.

Quality Control Samples

No accuracy or precision criteria have been established for any of the analytical methods used, but duplicate field samples, and matrix and surrogate spike analyses provide estimates of accuracy and precision. Results from these analyses are shown in Appendices D-1 (duplicates), D-2 (matrix spikes), and D-3 (surrogate spikes). In June, samples were collected simultaneously from Crab Creek Lateral for the WSPMP and by the USGS. Results from analysis of these samples are compared in Appendix D-4 to compare laboratory performance. In general, low relative percent difference (RPD) between duplicates indicates high precision and recoveries near 100% indicate good accuracy.

Precision of duplicate analyses was generally good. RPD values ranged from 0 to 129% and the average was 29%. Only three values were above 100%, and detections for these compounds were below quantitation limits.

Matrix spike recoveries were excellent. Only picloram and DCPA in the June and July/August samples had recoveries below 20%. Associated results were "J" or "NJ" qualified.

Surrogate recoveries were generally acceptable. June carbamate results were "J" qualified because of low surrogate recoveries in the method blanks. For the June Crab Creek Lateral duplicate sample, the chlorinated and organophosphorus pesticides analyses surrogate recoveries were 277% and 270% respectively. These high values were thought to be the result of double spiking. Low recoveries of the surrogate for nitrogen-containing pesticides in the July/August EL68D sample and the September/October Olequa Creek sample were due to the samples going dry during the concentration steps of the analysis. Affected results were "J" qualified.

Results from the interlaboratory comparison were in reasonably good agreement. Several of the detections were at or below quantitation limits, where accuracy is not expected to be high. Detection limits for the USGS sample tended to be lower than for the WSPMP, resulting in the detection of five compounds not found by the WSPMP. Linuron, an herbicide detected by the USGS, is not a target pesticide for the WSPMP. Pesticides that were found in the WSPMP sample that were not analyzed for by the USGS included 2,4-D, bentazon, and dicamba.

Appendix D-1. Duplicate Analysis Results for 1995 WSPMP Water Samples (µg/L, ppb)

Analyte	Sample 1	Sample 2	RPD[1]
June (Crab Creek Lateral)			
alachlor	0.02	0.023	14
atrazine	0.0073	0.018	85
azinphos-methyl	0.039	0.13	108
bentazon	0.13	0.11	17
chlorpyrifos	0.003	0.014	129
DCPA	0.011	0.0095	15
dicamba	0.006	0.0056	7
eptam	0.35	0.36	3
metolachlor	0.033	0.33 U[2]	NC[3]
simazine	0.02	0.039	64
terbacil	0.09	0.18	67
2,4-D	0.12	0.095	23
July/August (Yakima River)			
atrazine	0.0095	0.019	67
azinphos-methyl	0.021	0.021	0
bentazon	0.028	0.024	15
dimethoate	0.003	0.003	0
disulfoton	0.025	0.028	11
disulfoton sulfone	0.012	0.012	0
malathion	0.016	0.0049	106
terbacil	0.051	0.024	72
2,4-D	0.073	0.056	26
4,4'-DDE	0.0039	0.0038	3
Sept./October (GHCDD-1)			
azinphos-methyl	0.02	0.016	22
carbofuran	0.26	0.23	12
chlorpyrifos	0.015	0.016	6
diazinon	0.03	0.03	0
dichlobenil	0.87	0.96	10
dichlorprop	0.031	0.035	12
metribuzin	0.01	0.01	0
napropamide	0.25	0.26	4
norflurazon	0.51	0.46	10
terbacil	0.014	0.019	30
trichlopyr	0.046	0.043	7
2,4-D	0.15	0.12	22
4,4'-DDD	0.012	0.011	9
4,4'-DDE	0.004	0.0054	30

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

[2] - U = Undetected at or above reported value.

[3] - NC = Not Calculated.

Appendix D-2. Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

April	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Chlorinated Pesticides			
4,4'-DDD	97	109	12
4,4'-DDT	104	111	7
aldrin	35	90	88
alpha-BHC	95	104	9
beta-BHC	101	112	10
delta-BHC	97	108	11
endosulfan I	100	113	12
endosulfan II	107	117	9
endosulfan sulfate	108	116	7
endrin	101	111	9
endrin aldehyde	92	105	13
endrin ketone	105	115	9
gamma-BHC	92	107	15
heptachlor	57	100	55
heptachlor epoxide	99	106	7
methoxychlor	104	115	10
trans-chlordane	96	109	13
Organophosphorus Pesticides			
carbophenothion	89	99	11
chlorpyrifos	100	110	10
demeton-O	77	97	23
demeton-S	74	94	24
disulfoton	78	95	20
EPN	73	86	16
ethion	95	103	8
ethyl azinphos	95	113	17
fenitrothion	89	100	12
fonofos	89	101	13
malathion	102	110	8
merphos	71	85	18
methyl chlorpyrifos	90	110	20
sulfotepp	91	102	11

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

April	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Chlorinated Herbicides			
2,3,4,5-tetrachlorophenol	95	86	10
2,3,4,6-tetrachlorophenol	55	29	62
2,4,5-T	61	51	18
2,4,5-TB	87	81	7
2,4,5-TP	76	65	16
2,4,5-trichlorophenol	93	83	11
2,4,6-trichlorophenol	41	18	78
2,4-D	63	58	8
2,4-DB	86	78	10
3,5-dichlorobenzoic acid	83	65	24
4-nitrophenol	67	55	20
acifluorfen	32	31	3
bentazon	78	62	23
bromoxynil	102	98	4
DCPA	26	22	17
dicamba	80	61	27
dichlorprop	79	66	18
diclofop-methyl	77	66	15
dinoseb	27	26	4
ioxynil	84	73	14
MCPA	70	60	15
MCPP	80	68	16
pentachlorophenol	91	71	25
picloram	33	26	24
trichlopyr	79	65	19
Carbamates			
3-hydroxycarbofuran	93	108	15
aldicarb	59	58	2
aldicarb sulfone	119	126	6
aldicarb sulfoxide	83	104	22
carbaryl	105	92	13
carbofuran	104	105	1
methiocarb	78	72	8
methomyl	96	99	3
oxamyl	85	111	27
propoxur	104	105	1

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

June	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Chlorinated Pesticides			
2,4'-DDD	100	100	0
2,4'-DDE	85	87	2
2,4'-DDT	88	100	13
captafol	100	99	1
captan	100	110	10
kelthane	120	130	8
mirex	90	98	9
trans-nonachlor	90	93	3
Chlorinated Herbicides			
2,3,4,5-tetrachlorophenol	48	70	37
2,3,4,6-tetrachlorophenol	50	66	28
2,4,5-T	42	58	32
2,4,5-TB	42	76	58
2,4,5-TP	55	63	14
2,4,5-trichlorophenol	41	58	34
2,4,6-trichlorophenol	38	55	37
2,4-D	32	54	51
2,4-DB	52	64	21
3,5-dichlorobenzoic acid	46	58	23
4-nitrophenol	26	32	21
acifluorfen	40	55	32
bentazon	66	70	6
bromoxynil	64	72	12
DCPA	16	18	12
dicamba	43	47	9
dichlorprop	55	65	17
diclofop-methyl	52	65	22
dinoseb	22	59	91
ioxynil	57	65	13
MCPA	49	62	23
MCPP	55	63	14
pentachlorophenol	58	70	19
picloram	9	17	62
trichlopyr	50	61	20

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

June	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Nitrogen-Containing Pesticides			
cyanazine	150	160	6
diallate	170	94	58
diuron	100	120	18
metalaxyl	110	120	9
profluralin	89	100	12
Carbamates			
3-hydroxycarbofuran	110	104	6
aldicarb	50	87	54
aldicarb sulfone	119	108	10
aldicarb sulfoxide	116	107	8
carbaryl	116	108	7
carbofuran	103	95	8
methiocarb	104	107	3
methomyl	107	99	8
oxamyl	107	100	7
propoxur	95	95	0

July/August	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Organophosphorus Pesticides			
azinphos-ethyl	97	89	9
carbophenothion	144	92	44
chlorpyrifos	105	98	7
demeton-O	84	87	4
demeton-S	93	86	8
disulfoton	107	107	0
EPN	96	89	8
ethion	130	132	2
fenitrothion	108	98	10
fonofos	101	98	3
malathion	105	98	7
merphos	82	80	2
methyl chlorpyrifos	96	96	0
sulfotepp	103	101	2

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

July/August	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Nitrogen-Containing Pesticides			
alachlor	111	110	1
atrazine	115	101	13
bromacil	114	101	12
dichlobenil	90	99	10
diphenamid	117	114	3
ethalfluralin	124	90	32
fluridone	88	74	17
metolachlor	92	80	14
metribuzin	117	93	23
napropamide	119	106	12
norflurazon	120	105	13
oxyfluorfen	134	119	12
pendimethalin	131	104	23
prometryn	114	97	16
pronamide	138	101	31
propachlor	106	94	12
simazine	135	99	31
tebuthiuron	96	92	4
terbacil	114	88	26
trifluralin	124	98	23
Carbamates			
3-hydroxycarbofuran	99	89	11
aldicarb	107	51	71
aldicarb sulfone	127	144	13
aldicarb sulfoxide	106	99	7
carbaryl	96	84	13
carbofuran	96	79	19
methiocarb	67	46	37
methomyl	98	94	4
oxamyl	94	90	4
propoxur	96	77	22

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

July/August	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Chlorinated Herbicides			
2,3,4,5-tetrachlorophenol	79	100	23
2,3,4,6-tetrachlororophenol	74	84	13
2,4,5-T	70	86	21
2,4,5-TB	81	102	23
2,4,5-TP	77	92	18
2,4,5-trichlorophenol	81	97	18
2,4,6-trichlorophenol	64	68	6
2,4-D	70	84	18
2,4-DB	85	104	20
3,5-dichlorobenzoic acid	74	93	23
4-nitrophenol	55	64	15
acifluorfen	56	75	29
bentazon	79	95	18
bromoxynil	80	97	19
DCPA	14	21	40
dicamba	35	46	27
dichlorprop	75	91	19
diclofop-methyl	81	97	18
dinoseb	52	90	54
ioxynil	84	105	22
MCPA	69	83	18
MCPP	73	90	21
pentachlorophenol	81	93	14
picloram	11	15	31
trichlopyr	78	95	20

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

September/October	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Organophosphorus Pesticides			
butifos	112	111	1
dichlorvos	150	138	8
dimethoate	110	93	17
dioxathion	134	119	12
fenamiphos	123	102	19
methyl paraoxon	149	133	11
mevinphos	119	103	14
phosphamidan	131	110	17
propetamphos	144	124	15
temephos	109	96	13
tetrachlorvinphos	141	114	21
Nitrogen-Containing Pesticides			
benefin	108	130	18
butylate	97	105	8
chlorothalonil	112	126	12
chlorpropham	135	144	6
cycloate	109	116	6
eptam	87	93	7
hexazinone	137	161	16
molinate	86	97	12
pebulate	106	113	6
profluralin	115	139	19
propargite	104	116	11
triallate	126	138	9
vernolate	101	113	11
Carbamates			
3-hydroxycarbofuran	117	109	7
aldicarb	198	168	16
aldicarb sulfone	148	147	1
aldicarb sulfoxide	112	107	5
carbaryl	108	89	19
carbofuran	104	97	7
methiocarb	90	71	24
methomyl	110	105	5
oxamyl	117	113	3
propoxur	102	96	6

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-2 (cont.). Matrix Spike Recoveries for 1995 WSPMP Water Samples (%)

September/October	Matrix Spike	Matrix Spike Duplicate	RPD[1]
Chlorinated Herbicides			
2,3,4,5-tetrachlorophenol	78	88	12
2,3,4,6-tetrachlororophenol	78	85	9
2,4,5-T	82	90	9
2,4,5-TB	76	85	11
2,4,5-TP	90	98	9
2,4,5-trichlorophenol	74	76	3
2,4,6-trichlorophenol	70	74	6
2,4-D	82	90	9
2,4-DB	84	95	12
3,5-dichlorobenzoic acid	75	80	6
4-nitrophenol	43	47	9
acifluorfen	64	66	3
bentazon	95	93	2
bromoxynil	85	88	3
DCPA	35	37	6
dicamba	73	78	7
dichlorprop	84	88	5
diclofop-methyl	80	90	12
dinoseb	77	65	17
ioxynil	90	89	1
MCPA	75	83	10
MCPP	78	83	6
pentachlorophenol	85	93	9
picloram	21	29	32
trichlopyr	85	91	7

[1] - RPD = Relative Percent Difference (difference/mean) x 100.

Appendix D-3. Surrogate Recoveries for 1995 WSPMP Water Samples (%)

	DCBP	TCMX	TPP	DMNB	TBP	BDMC
April						
Clear Creek	97	32	144	88	119	67
GHCDD-1	99	34	115	84	106	77
Olequa Creek	92	37	89	74	87	74
Cherry Creek	102	92	117	107	121	89
Crab Creek Lateral	52	71	112	95	93	71
EL68D	63	53	111	82	32	79
Cowiche Creek	92	59	110	82	87	75
Yakima River	102	64	110	84	83	69
Yakima River Dup.	65	39	100	87	83	68
June						
Clear Creek	82	27	67	64	91	79
GHCDD-1	61	26	45	46	83	94
Olequa Creek	92	23	93	67	87	101
Cherry Creek	66	30	88	87	83	80
Crab Creek Lateral	66	35	76	77	74	91
Crab Creek Lat. Dup.	277	69	270	120	60	71
EL68D	66	28	87	65	59	113
Cowiche Creek	56	52	90	98	85	99
Yakima River	82	42	64	78	59	102
July/August						
Clear Creek	81	SNA[1]	130	59	115	109
GHCDD-1	43	SNA	119	58	91	84
Olequa Creek	132	SNA	178	98	94	74
Cherry Creek	75	SNA	112	72	59	84
Crab Creek Lateral	78	SNA	103	65	98	56
EL68D	96	SNA	107	0	95	69
Cowiche Creek	79	SNA	120	70	107	90
Yakima River	81	SNA	114	77	88	63
Yakima River Dup.	88	SNA	124	78	88	78
Sept./October						
Clear Creek	102	SNA	87	80	74	47
GHCDD-1	94	SNA	82	102	76	77
GHCDD-1 Dup.	101	SNA	85	87	52	80
Olequa Creek	82	SNA	90	1	90	122
Cherry Creek	108	SNA	103	91	71	37
Crab Creek Lateral	99	SNA	94	82	59	23
EL68D	111	SNA	99	94	83	84
Cowiche Creek	93	SNA	107	73	71	87
Yakima River	92	SNA	76	61	74	84

[1] - SNA = Surrogate Not Added

Appendix D-3 (cont.). Surrogate Recoveries for 1995 WSPMP Water Samples (%)

	DCBP	TCMX	TPP	DMNB	TBP	BDMC
April						
Lab Blank 1	97	63	103	89	76	74
Lab Blank 1 Duplicate	93	49	90	75	70	62
Lab Blank 2	88	29	101	76	6	NAF
Lab Blank 2 Duplicate	92	45	112	75	31	NAF
Matrix Spike	95	58	100	NAF[1]	76	77
Matrix Spike Duplicate	107	76	107	NAF	50	76
June						
Lab Blank 1	104	90	77	94	30	0
Lab Blank 1 Duplicate	87	45	76	72	43	0
Lab Blank 2	NAF	NAF	60	96	64	NAF
Lab Blank 2 Duplicate	NAF	NAF	86	83	50	NAF
Matrix Spike	87	31	NAF	60	57	98
Matrix Spike Duplicate	83	50	NAF	77	82	96
July/August						
Lab Blank 1	90	SNA[2]	102	81	75	73
Lab Blank 1 Duplicate	90	SNA	116	90	92	19
Lab Blank 2	88	SNA	117	78	51	NAF
Lab Blank 2 Duplicate	87	SNA	114	66	48	NAF
Matrix Spike	NAF	NAF	112	87	81	91
Matrix Spike Duplicate	NAF	NAF	103	84	94	67
Sept./October						
Lab Blank 1	126	SNA	90	100	56	61
Lab Blank 1 Duplicate	106	SNA	94	86	19	28
Lab Blank 2	106	SNA	101	106	44	NAF
Lab Blank 2 Duplicate	106	SNA	95	89	54	NAF
Matrix Spike	NAF	NAF	112	91	51	118
Matrix Spike Duplicate	NAF	NAF	96	89	63	88

[1] - NAF = Not Analyzed For

[2] - SNA = Surrogate Not Added

Surrogate Key

DCBP = Decachlorobiphenyl (chlorinated pesticides)

TCMX = Tetrachlorometaxylene (chlorinated pesticides)

TPP = Triphenyl Phosphate (organophosphorus pesticides)

DMNB = Dimethylnitrobenzene (nitrogen-containing pesticides)

TBP = 2,4,6-Tribromophenol (chlorinated herbicides)

BDMC = 4-Bromo-3,5-dimethylphenyl n-methylcarbamate (carbamates)

Appendix D-4. Interlaboratory Comparison Results (μg/L, ppb)

	USGS	WSPMP	RPD[1]
Insecticides			
azinphos-methyl	0.016 E	0.08 J	133
carbaryl	0.014 E	0.3 U	NC[2]
carbofuran	0.01 E	0.3 U	NC
chlorpyrifos	0.003 E	0.009 NJ	100
ethoprop	0.003 E	0.066 U	NC
Herbicides			
alachlor	0.013	0.02 J	42
atrazine	0.014	0.013 J	7
DCPA	0.028	0.01 J	95
EPTC	0.35	0.36	3
metolachlor	0.008	0.033 J	122
metribuzin	0.012	0.082 U	NC
simazine	0.028	0.03 J	7
terbacil	0.11 E	0.14 J	24
trifluralin	0.007	0.12 U	NC

[1] - RPD = Relative Percent Difference (difference/mean x 100).
[2] - NC = Not Calculated.
E = Estimated concentration.
J = The analyte was positively identified. The numerical value is an estimate.
U = The analyte was not detected at or above the reported value.
NJ = There is evidence that the analyte is present. The numerical value is an estimate.

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Appendix E-1. Pesticides Detected in Water Samples Collected for the 1992 WSPMP (µg/L,ppb)

	Mission Creek	Crab Creek	Walla Walla River	Glade Creek	Fishtrap Creek	Moxee Drain[1]
Insecticides						
4,4'-DDD						0.027
4,4'-DDE						0.018
4,4'-DDT						0.015
total DDT						**0.060**[3]
azinphos-methyl	**0.033**[2]					
diazinon						
malathion						**0.054**[4]
Herbicides						
2,4-D		0.980	0.055		0.27	0.16
atrazine		0.088		0.24	0.11	
atrazine desethyl				0.38		
bromacil						
chlorpropham						
DCPA (Dacthal)		1.24	12.1	0.028	0.006	0.011
dichloro-DCPA			0.046			
trichloro-DCPA			0.55			
dicamba[5]		0.080		0.019		
dichlobenil						
dichlorprop						
EPTC (Eptam)		0.31		0.20		
glyphosate	1.13	0.38	0.49			0.49
hexazinone			0.063			
MCPP					1.5	
metribuzin				0.043		
prometon						
simazine	0.041	0.033	0.078		0.091	
Fungicide						
pentachlorophenol	0.002					0.015

Values in bold exceed water quality criteria

[1] - Values are means of duplicate analyses

[2] - Exceeds USEPA, 1986 water quality criteria

[3] - Exceeds Washington State water quality standards

[4] - Exceeds NAS, 1973 recommended maximum concentrations

[5] - Listed as disugran in Davis, 1993

Appendix E-1 (cont.). Pesticides Detected in Water Samples Collected for the 1992 WSPMP (µg/L,ppb)

	Mercer Creek[1]	Thornton Creek	Sullivan Slough	Lake River	Tuttle Creek
Insecticides					
4,4'-DDD					
4,4'-DDE					
4,4'-DDT					
azinphos-methyl					
diazinon	**0.091**[2]	**0.077**[2]			
malathion					
Herbicides					
2,4-D	0.20	0.23	0.039		
atrazine			0.24		
atrazine desethyl					
bromacil			0.046		
chlorpropham			0.10		
DCPA (Dacthal)	0.061	0.066	0.017	0.011	
dicamba[3]		0.038			
dichlobenil	0.19	0.054			
dichlorprop		0.052			
EPTC (Eptam)					
glyphosate	0.78	0.58			
hexazinone					
MCPP	1.7				
metribuzin			0.036		
prometon	0.082				
simazine					
Fungicide					
pentachlorophenol					

Values in bold exceed water quality criteria

[1] - Values are means of duplicate analyses

[2] - Exceeds NAS, 1973 recommended maximum concentrations

[3] - Listed as disugran in Davis, 1993

Appendix E-2. Pesticides Detected in Water Samples Collected for the 1993 WSPMP (μg/L, ppb)

Sample Sites West of the Cascades

	Adna Creek				Fishtrap Creek				Mercer Creek				Salmon Creek				Joe Leary Slough	Lynch Coulee Creek
	April	June	Aug	Oct	April	June	Aug	Oct	April	June	Aug	Oct	April	June	Aug	Oct	June	June
2,4-D						0.069			0.05		0.039	0.29						
4-nitrophenol												0.22						
aldicarb														0.76				
atrazine					0.02	0.024	0.010	0.035		0.025			0.02					
bentazon																	0.08	
bromacil					0.03	0.054	0.047	0.058		0.11	0.037	0.073						
chlorpropham																	6.0	
chlorpyrifos																**0.044**[1]		
DCPA									0.06	0.041	0.032							0.20
diazinon										**0.03**[2]		**0.083**[2]				**0.022**[2]		
dichlobenil							0.035		0.17	0.11	0.034	0.09				0.039		
diuron										0.19								
eptam																	0.17	
malathion												**0.085**[2]						
MCPA												0.10						
MCPP						0.043					0.029	0.17						
methomyl															0.068			
mevinphos																	**11**[2]	
pentachlorophenol					0.008				0.007				0.005					
prometon										0.024		0.089						
propoxur											0.047							
simazine					0.02	0.011				0.048	0.018	0.029		0.38	0.044	0.039		

[1] - Exceeds Washington State Water Quality Standards

[2] - Exceeds NAS, 1973 recommended criteria

Values in bold exceed criteria

* - Values are means of duplicate analyses

Appendix E-2 (cont.). Pesticides Detected in Water Samples Collected for the 1993 WSPMP (µg/L, ppb)

Sample Sites East of the Cascades

	Crab Creek				Foster Creek				Misson Creek				Moxee Drain				Walla Walla River			
	April*	June	Aug	Oct	April	June	Aug	Oct	April	June*	Aug	Oct	April	June	Aug	Oct	April	June	Aug	Oct
2,4-D		0.34	0.090			0.035								0.23	0.24			0.024	0.25	
4,4'-DDD																0.002				
4,4'-DDE									0.002				0.006	0.029		0.003				
4,4'-DDT									0.002	0.018			0.002	0.028						
total DDT									**0.004**[1]	**0.018**[1]			**0.008**[1]	**0.057**[1]		**0.005**[1]				
atrazine	0.02	0.052	0.015	0.015															0.011	0.016
azinphos-methyl		**0.019**[3]				**0.016**[3]				**0.13**[3]		**0.012**[3]		**0.1**[3]	**0.056**[3]					
bentazon		0.093		0.11																
bromacil																	0.02		0.090	
bromoxynil					0.20	0.035	0.023													
chlorpyrifos									**0.14**[1]				**0.078**[1]	0.027	**0.29**[1]	0.01				
DCPA		0.59	0.49	0.96										0.015	0.033	0.009		2.2	3.9	2.7
diazinon												0.007		**0.14**[2]						
dicamba I		0.032												0.022					0.11	
dicamba II																			0.044	
dimethoate		0.022												0.037						
endosulfan I									0.031				0.031	0.012						
endosulfan II									0.013				0.014	0.013						
endosulfan sulfate									0.004				0.008	0.023						
total endosulfan									**0.048**[2]				**0.053**[2]	**0.048**[2]						
eptam		0.13																		
hexazinone		0.033																		
metribuzin																	0.16			
pentachlorophenol													0.005	0.012						
propargite															0.10	0.03				
simazine	0.02	0.016																	0.061	0.018
triallate																			0.034	

[1] - Exceeds Washington State Water Quality Standards

[2] - Exceeds NAS, 1973 recommended criteria

[3] - Exceeds EPA, 1986a criteria

Values in bold exceed criteria

* - Values are means of duplicate analyses

Appendix E-3. Pesticides Detected in Water Samples Collected for the 1994 WSPMP (µg/L, ppb)

	Sample Sites East of the Cascades											
	Mission Creek			Stemilt Creek			Stink Creek			Palouse River		
	April	June	October	April	June	October	April	June[1]	October	April	June	October
Insecticides												
3-hydroxycarbofuran			0.421					0.07				
4,4'-DDE		0.013										
4,4'-DDT		0.012						0.014				
total DDT		**0.025**[2]						**0.014**[2]				
azinphos-methyl (Guthion)	**0.004**[4]	**0.027**[3]		**0.010**[4]				**0.058**[3]				
carbaryl		**0.059**[4]										
chlorpyrifos	**0.02**[4]			**0.005**[4]			**0.056**[2]					
diazinon	**0.031**[4]			0.009			**0.021**[4]					
malathion					**0.012**[4]							
Herbicides												
2,4-D										0.028	0.069	
atrazine											0.053	0.069
bromacil		0.022	0.044									
bromoxynil				0.060			0.088					
DCPA (Dacthal)										0.012		
dichlobenil							0.017					
diclofop-methyl										0.030		
MCPA										0.036	0.020	
MCPP											0.029	
norflurazon									0.078			
norflurazon desmethyl									0.10			
simazine	0.25		0.011			0.006	0.025	0.092	0.075		0.55	
triallate										0.018	0.043	
Fungicide												
pentachlorophenol						0.0054					0.0091	

Values in bold exceed water quality criteria

[1] - Values are means of duplicate analyses

[2] - Exceeds Washington State water quality standards

[3] - Exceeds USEPA, 1986 water quality criteria

[4] - Exceeds NAS, 1973 recommended maximum concentrations

Appendix E-3 (cont.). Pesticides Detected in Water Samples Collected for the 1994 WSPMP (µg/L, ppb)

	Sample Sites West of the Cascades											
	GHCDD-1			Joe Leary Slough			Kearny Creek			Mercer Creek		
	April[1]	June	October	April	June	October	April	June	October	April	June	October[1]
Insecticides												
4-nitrophenol				0.084						0.13		
azinphos-methyl (Guthion)		**0.014**[2]										
carbofuran	0.08	0.054										
3-hydroxycarbofuran		0.054			0.059							
chlorpyrifos		**0.021**[3]	**0.03**[3]									
diazinon	**0.011**[3]		**0.029**[3]	**0.017**[3]						**0.032**[3]		**0.042**[3]
malathion										**0.028**[3]		
Herbicides												
2,4-D	0.11	0.22	0.091	0.077						0.17	0.014	0.035
atrazine							0.008					
bromacil										0.014	0.035	
chlorpropham					0.081							
DCPA (Dacthal)					0.0069					0.035	0.021	
dicamba				0.036						0.013		
dichlobenil	1.7	0.21	0.92							0.051	0.032	0.023
dichlorprop		0.011								0.018		
EPTC (Eptam)				0.060								
hexazinone							0.071	0.11	0.15			
MCPA				0.043								
MCPP					0.14						0.019	
metribuzin					0.076							
napropamide	0.20		0.17									
norflurazon	0.16	0.16	0.47									
prometon		0.021								0.012		
triclopyr		0.017			0.019	0.010				0.062	0.046	0.040
Fungicide												
pentachlorophenol					0.075	0.013			0.0047		0.023	0.024

Values in bold exceed water quality criteria

[1] - Values are means of duplicate analyses

[2] - Exceeds USEPA, 1986 water quality criteria

[3] - Exceeds NAS, 1973 recommended maximum concentrations