WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

WASHINGTON STATE PESTICIDE MONITORING PROGRAM 1993 SURFACE WATER SAMPLING REPORT

October 1994

Water Body Nos. (See Page iii for Numbers)

Publication No. 94-164

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Washington State Pesticide Monitoring Program 1993 Surface Water Sampling Report

by
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Olympia, Washington 98504-7710

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Abstract

The Washington State Pesticide Monitoring Program (WSPMP) was initiated in 1991 by the Department of Ecology to characterize pesticide residues geographically and over time in ground water and surface water throughout Washington. WSPMP surface water samples were collected at nine sites in April, June, August, and October of 1993, and from two additional sites in June only. Sites were selected to represent various pesticide uses; including agricultural use west of the Cascade Mountains, irrigated and dry-land agricultural use east of the Cascades, urban use, and use by forest practices. Samples were analyzed for 162 pesticides and breakdown products in the following chemical groups: chlorinated pesticides, organophosphorus pesticides, nitrogen-containing pesticides, pyrethroid pesticides, chlorinated herbicides, and carbamates. Conventional parameters included total suspended solids, total organic carbon, conductivity, nitrate+nitrite, temperature, pH, and flow.

A total of 38 pesticides and breakdown products were detected. The most frequently detected pesticides were the herbicides DCPA (Dacthal), simazine, atrazine, and 2,4-D. Washington State and/or EPA aquatic life criteria were exceeded at five sites. Pesticides above criteria were DDT, DDE, DDD, azinphos-methyl (Guthion), and chlorpyrifos (Dursban, Lorsban). Concentrations of four additional compounds exceeded National Academy of Sciences (NAS) recommendations to protect aquatic life and wildlife. Mevinphos (Phosdrin) was detected in Joe Leary Slough at a concentration that is acutely toxic to many fish and aquatic invertebrates.

Water Body Numbers

WA-01-1115
WA-03-0020
WA-08-2100
WA-23-1020
WA-28-1020
WA-32-1010
WA-37-1048
WA-41-1010
WA-45-1010
WA-50-1030

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- Kelly Carruth for preparation and proofing of the final report.

Summary

A total of 38 pesticides and breakdown products were detected in 38 surface water samples collected for the WSPMP from nine sites in April, June, August, and October and from two additional sites in June of 1993. Six of these sites had been previously sampled in 1992.

The pesticide 2,4-D was found at six sites, DCPA (Dacthal), simazine, and atrazine were found at five, and azinphos-methyl (Guthion), diazinon, and pentachlorophenol at four. Out of the 38 samples collected, DCPA was detected in 13 samples; simazine and atrazine were found in 12 samples; and 2,4-D in 11. Sixty-eight percent of the detected compounds were found in three or fewer samples.

Five pesticides were detected at concentrations exceeding Washington State and/or EPA aquatic life criteria (Table 1). An additional four compounds were above National Academy of Sciences (NAS, 1973) recommended maximum concentrations to protect aquatic life and wildlife.

Table 1. Pesticides Exceeding Water Quality Criteria in 1993 (µg/L, ppb)

Water Body	Pesticide	Date	Conc.	Criteria	Reference
Crab Creek	azinphos-methyl	June	0.019	0.01 (chronic)	EPA (1986)
Foster Creek	azinphos-methyl	June	0.016		
Mission Creek	azinphos-methyl	June	0.13		
		October	0.012		
	chlorpyrifos	April	0.14	0.083 (acute)	WAC 173-201A
	total DDT	April	0.004	0.001 (chronic)	WAC 173-201A
		June	0.018		
Moxee Drain	azinphos-methyl	June	0.1	0.01 (chronic)	EPA (1986)
		August	0.056		
	chlorpyrifos	April	0.078	0.041 (chronic)	WAC 173-201A
		August	0.29	0.083 (acute)	WAC 173-201A
	total DDT	April	0.008	0.001 (chronic)	WAC 173-201A
		June	0.057		
		October	0.005		
Salmon Creek	chlorpyrifos	October	0.044	0.041 (chronic)	WAC 173-201A

DDT and DDE (a DDT metabolite) were detected at concentrations above Washington State chronic water quality standards for protection of aquatic life in samples from Mission Creek and Moxee Drain. DDD (another DDT metabolite) was also found at levels above state standards at Moxee Drain. DDT was banned in 1972, but is extremely persistent and is transported into streams from soil erosion (Rinella *et al.*, 1993). Comparisons to Ecology historical data indicate that 1993 concentrations are similar to those identified in 1985.

Chlorpyrifos (Lorsban, Dursban), azinphos-methyl (Guthion), and endosulfan (Thiodan) were identified in samples from Mission Creek and Moxee Drain. All three were found at concentrations exceeding NAS recommended maximum concentrations for the protection of aquatic life and wildlife. Chlorpyrifos was also above state water quality standards (two detections were above the acute criterion) and azinphos-methyl exceeded the EPA chronic water quality criterion for the protection of aquatic life. Endosulfan concentrations were just below state chronic standards. These pesticides are used on fruit orchards to control aphids and codling moths. Azinphos-methyl was also found in Crab Creek above the EPA criterion and NAS recommendation, and may also be a result of orchard use.

The highest concentration detected in 1993 was from Joe Leary Slough, only sampled in June. Mevinphos (Phosdrin) was found at 11 μg/L (parts per billion), over 5,000 times higher than the NAS recommendation of 0.002 μg/L. There are no state or EPA criteria for mevinphos. Acutely toxic concentrations (96 hour LC_{50}[1]) for aquatic invertebrates are as low as 0.13 μg/L and 10.7 μg/L for rainbow trout (Johnson and Finley, 1980). Mevinphos is typically used on row crops, but the source of this pesticide at Joe Leary Slough is unknown.

Mevinphos is one of the most acutely toxic organophosphorus insecticides marketed (Smith, 1993) and is extremely toxic to aquatic organisms, birds, and mammals. The concentration detected in Joe Leary Slough was high enough to be lethal to many aquatic organisms. In addition to problems within the slough, this pesticide could be causing mortality to a variety of organisms in Padilla Bay, which is a productive rearing ground for aquatic life in Puget Sound (Bulthuis, 1993).

Diazinon and malathion are insecticides that are commonly used in residential and agricultural applications. Diazinon was found at levels above the NAS recommended maximum concentration in samples from Mercer Creek (residential) and Moxee Drain (agricultural). Malathion was also above the NAS recommendation in Mercer Creek.

In general, little is known about pesticides in surface waters and their effects on aquatic life and wildlife. Results from the 1992 and 1993 WSPMP samples collected from Mission Creek indicate that pesticides used on orchards within the Wenatchee Valley are being transported into adjacent streams. These streams are important salmon and steelhead habitat (Steele, 1994) and may be vulnerable to the potentially toxic pesticide concentrations identified in Mission Creek.

The problems associated with Moxee Drain have been well documented and are, to some extent, currently being addressed by state agencies and local farmers. Fifteen pesticides or

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[1] - 96 hour LC_{50} is the concentration of a specific compound that causes 50% mortality to test organisms during a test period of 96 hours.

breakdown products were identified in samples collected in 1993. Six of these were also found in 1992. Five of the 1993 compounds exceeded available criteria.

Fifteen pesticides were identified in samples from Mercer Creek. Two compounds exceeded NAS recommendations. These data indicate that urban pesticide use around Mercer Creek is a significant problem. Compounds that were consistently present in 1992 and 1993 were 2,4-D, DCPA, diazinon, dichlobenil, MCPP (Mecoprop), and prometon. Bromacil and simazine were also identified in three samples each in 1993.

DCPA was detected in 13 of 21 samples collected from five sites. This herbicide was also identified in samples collected by the WSPMP ground water unit at three of these sites (Walla Walla River, Moxee Drain, and Lynch Coulee Creek). The consistent presence of this pesticide in surface and ground water samples is a concern. Little is known about the effects of this pesticide on animals and data are inadequate to evaluate carcinogenicity.

Recommendations

Additional Sampling for the WSPMP

1) Continue Mission Creek as a long-term monitoring site representing orchard pesticide use, in order to document water quality violations or improvements. Move the sample site to the mouth of Mission Creek to include possible additional pesticide contamination from Brender Creek. Consider sampling other streams within the Wenatchee Valley.

2) Sample Moxee Drain every two to three years to evaluate the effectiveness of efforts to reduce pesticide contamination.

3) Collect additional water samples from Joe Leary Slough to confirm high pesticide concentrations.

4) Continue collecting water samples from Mercer Creek as a long-term monitoring site representing urban pesticide usage.

Intensive Surveys

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

1) Perform an intensive survey of streams within the Wenatchee Valley to assess the impacts of pesticides on aquatic life.

2) Obtain use information for mevinphos in the vicinity of Joe Leary Slough and attempt to identify possible sources of contamination.

Additional Recommendations

1) Identify DCPA (Dacthal) as a potential water quality concern and push for more studies to thoroughly evaluate its toxicity.

2) Provide training and/or information to farmers in the Skagit Valley regarding pesticide use and the possible consequences of aquatic contamination.

Introduction

The Washington State Pesticide Monitoring Program (WSPMP) was initiated in 1991 by the Department of Ecology (Ecology) to monitor ground water and surface water, including associated biota such as fish, shellfish, and waterfowl and bed sediments, for pesticide residues. Ground water and surface water monitoring are being implemented as separate tasks; this report addresses surface water sampling for 1993. Fish samples were collected in September of 1993 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.

Surface water samples were collected and analyzed from eleven sites in May and June of 1992 for a reconnaissance survey to refine methods and identify sampling sites for the WSPMP (Davis, 1993). Six of these sites were resampled in 1993, in addition to three new sites, for the first full season of water sampling. The results from these samples are presented herein.

Methods

Sampling Design

Samples were collected at nine sites (Figure 1) in April, June, August, and October of 1993. The number of sample sites and the frequency of sampling were determined primarily by the funding available. Extra funds in June allowed sampling of two additional sites for that month (Joe Leary Slough and Lynch Coulee Creek). Timing of collections coincided with the period of peak pesticide applications (late March through early July) and/or high runoff potential. Latitude, longitude, and state plane coordinates are listed for each site in Appendix A.

Samples were analyzed for 162 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

Sample sites were selected to represent various pesticide uses. Table 2 lists sites and pesticide uses that are typical of the site.

Table 2. 1993 Sampling Sites.

Sample Site	Represented Pesticide Use
Adna Creek	Forest practices
Fishtrap Creek	Berries and dairy support crops
Mercer Creek	Urban
Salmon Creek	Mix of various crops and urban
Joe Leary Slough	Row crops
Crab Creek	Row crops and some orchards
Foster Creek	Dry land agriculture
Mission Creek	Orchards
Moxee Drain	Mix of orchards and row crops
Walla Walla River	Mix of row crops and dry land agriculture
Lynch Coulee Creek	Row crops and some orchards

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

Washington State Pesticide Monitoring Program

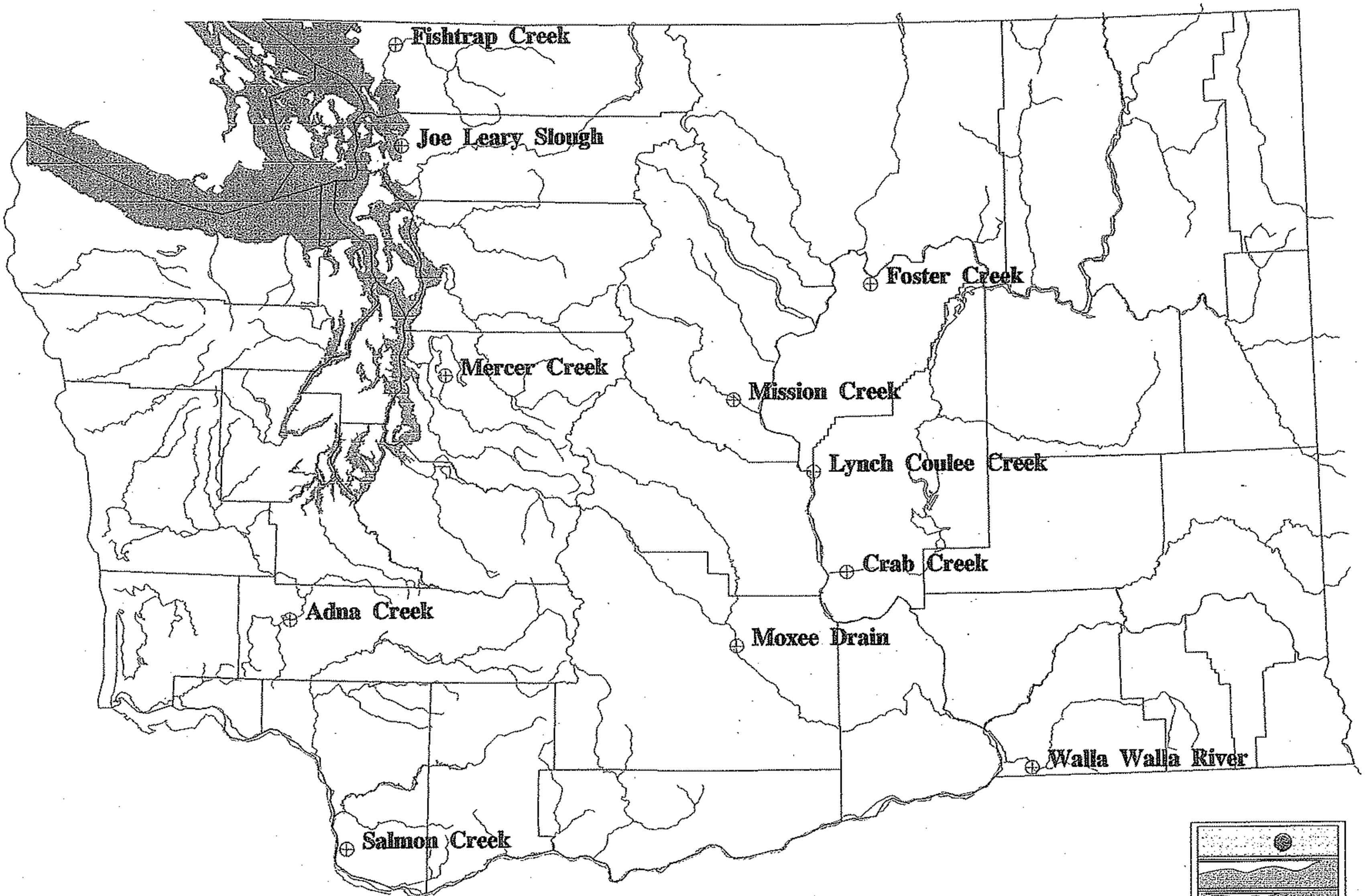

Figure 1 1993 Surface Water Sampling Sites

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 review is presented in Appendix D.

Results and Discussion

Pesticides Detected

A total of 38 pesticides and breakdown products were detected in water samples collected for the 1993 WSPMP (Table 3). The concentrations of most detected compounds were in the parts per trillion range. Only three pesticides (DCPA from the Walla Walla River and chlorpropham and mevinphos from Joe Leary Slough) were detected in the parts per billion range. Table 3 also lists the number of detections per month. Pesticides that exceed water quality criteria are highlighted with bold text in Table 3. Water quality criteria and aquatic toxicity data for detected pesticides are listed in Appendix I; sources for this information are included in the appendix. Supplemental information (e.g., trade names and applications) for each detected pesticide are presented in Appendix J. Pesticides detected in the 1992 WSPMP have been included in Appendix K for comparisons to the current data set.

Figure 2 illustrates detection frequencies for the 38 compounds. 2,4-D was found at the most sites (six), DCPA (Dacthal), simazine, and atrazine were found at five, and azinphos-methyl (Guthion), diazinon, and pentachlorophenol at four. Out of the 38 samples collected, DCPA was detected the most times (13 samples), simazine and atrazine were found in 12 samples, and 2,4-D in 11. Fifteen compounds (39%) were only detected in one sample, four (11%) in two, and seven (18%) in three; adding up to 68% of the detected analytes being found in three or fewer samples.

By sample period, the most detections were in June with 45. This agrees well with reports that indicate that the peak pesticide use period is in June (Tetra Tech, 1988; Maxwell, 1992). The number of detections in October (30) is unlikely to be due entirely to use during that time. Nine of the detections in October were at Mercer Creek, which was receiving storm runoff when sampled, and many of the compounds identified were probably residues from previously applied pesticides.

Breakdown Products

Four breakdown products of target pesticides were detected. DDE and DDD are metabolites of DDT and all three are persistent. Since the ban of DDT in 1972, it would be expected that

Table 3. Pesticides Detected in Water Samples Collected for the 1993 WSPMP ($\mu g/L$, ppb)

	Sample Sites West of the Cascades																	
	Adna Creek				Fishtrap Creek				Mercer Creek				Salmon Creek				Joe Leary Slough	Lynch Coulee Creek
	April	June	August	October	April	June	August	October	April	June	August	October*	April	June	August	October	June	June
2,3,4,6-tetrachlorophenol				0.025														
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																	0.075	
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		
Total Detections	0	0	0	1	4	5	3	2	4	8	7	10	2	2	2	4		

[1] - Exceeds Washington State Water Quality Standards

[2] - Exceeds NAS, 1973 recommended criteria

Values in bold exceed criteria

* - Values are means of duplicate analyses

Table 3 (cont.). Pesticides Detected in Water Samples Collected for the 1993 WSPMP ($\mu g/L$, ppb)

Sample Sites East of the Cascades

	Crab Creek				Foster Creek				Misson Creek				Moxee Drain				Walla Walla River			
	April*	June	August	October	April	June	August	October	April	June*	August	October	April	June	August	October	April	June	August*	October
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	
Total Detections	2	10	3	3	1	3	1	0	6	2	0	2	7	13	5	5	2	2	8	3

	April	June	August	October
Total detections per month	28	45	29	30

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

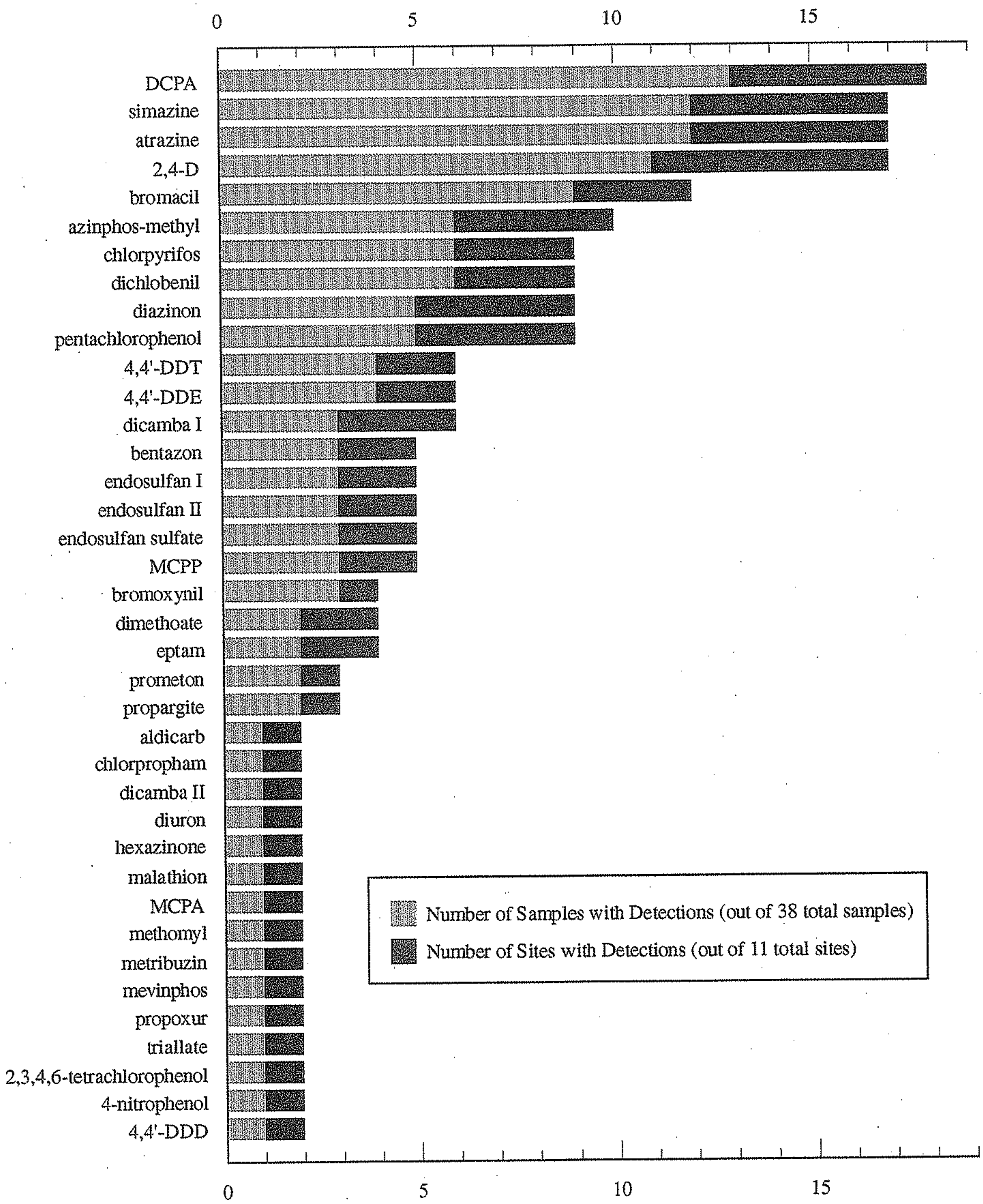

Figure 2. Detection Frequency of Pesticides in 1993 WSPMP Surface Water Samples

the proportion of metabolites would increase as the limited supply of the parent compound slowly degrades. This appears to be the case at Moxee Drain, where concentrations of DDE were slightly higher than DDT in April and June. In October DDE and DDD were present, but not DDT.

Endosulfan sulfate, a breakdown product of endosulfan, was detected in three samples from two sites. Endosulfan was also found in all three samples.

A degradation product of parathion, 4-nitrophenol was identified once, 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

Adna Creek

The stream identified here as Adna Creek is an unnamed stream that drains the Pleasant Hill area southwest of the town of Adna, which is east of Chehalis on highway 6. The stream runs through an area where a large proportion of the land is planted with christmas trees. Pesticide use in the area is probably limited to the christmas trees and a small amount of residential use (personal observation).

Only one pesticide was detected in samples from Adna Creek; 2,3,4,6-tetrachlorophenol in October. This compound is a wood preservative and may have leached from building materials in the area. No criteria are available for tetrachlorophenol.

Fishtrap Creek

Fishtrap Creek originates in Canada, flows through agricultural land used to grow dairy support crops and berries, through the northern edge of the town of Lynden, and into the Nooksack River. Ground water monitoring in this area in 1988 (Erickson and Norton, 1990) detected five pesticides in well water samples. Five different pesticides were detected in samples collected at Fishtrap Creek for the 1992 WSPMP Reconnaissance Survey (Davis, 1993).

Seven pesticides (Table 3) were detected in 1993 WSPMP samples from Fishtrap Creek. Four of the pesticides found in 1992 (atrazine, MCPP, simazine, and 2,4-D) were detected again in

Table 4. Results of Conventional Parameters for the 1993 WSPMP

Sample Site	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
Adna Creek	2.7	3.6	2.3	4.8	1	3	4	5	0.63	0.31	0.21	0.17	54	90	122	134
Fishtrap Creek	5.3	3.8	2.4	3.3	9	6	2	5	2.99	2.78	2.27	2.18	248	254	253	243
Mercer Creek	8.5	5.3	3.7	8.9*	5	2	1	6*	0.45	0.57	0.47	0.75*	149	213	219	115*
Salmon Creek	5.7	3.6	2.3	6.4	21	52	9	62	0.84	1.12	1.64	1.35	73	120	171	148
Crab Creek	9.5*	4.5	5.5	5.3	43*	70	18	30	2.31*	1.40	1.08	1.52	719*	504	552	571
Foster Creek	9.9	5.6	3.0	5.4	79	15	4	16	0.09	0.01u	0.01u	0.01u	907	803	795	860
Mission Creek	5.5	2.2*	1.7	2.4	83	46*	1u	1	0.30	0.39*	0.29	2.51	223	182*	95	376
Moxee Drain	3.9	5.7	3.5	3.2	218	378	81	16	1.31	1.79	1.37	4.64	318	311	288	669
Walla Walla River	6.4	3.3	8.7*	2.8	268	12	201*	21	0.63	0.55	1.11*	0.71	98	262	324*	343
Joe Leary Slough		5.3				19				0.30				393		
Lynch Coulee Creek		2.1				5				2.01				409		

Sample Site	Temperature (°C)				p H				Flow (CFS)			
	April	June	August	October	April	June	August	October	April	June	August	October
Adna Creek	8.2	13.4	11.5	11.6	5.23	7.25	6.75	7.49	7.08	1.48	0.14	0.50
Fishtrap Creek	11.3	14.9	14.4	12.1	7.12	7.96	7.50	7.85	99.25	39.53	15.01	12.01
Mercer Creek	10.7	14.0	13.9	12.2	6.64	6.78	7.31	7.32	30	8.2	7.3	42
Salmon Creek	10.4	17.0	15.7	12.9	6.47	7.14	7.65	7.57	375	131	63	38
Crab Creek	13.3	25.0	22.2	10.9	8.64	8.86	8.22	8.51	215.9	221.5	291.5	298.3
Foster Creek	11.8	27.0	23.9	10.6	8.81	8.87	8.54	8.82	11.60	1.30	0.76	1.78
Mission Creek	4.3	14.2	17.3	6.9	7.78	6.75	7.55	7.70	36.51	15.26	3.07	1.18
Moxee Drain	11.8	19.5	DNC[1]	10.1	8.18	8.51	7.15	8.16	32.30	31.75	60.70	11.10
Walla Walla River	9.0	22.9	DNC	9.7	8.29	8.73	7.53	8.27	1530	153	59	37
Joe Leary Slough		18.0				7.45				DNC		
Lynch Coulee Creek		17.9				8.72				8.85		

[1] - DNC = Data Not Collected

* - Values are means of duplicate analyses

1993. These four compounds, in addition to bromacil and dichlobenil, are herbicides. None of the detected pesticides were above criteria or approached acutely toxic concentrations (Appendix I).

Nitrate+nitrite levels in Fishtrap Creek were consistently above 2 mg/L, which is substantially above naturally occurring levels, but below the EPA water quality criterion of 10 mg/L for domestic water supplies (EPA, 1986a). These levels are not unexpected in streams receiving runoff from agricultural lands due to heavy fertilizer use in these areas.

Mercer Creek

Mercer Creek drains the Bellevue area east of Interstate-405, including surface street runoff, into Lake Washington. Much of this area is residential, but includes a bridle trail park, shopping centers and schools, and two golf courses.

Only two pesticides (diazinon and 2,4-D) were detected in samples collected from Mercer Creek by the EPA in 1990 (PTI, 1991). Seven were found in the 1992 WSPMP and 15 compounds were identified in 1993 WSPMP samples. Diazinon and 2,4-D were found in both WSPMP sample sets. Only seven of the 15 compounds detected in 1993 were target analytes for the EPA study and for four of the seven, the EPA detection limits were higher than the concentrations reported for the WSPMP.

While criteria are available for eight of the 15 compounds detected at Mercer Creek, only two exceeded criteria or approached acutely toxic concentrations. Diazinon, found at 0.03 μg/L in June and at 0.083 μg/L in October, exceeded the NAS recommended maximum concentration (0.009 μg/L) for protection of aquatic life and wildlife; malathion was also above the NAS recommended level (0.008 μg/L) in October at 0.085 μg/L. Both of these compounds are highly toxic organophosphorus insecticides that are heavily used in a number of applications, including several residential formulations. Detected concentrations approach acute toxicity values (*i.e.*, within an order of magnitude) for some invertebrates (96 hr LC_{50} for malathion is 0.63-0.92 μg/L and 0.15-0.28 μg/L for diazinon).

Salmon Creek

Salmon Creek is located in Clark County, just north of the city of Vancouver. Several small tributaries flowing from the south into Salmon Creek run through a mix of commercial and residential areas. Much of the main stem and tributaries from the north flow through rural areas with a number of small farms, cultivating various agricultural crops.

Eight compounds were detected, but only one (simazine) was found more than once. Two pesticides were above criteria. Chlorpyrifos (Dursban, Lorsban) was detected in October at

0.044 μg/L, which is slightly above the Washington State water quality standard (173-201 WAC) of 0.041 μg/L (chronic, 4 day average) and just below levels toxic to the freshwater amphipod *Gammarus lacustris* (96 hr LC_{50} 0.07-0.17 μg/L). Diazinon was also detected in October above the NAS recommendation at 0.022 μg/L. Like diazinon, chlorpyrifos is an organophosphorus insecticide that is used in a wide variety of applications.

Salmon Creek was not sampled for the 1992 WSPMP, but samples were collected from Lake River, which receives water from Salmon Creek. Only one pesticide (DCPA) was found in the 1992 samples from Lake River. DCPA was not found in samples from Salmon Creek.

Crab Creek

Crab Creek was sampled at a spot just above the town of Beverly near the mouth where it discharges into the Columbia River. This section of the creek is called Lower Crab Creek and consists primarily of irrigation return or waste water much of the year (Wagner, 1994). Most of the irrigation return water in Grant County either ends up in Potholes Reservoir or runs directly into Crab Creek. Its natural flow originates as Upper Crab Creek in Lincoln County, runs into Moses Lake and Potholes Reservoir, and then feeds a number of small lakes below the reservoir before eventually converging into a single stream as Lower Crab Creek.

The cities of Moses Lake, Ephrata, and Quincy are the major population centers near Lower Crab Creek. Some pesticide use may be attributed to these towns, but the vast majority undoubtedly comes from the intense and highly diverse agricultural practices throughout Grant County. Most of these crops are irrigated with water from the Columbia River.

Ten compounds were found in 1993 WSPMP samples from Crab Creek. Six of these were also detected in 1992 samples. Two of the six, atrazine and DCPA, were found in all four sampling periods in 1993. One pesticide, azinphos-methyl (Guthion), was detected at a concentration of 0.019 μg/L, exceeding the EPA (1986a) water quality criterion for the protection of aquatic life (0.01 μg/L) and approaching acute toxicity for invertebrates (96 hr LC_{50} 0.11-0.20 μg/L). Azinphos-methyl is an organophosphorus insecticide that is used on a number of crops to control biting and sucking insects (Smith, 1993). Apples, potatoes, cherries, and pears are the major use crops for Guthion in Washington and all four are grown in the vicinity of Crab Creek (WSDA, 1985).

Water temperatures in Crab Creek exceeded state water quality standards for a Class B stream (21.0°C) in June (25.0°C) and August (22.2°C). Some of this increase is likely to be a result of human activity, since many of the irrigation ditches are shallow and open. The temperature recorded in May of 1992 (21.8°C) also exceeded the state standard.

The USGS sampled Crab Creek monthly in 1993 (Wagner, 1994). Samples were analyzed for 47 target pesticides; most of these were also target compounds for the WSPMP. The WSPMP site near Beverly was not sampled. The nearest USGS site was located approximately 30 miles east of Beverly above Royal Lake and was selected because it is less diluted by wastewater than the Beverly site.

The USGS detected 30 pesticides in samples from the Royal Lake site. Only six of these were also detected in samples collected by the WSPMP in 1993. Four other compounds identified from Crab Creek by the WSPMP were not USGS targets.

Many of the additional pesticides detected by the USGS were found at concentrations below WSPMP detection limits or at different times of the year. However, the USGS identified four pesticides in samples collected about the same time as WSPMP samples and at concentrations well within WSPMP detection limits. These compounds may have been diluted to levels below detection limits by wastewater at the Beverly site.

Foster Creek

Foster Creek was sampled at the bridge on highway 17, just above the confluence with East Foster Creek. The middle and west forks of Foster Creek drain a large portion of northwestern Douglas County. Nearly all of this area represents dry land agriculture, primarily wheat.

This site was not sampled in 1992 and no other historical pesticide data are known to exist for Foster Creek. Only three compounds were detected in 1993. Azinphos-methyl, found only in June at a concentration of 0.016 μg/L, exceeded the EPA (1986a) criterion. Bromoxynil was detected in April, June, and August, but water quality criteria have not been established for this herbicide. The 96 hr LC_{50} for rainbow trout is 50 μg/L, well above any of the detected concentrations. Bromoxynil is a herbicide commonly used on wheat and other grain crops for post-emergent control of a variety of weeds.

Water temperatures in Foster Creek were above state standards in June (27.0°C) and August (23.9°C). These exceedances were probably not due to human activities. This stream is small, shallow, and is unprotected by vegetation throughout most of its course.

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. The sampling site was above the confluence with Brender Creek, at a bridge near the intersection of Meadow Sweet Place and Mission Creek Road. 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.

Eight compounds were detected in 1993 water samples, five of these exceeded water quality criteria. DDT was found in April and June and DDE was found in April. Prior to its ban in 1972, DDT was used extensively on orchards for control of a variety of insects. This pesticide and its breakdown product, DDE, bind tightly to soil and are extremely persistent (Rinella *et al.*, 1993). In the spring, heavy rains and snow melt can cause runoff and erosion that transports DDT and DDE into streams. The concentrations found were above Washington State water quality standards for the protection of aquatic life (chronic, 24-hour average), but below acute toxicity values.

The presence of other pesticides exceeding criteria can be associated with current use on the orchards (Smith, 1994). Chlorpyrifos (Lorsban) and endosulfan (Thiodan) were detected in April and are used at that time to control aphids. Azinphos-methyl (Guthion) was found in June when it is used to control codling moths. A low concentration of azinphos-methyl was also found in October, but no insecticides are applied to the orchards that late in the year.

Chlorpyrifos was found at a concentration of 0.14 μg/L, exceeding the state acute standard of 0.083 μg/L, and within the range that is toxic to *Gammarus lacustris* (0.07-0.17 μg/L). Endosulfan is a mixture of two isomers, endosulfan I and II. Both isomers breakdown to endosulfan sulfate, which is similar in toxicity to the parent compounds (Hayes and Laws, 1991). Available criteria are for total endosulfan, which includes both isomers and the sulfate form. Total endosulfan found at Mission Creek was 0.048 μg/L. The NAS (1973) recommended maximum concentration for endosulfan is 0.003 μg/L, and the Canadian water quality guideline (CCREM, 1987) for protection of aquatic life is 0.02 μg/L. Both detections of azinphos-methyl (0.13 μg/L in June and 0.012 μg/L in October) exceeded the EPA (1986a) water quality criterion of 0.01 μg/L. The level found in June was above concentrations toxic to some invertebrates and approaches concentrations acutely toxic to fish.

Samples collected from this same site in June for the 1992 WSPMP contained four pesticides. Only one of these, azinphos-methyl, was detected again in 1993. The concentration of azinphos-methyl in 1992 also exceeded the EPA criterion.

Moxee Drain

Moxee Drain receives irrigation return water from a large agricultural area east of Yakima in the Moxee Valley. A small amount of the flow is probably from natural runoff from the surrounding hills, but the flow is highest in the summer when there is very little rain fall, indicating that most of the water in Moxee Drain is from irrigation. The major crops grown in

Moxee Valley are hops and fruit. Residential pesticide use in the area may also be fairly heavy, since many of the homes in the area have gardens and/or fruit trees.

Fifteen pesticidal compounds were detected in 1993. Eight were found in 1992 and six of the eight were found again in 1993. Seven compounds exceeded water quality criteria in 1993 samples.

As discussed under Mission Creek, DDT and its breakdown products DDE and DDD, continue to be a problem in areas with heavy historical use and soil erosion. DDT compounds in Moxee Drain were apparently associated with the total suspended solids (TSS) load. The concentration of DDT was highest in June when the TSS load was also the highest. For a number of reasons, increased flow in the Moxee Drain does not always result in increased erosion (Tobin, 1994). Flow was highest in August, but TSS was low and DDT was not detected. Concentrations in April, June, and October exceeded Washington State chronic standards.

The recommended maximum concentration for total endosulfan was exceeded in April and June. The remaining three pesticides above criteria or recommendations were all organophosphorus insecticides; azinphos-methyl in June and August, chlorpyrifos in April and August, and diazinon in June.

DCPA was detected in low concentrations in June, August, and October. This widely used herbicide was also identified in initial samples from the Moxee surficial aquifer, collected by Ecology's WSPMP ground water unit in 1992 (Larson, 1993). A second round of sampling in early 1993 failed to detect DCPA.

Moxee Drain was sampled for pesticides in 1988-89 by the U.S. Geological Survey (USGS) (Rinella, *et al.*, 1992). Eight compounds detected in 1993 WSPMP samples were also identified in USGS samples; they are: DDT, DDE, DDD, 2,4-D, dicamba, endosulfan, diazinon, and chlorpyrifos. An additional five pesticides were found in WSPMP samples that were not target analytes for the USGS study. Ten other pesticides were identified in USGS samples, but not by the WSPMP. All ten were target analytes for the WSPMP, but USGS detection limits were lower for some of the compounds, and the USGS sampled Moxee Drain a total of seven times, increasing the probability of detecting more pesticides.

A survey of the Yakima River performed in 1985 by Ecology (Johnson, *et al.*, 1986) to identify sources of DDT, showed that Moxee Drain was a major contributor to the DDT load in the Yakima River, second only to Sulfur Creek. Concentrations detected in 1985 are similar to those found in 1988-89 by the USGS and in 1992-93 by the WSPMP.

Walla Walla River

The Walla Walla River originates in Oregon, flows through the Walla Walla Valley, and discharges into the Columbia River. The flow where the river crosses the border is generally very small. As the river runs through the Walla Walla Valley, several small creeks and the Touchet River add to the flow. A wide variety of row crops, in addition to peas, wheat, and alfalfa, are grown throughout the Walla Walla Valley. Nearly all of these crops are irrigated from wells or directly from the river. Most of the land that drains into the Touchet River supports dry-land wheat cultivation.

Nine pesticides were detected in 1993 WSPMP samples from the Walla Walla River. Five were found in 1992 and three of these were detected again in 1993. None of the pesticides in 1992 or 1993 exceeded state or federal water quality criteria.

The concentration of DCPA in 1992 was the highest of the eleven sites sampled (12.1 μg/L). This was true for the 1993 samples as well, DCPA was detected in June, August, and October at some of the highest concentrations found in 1993. DCPA is considered only slightly toxic to rainbow trout (96 hr LC_{50} 30,000 μg/L).

In addition to the consistently high concentrations in surface water samples, DCPA was also detected in samples collected in the Walla Walla Valley by the WSPMP ground water unit in 1993 (Larson, 1994). Sampling to verify detected pesticides is scheduled for late summer in 1994.

Total suspended solids were high in the Walla Walla River in April and again in August. Concentrations were above the NAS (1973) recommended level for moderate protection of aquatic communities (80 mg/L), but were lower than the recommendation that provides a low level of protection (400 mg/L). The high level in April was probably from stormwater or snow melt runoff, indicated by the extremely high flow then of 1,530 CFS. High TSS in August was probably due to irrigation runoff, evidenced by the low flow (59 CFS) and the higher number of pesticide detections.

Joe Leary Slough and Lynch Coulee Creek

Joe Leary Slough and Lynch Coulee Creek were sampled once in June of 1993. Joe Leary Slough drains the Olympia Marsh, northwest of Mount Vernon, into Padilla Bay. Land use adjacent to the slough is predominantly agricultural. Four pesticides were detected. The concentrations of two compounds, chlorpropham (6.0 μg/L) and mevinphos, (11 μg/L), were the highest found in 1993 WSPMP samples. The concentration of mevinphos, an organophosphorus insecticide, was over 5,000 times higher than the NAS recommended maximum concentration for protection of aquatic life and wildlife of 0.002 μg/L. Mevinphos is extremely toxic to aquatic invertebrates (96 hr LC_{50} for *Daphnia pulex* 0.13-0.25 μg/L) and fish (96 hr LC_{50} for rainbow trout 10.7-13.2 μg/L). No water quality criteria exist for chlorpropham, a herbicide; the 96 hr LC_{50} for rainbow trout is 3,020-5,700 μg/L.

The stream identified here as "Lynch Coulee Creek" is unnamed on available maps. The source of the stream is Crater and Babcock Ridge Lakes west of Quincy, which flow into and through Lynch Coulee, discharging into the Columbia River just north of Crescent Bar. The stream travels underground throughout much of this course. These lakes probably did not exist prior to initiation of intense irrigation in the area. Once irrigation begins in the spring each year, wastewater also flows into Lynch Coulee. Flow from the lakes probably also increases at that time. Land in this area is heavily cultivated with a variety of crops, but little of the water that ends up in Crater and Babcock Ridge Lakes is from direct surface run off (personal observation).

Only one pesticide (DCPA) was identified in samples from Lynch Coulee Creek. Samples collected from 27 wells around Quincy in 1991 by the WSPMP ground water unit (Larson and Erickson, 1993) contained five pesticides. DCPA was found in 16 of the wells at concentrations up to 8.30 μg/L.

Geographical Distribution of Pesticides

In Table 3, sample sites are separated into groups based on location, east or west of the Cascade Mountains. Thirteen (57%) of the pesticides detected west of the Cascades were not found in the east, and 15 (60%) east side compounds were not found in the west. Most of the pesticides unique to the west side were only detected once or twice and relationships to specific uses are not apparent. Dichlobenil (Casoron) was detected six times and is probably used primarily for residential weed control. Some of the compounds unique to the east side of the Cascades (e.g., azinphos-methyl and endosulfan) are heavily used on fruit orchards, which are predominantly found east of the mountains. The total number of pesticides detected at agricultural sites on the west side of the Cascades is similar to the number found at east side agricultural sites with irrigated crops.

On the west side, distinctions between pesticide use categories based on detected pesticides are vague. Compounds detected at agricultural sites were also found in Mercer Creek, an urban site. Many more analytes were identified in samples from Mercer Creek than the other west side sites, or even most east side sites. Few, if any, compounds from Mercer Creek are exclusively urban pesticides, but apparently the diversity of pesticides used here is substantially higher than for most agricultural settings.

Distinctions between pesticide use categories east of the Cascades are more apparent. Agriculture around Crab Creek and the Walla Walla River consists primarily of irrigated row crops. Dry-land agriculture predominates adjacent to Foster Creek. Mission Creek is surrounded by fruit orchards and orchards and hops are the major crops within Moxee Valley. As indicated above, several detected pesticides can be attributed to orchard use. Diazinon is commonly used on hops and bromoxynil is used to control weeds in dry-land wheat fields. Atrazine, 2,4-D, DCPA, and simazine appear to be used primarily on row crops.

The geographical distribution of many pesticides is clearly related to specific uses near the water bodies sampled. Other pesticides are so widely used that their presence in a stream generally cannot be attributed to a single use category or source.

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Appendices

Appendix A. Sample Site Positions

Site Name	Latitude deg	Latitude min	Latitude sec	Longitude deg	Longitude min	Longitude sec	State Plane X	State Plane Y
Adna Creek at Highway 6	46	37	39.6	123	03	48.1	1356091	482458
Fishtrap Creek at River Road Bridge	48	54	51.6	122	31	12.0	1513911	1312517
Mercer Creek at mouth	47	36	6.0	122	10	58.2	1584813	831668
Salmon Creek at Seward Road Bridge	45	43	22.1	122	42	22.4	1436550	149908
Crab Creek at 1st bridge on Crab Creek Road	46	49	54.6	119	48	51.6	2171619	547197
Foster Creek at Highway 17	47	58	7.8	119	39	0.4	2208252	962315
Mission Creek at Mission Creek Road	47	30	43.5	120	28	18.5	2006970	794559
Moxee Drain near mouth	46	32	28.8	120	27	39.6	2009814	440513
Walla Walla River at Cummins Road Bridge	46	02	14.4	118	45	52.2	2440731	261571
Joe Leary Slough at Bayview-Edison Road	48	31	2.7	122	28	17.3	1521965	1167366
Lynch Coulee Creek at mouth	47	13	31.3	120	00	4.7	2123914	690367

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 µg/L
2,4'-DDT	0.05	chlordene-gamma	0.05
2,4'-DDE	0.05	dicofol (kelthane)	0.20
2,4'-DDD	0.05	dieldrin	0.05
4,4'-DDT	0.12	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	0.05	heptachlor epoxide	0.05
BHC-gamma (lindane)	0.05	methoxychlor	0.05
captafol	0.60	mirex	0.05
captan	0.40	nonachlor-cis	0.05
chlordane-alpha	0.05	nonachlor-trans	0.05
chlordane-gamma	0.05	oxychlordane	0.05
chlordene-alpha	0.05	toxaphene	1.50

Pyrethroid Pesticides
(one analysis)

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

* - 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	fensulfothion	0.13
azinphos-ethyl	0.20	fenthion	0.08
azinphos-methyl (guthion)	0.16	fonofos	0.05
carbophenothion	0.11	imidan (phosmet)	0.09
chlorpyrifos (dursban)	0.05	malathion	0.08
chlorpyrifos-methyl	0.04	merphos	0.13
coumaphos	0.11	mevinphos	0.08
DEF (tribufos)	0.18	monocrotophos	0.58
demeton-o	0.05	paraoxon-methyl	0.15
demeton-s	0.05	parathion	0.07
diazinon	0.07	parathion-methyl	0.06
dichlorvos	0.07	phorate	0.04
diethyl fumarate	0.25	phosphamidan	0.20
dimethoate	0.08	propetamphos	0.18
dioxathion	0.14	ronnel	0.05
disulfoton	0.05	sulfotepp	0.05
ethion	0.06	sulprofos	0.05
ethoprop	0.07	tetrachlorvinphos (gardona)	0.18
fenamiphos	0.13	tetraethyl pyrophosphate (TEPP)	0.05
fenitrothion	0.06		

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 μg/L	Compound	Quantitation Limits μg/L
Triazines			
ametryn	0.08	cycloate	0.13
atraton	0.25	di-allate (avadex)	0.29
atrazine	0.08	EPTC (eptam)	0.13
cyanazine	0.11	triallate (fargo)	0.22
hexazinone	0.13	vernolate	0.13
metribuzin	0.08		
prometon	0.08	**Substituted Amides**	
prometryn	0.08	diphenamid	0.25
propazine	0.08	napropamide	0.25
simazine	0.08	pronamide	0.25
terbutryn	0.08		
		Uracils	
Anilines		bromacil	0.50
benfluralin (benefin)	0.13	terbacil	0.42
ethalfluralin	0.13		
pendimethalin	0.13	**Ureas**	
profluralin	0.20	diuron	0.45
trifluralin	0.13	tebuthiuron	0.08
Anilides		**Miscellaneous**	
alachlor	0.20	carboxin	0.92
butachlor	0.29	chlorpropham	0.42
metolachlor	0.25	fenarimol	0.25
propachlor	0.17	fluridone	0.67
		metalaxyl	0.52
Cyano		MGK264	0.58
chlorothalonil	0.20	molinate	0.22
dichlobenil	0.10	norflurazon	0.13
		oxyfluorfen	0.28
Thiocarbamates		pebulate	0.20
butylate	0.13	triadimefon	0.22

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

EPA Method 615
(one extraction, one analysis)

Chlorinated Herbicides

Compound	Quantitation Limits μg/L	Compound	Quantitation Limits μg/L
2,4-D	0.07	DCPA (dacthal)	0.01
2,4-DB	0.05	dalapon (DPA)	0.07
2,4,5-TB	0.01	dicamba I	0.01
2,4,5,-TP	0.13	dicamba II (dicamba isomer)	0.05
2,4,5-trichlorophenol	0.028	dichlofop-methyl	0.03
2,4,6-trichlorophenol	0.028	dichlorprop	0.03
2,3,4,6-tetrachlorophenol	0.026	dinoseb	0.01
3,5-dichlorobenzoic acid	0.03	ioxynil	0.02
4-nitrophenol	0.03	MCPA	0.15
5-hydroxydicamba	0.02	MCPP	0.15
acifluorfen (blazer)	0.19	pentachlorophenol	0.01
bentazon	0.10	picloram	0.01
bromoxynil	0.01	trichlopyr (garlon)	0.03
chloramben	0.02		

EPA Method 531.1
(direct injection, one analysis)
Carbamates

Compound	Quantitation Limits μg/L	Compound	Quantitation Limits μg/L
1-napthol	0.05	carbofuran	0.3
3-hydroxycarbofuran	0.15	methiocarb	0.5
aldicarb	0.5	methomyl	0.15
aldicarb sulfone	0.15	oxamyl	0.15
aldicarb sulfoxide	0.15	propoxur (baygon)	0.3
carbaryl	0.3		

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

EPA Method 547 (April), Monsanto Method (June)
(one extraction, one analysis)

Compound	Quantitation Limits µg/L
glyphosate	25 (April), 1.0 (June)

Due to poor and variable quantitation limits, the glyphosate analysis was dropped for the August and October sample periods. Glyphosate was not detected in samples collected in April and June.

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). Chlorinated herbicides were analyzed using EPA Method 615 and carbamates with EPA Method 531.1. Three pesticide groups (urea pesticides, volatile organics, and diquat/paraquat) were dropped from the 1993 target list, due to poor detection limits and a lack of detections in 1992. Glyphosate was included in the April and June analyses, but was dropped for the August and October samples due to poor and variable detection limits.

The analytical method for carbamates was modified in 1993 to improve detection limits. Rather than direct water injection, as was done in 1992, samples were extracted with methylene chloride using a procedure developed by the California Department of Food and Agriculture (CDFA, 1991). Detection limits improved by approximately an order of magnitude with the new method, but these levels are still substantially higher than water quality criteria for carbamates.

Carbamate extracts from the April samples were concentrated using a nitrogen evaporator, but this required nearly eight hours for each sample and there was a concern that target analytes were degrading. The remaining extracts for 1993 were concentrated using Kurderna-Danish concentrators and Snyder columns on a steam bath, followed by removal of the last 50 mLs with a nitrogen evaporator. Surrogate recoveries were markedly improved using the latter method. October carbamate samples were collected in 4 oz. bottles with monochloroacetic acid added as a preservative.

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 Crab Creek, from Mission Creek in June, the Walla Walla River in August, 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.

Appendix C (cont.).

A transfer/bottle blank was prepared in June to ensure that decontamination procedures were effective.

Reagent water was spiked with known pesticide concentrations and submitted as blind duplicates to evaluate method precision and accuracy. The samples were prepared in the field to evaluate possible analyte loss from breakdown during the period between sample collection and analysis. A field spike kit for method 1618 (chlorinated pesticides, organophosphorus pesticides, nitrogen- and sulfur-containing pesticides, and pyrethroid pesticides) was obtained from the USGS National Water Quality Laboratory, Arvada, Colorado (lot no. LA35685). Carbamate (lot no. 3201) and chlorinated herbicide (lot no. 01092) quality control standards were obtained from Environmental Resource Associates, Arvada, Colorado. The material from the USGS is specially prepared for the National Water Quality Assessment (NAWQA) program.

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. Results from the glyphosate analyses, which were contracted out to Water, Food and Research Lab, Inc., Tigard, Oregon for the April samples and A & S Environmental Testing, Inc., Reading, Pennsylvania for the June samples, were reviewed and assessed by Stuart Magoon of Manchester Laboratory.

No significant problems were encountered for any of the analyses. DCPA (Dacthal) was detected in one laboratory blank in April, but not in the duplicate. Applying the EPA five times rule, compounds detected in a sample are considered real and not the result of contamination if the concentration is greater than or equal to five times the amount in the blank. DCPA was detected at two sites in April, Crab Creek and the Walla Walla River, but the concentrations were both less than five times the amount in the blank and so are not reported here.

Quality Control Samples

No accuracy or precision criteria have been established for any of the analytical methods used, but duplicate field samples and reference material, and matrix and surrogate spike analyses provide estimates of accuracy and precision. Results are shown in Appendices E (duplicates), F (field spikes), G (matrix spikes), and H (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 excellent. RPD values ranged from 0 to 62% with the exception of a single value of 164% and the average was 21%.

The field spike mix for method 1618 contained 41 target analytes. Multipoint calibration was not feasible for such a large number of analytes and either a single point calibration or the atomic emission detector calibration mix was used to quantitate the spiked compounds. All results were qualified as estimates (J). Reported concentrations for the 41 spiked compounds were very close to the expected value. When these results were rounded to the same decimal place as the expected values, all but four were identical to the expected concentrations. These results indicate excellent accuracy for method 1618 (modified).

RPDs for the chlorinated herbicide and carbamate field spikes ranged from 60 to 156, with an average of 82, indicating fair accuracy. The poorer accuracy observed for chlorinated herbicides and carbamates reflects the typically low surrogate recoveries for these analyses. Although low, results for the chlorinated herbicides were still within expected ranges. Carbamate spike results were all below expected ranges, suggesting that there is some analyte loss occurring, probably during the analytical process, judging from the low surrogate recoveries. Field spike results do not indicate any significant analyte loss between sample collection and analysis.

Matrix spike recoveries for metolachlor, hexazinone, dimethoate, mevinphos, and phosphamidan in October were very low for one sample and greater than 90% in the other. No explanation could be found for this anomaly. None of these pesticides were detected in October. Otherwise, matrix spike and duplicate recoveries were acceptable.

Most surrogate recoveries were between 50% and 135% for method 1618, except for 4,4-dibromooctafluorobiphenyl in October, which were all below 30%. As indicated above, recovery of surrogates for chlorinated herbicides and carbamates was typically lower than for method 1618 recoveries. Most were still satisfactory. Carbamate surrogate recoveries in April were substantially lower than for the other sample periods, reflecting the change in the method for concentrating the extraction solvent. 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). Carbamate detections in August were "N" qualified (there is evidence the analyte is present). These qualifiers have not been included in this report for clarity of presentation. Complete results are available on request.

Appendix E. Duplicate Analysis Results for 1993 WSPMP Surface Water Samples (μg/L, ppb)

Analyte	Sample 1	Sample 2	RPD[1]
April (Crab Creek)			
atrazine	0.02	0.02	0
DCPA	0.4	0.04	164
simazine	0.02	0.02	0
June (Mission Creek)			
azinphos-methyl	0.13	0.12	8
4,4'-DDT	0.023	0.013	56
August (Walla Walla River)			
atrazine	0.011	0.078u[2]	NC[3]
bromacil	0.082	0.097	17
DCPA	4.1	3.6	13
dicamba I	0.1	0.11	10
dicamba II	0.044	0.044	0
October (Mercer Creek)			
bromacil	0.078	0.068	14
diazinon	0.09	0.076	17
dichlobenil	0.1	0.086	15
malathion	0.088	0.081	8
MCPA	0.071	0.13	59
MCPP	0.14	0.2	35
prometon	0.082	0.095	15
simazine	0.028	0.029	4
2,4-D	0.29	0.40u	NC
4-nitrophenol	0.15	0.28	60

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

[2] - Not detected at or above reported value

[3] - NC = Not Calculated

Appendix E (cont.). Duplicate Analysis Results for 1993 WSPMP Surface Water Samples (μg/L, ppb)

Analyte	Sample 1	Sample 2	RPD[1]
Field Spikes			
chlorinated pesticides			
alpha-BHC	0.086	0.090	5
gamma-BHC	0.093	0.091	2
dieldrin	0.072	0.073	1
4,4'-DDE	0.11	0.11	0
organophosphorus pesticides			
azinphos-methyl	0.060	0.043	33
chlorpyrifos	0.11	0.11	0
diazinon	0.068	0.075	10
dimethoate	0.030	0.022	31
disulfoton	0.070	0.043	48
ethoprop	0.069	0.062	11
fonofos	0.091	0.094	3
malathion	0.079	0.066	18
methyl parathion	0.067	0.061	9
parathion	0.095	0.092	3
phorate	0.077	0.066	15
nitrogen-containing pesticides			
alachlor	0.11	0.14	24
atrazine	0.086	0.097	12
benefin	0.076	0.071	7
butylate	0.073	0.077	5
cyanazine	0.10u[2]	0.054	NC[3]
eptam	0.083	0.085	2
ethafluralin	0.084	0.094	11
linuron	0.12	0.088	31
metolachlor	0.11	0.11	0
metribuzin	0.10	0.079	23
molinate	0.078	0.093	18
napropamide	0.15	0.10	40
pebulate	0.075	0.087	15
pendimethalin	0.097	0.092	5
prometon	0.048	0.042	13
pronamide	0.10	0.13	26
propachlor	0.12	0.097	21
propazine	0.032	0.017	61
simazine	0.070	0.077	10
tebuthiuron	0.021	0.014	40
terbacil	0.061	0.047	26
terbufos	0.062	0.066	6
treflan	0.068	0.055	21
triallate	0.098	0.099	1

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

2 - Not detected at or above reported value

3 - NC = Not Calculated

Appendix E (cont.). Duplicate Analysis Results for 1993 WSPMP Surface Water Samples (μg/L, ppb)

Analyte	Sample 1	Sample 2	RPD[1]
Field Spikes			
pyrethroids			
cis-permethrin	0.17u[2]	0.17u	NC[3]
sulfur-containing pesticides			
propargite	0.12	0.12	0
chlorinated herbicides			
2,4-D	0.20	0.11	58
2,4,5-TP (silvex)	0.038	0.033	14
pentachlorophenol	0.36	0.19	62
carbamates			
aldicarb	0.239	0.214	11
aldicarb sulfoxide	0.044	0.059	29
aldicarb sulfone	0.067	0.096	36
carbofuran	0.151	0.094	47

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

[2] - Not detected at or above reported value

[3] - NC = Not Calculated

Appendix F. Comparison of Field Spike Analysis Results to Expected and Certified Values (μg/L, ppb)

Analyte	Reported Mean Concentration (± ½ duplicate range)		Rounded Mean Concentration	Expected Value[1]
chlorinated pesticides				
alpha-BHC	0.088	±0.022	0.1	0.1
gamma-BHC	0.092	±0.001	0.1	0.1
dieldrin	0.073	±0.001	0.1	0.1
4,4'-DDE	0.11	±0.0	0.1	0.1
organophosphorus pesticides				
azinphos-methyl	0.052	±0.009	0.1	0.1
chlorpyrifos	0.11	±0.0	0.1	0.1
diazinon	0.072	±0.004	0.1	0.1
dimethoate	0.026	±0.004	0.03	0.1
disulfoton	0.057	±0.014	0.1	0.1
ethoprop	0.066	±0.004	0.1	0.1
fonofos	0.093	±0.002	0.1	0.1
malathion	0.073	±0.007	0.1	0.1
methyl parathion	0.064	±0.003	0.1	0.1
parathion	0.094	±0.002	0.1	0.1
phorate	0.072	±0.006	0.1	0.1
nitrogen-containing pesticides				
alachlor	0.125	±0.015	0.1	0.1
atrazine	0.092	±0.011	0.1	0.1
benefin	0.074	±0.003	0.1	0.1
butylate	0.075	±0.002	0.1	0.1
cyanazine	0.052	±0.002	0.1	0.1
eptam	0.084	±0.001	0.1	0.1
ethalfluralin	0.089	±0.005	0.1	0.1
linuron	0.104	±0.016	0.1	0.1
metolachlor	0.11	±0.0	0.1	0.1
metribuzin	0.090	±0.021	0.1	0.1
molinate	0.086	±0.008	0.1	0.1
napropamide	0.125	±0.025	0.1	0.1
pebulate	0.081	±0.006	0.1	0.1
pendimethalin	0.095	±0.003	0.1	0.1

[1] - Expected values are the spiked concentrations and are not based on analytical results

Appendix F (cont.). Comparison of Field Spike Analysis Results to Expected and Certified Values (μg/L, ppb)

Analyte	Reported Mean Concentration (± ½ duplicate range)		Rounded Mean Concentration	Expected Value
nitrogen-containing pesticides (cont.)				
prometon	0.045	±0.003	0.05	0.1
pronamide	0.115	±0.015	0.1	0.1
propachlor	0.109	±0.012	0.1	0.1
propazine	0.025	±0.008	0.03	0.1
simazine	0.074	±0.004	0.1	0.1
tebuthiuron	0.018	±0.004	0.02	0.1
terbacil	0.054	±0.007	0.1	0.1
terbufos	0.064	±0.002	0.1	0.1
treflan	0.062	±0.007	0.1	0.1
triallate	0.099	±0.001	0.1	0.1
pyrethroids				
cis-permethrin	0.17u	±0.0	0.2u	ND[1]
sulfur-containing pesticides				
propargite	0.12	±0.0	0.1	0.1

Analyte	Mean Concentration (± ½ duplicate range)		Expected Range	Certified Value	RPD[2]
chlorinated herbicides					
2,4'-D	0.16	±0.05	0.14-0.39	0.298	60
2,4,5'-TP (silvex)	0.036	±0.003	0.03-0.09	0.069	63
pentachlorophenol	0.28	±0.09	0.24-0.88	0.655	80
carbamates					
aldicarb	0.227	±0.013	0.31-0.58	0.443	64
aldicarb sulfoxide	0.052	±0.008	0.08-0.14	0.109	71
aldicarb sulfone	0.082	±0.029	0.46-0.86	0.660	156
carbofuran	0.123	±0.029	0.21-0.39	0.299	83

[1] ND = Not Detected
[2] RPD = Relative Percent Difference, (difference/mean) x 100.

Appendix G. Matrix Spike Recoveries for 1993 WSPMP Surface Water Samples (%)

	April			June			August			October		
	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD
chlorinated pesticides												
4,4'-DDT	62	58	7	104	100	4	105	103	2	108	91	17
aldrin	37	52	34	57	63	10	90	93	3	61	87	35
trans-chlordane	65	71	9	94	89	5	94	95	1	110	104	6
endosulfan I	75	80	6	97	93	4	94	95	1	NAF	NAF	
endrin	79	77	3	101	94	7	94	93	1	120	108	11
gamma-BHC	77	77	0	95	93	2	95	93	2	120	117	3
heptachlor	46	57	21	73	74	1	85	86	1	68	86	23
methoxychlor	69	62	11	100	97	3	106	103	3	116	103	12
organophosphates												
azinphos-ethyl	84	84	0	94	94	0	108	103	5	NAF	NAF	
chlorpyrifos	74	70	6	84	84	0	101	100	1	112	109	3
diazinon	80	76	5	88	88	0	113	110	3	NAF	NAF	
ethion	77	75	3	92	91	1	98	96	2	109	107	2
ethoprop	78	79	1	89	92	3	94	94	0	103	104	1
fonofos	80	77	4	90	92	2	98	98	0	NAF	NAF	
malathion	84	82	2	88	89	1	106	103	3	115	115	0
methyl parathion	83	80	4	87	88	1	104	101	3	112	111	1
phorate	70	69	1	89	92	3	96	95	1	90	88	2
abate	NAF[1]	NAF		NAF	NAF		NAF	NAF		74	47	45
butifos	NAF	NAF		NAF	NAF		NAF	NAF		114	106	7
dichlorvos	NAF	NAF		NAF	NAF		NAF	NAF		78	109	33
dimethoate	NAF	NAF		NAF	NAF		NAF	NAF		5	84	178
dioxathion	NAF	NAF		NAF	NAF		NAF	NAF		115	120	4
fenamiphos	NAF	NAF		NAF	NAF		NAF	NAF		111	105	6
fensulfothion	NAF	NAF		NAF	NAF		NAF	NAF		86	107	22
mevinphos	NAF	NAF		NAF	NAF		NAF	NAF		14	108	154
phosphamidan	NAF	NAF		NAF	NAF		NAF	NAF		8	116	174
tetrachlorvinphos	NAF	NAF		NAF	NAF		NAF	NAF		115	110	4

[1] - NAF = Not Analyzed For

Appendix G (cont.). Matrix Spike Recoveries for 1993 WSPMP Surface Water Samples (%)

	April			June			August			October		
	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD
nitrogen-containing pesticides												
alachlor	69	87	23	108	95	13	66	82	22	106	108	2
bromacil	83	81	2	101	106	5	89	86	3	4	90	183
dichlobenil	75	77	3	87	89	2	113	112	1	131	127	3
hexazinone	109	94	15	121	120	1	93	89	4	0	99	200
metribuzin	78	80	3	87	91	4	94	95	1	42	90	73
pronamide	84	74	13	99	98	1	87	91	4	81	96	17
simazine	85	86	1	105	102	3	108	102	6	78	103	28
trifluralin	61	67	9	82	84	2	83	87	5	35	32	9
ametryn	98	113	14	NAF	NAF		NAF	NAF		NAF	NAF	
benefin	61	72	17	NAF	NAF		NAF	NAF		NAF	NAF	
butylate	87	79	10	NAF	NAF		NAF	NAF		NAF	NAF	
chlorothalonil	50	42	17	NAF	NAF		NAF	NAF		NAF	NAF	
cycloate	69	72	4	NAF	NAF		NAF	NAF		NAF	NAF	
eptam	74	76	3	NAF	NAF		NAF	NAF		NAF	NAF	
propazine	128	79	47	NAF	NAF		NAF	NAF		NAF	NAF	
triallate	79	55	36	NAF	NAF		NAF	NAF		NAF	NAF	
vernolate	80	64	22	NAF	NAF		NAF	NAF		NAF	NAF	
di-allate	NAF[1]	NAF		78	98	23	NAF	NAF		NAF	NAF	
diuron	NAF	NAF		84	91	8	NAF	NAF		NAF	NAF	
metalaxyl	NAF	NAF		92	99	7	NAF	NAF		NAF	NAF	
profluralin	NAF	NAF		79	85	7	NAF	NAF		NAF	NAF	
tebuthiuron	NAF	NAF		NAF	NAF		107	115	7	34	67	65
pyrethroids												
fenvalerate	76	78	3	89	86	3	101	99	2	107	104	3
sulfur-containing pesticides												
propargite	121	116	4	79	80	1	NAF	NAF		NAF	NAF	

[1] - NAF = Not Analyzed For

Appendix G (cont.). Matrix Spike Recoveries for 1993 WSPMP Surface Water Samples (%)

	April			June			August			October		
	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD
chlorinated herbicides												
2,4-D	72	92	24	52	47	10	68	85	22	150	140	7
2,4,5-TP	64	81	23	43	40	7	55	62	12	100	89	12
2,4,6-trichlorophenol	49	62	23	51	44	15	47	53	12	50	51	2
dalapon	103	96	7	20	14	35	25	29	15	14	14	0
DCPA	164	411	86	44	40	10	267	310	15	101	76	28
dicamba I	98	98	0	49	45	9	67	78	15	102	90	13
dinoseb	49	58	17	4	5	22	8	10	22	NAF	NAF	
MCPA	59	66	11	50	44	13	67	75	11	78	83	6
pentachlorophenol	49	63	25	41	33	22	23	25	8	58	48	19
picloram	74	103	33	53	50	6	54	63	15	68	60	13
2,3,4,5-tetrachlorophenol	NAF[1]	NAF		47	47	0	34	41	19	71	71	0
2,4-DB	NAF	NAF		42	40	5	50	52	4	93	87	7
2,4,5-T	NAF	NAF		48	41	16	54	66	20	92	90	2
2,4,5-TB	NAF	NAF		52	54	4	48	48	0	136	91	40
2,4,5-trichlorophenol	NAF	NAF		44	37	17	41	45	9	100	57	55
3,5-dichlorobenzoic acid	NAF	NAF		52	47	10	55	66	18	82	77	6
4-nitrophenol	NAF	NAF		38	26	38	25	20	22	91	29	103
5-hydroxydicamba	NAF	NAF		37	33	11	33	37	11	82	59	33
acifluorfen	NAF	NAF		10	12	18	25	28	11	18	23	24
bentazon	NAF	NAF		64	44	37	41	57	33	84	59	35
bromoxynil	NAF	NAF		48	35	31	56	67	18	50	49	2
chloramben	NAF	NAF		NAF	NAF		57	64	12	NAF	NAF	
dichlorprop	NAF	NAF		48	42	13	61	73	18	106	94	12
diclofop-methyl	NAF	NAF		57	61	7	50	55	10	93	91	2
ioxynil	NAF	NAF		28	21	29	38	44	15	45	25	57
MCPP	NAF	NAF		19	17	11	57	52	9	39	50	25
trichlopyr	NAF	NAF		44	39	12	37	48	26	114	108	5

[1] - NAF = Not Analyzed For

Appendix G (cont.). Matrix Spike Recoveries for 1993 WSPMP Surface Water Samples (%)

	April			June			August			October		
	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD	MS	MSD	RPD
carbamates												
aldicarb sulfoxide	50	54	8	37	50	30	43	22	65	119	119	0
aldicarb sulfone	42	41	2	70	37	62	20	9	76	145	127	13
aldicarb	89	104	16	24	51	72	50	31	47	67	85	24
oxamyl	4	5	22	35	32	9	43	21	69	113	111	2
methomyl	58	67	14	59	53	11	68	52	27	107	108	1
3-hydroxycarbofuran	17	20	16	64	48	29	55	34	47	80	76	5
propoxur	38	48	23	65	56	15	76	36	71	91	117	25
carbofuran	38	47	21	90	59	42	65	33	65	89	101	13
carbaryl	13	17	27	89	49	58	63	28	77	106	115	8
methiocarb	12	21	55	80	43	60	46	26	56	95	103	8

MS = Matrix Spike

MSD = Matrix Spike Duplicate

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

Appendix H. Surrogate Recoveries for 1993 WSPMP Surface Water Samples (%)

	DBC	DCBP	DBOFBP	TPP	DMNB	TBP	BDMC	AMPA
April								
Adna Creek	87	88	45	110	60	35	31	67
Fishtrap Creek	77	73	32	108	65	35	12	67
Mercer Creek	82	80	48	117	85	37	70	58
Salmon Creek	82	77	43	105	71	32	0	58
Crab Creek	72	73	40	106	71	45	1	140
Crab Creek Dup.	67	67	39	98	66	76	36	58
Foster Creek	79	77	33	87	66	66	59	145
Mission Creek	76	74	23	92	55	32	47	109
Moxee Drain	75	79	27	109	65	45	0	58
Walla Walla River	82	82	37	93	71	46	5	100
June								
Adna Creek	67	68	28	102	72	34	65	SNA[1]
Fishtrap Creek	51	51	23	91	77	34	77	SNA
Mercer Creek	64	64	33	116	85	61	90	SNA
Salmon Creek	68	70	47	98	81	47	74	SNA
Crab Creek	76	79	18	96	64	54	53	SNA
Foster Creek	47	46	14	91	58	53	5	SNA
Mission Creek	71	74	20	88	70	75	41	SNA
Mission Creek Dup.	64	64	28	88	65	51	50	SNA
Moxee Drain	53	53	18	89	69	68	34	SNA
Walla Walla River	54	51	18	91	64	69	36	SNA
Joe Leary Slough	63	67	36	97	79	26	76	SNA
Lynch Coulee Creek	75	72	18	86	72	50	63	SNA
August								
Adna Creek	127	125	75	138	95	56	66	NAF[2]
Fishtrap Creek	124	124	75	135	103	85	18	NAF
Mercer Creek	122	119	78	138	93	66	36	NAF
Salmon Creek	142	142	85	152	96	55	39	NAF
Crab Creek	114	117	75	127	83	41	50	NAF
Foster Creek	105	99	52	112	91	53	29	NAF
Mission Creek	106	106	68	114	108	34	31	NAF
Moxee Drain	102	106	50	125	93	56	52	NAF
Walla Walla River	108	107	32	137	87	32	65	NAF
Walla Walla River Dup.	103	95	45	125	87	43	78	NAF
October								
Adna Creek	SNA[1]	73	8	78	46	68	116	NAF
Fishtrap Creek	SNA	70	6	66	52	39	117	NAF
Mercer Creek	SNA	67	8	70	46	64	22	NAF
Mercer Creek Dup.	SNA	60	9	55	46	85	92	NAF
Salmon Creek	SNA	70	6	65	42	SNA	140	NAF
Crab Creek	SNA	76	11	83	57	60	73	NAF
Foster Creek	SNA	94	14	92	59	45	10	NAF
Mission Creek	SNA	93	27	88	73	41	82	NAF
Moxee Drain	SNA	85	9	93	53	34	56	NAF
Walla Walla River	SNA	86	12	89	67	35	78	NAF

Appendix H (cont.). Surrogate Recoveries for 1993 WSPMP Surface Water Samples (%)

	DBC	DCBP	DBOFBP	TPP	DMNB	TBP	BDMC	AMPA
April								
Lab Blank 1	85	85	27	68	64	45	0	96
Lab Blank 1 Dup.	92	93	31	89	67	76	40	NAF
Lab Blank 2	103	104	65	99	88	50	SNA	NAF
Lab Blank 2 Dup.	94	100	56	84	77	37	SNA	NAF
Matrix Spike	76	82	66	94	73	93	65	92
Matrix Spike Dup.	88	92	63	94	73	73	84	75
June								
Lab Blank 1	80	85	42	96	74	63	78	SNA
Lab Blank 1 Dup.	77	76	26	83	61	96	83	SNA
Lab Blank 2	80	83	17	87	64	90	100	NAF
Lab Blank 2 Dup.	73	72	21	83	63	112	34	NAF
Field Blank	78	63	35	76	64	132	50	SNA
Matrix Spike	88	87	30	93	86	33	104	SNA
Matrix Spike Dup.	86	86	34	99	87	36	55	SNA
Field Spike	58	45	21	96	74	58	79	NAF
Field Spike Dup.	79	57	26	96	88	43	39	NAF
August								
Lab Blank 1	128	121	50	104	105	71	62	NAF
Lab Blank 1 Dup.	128	128	54	138	112	67	62	NAF
Lab Blank 2	137	139	76	142	115	80	35	NAF
Lab Blank 2 Dup.	129	123	28	129	81	83	45	NAF
Matrix Spike	129	115	69	134	114	37	58	NAF
Matrix Spike Dup.	125	103	90	134	118	38	33	NAF
October								
Lab Blank 1	SNA	92	14	81	70	71	95	NAF
Lab Blank 1 Dup.	SNA	80	12	56	57	36	69	NAF
Lab Blank 2	SNA	75	13	74	62	72	SNA	NAF
Lab Blank 2 Dup.	SNA	82	14	84	70	65	SNA	NAF
Matrix Spike	SNA	105	13	119	70	94	115	NAF
Matrix Spike Dup.	SNA	95	17	114	67	71	112	NAF

[1] - SNA = Surrogate Not Added

[2] - NAF = Not Analyzed For

Surrogate Key

DBC = Dibutylchlorendate (Chlorinated Pesticides)

DCBP = Decachlorobiphenyl (Chlorinated Pesticides)

DBOFBP = 4,4-Dibromooctafluorobiphenyl (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)

AMPA = Aminomethylphosphonic Acid (Glyphosate)

Appendix I-1. Water Quality Criteria and Recommended Maximum Concentrations for Pesticides Detected in 1993 WSPMP Surface Water Samples (μg/L, ppb)

Pesticide	WAC 173-201A Freshwater Acute	WAC 173-201A Freshwater Chronic	EPA 40 CFR Part 131 Freshwater Maximum Conc.[3]	EPA 40 CFR Part 131 Freshwater Continuous Conc.[1]	EPA,1986 Freshwater Acute	EPA,1986 Freshwater Chronic[2]	NAS, 1973 Maximum Conc.	CCREM, 1987 Maximum Conc.	Norris and Dost, 1991 Invertebrates Acute	Norris and Dost, 1991 Invertebrates Chronic[2]	Norris and Dost, 1991 Fish Acute	Norris and Dost, 1991 Fish Chronic[2]
chlorpyrifos	0.083	0.041[1]					0.001					
total DDT	1.1	0.001[2]			1.1	0.001	0.002	0.001				
4,4'-DDT			1.1	0.001								
total endosulfan	0.22	0.056[2]			0.22	0.056	0.003	0.02	0.04	0.004	0.02	0.002
endosulfan I			0.22	0.056								
endosulfan II			0.22	0.056								
azinphos-methyl						0.01	0.001					
malathion						0.01	0.008					
diazinon							0.009					
dicamba							200		390	39	3500	350
dichlobenil							37.0					
diuron							1.6					
simazine							10.0	10	20	2	50	5
2,4-D							4.0		120	12	60	6
atrazine								2.0	14	1	90	9
metribuzin								1.0				
pentachlorophenol								0.5				
triallate								0.24				
hexazinone									1120	110	6400	640
propargite											2	0.2

[1] - 4 day average

[2] - 24 hour average

[3] - 1 hour average

Appendix I-2 (cont.). Acute Toxicity of Pesticides Detected in 1993 WSPMP Surface Water Samples (μg/L, ppb; 96 hour LC_{50})

Pesticide	Rainbow Trout	Bluegill	Invertebrates	Reference
aldicarb	390-800	30-80	411	EPA, 1984
atrazine	4,500-8,800	116,000	NA[1]	Tetra Tech, 1988
bentazon	>100,000	NA	slightly toxic	EPA, 1985
bromacil	28,000	71,000	non-toxic (bees)	FCH, 1991
bromoxynil	50	NA	non-toxic (bees)	FCH, 1991
chlorpropham	3,020-5,700	6,300-6,800	NA	EPA, 1987
DCPA	30,000	>100,000	6,200- >100,000	EPA, 1988
hexazinone	320,000-420,000	370,000-420,000	NA	Tetra Tech, 1988
MCPA	non-toxic	NA	non-toxic (bees)	FCH, 1991
MCPP	115,000	NA	NA	Tetra Tech, 1988
metribuzin	76,000	80,000	NA	Tetra Tech, 1988
prometon	12,000	40,000	NA	Tetra Tech, 1988
propargite	118	167	92	EPA, 1986b
triallate	1,500	2,400	NA	FCH, 1991

[1] - NA = Not Available

Appendix I-2. Acute Toxicity (Johnson and Finley, 1980) of Pesticides Detected in 1993 WSPMP Surface Water Samples (μg/L, ppb; 96 hour LC_{50})

Pesticide	Aquatic Invertebrates Most Sensitive sp.	Aquatic Invertebrates *Gammarus* spp.	Fish Most Sensitive sp.	Fish Rainbow Trout
azinphos-methyl	0.11-0.16	0.11-0.20	0.27-0.48	3.0-6.4
chlorpyrifos	0.07-0.17	NA[1]	1.1-5.1	6.0-8.4
DDD	0.1-1.2	same	11-19	57-87
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
dimethoate	36-51	150-270	6,000	4,100-9,300
diuron	130-190	same	1,100-1,900	4,100-5,900
endosulfan	1.6-3.3	4.1-8.1	0.9-1.7	1.2-1.6
eptam	15,000-36,000	66,000	14,800-17,700	same
malathion	0.63-0.92	same	59-70	160-240
methomyl	4.1-19	424-2,600	589-979	1,100-1,400
mevinphos	0.13-0.25	3.1-3.9	10.7-13.2	same
pentachlorophenol	NA	NA	23-44	48-56
propoxur	18	29-39	4,800	8,200
simazine	560-2,200	>100,000	>100,000	same
2,4-D	90-1,400	1,900-3,000	190-330	same

[1] - NA = Not Available

Appendix J. Supplemental Information for Pesticides Detected in the 1993 WSPMP

Common Name	Trade Name[1]	Chemical Group	Activity	Application
2,3,4,6-tetrachlorophenol	Dowicide	phenol	fungicide, insecticide	wood preservative
2,4-D	Weed-B-Gon	chlorophenoxy herbicide	hormone-type herbicide	postemergent control of broadleaf weeds
DDT	Genitox	chlorinated pesticide	insecticide	all use banned in 1972
DDE				breakdown product of DDT
DDD	Rhothane	chlorinated pesticide	insecticide	breakdown product of DDT
atrazine	Gesaprin	triazine	selective herbicide	weed control on corn and other crops
azinphos-methyl	Guthion	organophosphate	broad spectrum insecticide	insect control on fruit, melons, nuts, & field crops
aldicarb	Temik	carbamate	systemic insecticide, acaricide	soil application
bentazon	Basagran	chlorinated herbicide	selective herbicide	postemergent control of many broadleaf weeds
bromacil	Bromax	uracil	broad spectrum herbicide	general control of weeds and brush
bromoxynil	Brominex	nitrile	selective herbicide	postemergent control of weeds in grain crops
chlorpropham	CIPC	carbamate	plant growth regulator	preemergent weed control
chlorpyrifos	Dursban, Lorsban	organophosphate	broad spectrum insecticide	use on a wide variety of agricultural and household pests
DCPA	Dacthal	benzoic acid	selective herbicide	preemergent control of grasses
diazinon	Knox-out	organophosphate	broad spectrum insecticide	use on a wide variety of agricultural and household pests
dicamba	Brushmaster	benzoic acid	herbicide	pre- or postemergent control of weeds on crop and noncrop sites
dichlobenil	Casoron	benzonitrile	broad spectrum herbicide	controls grasses, broadleaf weeds, and aquatic weeds
dimethoate	Devigon	organophosphate	systemic insecticide/acaricide	effective on a wide range of insects
diuron	Herbixol	uracil	herbicide	postemergent control of grasses and broadleaf weeds
endosulfan	Thiodan	chlorinated cyclodiene	insecticide, acaricide	for control of aphids on fruit trees
EPTC	Eptam	thiocarbamate	selective herbicide	controls grassy weeds in corn, potatoes, beans, etc.
hexazinone	Velpar	triazine	contact and residual herbicide	controls many annual, biennial, and perennial weeds
malathion	Cythion	organophosphate	insecticide	control of sucking and chewing insects on fruits, vegetables, & ornamentals
MCPA	Bordermaster	chlorophenoxy herbicide	hormone-type herbicide	postemergent control of broadleaf weeds on small grains
MCPP	Mecoprop	chlorophenoxy herbicide	hormone-type herbicide	control of broadleaf weeds on ornamentals
methomyl	Methomex	carbamate	broad spectrum insecticide	control of insects in field and fruit crops and ornamentals
metribuzin	Sencor	triazine	herbicide	controls grasses and broadleaf weeds in agricultural crops
mevinphos	Duraphos	organophosphate	contact & systemic insecticide	controls a wide range of insects on many crops
pentachlorophenol	Dowicide	phenol	fungicide, molluscicide	wood preservative
prometon	Pramitol	triazine	nonselective herbicide	pre- and postemergent control of most grasses & broadleaf weeds
propoxur	Baygon	carbamate	insecticide	mosquitoe control
propargite	Comite	sulfite ester	acaricide	controls mites & spiders on many crops
simazine	Simanex	triazine	selective herbicide	controls most annual grasses & broadleaf weeds
triallate	Far-Go	thiocarbamate	selective herbicide	preemerent control of wild oats in other field crops

1 - Each trade name listed is typically one of many available formulations and is the name most familiar to the first author.

Detected pesticides are not necessarily residues from use of the specific formulations listed here.

Appendix K. Compounds Detected in the 1992 WSPMP Reconnaissance Survey (Davis, 1993)

Site Name	Date Sampled	Compound Detected	Concentration (μg/L)
Misson Creek	May 30	azinphos-methyl	**0.033**
		glyphosate	1.13
		pentachlorophenol	0.002
		simazine	0.041
Crab Creek	May 30	atrazine	0.088
		dacthal (DCPA)	1.24
		dicamba	0.012
		disugran *	0.080
		EPTC (eptam)	0.31
		glyphosate	0.38
		simazine	0.033
		2,4-D	0.980
Walla Walla River	May 30	dacthal (DCPA)	12.1
		dichloro-DCPA *#	0.046
		trichloro-DCPA *#	0.55
		glyphosate	0.49
		hexazinone	0.063
		simazine	0.078
		2,4-D	0.055
Glade Creek	May31	atrazine	0.24
		atrazine desethyl *#	0.38
		dacthal (DCPA)	0.028
		dichloroisocyanatobenzene *#	0.11
		disugran *	0.019
		EPTC (eptam)	0.20
		metribuzin	0.043
Fishtrap Creek	June 14	atrazine	0.11
		dacthal (DCPA)	0.006
		MCPP	1.5
		simazine	0.091
		2,4-D	0.27
		tributyl phosphate *	0.018
		ethanol-2-chlorophosphate *	0.11

Appendix K (cont.). Compounds Detected in the 1992 WSPMP Reconnaissance Survey

Site Name	Date Sampled	Compound Detected	Concentration (μg/L)
Moxee Drain	May 31	dacthal (DCPA)	0.011
		glyphosate	0.65
		malathion	0.048
		pentachlorophenol	0.016
		2,4-D	0.16
		4,4'-DDT	**0.015**
		4,4'-DDD	**0.026**
		4,4'-DDE	**0.017**
Moxee Drain Duplicate	May 31	dacthal (DCPA)	0.011
		glyphosate	0.33
		malathion	0.059
		pentachlorophenol	0.014
		2,4-D	0.15
		4,4'-DDT	**0.015**
		4,4'-DDD	**0.028**
		4,4'-DDE	**0.018**
Mercer Creek	June 14	dacthal (DCPA)	0.060
		diazinon	0.088
		dichlobenil	0.20
		glyphosate	1.07
		prometon	0.074
		2,4-D	0.19
		tributyl phosphate *	0.36
		ethanol-2-chlorophosphate *	0.11
Mercer Creek Duplicate	June 14	dacthal (DCPA)	0.061
		diazinon	0.094
		dichlobenil	0.17
		glyphosate	0.48
		MCPP	1.7
		prometon	0.090
		2,4-D	0.20
		tributyl phosphate *	0.40
		ethanol-2-chlorophosphate *	0.099

Appendix K (cont.). Compounds Detected in the 1992 WSPMP Reconnaissance Survey

Site Name	Date Sampled	Compound Detected	Concentration (µg/L)
Thornton Creek	June 14	dacthal (DCPA)	0.066
		diazinon	0.077
		dichlobenil	0.054
		dichlorprop	0.052
		disugran *	0.038
		glyphosate	0.58
		2,4-D	0.23
		tributyl phosphate *	1.1
		ethanol-2-chlorophosphate *	0.013
Sullivan Slough	June 14	atrazine	0.24
		bromacil	0.046
		chlorpropham	0.10
		dacthal (DCPA)	0.017
		metribuzin	0.036
		2,4-D	0.039
		trichloroaniline *	0.086
		pentachloroaniline *#	0.39
Lake River	June 15	dacthal (DCPA)	0.011
Tuttle Creek	June 15	no detections	

* - Non-target compounds detected and quantified by AED.
# - Suspected breakdown products.

Concentrations in **bold** are values that exceed EPA (1986a) and/or Washington State water quality criteria.