

# Washington State Pesticide Monitoring Program

# 1994 Surface Water Sampling Report

February 1996

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# Washington State Pesticide Monitoring Program 1994 Surface Water Sampling Report

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February 1996

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# **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 of distribution are changing over time.

WSPMP surface water samples were collected at eight sites in April, June, and October of 1994 Sites were selected to represent various pesticide uses including agricultural use west of the Cascade Mountains, irrigated and dry-land agriculture east of the Cascades, use on orchards, urban use, and use 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

A total of 33 pesticides and breakdown products were detected. The most frequently detected pesticides were 2,4-D, diazinon, dichlobenil, pentachlorophenol, and simazine. Washington State and/or U.S. Environmental Protection Agency (USEPA) aquatic life criteria were exceeded at three sites. Pesticides above criteria were DDT, DDE, azinphos-methyl (Guthion), and chlorpyrifos (Dursban, Lorsban). Levels of carbaryl, diazinon, and malathion exceeded National Academy of Sciences (NAS) recommended maximum concentrations to protect aquatic life and wildlife

Azinphos-methyl and chlorpyrifos have been detected consistently in streams adjacent to orchards at concentrations exceeding water quality criteria DDT, diazinon, carbaryl, malathion, and endosulfan are other insecticides that have been found in samples from streams running through orchards; most at levels above USEPA, Washington State, and/or NAS standards Mixtures of these insecticides are likely to be more toxic than the individual compounds

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). Three compounds were detected in all three sample periods and four were found in two periods. Urban use seems to result in a similar pattern of detections. Six pesticides were found in Mercer Creek each of the three years it was sampled. Four additional compounds were identified in two of the years.

Recommendations include additional sampling in GHCDD-1 and urban streams, an intensive survey of streams flowing through orchards to assess impacts of orchard pesticides on biota, development of BMPs for orchard pesticide use, development of state water quality criteria for selected pesticides, addition of Mission Creek to the 303(d) water quality limited list for total DDT, and improved interagency coordination to reduce pesticide related environmental impacts

# **Acknowledgments**

The following persons deserve recognition for their contributions to this study:

- 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.
- John and Cora Picken for allowing access to their property so samples could be collected from Stink Creek
- Larry Goldstein, Bill Yake, and Art Johnson for providing valuable review comments for the draft report.
- Joan LeTourneau for preparing and proofing the final report

# Summary

A total of 33 pesticides and breakdown products were detected in 24 surface water samples collected for the WSPMP from eight sites in April, June, and October of 1994. Three of these sites had been previously sampled in 1992 and/or 1993.

The herbicide 2,4-D was found in nine samples from four sites, diazinon in eight from six sites, and dichlobenil (Casoron), simazine, and pentachlorophenol were identified in seven samples from three, four, and five sites, respectively. Azinphos-methyl (Guthion) and chlorpyrifos (Lorsban) were each found five times at four sites, and all detections exceeded water quality guidelines. Sixty-four percent of the detected compounds were in three or fewer samples.

Three pesticides were detected at concentrations exceeding Washington State and/or USEPA aquatic life criteria (Table 1) An additional three compounds, carbaryl, diazinon, and malathion, were above National Academy of Sciences (NAS, 1973) recommended maximum concentrations to protect aquatic life and wildlife

Table 1. Pesti	cides Exceeding W	ater Qualit	y Criteria in 19	94 (μg/L, ppb)	
Water Body	Pesticide	Date	Concentration	Criteria (chronic)	Reference
Mission Creek	total DDT	June	0.025	0.001	WAC 173-201A
	azinphos-methyl	June	0.027	0.01	USEPA, 1986
Stink Creek	chlorpyrifos	April	0 056	0.041	WAC 173-201A
	azinphos-methyl	June	0.058	0.01	USEPA, 1986
	total DDT	June	0 014	0001	WAC 173-201A
GHCDD-1	azinphos-methyl	June	0.014	0.01	USEPA, 1986

Three sites, Mission, Stemilt, and Stink Creeks, were sampled to represent orchard pesticide use. Azinphos-methyl, chlorpyrifos, and diazinon were detected at all three sites. These three pesticides were also found in samples from Mission Creek collected in 1993, and azinphos-methyl was detected in Mission Creek in 1992. DDT was found in Mission Creek in 1993 and 1994, and in Stink Creek in 1994. Carbaryl and malathion were each identified once. In 1993, endosulfan was also found in a sample from Mission Creek.

Insecticides used on orchards appear to be a chronic problem in adjacent streams. Concentrations of some compounds are high enough to cause significant adverse effects to resident stream fauna. 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.

The Palouse River was sampled to represent dry-land agriculture. Nine pesticides were detected; eight were herbicides and the ninth was pentachlorophenol, a fungicide. None exceeded water quality standards.

Numerous pesticides are present consistently in water draining from cranberry bogs in Grayland. In Grays Harbor County Drainage Ditch No 1 (GHCDD-1), 12 compounds were detected in water samples collected in 1994. Azinphos-methyl exceeded the USEPA (1986) water quality criterion, and chlorpyrifos and diazinon were above NAS recommendations. Three of the 12 pesticides were detected in all three sample periods and four were found in two periods, which is the second 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.

In 1993, mevinphos (Phosdrin) was found at a very high concentration in Joe Leary Slough, which prompted additional sampling in 1994. Thirteen pesticides were found in samples collected in 1994, but mevinphos was not detected Diazinon was above the NAS recommended maximum concentration in April.

In coordination with the Washington State Department of Agriculture (WSDA), samples were collected from Kearny Creek to assess potential water quality impacts from pesticide use on Christmas tree plantations. Only three compounds were detected: atrazine, hexazinone (Velpar), and pentachlorophenol. Hexazinone was found in all three sample periods, and was also detected in one sample collected by the WSDA in June. Detected concentrations were well below any applicable water quality criteria. Water quality impacts appear to be minimal.

Mercer Creek was sampled in 1994 to verify detections from samples collected in 1992 and 1993 2,4-D, DCPA, diazinon, dichlobenil, MCPP, and prometon were detected all three years Concentrations of diazinon were above the NAS recommended maximum for all detections Malathion was found once each year in 1993 and 1994, and both detections were above the NAS recommendation. Of 13 pesticides found in 1994, three were detected in all three sample periods and four were found in two sample periods. A high proportion of the pesticides identified in 1993 were also detected multiple times. Flora and fauna in Mercer Creek may be experiencing adverse effects from long-term exposure to multiple pesticides.

# Recommendations

# Additional Sampling for the WSPMP

- Continue sampling Grays Harbor County Drainage Ditch No.1 to verify the high number and frequency of detections.
- Sample additional streams that are representative of urban pesticide usage to determine if the compounds and concentrations found in Mercer Creek are typical of urban use.

# **Intensive Surveys**

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

• Perform an intensive survey of streams that flow through orchards to assess the impacts of high concentrations of multiple insecticides on stream biota and associated wildlife.

#### **Additional Recommendations**

- Develop and implement Best Management Practices (BMPs) that will minimize pesticides used on orchards from entering waters of the state
- Develop Washington State Water Quality Criteria for the following insecticides that are frequently detected at concentrations potentially harmful to aquatic life: azinphos-methyl (Guthion), carbofuran, diazinon, and malathion
- Develop Washington State Water Quality Criteria 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 Criteria that address additivity for cases where multiple pesticides are detected in the same sample.
- Develop a fact sheet, pamphlet, or other public education medium that identifies urban pesticide use as a significant problem and lists "BMPs" that will reduce the number and amount of pesticides entering waters of the state

## 303(d) Listing

 Mission Creek should be evaluated for potential listing on the Federal Clean Water Act, water quality limited 303(d) list, based on three water samples (two in 1993 and one in 1994) that contained concentrations of total DDT that exceeded Washington State Water Quality Criteria

# **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 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 1994. Fish samples were collected in September of 1994 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 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

# Methods

# Sampling Design

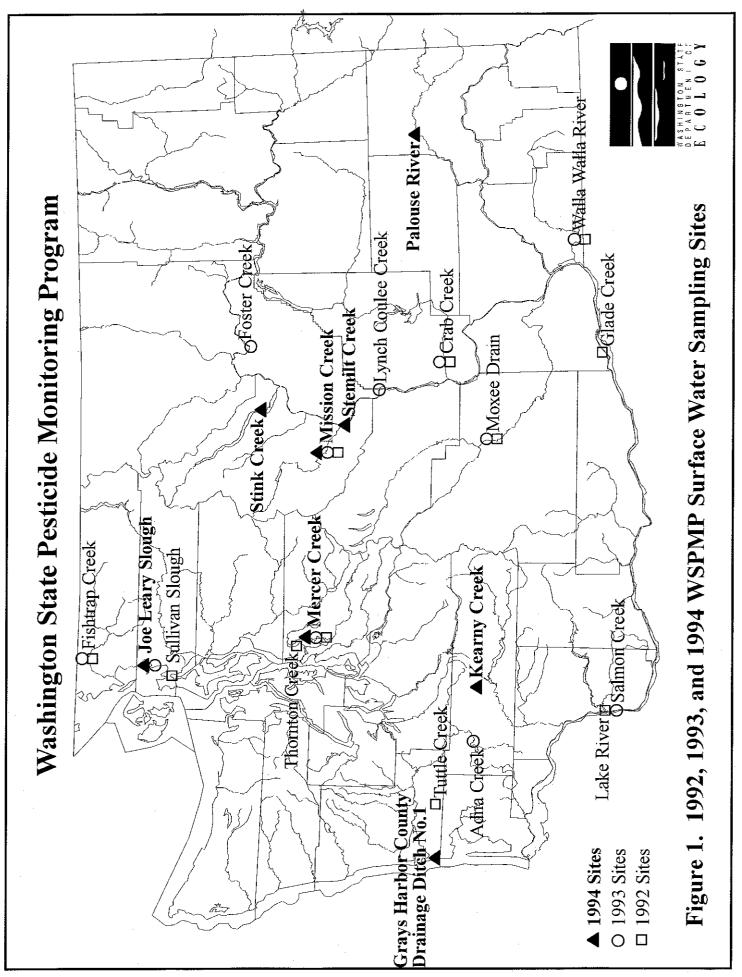
Samples were collected at eight sites (Figure 1) in April, June, and October of 1994. April and June represent the peak pesticide application period (late-March to early-July). Sampling in October is conducted to represent previously applied pesticide residues transported to streams in fall storm-water runoff. The number of sample sites and the frequency of sampling were determined primarily by the funding available. Latitude, longitude, and state plane coordinates are listed for each site in Appendix A.

Sampling for the WSPMP is currently being integrated into the five-year cycle developed for Ecology's watershed approach to water quality management. Pesticide sampling for each watershed is implemented one year prior to the scoping period scheduled for that watershed. Results from the WSPMP are used to identify areas with potential pesticide-related problems. These results are presented during the scoping sessions so needs can be assessed more effectively using recent, pertinent data.

The sampling emphasis for the 1994 WSPMP was within the Wenatchee, Western Olympic, and Upper and Lower Snake River watersheds. The Nooksack/San Juan watershed is also included in this group, but higher priority sites were identified in the other watersheds. In addition, sites within the Nooksack watershed were sampled in 1992 and 1993.

Two of the eight sites, Mercer Creek and Mission Creek, were sampled for the third year to verify detections. Verification sampling does not necessarily follow the watershed approach cycle. Mission Creek is within the Wenatchee watershed, but Mercer Creek is in the Cedar River watershed, which is not scheduled to be sampled until 1996 in the watershed cycle.

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



Page 3

# **Sampling Sites**

Sample sites were selected to represent various pesticide uses (Table 2).

Table 2. List of Sample	e Sites, Locations, and Pesticide U	ses Typical of the Site
Sample Site	Location	Represented Pesticide Use
Mission Creek	at Cashmere, Chelan Co.	orchards
Stemilt Creek	near Wenatchee, Chelan Co	orchards
Stink Creek	near Manson, Chelan Co	orchards
Palouse Creek	at Winona, Whitman Co.	dry-land agriculture
GHCDD-1	at Grayland, Grays Harbor Co	cranberries
Joe Leary Slough	near Sedro Wooley, Skagit Co.	various row crops
Kearny Creek	near Alpha, Lewis Co.	Christmas tree farms
Mercer Creek	near Bellevue, King Co	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 33 pesticides and breakdown products were detected in water samples collected for the 1994 WSPMP (Table 3). The concentrations of most compounds were in the parts per trillion range. Only dichlobenil from GHCDD-1 in April was detected in the parts per billion range (1.7 µg/L). Pesticides that exceed water quality criteria are highlighted with bold type in Table 3.

Water quality criteria and aquatic toxicity data for detected pesticides are listed in Appendix H; sources for this information are included in this Appendix Supplemental information (e.g., trade names and applications) for each detected pesticide are presented in Appendix I. For reference, pesticides detected in the 1992 and 1993 WSPMP have been included in Appendix J-1 and J-2

Detection frequencies in samples collected in 1994 were similar to results from 1992 and 1993. Figure 2 illustrates detection frequencies for all pesticides identified by the WSPMP in surface water samples (1992-1994). For the 1994 data, 2,4-D was found most often, being detected in nine of the 24 samples (38%) at four of the eight sites. Diazinon was found in eight samples and at six sites. Dichlobenil (Casoron), simazine, trichlopyr, and pentachlorophenol were detected in at least 25% of the samples (6 out of 24). Azinphos-methyl and chlorpyrifos were each found five times at four sites, and all detections exceeded water quality guidelines. Sixty-four percent of the detected compounds were found in three or fewer samples.

For the combined data in Figure 2, 2,4-D was the most frequently detected compound, being found in 27 of the 73 samples analyzed (37%) DCPA (Dacthal), atrazine, simazine, diazinon, and dichlobenil were identified in at least 20% (15) of the samples. Azinphos-methyl (Guthion) and chlorpyrifos (Lorsban) were detected in 16% and 15% of the samples, respectively, and were the two pesticides that exceeded water quality criteria most often. Forty-three percent of the detected pesticides were identified in three or fewer samples.

#### **Breakdown Products**

Four breakdown products of target pesticides were detected DDE is a metabolite of DDT and is 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 was detected in the sample from Mission Creek collected in June at a concentration similar to DDT DDT was identified in Stink Creek in June, but no DDT metabolites were detected

The breakdown product of carbofuran, 3-hydroxycarbofuran, was found in four samples, but carbofuran was detected in only one of the four samples. 3-hydroxycarbofuran is less toxic than the parent compound (USEPA, 1984a).

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

					Sample	Sample Sites East of the Cascades	of the Ca	ascades				
	Mi	Mission Creek	sek	Ste	Stemilt Creek	ek.	Š	Stink Creek	k	Pal	Palouse River	er
	April	June	October	April	June	October	April	$\mathrm{June}^{\scriptscriptstyle 1}$	October	April	June	October
Insecticides										i.		
3-hydroxycarbofuran			0.421					0,07				
4,4'-DDE		0.013										
4,4'-DDT		0.012						9014				
total DDT		$0.025^{2}$						$0.014^{2}$				
tzinphos-methyl (Guthaen)	0.004	0.027		.010				0.058				
carbaryl		$0.059^{4}$										
chlorpyrifos	6.024			4.005			0.056					
diazinon	$0.031^{4}$			0.00			0.0214					
malathien					0.0124							
Herbicides												
2,4-D										0.028	6900	
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			900.0	0.025	0.092	0.075		0.55	
trailate										8100	0.043	
Fungicide												
pentachlorophenol						0,0054					16000	
Walnes in hold exceed meters candida	· onitonio											

Values in bold exceed water quality criteria

- Values are means of duplicate analyses

\* - Exceeds Washington State water quality standards

\* - Exceeds USEPA, 1986 water quality enteria

\*- Exceeds NAS, 1973 recommended maximum concentrations

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

Sample Sites West of the Cascades

•					Sample	Sites Wes	Sample Sites West of the Cascades	ades				
		GHCDD-1		Joe I	Joe Leary Slough	ngh	Kean	Kearny Creek		Me	Mercer Creek	~
	April <sup>1</sup>	June	October	April	June	October	April	June O	October	April	June	October <sup>1</sup>
Insecticides												
4-ntrophenol				0.084						0.13		
azınphos-methyl (Guthion)		$0.014^{2}$										
carbofinan	900	0.054										
3-hydroxycarbofuran	)	0.054			0.059		V0000000000000000000000000000000000000	000000000000000000000000000000000000000				000000000000000000000000000000000000000
chlapynios		0.0213	0.03									
diazınon	$0.011^{3}$		$0.029^{3}$	$0.017^{3}$						$0.032^{3}$		0.0423
malathon										0.028		
Herbicides												
2,4-D	0.11	0.22	1600	6.077						0.17	0.014	0.035
atrazine							0.008					
bromacil										0.014	0.035	
chlorpropham	-				0.081							
DCPA (Daothal)					69000					0.035	0.021	
dicamba				0.036						0.013		
dichlohenil	1.7	0.23	0.92							190'0	0.032	0.023
dichlorprop	)	0.011								0.018		
EPIC (Eptam)				0.060								
hexazınone		No. of Contract of					0.071	0.11	0.15			
MCPA				6003								
MCPP					0.14						0.019	
metribuzin					0.076							
napropamide	0.20		0.17									
norflurazon	0.16	910	C 47									
prometon	)	0.021								0.012		
trelopyr		7100			6100	0:010				0.062	0.046	0.040
Fungicide	***************************************	***************************************										-
pentachlorophenol					0.075	0.013		Đ	0047		0.023	#Z00
Volume in hold agreed weeks assalita-	oine bire											

Values in bold exceed water quality criteria

- Values are means of duplicate analyses

\* - Exceeds USEPA, 1986 water quality criteria

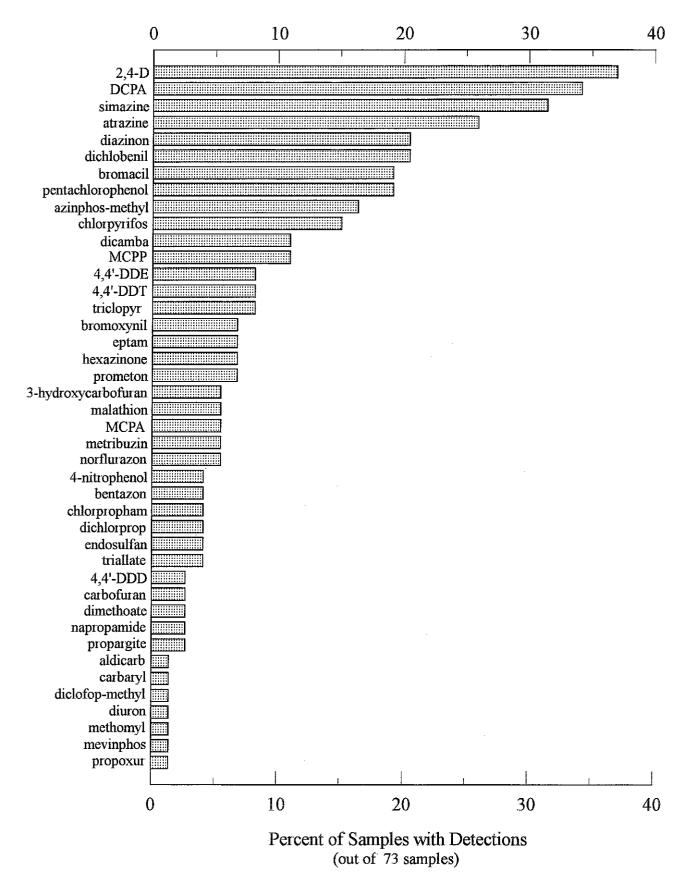


Figure 2. Detection Frequency of Pesticides in 1992, 1993, and 1994 WSPMP Surface Water Samples

Norflurazon desmethyl, a metabolite of norflurazon, was found once in a sample from Stink Creek Norflurazon was also detected Norflurazon was found in all three samples from GHCDD-1, but no breakdown products were detected.

A degradation product of parathion, 4-nitrophenol, was identified twice, once at Joe Leary Slough and once at Mercer Creek, but the parent compound was not detected.

#### **Conventional Parameters**

Results of conventional parameter analyses and field measurements are presented in Table 4 Significant findings are discussed in the next section

#### Site Evaluations

#### Mission Creek

The source of Mission Creek extends high into the Wenatchee Mountains south of Cashmere Mission Creek also receives water from Little Camas Creek and Sand Creek Most of Mission Creek runs through uninhabited land, but the lower section flows directly through several pear and apple orchards and then discharges into the Wenatchee River. The sampling site in 1994 was at the mouth, below the confluence with Brender Creek. Mission Creek was also sampled for the WSPMP in 1992 and 1993, but the sample site was upstream from Brender Creek, at a bridge near the intersection of Meadow Sweet Place and Mission Creek Road.

Azinphos-methyl exceeded USEPA (1986) water quality criteria in WSPMP samples collected from Mission Creek in 1992 and 1993 Chlorpyrifos, endosulfan (Thiodan), and total DDT (t-DDT = DDT+DDE+DDD) concentrations were above Washington State water quality standards for the protection of aquatic life (WAC 173-201A) in 1993 (Davis, 1993; Davis and Johnson, 1994) Mission Creek was sampled again in 1994 to determine if these pesticides are consistently present from year to year. Stemilt and Stink Creeks were sampled in 1994 to determine if the same pesticides that exceeded water quality criteria in Mission Creek were also present in other streams that flow through orchards

In 1994, azinphos-methyl and total DDT were detected in samples from Mission Creek at 0 027 and 0 025 µg/L, respectively, which again exceeded USEPA or Washington State water quality criteria. In addition, levels of carbaryl (Sevin), chlorpyrifos, and diazinon were above the National Academy of Sciences (NAS, 1973) recommended maximum concentrations for the protection of aquatic life and wildlife.

Chlorpyrifos and azinphos-methyl are heavily used on the orchards that Mission Creek flows through (Smith, 1994). Chlorpyrifos is used in early spring to control aphids. Azinphos-methyl is used in late spring to control codling moths. DDT was heavily used on orchards prior to its ban in 1972, and it is still commonly found where there is soil erosion from the orchards.

Table 4. Results of Conventional Parameters for the 1994 WSPMP

Conductivity (µmho/cm) April June October	150 193 501	667 381 790	$626   652^1   631$	122 238 522	$228^{1}$ $234$ $225$	362 403 8070	464 56.5 69.4	$211 - 223 - 204^{1}$											
	3.38	3,40	3.29	0.37		0.52	0.23	0.40		_	October	1.8	70	0.21	116	3.0	DNC	2.1	7.12
Nitrate+Nitrite (mg/L-N) April June October	0.75	0.21	$2.70^{1}$	0.08	0.08	0.35	0.25	0.52		Flow (CFS)	June	12.8	য ব	0.51	28.6	1.2		4.8	6.93
Nitrate+ April	0.26	28	0.05	0.23	$0.18^{1}$	030	0.47	0.72		丘	April	42.9	0.0	1.4	266	3.8	DNC	11.7	15.70
) October	5	10	10	00	8	2	3	Ç)			October	7.8	8.3	8.1	8.6	6.5	89	7.3	99
TSS (mg/L) June	10	स	$12^{i}$	23	5	104	4	а		hД	June	8.5	23	7.8	8.3	7.4	6.5	6.2	6.5
T\$ April	1850	IL <sup>2</sup>	31	31	51	139	5	50			April	8.0	8	7.6	7.1	6.3	6.7	7.4	6.8
) October	1.3	0	3.2	4,5	10.7	3.1	2.8	1,7,1	(	_ (၁	October	11.5	<del>7</del> 7	13.6	13.0	10.6	9.0	7.7	9.2
TOC (mg/L) June O	1.4	18	5.31	5,5	9.8	06	2.1	3,5		Temperature (°C)	June	13.5	5.5	21.3	23.4	14.3	9.61	16.8	14.8
TC April	13.8	£3	12.7	e 8	11.51	17.4	2.4	103		Tem	April	9.4	16.7	10.0	20.7	11.8	13.8	12.2	11.7
Sample Site	Mission Creek	Stemilt Creek	Stink Creek	Palouse River	GHCDD-1	Joe Leary Slough	Kearny Creek	Mercer Creek			Sample Site	Mission Creek	Stemilt Creek	Stink Creek	Palouse River	GHCDD-1	Joe Leary Slough	Kearny Creek	Mercer Creek

<sup>1 -</sup> Values are means of duplicate analyses

<sup>&</sup>lt;sup>2</sup> - Not detected at or above the reported value

 $<sup>^{\</sup>circ}$  - Data not collected

Measured concentrations of azinphos-methyl, carbaryl, chlorpyrifos, diazinon, and DDT approach acute toxicity values (i.e., within an order of magnitude) for some invertebrates (Appendix H) All of these pesticides are highly toxic insecticides, and all except DDT are acetylcholinesterase (AChE) inhibitors. The toxicity of insecticide mixtures is generally at least additive, and mixtures of AChE inhibitors are often synergistic (Macek, 1975, Faust et al., 1994). Although the detected concentrations of the individual pesticides are lower than published toxicity values, combinations of the insecticides are likely to be acutely toxic to some aquatic fauna

Total suspended solids (TSS) in the sample from Mission Creek collected in April were extremely high (1850  $\mu$ g/L, Table 4) Flow was also very high at that time. These high values were probably due to snow-melt runoff in the mountains above the orchards. Aquatic communities may have been impacted by the high suspended solids. The concentration of TSS was in the range as determined by the NAS (1973) that provides a very low level of protection for aquatic communities (>400  $\mu$ g/L)

#### Stemilt Creek

Like Mission Creek, Stemilt Creek starts in the Wenatchee Mountains and flows through orchards in the Wenatchee Valley. Orr and Middle Creeks are tributaries and enter Stemilt Creek above the orchards in Wenatchee Heights. The sampling site was at the bridge on the Malaga-Alcoa Highway just before the creek discharges into the Columbia River.

Four insecticides, azinphos-methyl, chlorpyrifos, diazinon, and malathion, and two herbicides, bromoxynil and simazine, were identified in samples from Stemilt Creek Pentachlorophenol was also detected Azinphos-methyl, chlorpyrifos, and malathion at 0 010, 0 005, and 0 012  $\mu$ g/L, respectively, exceeded NAS (1973) recommended maximum concentrations, and approach acute toxicity values for some invertebrates

Stemilt Creek is a very small stream with a flow of less than one cubic foot per second (CFS) most of the year. However, the flow in June went up to 4.4 CFS, indicating that irrigation accounts for most of the flow in the summer. It should be noted that only malathion was detected in June. This suggests that the irrigation water does not run directly off into the creek. If it did, more and higher concentrations of pesticides would be expected as the flow increased.

#### Stink Creek

Stink Creek is another stream that flows through orchards. Stink Creek is only about a mile long and drains Roses and Dry Lakes. These lakes sit in a small valley above the north shore of Lake Chelan near Manson, and are surrounded by orchards. Near Lake Chelan, the creek enters a pipe that discharges into the lake. Samples were collected just upstream of the pipe.

Ten compounds were detected in water samples. Four were insecticides, four were herbicides, and two were breakdown products. All four insecticides exceeded water quality criteria. Chlorpyrifos was found in April at a concentration of 0.056 µg/L, and 4,4'-DDT was detected in June at 0.014 µg/L; both pesticides were above Washington State chronic standards. The

USEPA (1986) criterion for azinphos-methyl was exceeded in June (0.058 μg/L), and in April diazinon, at 0.021 μg/L, was above the NAS (1973) recommended maximum concentration. All four also approach acute toxicity values, particularly chlorpyrifos which was at the low end of the range of the 96 hour LC<sub>50</sub> for *Gammarus lacustris* (0.07 to 0.17 μg/L, Johnson and Finley, 1980).

In sediment samples collected from Roses Lake by Ecology (Serdar et al, 1994), total DDT concentrations were extremely high (average of 1600 µg/Kg, ppb). Water from Roses Lake passes into Dry Lake before discharging into Stink Creek. Vegetation in Dry Lake is very thick at the end where it discharges into Stink Creek, and most particulates carrying DDT would be filtered out by the vegetation. However, during a storm event that substantially increases flow through the lakes, high concentrations of DDT may be carried into the creek.

Stink Creek is classified as a AA stream (feeder to a lake) As such, the maximum temperature should not exceed 16.0°C. In June, the temperature in Stink Creek was 21.3°C, but this high value was probably not the result of human activity. Dry Lake, which feeds Stink Creek, is shallow and probably heats up quickly in the hot summer sun.

## Orchard Pesticide Use Summary

Six insecticides were identified in samples from the three sites representing orchard pesticide use. All detections for these six compounds exceeded water quality criteria. Azinphos-methyl, chlorpyrifos, and diazinon were found at all three sites. These three pesticides were also found in samples from Mission Creek collected in 1993. In addition, azinphos-methyl was detected in Mission Creek in 1992. DDT was found in Mission Creek in 1993 and 1994, and in Stink Creek in 1994. Carbaryl and malathion were each identified once. In 1993, endosulfan was also found in a sample from Mission Creek.

Azinphos-methyl is the most consistently detected insecticide in samples from orchard use areas. Most concentrations of azinphos-methyl have exceeded the USEPA (1986) water quality criterion for protection of aquatic wildlife; the remainder have been above the NAS (1973) recommended maximum concentration. The level of azinphos-methyl detected in June of 1993 was above concentrations toxic to some invertebrates (Davis and Johnson, 1994).

Chlorpyrifos has been found consistently in samples collected in April from orchard use areas. It is used from late March through April to control aphids in orchards. Chlorpyrifos is moderately persistent, but it generally does not reach surface waters because it is not readily soluble in water and it adsorbs strongly to organic matter (Seyler et al., 1994). Apparently, some makes its way into the streams in detectable concentrations during application periods, but residues have not been detectable shortly thereafter. Some levels of chlorpyrifos have exceeded the Washington State water quality standard for protection of aquatic wildlife (WAC 173-201A); others were above the NAS recommended maximum concentration.

DDT is apparently associated with soil particles originating from the orchards. It is detected most frequently in June, probably from storm-water runoff. Orchard runoff also occurs in April, but

snow melt probably dilutes the concentrations below detectable levels DDT in Stink Creek will probably increase substantially during any high flow event

Diazinon has also been detected consistently in orchard area streams. Some concentrations have exceeded the NAS recommendation; no state or federal criteria exist.

Azinphos-methyl and chlorpyrifos appear to be chronic problems in orchard streams, and either individually or in combination have the potential, at the concentrations detected, to cause significant adverse effects to the resident stream fauna. By itself, diazinon does not appear to be a problem in orchard streams. If the effects of insecticides are additive, then the presence of diazinon, along with azinphos-methyl, chlorpyrifos, and/or any other insecticides, may result in significant adverse effects to the aquatic fauna.

#### Palouse River

The south fork of the Palouse River originates southeast of Pullman and runs northwest through Pullman to Colfax, where it joins with the north fork. The north fork originates in Idaho and flows westward through the town of Palouse and on to Colfax. After the confluence, the river flows northwest for a few miles and then begins turning southwest until it flows into the Snake River

Samples for the WSPMP were collected at Winona, upstream of the confluence with Rebel Flat Creek. The Palouse River was chosen to represent dry-land agriculture pesticide use, which is the predominant land use upstream from Winona. Downstream from Winona the river receives water from streams that are not primarily representative of dry-land agriculture.

Nine pesticides were detected in water samples from the Palouse River collected in 1994. Eight of these were herbicides that are typically used on grain crops. Pentachlorophenol, a fungicide/molluscicide used to treat wood, was also found. Concentrations of all detected pesticides were well below any criteria or toxicity values.

The temperature in June (23.4°C) exceeded the Washington State water quality standard for Class B surface waters (21.0°C, WAC 173-201A) High temperatures in this river may be partially the result of human activities Air temperatures during the summer in this watershed become quite high and much of the protective vegetation along the river has been removed or disturbed by human activity

# Grays Harbor County Drainage Ditch No.1

This ditch drains cranberry bogs in the northern portion of the Grayland area and flows north into South Bay 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.

Cranberry bogs in the southern part of Grayland drain into another ditch (Pacific County Drainage Ditch No 1) that flows south into Willapa Bay near Tokeland. Discharge from this ditch has been sampled by the USEPA (Watson, 1995), but the data are not yet available.

Twelve pesticides were found in samples collected for the WSPMP. Seven of these are recommended for use on cranberries by the Washington State University Cooperative Extension (Antonelli *et al.*, 1995). Azinphos-methyl was detected in June at 0.014  $\mu$ g/L, slightly above the criterion set by the USEPA (1986) of 0.01  $\mu$ g/L. Detections of chlorpyrifos in June (0.021  $\mu$ g/L) and October (0.03  $\mu$ g/L), and diazinon in April (0.011  $\mu$ g/L) and October (0.029  $\mu$ g/L) exceeded NAS recommended concentrations. All three of these insecticides approach toxicity values for some invertebrates.

Of the 12 pesticides detected in GHCDD-1, three insecticides, carbofuran, chlorpyrifos, and diazinon were each found in two of the three sample periods. Three of the herbicides, 2,4-D, dichlobenil, and norflurazon, were present in all three sample periods. Napropamide was also found in two sample periods. Multiple detections are important because it suggests that the flora and fauna are being exposed to these pesticides for long periods of time. Water quality criteria for chronic exposures are typically based on relatively short durations, such as 24 to 96 hours. Little information is available for longer exposures, but the toxicity of some pesticides is likely to be higher for durations on the order of months as suggested by multiple detections. Flora and fauna in GHCDD-1 appear to be exposed to multiple pesticides for extended periods of time, and may be experiencing adverse effects that would not be expected for short duration exposures

Multiple detections of insecticides can be explained by reviewing the pesticide application schedule recommended by the WSU Cooperative Extension (Antonelli et al., 1995). Four time periods for insecticide application are recommended throughout the growing season to control various pests. However, multiple detections of herbicides are not so easily explained. Herbicide application takes place primarily in the winter and early spring when the cranberry plants are dormant, and generally ends by late April.

The pH for GHCDD-1 in April was 6.3, which is slightly below the state standard for class A waters of 6.5 to 8.5 (WAC 173-201A-030). The reason for this low pH is not known

## Joe Leary Slough

Joe Leary Slough drains the Olympia Marsh, northwest of Mount Vernon, into Padilla Bay Land use adjacent to the slough is predominantly agriculture, including orchards, caneberries, pasture land, and a variety of row crops

This slough was sampled once in June of 1993, and mevinphos (Phosdrin) was found at a very high concentration (Davis and Johnson, 1994) Mevinphos is a highly toxic organo-phosphorus insecticide, and it was found at a level high enough to kill some fish. Joe Leary Slough was resampled in 1994 to determine if mevinphos continued to be present at high concentrations

Thirteen pesticides were detected in water samples from Joe Leary Slough in 1994. Diazinon, at 0 017  $\mu$ g/L, was above the NAS recommended maximum concentration. No other pesticides were above water quality criteria, and none exceeded acute toxicity values. Only two of the compounds detected were found in more than one sampling period. Mevinphos was not detected in 1994, probably because most uses were canceled by the Washington State Department of Agriculture (AENews, 1994).

Joe Leary Slough is classified as a Class A water body. The water temperature in June (19.6°C) exceeded the state standard of 18.0°C. Historically, this area was an estuary/wetland Agricultural practices in the area have modified this water body so extensively that for most of its length it is little more than a drainage ditch with little or no protective vegetation. It is probably safe to assume that the high temperature is due to human activity.

#### Kearny Creek

Sampling of Kearny Creek was coordinated with the Washington State Department of Agriculture (WSDA). The WSDA was investigating potential water quality impacts from pesticide use on Christmas tree plantations. Coordination consisted of sampling of the same stream and sharing the results. Sampling sites and schedules, target analyte lists, and analytical methods were different

Kearny Creek originates in the foothills north of highway 508 near Cinebar, runs through about four miles of Christmas tree and "hobby" farms, and then flows into the south fork of the Newaukum River About a mile and a half upstream from the confluence with the river, Door Creek flows into Kearny Creek The sample site for the WSPMP was at the bridge on Frase Road, just downstream of the confluence with Door Creek The WSDA collected samples at two sites, one on Kearny Creek about one mile upstream of the WSPMP site and one on Door Creek about a mile and a half upstream from the confluence with Kearny Creek

Only three pesticides were detected in samples collected for the WSPMP Atrazine was found in April and hexazinone (Velpar) was identified in samples from all three sampling periods. Pentachlorophenol was also detected at a low level in October In samples collected by the WSDA on June 8, hexazinone was detected in Door Creek at 0.77 µg/L, but nothing was found in Kearny Creek (Foss, 1994). All concentrations were well below any applicable criteria.

The hexazinone detected at the WSPMP site was probably from Door Creek. During a reconnaissance of the area on April 8, 1994, signs were seen posted around a large Christmas tree farm along the upper end of Door Creek that indicated that the farm had been treated with Velpar The WSDA data support this with a detection of hexazinone in Door Creek, but not in Kearny Creek.

Kearny Creek is a Class A water body. The acceptable pH range for class A waters is 6.5 to 8.5. In June, the pH in Kearny Creek was 6.2. The reason for this low value is not known.

Kearny Creek is the third stream sampled by the WSPMP representing forest practices pesticide use. Tuttle Creek was sampled in 1992 (Davis, 1993) and Adna Creek was sampled in 1993 (Davis and Johnson, 1994). No pesticides were detected in Tuttle Creek and only one, 2,3,4,6-tetrachlorophenol, was found in samples from Adna Creek.

The low concentrations and number of detections at these sites appear to indicate that forest practices pesticide use is having little impact on surface waters and associated biota. In general, this may be true because few pesticides are regularly used on forest practices applications, pesticide applications are made infrequently on individual sites, and sites are typically isolated from one another. However, under certain circumstances some pesticides may reach concentrations that could adversely impact stream biota. Shortly after application on a Christmas tree farm, levels of chlorothalonil (Daconil) and oxydemeton-methyl (Metasystox-R) in a stream flowing through the farm were found to be higher than recommended maximum concentrations (Rashin and Graber, 1993). While impacts from forest practices pesticide use do not appear to be common, isolated incidents do take place.

#### Mercer Creek

Mercer Creek drains the Bellevue area east of Interstate-405, including street runoff, into Lake Washington, and represents urban pesticide use. Much of this area is residential, but includes a bridle trail park, shopping centers, schools, and two golf courses. The creek was sampled at the mouth where it flows into Mercer slough.

This site was also sampled in 1992 and 1993 for the WSPMP (Davis, 1993; Davis and Johnson, 1994), and was sampled again in 1994 to verify detections. Thirteen pesticides were detected in samples collected in 1994. Ten of these were also found in 1993. Only one sample was collected in 1992, but all of the six target compounds that were detected were also found in 1993 and 1994. These six were 2,4-D, DCPA, diazinon, dichlobenil, MCPP, and prometon 2,4-D, DCPA, and dichlobenil were the most consistently detected pesticides at Mercer Creek. Other frequently detected compounds were bromacil, pentachlorophenol, simazine, and trichlopyr

Diazinon was found above the NAS (1973) recommended maximum concentration for every detection over the three years. Malathion was found once each in 1993 and 1994, and both detections exceeded the NAS recommendation. Although the concentrations of diazinon and malathion approached toxicity values for some invertebrates, none were above LC<sub>50</sub> values (Appendix H).

Of the 13 pesticides found in 1994, three were detected in all three sample periods and four were found in two sample periods. A high proportion of the pesticides identified in 1993 were also detected multiple times. Flora and fauna in Mercer Creek may be experiencing adverse effects from long-term exposure to multiple pesticides

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**Appendices** 

Appendix A. Surface Water Sampling Site Positions for the 1994 WSPMP

Site Name	]	Latitud	<u>е</u>	L	ongitu	de	State	Plane
	deg	min	sec	deg	min	sec	X	<u>Y</u>
Mission Creek at Mission Creek R	47 .oad	30	43.5	120	28	18.5	2006970	794559
Stemilt Creek at Malga-Alcoa Hig	47 ghway	22	31	120	14	47	2062841	744759
Stink Creek at mouth	47	55	48	120	11	26	2075881	947173
Palouse River at Winona	46	56	44	117	48	13	2673351	599435
GHCDD-1 at Schmid Road	46	48	58	124	05	25	1101412	561171
Joe Leary Slough at Bayview-Edison	48 Road	31	2 7	122	28	173	1521965	1167366
Kearny Creek at Frase Road	46	36	38	122	36	10	1471591	472798
Mercer Creek at mouth	47	36	6.0	122	10	58 2	1584813	831668

#### Appendix B. Target Pesticides List for Surface Water

#### EPA Method 1618 - Modified

(one extraction)

#### **Chlorinated Pesticides**

(one analysis)

Compound	Quantitation Limits* μg/L	Compound	Quantitation Limits $\mu$ g/L
2,4'-DDT	0.05	chlordene-gamma	0.05
2,4'-DDE	0.05	dicofol (Kelthane)	0.50
2,4'-DDD	0.05	dieldrin	0.05
4,4'-DDT	0.05	endrin	0.05
4,4'-DDE	0.05	endrin aldehyde	0.05
4,4'-DDD	0.05	endrin ketone	0,05
DDMU	0.05	endosulfan I	0.05
aldrin	0.05	endosulfan II	0.05
BHC-alpha	0.05	endosulfan sulfate	0.05
BHC-beta	0.05	heptachlor	0.05
BHC-delta	005	heptachlor epoxide	0.05
BHC-gamma (Lindane)	005	methoxychlor	008
captafol	0.25	mirex	0.05
captan	0.15	nonachlor-cis	005
chlordane-alpha	0.05	nonachlor-trans	005
chlordane-gamma	005	oxychlordane	005
chlordene-alpha	005	toxaphene	1.,00

## **Pyrethroid Pesticides**

(one analysis)

Compound	Quantitation Limits μg/L	Compound	Quantitation Limits μg/L
cis-permethrin	0.17	phenothrin	0.17
fenvalerate	0.30	resmethrin	0.17

<sup>\* -</sup> Quantitation limits are approximate and may change between samples.

## Appendix B (cont.). Target Pesticides List for Surface Water

#### EPA Method 1618 - Modified (cont.)

# Organo-Phosphorus Pesticides

(one analysis)

Compound	Quantitation Limits μg/L	Compound	Quantitation Limits μg/L
abate (Temephos)	0.75	fenamiphos	0.13
azinphos-ethyl	0.13	fenitrothion	0.15
azinphos-methyl (Guthion)	0.16	fensulfothion	0.00
carbophenothion	0.10	fenthion	0.08
chlorpyrifos (Lorsban)	0.06	fonofos	0.05
chlorpyrifos-methyl	0.06	imidan (Phosmet)	0.09
coumaphos	0.09	malathion	0.09
DEF (Tribufos)	0.11	merphos	0.13
demeton-o	0.11	mevinphos	008
demeton-s	0.06	-	0.58
diazinon	0.08	monocrotophos	0.38 0.15
dichlorvos		paraoxon-methyl	
	0.07	parathion	0.06
diethyl fumarate	0.25	parathion-methyl	0.06
dimethoate	0.06	phorate	0.06
dioxathion	0.14	phosphamidan	0.19
disulfoton	0.05	propetamphos	0.16
EPN	0.08	ronnel	0.06
ethion	006	sulfotepp	0.05
ethoprop	0.07	sulprofos	0.06
		tetrachlorvinphos (Gardona)	0.17

# **Sulfur-Containing Pesticides**

(one analysis)

Compound	Quantitation Limits µg/L	
propargite	0.18	

# Appendix B (cont.). Target Pesticides List for Surface Water

## EPA Method 1618 - Modified (cont.)

# Nitrogen-Containing Pesticides

(one analysis)

Compound	Quantitation Limits $\mu$ g/L	Compound	Quantitation Limits $\mu$ g/L
Triazines			***
ametryn	0.08	cycloate	0.13
atraton	0.25	di-allate (Avadex)	030
atrazine	008	EPTC (Eptam)	0.14
cyanazine	0.12	triallate (Fargo)	0.20
hexazinone	0.13	vernolate	0.14
metribuzin	0.08	•	
prometon	008	Substituted Amides	
prometryn	008	diphenamid	0.25
propazine	008	napropamide	0.25
simazine	0.08	pronamide	0.25
terbutryn	008		
		Uracils	
Anilines		bromacil	0.50
benfluralin (Benefin)	0.12	terbacil	0.25
ethalfluralin	0.12		
pendimethalin	0.12	Ureas	
profluralin	0.19	diuron	0.45
trifluralin	0.12	tebuthiuron	008
Anilides		Miscellaneous	·
alachlor	0.20	carboxin	0.86
butachlor	0.29	chlorpropham	035
metolachlor	0.25	fenarimol	0.25
propachlor	017	fluridone	055
		metalaxyl	0.52
Cyano		MGK264	0.55
chlorothalonil	0.20	molinate	020
dichlobenil	010	norflurazon	0.13
		oxyfluorfen	0.25
Thiocarbamates		pebulate	0.20
butylate	0.13	triadimefon	0.22

#### Appendix B (cont.). Target Pesticides List for Surface Water

#### EPA Method 515.1

(one extraction, one analysis)

#### **Chlorinated Herbicides**

Compound	Quantitation Limits μg/L	Compound	Quantitation Limits μg/L
2,4-D	0.04	chloramben	0.04
2,4-DB	0.05	DCPA (Dacthal)	0.03
2,4,5-TB	004	dalapon (DPA)	0.11
2,4,5,-TP	0.03	dicamba	0.04
2,4,5-trichlorophenol	0.02	dichlofop-methyl	0.06
2,4,6-trichlorophenol	002	dichlorprop	0.04
2,3,4,6-tetrachlorophenol	002	dinoseb	0.06
3,5-dichlorobenzoic acid	0.04	ioxynil	004
4-nitrophenol	0.07	MCPA	0.08
5-hydroxydicamba	004	MCPP	008
acifluorfen (Blazer)	0.16	pentachlorophenol	002
bentazon	006	picloram	0.04
bromoxynil	0.04	triclopyr (Garlon)	003

# EPA Method 531.1 (one extraction, one analysis)

#### Carbamates

Compound	Quantitation Limits $\mu$ g/L	Compound	Quantitation Limits μg/L
1-napthol	0.04	carbofuran	0.04
3-hydroxycarbofuran	0.04	methiocarb	004
aldicarb	0.04	methomyl	004
aldicarb sulfone	0.04	oxamyl	004
aldicarb sulfoxide	004	propoxur (Baygon)	0.04
carbaryl	004	x x \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	2,0

## 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). Chlorinated herbicides were analyzed using EPA Method 615 and carbamates with EPA Method 531 1. Methods were not modified from those reported in 1993 (Davis and Johnson, 1994)

## **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 GHCDD-1, from Stink Creek in June, and from Mercer Creek in October MS/MSD samples were used to estimate analytical precision and accuracy Field duplicates were also used to assess analytical precision.

In 1993, a field spike was submitted to the laboratory to assess analytical accuracy and loss of target analytes in the period from collection to analysis. Out of 41 target analytes submitted in the field spike, all but one was detected, and reported concentrations were very close to the expected values (Davis and Johnson, 1994), indicating excellent accuracy

A transfer/bottle blank was prepared in June of 1993 to ensure that decontamination procedures were effective. No target analytes were detected in the blank.

#### **Data Review**

Data packages and quality control results from samples analyzed by Ecology's Manchester Environmental Laboratory were reviewed and assessed by Dickey Huntamer

No significant problems were encountered for most of the analyses Problems with a new HPLC system used to analyze carbamate samples resulted in loss of most October carbamate data. The computer system was not set up correctly causing it to overwrite raw data from the previous analysis. Results from only one sample and one matrix spike were recovered. During the analysis, an incorrect autosampler pump setting resulted in oversampling so there was not enough sample remaining to permit reanalysis. During the chlorinated herbicides analysis for October the Mission Creek sample was contaminated by the carry over of methylation reagent during the methylation process, resulting in loss of all data from that sample

### **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 are shown in Appendices E (duplicates), F (matrix spikes), and G (surrogate spikes). 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 excellent. RPD values ranged from 0 to 64% and the average was 18%.

Matrix spike recoveries for chlorinated herbicides in June were low, ranging from 8 to 51%, with four compounds below 20%. These four compounds were "J" qualified (the analyte was positively identified and the associated value is an estimate) in the matrix spike source sample. Aldicarb had a recovery of 15% in the June carbamate matrix spike, but was 52% in the spike duplicate. The laboratory explained this as the result of aldicarb breaking down to aldicarb sulfoxide, which had a recovery of 151% in the matrix spike. Otherwise, matrix spike and duplicate recoveries were acceptable.

Surrogate recoveries ranged between 0 and 136%, and averaged 76%. Samples were qualified with a "J" when the surrogate recovery was less than 20%. No pesticides were detected in samples with surrogate recoveries less than 20%.

Many of the detected compounds were qualified as estimates (J or NJ) These qualifiers have not been included in this report for clarity of presentation. Complete results are available from the author on request

Appendix E. Duplicate Analysis Results for 1994 WSPMP Surface Water Samples (µg/L, ppb)

Analyte	Sample 1	Sample 2	RPD <sup>1</sup>
April (GHCDD-1)			
2,4-D	0.11	0.11	0
carbofuran	0.08	0.08	0
diazinon	0.011	0.011	0
dichlobenil	2.1	1.3	47
napropamide	0.19	0.20	5
norflurazon	0.16	0.15	6
simazine	0.086 U²	0.015	NC3
June (Stink Creek)			
3+hydroxycarbofuran	0.09	0.059	42
4,4'-DDD	0.011	0.055 U	NC
4,4'-DDT	0.019	0.0098	64
azinphos-methyl	0.054	0.062	14
simazine	0.085	0.099	15
October (Mercer Creek)		,	
2,4-D	0.037	0.033	11
diazinon	0.044	0.040	10
dichlobenil	0.024	0.021	13
pentachlorophenol	0.025	0.022	13
triclopyr	0.045	0.035	25

<sup>&</sup>lt;sup>1</sup> - RPD = Relative Percent Difference, (difference/mean) x 100

<sup>&</sup>lt;sup>2</sup> - Not detected at or above reported value

 $<sup>^{3}</sup>$  - NC = Not Calculated

Appendix F. Matrix Spike Recoveries for 1994 WSPMP Surface Water Samples (%)

		April			June			October	
***************************************	MS	$MSD^2$	$RPD^3$	MS	MSD	RPD	MS	MSD	RPD
chlorinated pesticides									
2,4'-DDT	NAF⁴	NAF		102	78	27	NAF	NAF	
4,4'-DDT	83	98	<b>&amp;</b>	68	75	17	NAF	NAF	
2,4'-DDE	NAF	NAF		68	72	21	NAF	NAF	
2,4'-DDD	NAF	NAF		92	72	24	NAF	NAF	
aldrin	99	24	80	42	51	19	NAF	NAF	
BHC-gamma (lindane)	94	87	<b>∞</b>	85	72	17	NAF	NAF	
captafol	NAF	NAF		06	71	24	NAF	NAF	
captan	NAF	NAF		85	71	18	NAF	NAF	
chlordane-gamma	87	82	.9	81	72	12	NAF	NAF	٠
endrin	86	87	12	91	11	17	NAF	NAF	
endosulfan I	68	06		87	75	15	NAF	NAF	
heptachlor	63	38	50	59	62	5	NAF	NAF	
kelthane	NAF	NAF		115	82	34	NAF	NAF	
nonachlor-trans	NAF	NAF		16	73	22	NAF	NAF	
methoxychlor	66	83	18	91	9/	18	NAF	NAF	
mirex	NAF	NAF		26	11	23	NAF	NAF	
pyrethroid pesticides									
fenvalerate	85	98	<b>=</b>	85	73	15	NAF	NAF	
sulfur-containing pesticides									
propargite	88	102	. 15	NAF	NAF		NAF	NAF	
' - MS = Matrix Spike		3 - RPD = Relativ	- RPD = Relative Percent Difference, (difference/mean x 100)	ice, (difference/n	nean x 100)				

4 - NAF = Not Analyzed For

. - MSD = Matrix Spike Duplicate

Appendix F (cont.). Matrix Spike Recoveries for 1994 WSPMP Surface Water Samples (%)

	-	April			June			October	
	MS	$\mathrm{MSD}^2$	${ m RPD}^3$	MS	MSD	RPD	MS	MSD	RPD
organo-phosphorus pesticides									
abate	NAF⁴	NAF		94	98	6	NAF	NAF	
azınphos-ethyl	87	96	3	98	75	14	NAF	NAF	
azınphos-methyl	NAF	NAF		NAF	NAF		107	100	7
chlorpyrifos	68	107	18	93	78	18	NAF	NAF	
coumaphos	NAF	NAF		NAF	NAF		107	112	S
DEF	NAF	NAF		68	71	23	NAF	NAF	
diazinon	98	102	17	75	89	10	110	106	4
dichlorvos	NAF	NAF		84	85	_	NAF	NAF	
dimethoate	NAF	NAF		84	72	15	104	105	_
dioxathion	NAF	NAF		92	74	22	NAF	NAF	
ethion	88	95	∞	90	2/2	17	NAF	NAF	
ethoprop	78	91	15	95	83	13	94	101	7
fenamiphos	NAF	NAF		98	69	22	NAF	NAF	
fensulfothion	NAF	NAF		88	72	20	104	101	ю
fenthion	NAF	NAF		NAF	NAF		100	26	т
fonofos	82	26	13	NAF	NAF		NAF	NAF	
imidan	NAF	NAF		NAF	NAF		112	105	9
malathion	88	105	18	95	80	17	NAF	NAF	
parathion	NAF	NAF		NAF	NAF		103	66	4
mevinphos	NAF	NAF		87	78	11	NAF	NAF	
parathion-methyl	77	24	23	95	80	17	901	107	1
phorate	78	92	16	92	9/	19	110	107	m
phosphamidan	NAF	NAF		101	81	22	NAF	NAF	
ronnel	NAF	NAF		NAF	NAF		104	104	0
sulprofos	NAF	NAF		NAF	NAF		101	107	9
tetrachlorvinphos	NAF	NAF		90	74	70	NAF	NAF	
' - MS = Matrx Spike		'-RPD = Relativ	- RPD = Relative Percent Difference, (difference/mean $\times$ 100)	nce, (difference/n	nean x 100)				
in the second se									

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<sup>&</sup>lt;sup>2</sup> - MSD = Matrix Spike Duplicate

<sup>4 -</sup> NAF = Not Analyzed For

Appendix F (cont.). Matrix Spike Recoveries for 1994 WSPMP Surface Water Samples (%)

		April	-		June			October	
	MS¹	$MSD^2$	$RPD^3$	MS	MSD	RPD	MS	MSD	RPD
nitrogen-containing pesticides									
alachlor	93	85	6	62	09	m	NAF	NAF	
ametryn	NAF⁴	NAF		NAF	NAF		103	68	15
benfluralin	NAF	NAF		NAF	NAF		100	87	14
bromacil	82	100	20	82	73	12	NAF	NAF	
butylate	NAF	NAF		NAF	NAF		68	87	7
chlorothalonil	NAF	NAF		NAF	NAF		105	103	2
cycloate	NAF	NAF		NAF	NAF		109	108	-
di-allate	81	99	20	NAF	NAF		NAF	NAF	
dichlobenil	NAF	NAF		26	81	13	NAF	NAF	
diuron	08	83	4	NAF	NAF		NAF	NAF	
eptam	NAF	NAF		NAF	NAF		86	86	0
hexazmone	128	130	7	101	94	7	137	131	4
metalaxyl	62	104	7	NAF	NAF		NAF	NAF	
metribuzin	102	109	7	69	63	6	NAF	NAF	
profluralin	87	78	5	NAF	NAF		NAF	NAF	
prometon	NAF	NAF		NAF	NAF		80	74	<b>∞</b>
pronamide	93	92	-	66	88	12	NAF	NAF	
propazine	NAF	NAF		NAF	NAF		119	122	2
simazine	6	106	6	92	11	18	NAF	NAF	
tebuthiuron	NAF	NAF		69	09	14	NAF	NAF	
terbutryn	NAF	NAF		NAF	NAF		96	22	19
triallate	NAF	NAF		NAF	NAF		85	98	
trifluralin	84	84	0	20	48	4	NAF	NAF	
vernolate	NAF	NAF		NAF	NAF		94	96	4
. MS = Matry Snike		PDD = Polotin	o Dorcont Differs	nos (difforence/n	100 x 100				

' - MS = Matrix Spike

\* - MSD = Matrix Spike Duplicate

- RPD = Relative Percent Difference, (difference/mean x 100)

4 - NAF = Not Analyzed For

Appendix F (cont.). Matrix Spike Recoveries for 1994 WSPMP Surface Water Samples (%)

		April			Inne			October	
	MS <sup>1</sup>	$MSD^2$	$RPD^3$	MS	MSD	RPD	MS	MSD	RPD
chlorinated herbicides									
2,4-D	77	104	30	33	52	45	80	93	15
2,4-DB	59	87	38	32	48	40	72	85	16
2,4,5-T	99	2/2	30	37	46	22	78	16	16
2,4,5-TB	58	98	39	36	45	22	99	80	20
2,4,5-TP	58	68	42	NAF <sup>4</sup>	57		98	101	16
2,4,5-trichlorophenol	52	11	39	34	33	Ю	78	95	19
2,4,6-trichlorophenol	44	99	24	35	47	29	83	105	23
2,3,4,5-tetrachlorophenol	64	96	40	32	44	32	80	86	20
3,5-dichlorobenzoic acid	48	82	52	37	50	30	84	110	26
4-nıtrophenol	52	89	27	56	25	4	47	91	64
5-hydroxydicamba	26	75	53	30	32	9	63	82	26
acifluorfen	09	48	22	10	14	33	12	15	28
bentazon	54	63	15	40	48	18	65	55	17
bromoxynil	64	83	26	37	51	32	9/	68	16
chloramben	39	79	89	21	16	27	30	49	50
DCPA (dacthal)	26	40	42	23	24	4	34	40	15
dalapon	47	45	4	<b>«</b>	7	13	NAF	NAF	
dicamba	57	83	37	36	51	34	85	86	16
dichlofop-methyl	61	84	32	32	51	46	49	80	22
dichlorprop	57	98	41	36	48	29	82	93	13
dinoseb	54	28	7	∞	∞	0	14	19	31
ıoxynil	59	79	56	35	20	35	57	70	21
MCPA	59	84	35	34	49	36	75	91	19
MCPP	58	68	42	34	52	42	83	96	15
pentachlorophenol	59	92	44	37	20	30	84	102	19
picloram	40	44	10	78	39	33	57	58	2
triclopyr	57	98	41	37	51	32	81	94	16
'- MS = Matrx Spike		<sup>3</sup> - RPD = Relative Percent Differ	Percent Differer	ice, (difference/r	nean x 100)				

<sup>&#</sup>x27; - MS = Matrx Spike 2 - MSD = Matrx Spike Duplicate

 $<sup>^{3}</sup>$  - RPD = Relative Percent Difference, (difference/mean  $\times$  100)

<sup>4 -</sup> NAF = Not Analyzed For

Appendix F (cont.). Matrix Spike Recoveries for 1994 WSPMP Surface Water Samples (%)

		April			June			October	
	MS1	$MSD^2$	RPD <sup>3</sup>	MS	MSD	RPD	MS	MSD	RPD
carbamates									
3-hydroxycarbofuran	97	64	0	84	91	8	78	NAF⁴	
aldicarb	72	74	2	15	52	110	30	NAF	
aldicarb sulfone	91	91	0	93	91	0.1	68	NAF	
aldicarb sulfoxide	8	84	9	151	111	31	88	NAF	
carbaryl	92	93	2	06	88	7	94	NAF	
carbofuran	96	92	2	85	81	5	49	NAF	
methiocarb	95	85	12	75	9/	0.3	22	NAF	
methomyi	96	68	1	06	87	4	65	NAF	
oxamyl	66	95	4	92	86	cc	61	NAF	
propoxur	87	87	0	91	81	11	36	NAF	

<sup>-</sup> MS = Matrix Spike

<sup>\* -</sup> MSD = Matrix Spike Duplicate

 $<sup>^3</sup>$  - RPD = Relative Percent Difference, (difference/mean x 100)

<sup>4 -</sup> NAF = Not Analyzed For

Appendix G. Surrogate Recoveries for 1994 WSPMP Surface Water Samples (%)

	DCBP	TCMX	TPP	DMNB	IBP	BDMC
April						
Mission Creek	67	$SNA^1$	68	49	59	79
Stemilt Creek	73	SNA	76	50	65	71
Stink Creek	30	SNA	77	60	122	52
Palouse River	70	SNA	101	66	65	86
GHCDD-1	89	SNA	108	59	41	83
GHCDD-1 Dup	93	SNA	103	51	63	77
Joe Leary Slough	108	SNA	119	56	118	84
Kearny Creek	80	SNA	91	42	52	70
Mercer Creek	75	SNA	87	54	58	79
June						
Mission Creek	88	79	119	95	57	72
Stemilt Creek	89	72	98	99	86	77
Stink Creek	90	25	95	0	59	96
Stink Creek Dup	83	60	95	76	86	75
Palouse River	86	71	98	80	68	102
GHCDD-1	84	73	105	95	61	67
Joe Leary Slough	95	77	107	98	65	72
Kearny Creek	106	87	125	107	86	29
Mercer Creek	112	91	136	106	118	82
October						
Mission Creek	65	60	99	68	$DL^2$	96
Stemilt Creek	77	73	112	89	93	DL
Stink Creek	72	69	114	67	93	DL
Palouse River	75	65	112	70	75	DL
GHCDD-1	63	9	127	72	88	DL
Joe Leary Slough	68	59	105	67	81	DL
Kearny Creek	81	11	113	58	88	DL
Mercer Creek	78	54	107	48	106	DL
Mercer Creek Dup.	48	42	96	59	95	DL

<sup>1 -</sup> SNA = Surrogate Not Added

<sup>&</sup>lt;sup>2</sup> - DL = Data Lost, an analytical problem resulted in a loss of data

# Appendix G (cont.). Surrogate Recoveries for 1994 WSPMP Surface Water Samples (%)

	DCBP	TCMX	TPP	DMNB	TBP	BDMC
April						
Lab Blank 1	95	$SNA^1$	85	71	81	76
Lab Blank 1 Duplicate	91	SNA	87	64	75	84
Lab Blank 2	95	SNA	110	57	60	$NAF^2$
Lab Blank 2 Duplicate	116	SNA	114	73	76	NAF
Matrix Spike	109	SNA	110	56	58	85
Matrix Spike Duplicate	93	SNA	97	61	85	97
June						
Lab Blank 1	69	43	84	76	54	70
Lab Blank 1 Duplicate	46	24	59	53	64	79
Lab Blank 2	82	19	97	87	68	NAF
Lab Blank 2 Duplicate	84	21	105	84	74	NAF
Matrix Spike	80	29	96	66	71	84
Matrix Spike Duplicate	73	28	80	61	51	72
October						
Lab Blank 1	66	46	110	58	87	$DL^3$
Lab Blank 1 Duplicate	80	65	105	78	94	DL
Lab Blank 2	89	29	96	65	91	DL
Lab Blank 2 Duplicate	75	8	109	60	92	DL
Matrix Spike	NAF	NAF	106	61	91	100
Matrix Spike Duplicate	NAF	NAF	102	61	106	DL

<sup>&</sup>lt;sup>1</sup> - 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)

<sup>&</sup>lt;sup>2</sup> - NAF = Not Analyzed For

 $<sup>^3</sup>$  - DL = Data Lost, an analytical problem resulted in a loss of data

Appendix H-1. Water Quality Criteria and Recommended Maximum Concentrations of Pesticides Detected in 1994 WSPMP Surface Water Samples for the Protection of Aquatic Life (μg/L, ppb)

11 Fish Chronic <sup>3</sup>			o.		7				350			049					5		7
Norris and Dost, 1991 ates Chronic <sup>3</sup> Acute	09		06		70				3500			6400					50		70
Norris and Invertebrates ute Chronic³	12		1		0.06				39			110					2		m
Ac			14		9.0				390			1120					20		30
CCREM, 1987 Maximum Conc.	4	0.001	2.0	S		1.75			10		6.1			5.6	1.0	90	10	0.24	
NAS, 1973 Maximum Conc.	3	0.002		0.001	0.02		0.001	6000	200	37.0			0.008				10.0		
EPA, 1986 Freshwater tte Chronic³		0.001		0.01									0.1			3.54			
EPA, Fresh Acute		1.1														\$5.5			
WAC 173-201A  Freshwater cute Chronic		0.001 <sup>3</sup>					$0.041^{2}$									3.54			
WAC 17 Fresh Acute		1.1					0.083									\$35			
Pesticide	2,4-D	4.4DDI total DDT	atrazme	azinphos-metnyi bromoxynil	carbaryl	carbofuran	chlorpyrifos	diazinon	dicamba	dichlobenii	diclofop-methyl	hexazinone	malathion	MCPA	metribuzm	pentachlorophenol	simazine	triallate	triclopyr

- I hour average

² - 4 day average

<sup>3</sup> - 24 hour average

 $^{\rm 4}$  - at pH 6.5 (minimum pH of sites where pentachlorophenol was detected)

Appendix H-2. Acute Toxicity (Johnson and Finley, 1980) of Pesticides Detected in 1994 WSPMP Surface Water Samples (μg/L, ppb; 96 hour LC<sub>50</sub>)

	Aquatic In	vertebrates	Fis	sh
Pesticide	Most Sensitive sp.	Gammarus spp.	Most Sensitive sp.	Rainbow Trout
azinphos-methyl	0.11 - 0 16	0.11 - 0.20	0 27 - 0.48	3.0 - 64
carbaryl	14-24	16 - 39	520 - 910	1,450 - 2,630
carbofuran	NA <sup>1</sup>	NA	115 - 188	272 - 531
chlorpyrifos	0.07 - 0 17	same	1.1 - 5.1	6.0 - 8 4
DDE	NA	NA	26 - 40	same
DDT	0.12 - 0.30	0.7 - 1 5	0 9 - 2.4	6.8 - 11.4
diazinon	0.15 - 0 28	same	90	same
dicamba	>56,000	>100,000	28,000	same
dichlobenil	3,300 - 4,200	8,000 - 15,000	4,000 - 9,100	4,700 - 8,400
eptam	15,000 - 36,000	66,000	14,800 - 17,700	same
malathion	0.63 - 0.92	same	59 - 70	160 - 240
pentachlorophenol	NA	NA	23 - 44	48 - 56
simazine	560 - 2,200	>100,000	>100,000	same
2,4-D	90 - 1,400	1,900 - 3,000	190 - 330	same

<sup>1 -</sup> NA = Not Available

Appendix H-2 (cont.). Acute Toxicity of Pesticides Detected in 1994 WSPMP Surface Water Samples (µg/L, ppb; 96 hour LC<sub>50</sub>)

Pesticide	Most Sensitiv	ve Species Tested Invertebrates	References
atrazine	4,500	$NA^1$	Tetra Tech, 1988
bromacil	28,000	non-toxic (bees)	FCH, 1991
bromoxynil	63	non-toxic (bees)	Seyler et al., 1994
carbofuran	94	9.8	USEPA, 1984a
chlorpropham	3,020	NA	USEPA, 1987
DCPA (dacthal)	30,000	6,200	USEPA, 1988a
diclofop-methyl	toxic <sup>2</sup>	non-toxic (bees)	FCH, 1991
hexazinone	320,000	NA	Tetra Tech, 1988
MCPA	89,000	>180,000	USEPA, 1989
MCPP	115,000	NA	USEPA, 1988b
metribuzin	>10,000	4,180	USEPA, 1985
napropamide	9,400	14,300	Seyler et al , 1994
norflurazon	8,100	15,000 (NOEL <sup>3</sup> )	USEPA, 1984b
prometon	12,000	NA	Tetra Tech, 1988
triallate	1,200	430	Seyler et al., 1994
triclopyr	117,000	1,170,000	Seyler et al., 1994

<sup>1 -</sup> NA = Not Available

<sup>&</sup>lt;sup>2</sup> - I oxicity to fish not measurable due to insolubility of the compound in water

<sup>&</sup>lt;sup>3</sup> - NOEL = No Observed Effects Level

Appendix I. Supplemental Information for Pesticides Detected in 1994 WSPMP Surface Water Samples

Application	systemic control of broadleaf weeds	all use banned in 1972	breakdown product of DDT	Wassi Company on come and other course	The second control with a second control of the second control of	insect control on tree fruit, melons, nuts, and field crops	general control of weeds and brush	postemergent control of weeds in grain crops	insect control on that, forests, lawns, livestock, etc	controls insects, mites, and nematodes on crops	precinerant weed control	control of a wide variety of agricultural and household pests	preemergent control of grasses	control of a wide variety of agricultural and household pests	control of brush and broadlest weeds	control of grasses, and broadleaf and aquatic weeds	controls anitial grassit weeds	systemic control of brush and weeds	control of grasses in corn, potatoes, beans, etc.	controls many annual, biennial, and perennial weeds	control of sucking and chewing insects on fruits and vegetables	postemergent control of broadleaf weeds on small grains	control of broadleaf weeds on ornamentals and grasses	control of annual grasses and broadleaf weeds	systemic control of some annual grasses and broadleaf weeds	preemergent control of annual grasses and broadleaf weeds	wood preservante	pre- and postemergent control of most grasses & broadleaf weeds	control of annual grasses and broadleaf weeds	preemergent control of grass weeds	Chofernson montree of these drams become to the
Activity	hormone-type herbicide	insecticide		selective herbicide	hanne de management et en	broad spectrum insecticide	broad spectrum herbreide	selective herbicide	broad spectrum insecticade	broad spectrum insecticide	plant growth regulator	broad spectrum insecticide	selective herbicide	broad spectrum insecticide	selective herbicide	broad spectrum herbicide	selective herbicide	hormone-type herbicide	selective herbicide	contact and residual herbicide	broad spectrum insecticade	hormone-type herbicide	hormone-type herbivide	selective herbicide	selective herbicide	selective herbicide	fingicide, molluscicide	nonselective herbicide	selective herbicide	selective herbicide	collection bearles will
Chemical Group	chlorinated phenoxy	chlormated pesticide		triazine	and the second s	organopnospnate	uracil	nitrile	carbamate	carbamate	carbamate	organophosphate	benzoic acid	organophosphate	benzoic acid	benzontrile	chiorinated phenoxy	chlormated phenoxy	thiocarbamate	triazine	organaphasphate	chlormated phenoxy	chlorinated phenoxy	triazinone	amide	fluorinated pyridazinone	phenol	triazine	triazine	thiocarbamate	and dead
Trade Name	Aqua-Kleen	Genitox		Gesaorin	Carthian	Califion	Bromax	Brommex	Sevin	Furadan	Chloro IPC	Dursban, Lorsban	Dacthal	Knox-Out	Banvel	Casoron	Hoclon	2,4-DP, Weedone	Eptani	Velpar	Cythion	Agritox	Mecoprop	Lexone, Sencor	Devrinol	Telok, Solicam	Dowlede	Pramitol	Simanex, Aquazine	Avadex, Far-Go	Garton
Common Name	2,4-D	DDI	DDE	attazine	orientics mother	aznipilos-illeulyi	bromacil	bromoxynil	carbaryl	carbofuran	chlotptopham	chlorpyrifos	DCPA	diazmon	dicamba	dichlobenil	dichlofop-methy!	dichlorprop	EPTC	hexazinone	malathion	MCPA	MCPP	metribuzın	napropamide	norflurazon	pentachlorophenoi	prometon	simazine	triallate	triclowe

<sup>-</sup> Each trade name listed is typically one of many available formulations using the same active ingredient and is the trade name most familiar to the author Detected pesticides are not necessarily residues from use of the specific formulations listed here

Appendix J-1. Pesticides Detected in Water Samples Collected for the 1992 WSPMP ( $\mu g/L$ ,ppb)

	Mission Creek	Crab Creek	Walla Walla River	Glade Creek	Fishtrap Creek	Moxee Drain <sup>1</sup>
Insecticides	Creek	CIECK	Kivei	CIECK	CICCK	Diani
Insecticides 4.4'-DDD						0.027
-0.00f000000000000000000000000000000000						0.018
4,4'-DDE 4,4'-DDT						0.018
//0/501/0/00/00/00/00/00/00/00/00/00/00/00/00						$0.060^3$
total DDT	_ <b>-</b>					0.060
azinphos-methyl	0.0332					
diazinon						
malathion						0.054 <sup>4</sup>
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 <sup>5</sup>		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

<sup>&</sup>lt;sup>1</sup> - Values are means of duplicate analyses

<sup>&</sup>lt;sup>2</sup> - Exceeds USEPA, 1986 water quality criteria

<sup>&</sup>lt;sup>3</sup> - Exceeds Washington State water quality standards

<sup>&</sup>lt;sup>4</sup> - Exceeds NAS, 1973 recommended maximum concentrations

<sup>&</sup>lt;sup>5</sup> - Listed as disugran in Davis, 1993

## Appendix J-1 (cont.). Pesticides Detected in Water Samples Collected for the 1992 WSPMP ( $\mu g/L,ppb$ )

	Mercer	Thornton	Sullivan	Lake	Tuttle
	Creek <sup>1</sup>	Creek	Slough	River	Creek
Insecticides					
4,4'-DDD					
4,4'-DDE					
4,4'-DDT					
azinphos-methyl	•				
diazinon	$0.091^2$	0.0772			
malathion		************************			
and a con					
Herbicides	0.20	0.23	0.039		
2,4-D atrazine	0.20	0.23	0.24		
atrazine desethyl			0.24		
bromacil			0.046		
chlorpropham			0.10		
DCPA (Dacthal)	0.061	0 066	0.017	0.011	
dicamba		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					
Funcicido					
Fungicide					
pentachlorophenol					

Values in bold exceed water quality criteria

<sup>&</sup>lt;sup>1</sup> - Values are means of duplicate analyses

<sup>&</sup>lt;sup>2</sup> - Exceeds NAS, 1973 recommended maximum concentrations

<sup>&</sup>lt;sup>3</sup> - Listed as disugran in Davis, 1993

Appendix J-2. Pesticides Detected in Water Samples Collected for the 1993 WSPMP ( $\mu g/L$ , ppb)

			Sample	sites West of t	Sample Sites West of the Cascades				Leary	Coulee
			Fishtrap Creek	reek	Mercer Creek	Creek	Salmon Creek			Creek
	April	June August October	April June A	August October	April June	August October*	April June August	October	June	
Insecticides 4-nitrophenol	000000 000000 000000 000000 000000	-				0.22				
chlorpyrifos diazinon	50000 50000 50000 50000 50000 50000				0.032	0		0.0441		
malathion methomyl					00000	0.0852	890 0			-000 -000 -000
mevinphos propoxur						0.047			111	
Herbicides	00000 00000 00000 00000 00000 00000 0000			1300						
2,4-D aldicarb	86.65 200.00 200.00 200.00 200.00 200.00		0000000 0000000		0.05	0.039 0.29	0.76			1000
afrazine bentazon	9000		0.02 0.024	0.010 0.035	0.025		0.02		0.075	360
bromacil chlorpropham	01000 01000 01000 01000 00100 00100		0.03 0.054	0.047 0.058	0.11	0.037 0.073	,		0.9	
DCPA (Dacthal) dichlobenil				0.035	0.06 0.041 0.11	0.032 0.034 0.09		0.039		0.20
diuron EPTC (Eptam)	000000					33333			0.17	
MCPA	00000		0.043			0.029 0.17				0.000
Sinazine	100000		0.02 0.011		0.024 0.048	0.018	0.38 0.044	0:030		500000 000000 000000 000000
Fungicides	60 (60) 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00 00	300.0								
pentachlorophenol	1000	200000	80070		0.007		0.005		200 200 200 200 200 200 200 200 200 200	

\* - Values are means of duplicate analyses

· - Exceeds Washington State Water Quality Standards

- - Exceeds NAS, 1973 recommended maximum concentrations

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

## August October April	June August October	April June* August October  0.002 0.002 0.003 0.13* 0.13* 0.14* 0.03* 0.003 0.004 0.048*	April         June         August         October           0.006         0.029         0.002           0.008         0.058         0.005           0.008         0.057         0.005           0.078         0.027         0.01           0.037         0.037         0.03           0.048         0.013         0.03           0.053         0.048         0.03           0.053         0.048         0.03	April June August* October
ethtyl  sulfan  0.022  1  1  1  1  1  1  1  1  1  1  1  1		0.018 <sup>1</sup> 0.113 <sup>2</sup>	0.006 0.029 0.002 0.0028 0.008 0.057 0.078 0.027 0.14 0.031 0.031 0.014 0.013 0.014 0.013 0.014 0.013	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
etttyt s  0.022  I II sulfan  0.34 0.090  0.34 0.090  0.05 0.05 0.015  0.093 0.49 0.96  0.032  am)  0.13		0.018 0.018* 0.13*	0.006 0.029 0.002 0.028 0.008* 0.057* 0.07* 0.027 0.07* 0.037 0.031 0.012 0.014 0.013 0.014 0.013 0.008 0.023 0.053* 0.048*	
entryit 6.0192  I  II  sulfain  1.0.022  0.034  0.034  0.035  0.030  0.030  0.030  0.030  0.030  0.033  0.033		0.018 0.018 <sup>1</sup> 0.13 <sup>2</sup>	0.002 0.028 0.008* 0.057* 0.100 0.078* 0.027 0.29* 0.037 0.037 0.037 0.014 0.013 0.063* 0.048* 0.010	
eethy:  s  0.022  I  II  sulfate  0.034  0.093  0.11  0.032  0.013  enthy:  0.033  0.033		0.03%	0.008* 0.057* 0 0.078* 0.027 0.29* 0.037 0.037 0.037 0.037 0.012 0.012 0.012 0.014 0.014 0.013 0.014 0.013 0.008 0.023 0.048* 0.10	
am) 0.032  1  1  1  1  1  1  1  1  1  1  1  1  1		3	0.078	
am) 0.022  1  1  1  1  1  1  1  1  1  1  1  1			0.078* 0.027 0.29* 0.14* 0.037 0.014 0.013 0.008 0.023 0.053* 0.048* 0.10	
I II			0.037 0.031 0.012 0.014 0.013 0.008 0.023 0.053 0.0483	
III suifate  lifan  0.34 0.090  0.02 0.052 0.015 0.015  0.093 0.49 0.96  cthal)  0.032  0.13  0.13		0.031 0.013 0.004 0.048°	0.012 0.013 0.023 0.048° 0.10	ANT MANAGEMENT CONTRACTOR CONTRAC
auffan  0.34 0.090  0.02 0.052 0.015  0.093 0.11  0.059 0.49 0.96  0.032  0.13  0.033		0.013 0.004 0.048*	0.013 0.023 0.0483 0.10	
of the control of the		0.048°	0.023 0.048³ 0.10	
0.34 0.090 0.02 0.052 0.015 0.015 0.093 0.11 0.059 0.49 0.96 0.032 0.13 0.033		0.0483	010	
0.34 0.090 0.02 0.052 0.015 0.015 0.093 0.11 0.059 0.49 0.96 0.032 0.13 0.033				
0.34 0.090 0.02 0.052 0.015 0.015 0.093 0.11 0.20 cthat) 0.59 0.49 0.96 0.032 am) 0.13				
0.02 0.052 0.015 0.015 0.093 0.11 0.20 cthal) 0.59 0.49 0.96 0.032 am) 0.13	0.035		0.03 0.04	
0.093 0.11  1 0.20 ctital) 0.032 am) 0.13  0.033				0.024 0.23
1 0.20 cthal) 0.59 0.49 0.96 0.20 0.032 0.033 0.033				0
ctital) 0.59 0.49 0.96 0.20 0.032 0.032 0.032 0.032 0.033 0.033				0.02
cthal) 0.59 0.49 0.032 am) 0.13 0.033	20 0.035 0.023			
am)			0.015 0.033 0.009	2.2 3.9 2.7
am)				0.11
C		•		
Authorities V.U.Z. U.U.D.				0.061 0.018
Unitable Committee Committ				0.034
rungkrue pentachlorophenol /			0.005 0.012	

<sup>\* -</sup> Values are means of duplicate analyses

<sup>· -</sup> Exceeds Washington State Water Quality Standards

<sup>2 -</sup> Exceeds EPA, 1986 water quality criteria

<sup>2 -</sup> Exceeds NAS, 1973 recommended maximum concentrations