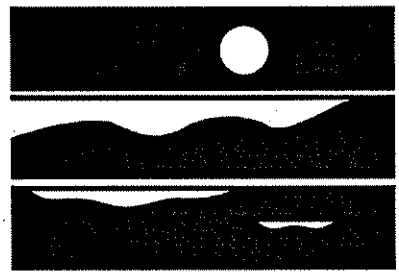

Washington State Pesticide Monitoring Program

1993 Fish Tissue Sampling Report

October 1995

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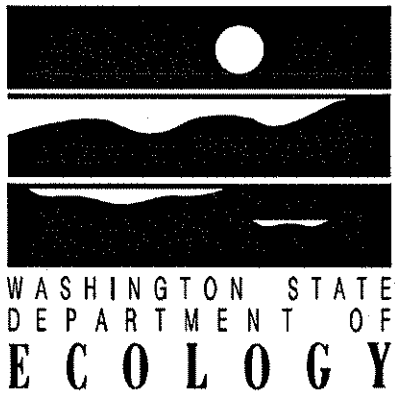

Washington State Pesticide Monitoring Program

1993 Fish Tissue Sampling Report

by
Dale Davis
Art Johnson
Dave Serdar

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

October 1995

Water Body Numbers

WA-01-1010	WA-32-1010
WA-01-1115	WA-45-1010
WA-23-1020	WA-45-1011
WA-28-1020	WA-57-1010
WA-28-9090	

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Abstract

Eighteen fish tissue samples were collected from six sites in September 1993 for the Washington State Pesticide Monitoring Program. Samples were analyzed for 43 target pesticides and breakdown products, and seven polychlorinated biphenyls (PCBs). Thirty-four of the target pesticides are chlorinated insecticides or their breakdown products, five are organophosphorus insecticides, two are chlorinated herbicides, and two are chlorinated fungicides. Total lipid content was also determined for each sample.

A total of 20 pesticides and breakdown products, and three PCBs (Aroclor equivalents), were detected in fish tissue samples. The majority of compounds identified were DDT, chlordane, or their metabolites. Only three of the detected pesticides, DCPA (Dacthal), ethion, and endosulfan sulfate (a breakdown product of endosulfan), are currently registered for use in Washington. A breakdown product of DDT, 4,4'-DDE, was the only target analyte detected at all sites. Other frequently detected compounds were 4,4'-DDD, 4,4'-DDT, cis- and trans-chlordane, and PCB-1260 and -1254. The most commonly detected commercially formulated pesticide was chlordane. Other formulated pesticides frequently found in fish tissue were 4,4'-DDT, hexachlorobenzene, and dieldrin.

Results were compared to USEPA screening values, proposed wildlife criteria, and to 85th percentiles calculated from statewide data. In fillet samples from the Walla Walla River, screening values were exceeded for total DDT (t-DDT), t-chlordane, dieldrin, heptachlor epoxide, hexachlorobenzene, and t-PCBs. Concentrations of t-DDT, dieldrin, and t-PCBs from the Walla Walla River, and t-PCBs from the Spokane River, were substantially higher than screening values. Wildlife criteria were exceeded for DDE, t-DDT, and t-PCBs in whole-fish samples from the Walla Walla and Wenatchee Rivers. Total PCBs were also above criteria in samples from Vancouver Lake and the Spokane River. Concentrations of t-DDT, t-chlordane, dieldrin, hexachlorobenzene, lindane, heptachlor epoxide, and t-PCBs in samples from the Walla Walla River, and t-PCBs in samples from the Wenatchee, Chehalis, and Spokane Rivers, and Vancouver Lake were above the state 85th percentile. Some piscivorous wildlife within the Walla Walla, Wenatchee, and Spokane River basins may be at risk from consumption of contaminated fish.

Acknowledgements

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

- Stuart Magoon and Karin Feddersen of Ecology's Manchester Environmental Laboratory for their extra efforts to provide exceptional analytical services and for their valuable technical advice.

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Summary

The Washington State Pesticide Monitoring Program (WSPMP) was initiated in 1991 by the Department of Ecology to monitor surface water and ground water for pesticide residues. This report describes tissue monitoring results for 1993. Tissue samples were also collected in 1992 and results are reported by Davis and Johnson (1994a)

Whole samples of bottom feeding fish were collected to assess wildlife impacts, and sport fish were collected to evaluate potential risk to human health. Largescale suckers were chosen as the bottom feeding species. Sport fish species collected included rainbow and steelhead trout, mountain whitefish, largemouth bass, and carp. Composite samples of five individuals were collected for each species. Samples were analyzed for 43 pesticides and breakdown products, and seven PCB mixtures (as Aroclor equivalents).

A total of 20 pesticides and breakdown products, and three PCBs were detected in 18 fish tissue samples collected from six sites in September of 1993. A minimum of five target analytes were detected per sample site, with a maximum of 19 and an average of 11. The majority of compounds identified were DDT, chlordane, or their metabolites. Only three of the detected pesticides, DCPA (Dacthal), ethion, and endosulfan sulfate (a breakdown product of endosulfan), are currently registered for use in Washington. Other detected compounds breakdown slowly and are present due to historical use.

A breakdown product of DDT, 4,4'-DDE, was the only target analyte detected at all sites. Other frequently detected compounds were 4,4'-DDD, 4,4'-DDT, cis- and trans-chlordane, and PCB-1260 and -1254. The most commonly detected commercially formulated pesticide was chlordane. Other formulated pesticides frequently found in fish tissue were 4,4'-DDT, hexachlorobenzene, and dieldrin.

Screening values were used to identify and prioritize problem areas that are potential human health risks. These values were exceeded in fillet samples from five sites. In samples from the Walla Walla River, screening values were exceeded for total DDT (t-DDT), t-chlordane, dieldrin, heptachlor epoxide, hexachlorobenzene, and t-PCBs. Concentrations of t-DDT, dieldrin, and t-PCBs from the Walla Walla River, and t-PCBs from the Spokane River, were substantially higher than screening values.

Sites with fillet samples exceeding National Toxics Rule (NTR) criteria were recommended for addition to the 303(d) water quality limited list. Samples from the Walla Walla River (carp and steelhead trout), Mission Creek (rainbow trout), the Chehalis River (mountain whitefish), Vancouver Lake (largemouth bass), and the Spokane River (rainbow trout) all had one or more compounds exceeding NTR criteria.

Proposed wildlife criteria developed for the Niagara River were exceeded for DDE, t-DDT, and t-PCBs in whole-fish samples from the Walla Walla and Wenatchee Rivers. Total PCBs were also above criteria in samples from Vancouver Lake and the Spokane River.

Bald eagles and ospreys nesting in the Walla Walla and Wenatchee River basins may be experiencing eggshell thinning and reduced hatching success due to t-DDT contamination in fish the birds are consuming. DDT contamination in eggs of fish in these rivers may also be causing increased mortality at the fry stage of development.

Mink and river otters consuming fish from the Spokane, Wenatchee, and Walla Walla Rivers could be experiencing some degree of reproductive impairment due to PCB contamination. In addition, PCB levels were high enough in fish from the Spokane River to cause reduced hatching success of fish eggs.

Statewide pesticide data were pooled to calculate an 85th percentile for comparison to WSPMP data. The 85th percentile was selected to indicate when the concentration of a compound is substantially elevated above the median. Concentrations of t-DDT, t-chlordane, dieldrin, hexachlorobenzene, lindane, heptachlor epoxide, and t-PCBs in samples from the Walla Walla River exceeded 85th percentiles. Total PCBs in samples from the Wenatchee, Chehalis, and Spokane Rivers, and Vancouver Lake were also above the 85th percentile.

Recommendations

Walla Walla River

High concentrations of several toxic contaminants indicate that there is a potential risk to human health and aquatic wildlife from consumption of contaminated fish tissue.

- Consult with the Washington State Department of Health on the need for an intensive survey to evaluate potential risks to human health from contaminated fish tissue.
- At a minimum, assess contamination in other species of sport fish.
- Resample every three to five years as a trend site.
- Conduct a joint study with the Washington State Department of Fish and Wildlife to determine if piscivorous wildlife are being adversely affected by these toxic contaminants.

Mission Creek / Wenatchee River

Total DDT concentrations in fish from both streams may be a risk to some aquatic wildlife. Piscivorous mammals may also be affected by PCBs in the river. Possible endosulfan contamination deserves attention.

- Conduct a joint study with the Washington State Department of Fish and Wildlife to determine if piscivorous wildlife are being adversely affected.
- At a minimum, sample additional sites within the Wenatchee River basin to determine the extent of contamination.
- Sample Mission Creek in the spring immediately after endosulfan applications to assess the extent of fish contamination.

Spokane River

PCB contamination in fish poses a possible threat to fish productivity, and may be a considerable hazard to some piscivorous aquatic wildlife, particularly mink.

- If Ecology sampling scheduled for the Spokane River in 1996 shows continued high levels of PCBs in fish, sample representative piscivorous wildlife to determine if PCBs are being accumulated to hazardous levels.

303(d) Listing

Sites that qualify for addition to the 303(d) water quality limited list are the Walla Walla, Chehalis, and Spokane Rivers, Mission Creek, and Vancouver Lake.

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 bed sediments and associated biota such as fish, shellfish, and waterfowl, for pesticide residues. Ground water and surface water monitoring are being implemented as separate tasks. 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.

In a guidance document for assessing chemical contaminants in fish tissue, the U.S. Environmental Protection Agency (USEPA, 1993) describes two types of surveys. Initially, screening surveys are designed to identify potential problem areas by collecting one or two composite samples from a number of water bodies. These data are used to determine where more intensive surveys should be implemented to thoroughly investigate the extent and severity of the problem. The surface water portion of the WSPMP is essentially an ongoing screening survey.

The first set of fish tissue and sediment samples was collected in 1992 (Davis and Johnson, 1994a). This report addresses fish tissue sampling for 1993; no sediment samples were collected. Surface water samples were collected in April, June, August, and October of 1993, and results have been summarized in a report by Davis and Johnson (1994b).

Methods

Sampling Design

Fish tissue samples were collected for the WSPMP at six primary and three secondary sites (Figure 1) in September of 1993. Secondary sites were used to supplement samples from nearby primary sites that lacked desired target species. Table 1 lists sample sites, their location, and the number and type of samples collected. Latitude, longitude, and state plane coordinates are listed for each site in Appendix A.

Samples were analyzed for 43 pesticides and breakdown products, and seven polychlorinated biphenyls (PCBs) (Appendix B). Tissue was also analyzed for percent total lipids. The length and weight of each fish were recorded in the field and are summarized in Appendix C. Scientific names for each species collected are also listed in Appendix C.

The timing for sample collection was intended to allow spring spawners to rebuild lipid reserves, which concentrate bioaccumulative pesticides, and take place before fall spawning occurred. In addition, stream flows are lower in late summer, allowing easier and safer access.

For a screening survey, the USEPA recommends collecting one composite for each of two species at each sample site (USEPA, 1993). One species should be a bottom feeder and the other a sport fish. The USEPA document was written for use in developing advisories regarding human consumption of fish fillets. The WSPMP is designed as a screening survey, but also to provide data to evaluate the effects of pesticides in the environment. Thus, samples of whole bottom feeding fish were collected to assess wildlife impacts, and sport fish fillets were collected to evaluate potential risk to human health.

Target species were selected based on the following criteria:

- have a wide geographic distribution (statewide is desirable)
- potential to bioaccumulate high concentrations of pesticides (have a high lipid content)
- be a popular resident sport fish
- be easily identified
- be abundant, easy to capture, and large enough to provide an adequate sample size

Largescale suckers were chosen as the bottom feeding species because they possess all of the desired attributes of a target species. No single species of sport fish is widely distributed throughout Washington, so the species of opportunity was collected: rainbow and steelhead trout, mountain whitefish, largemouth bass, and carp.

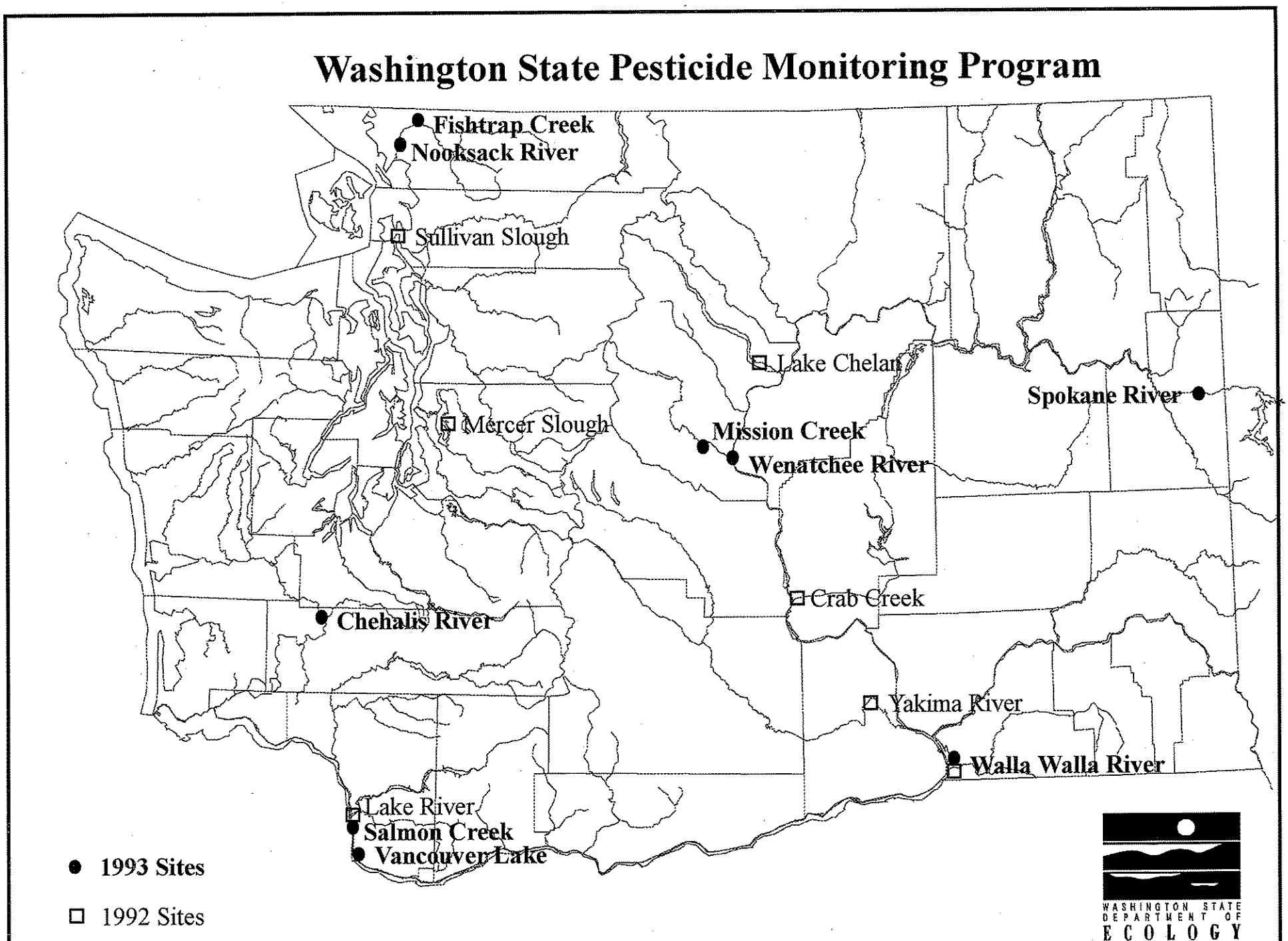

Figure 1. 1992 and 1993 WSPMP Fish Tissue Sampling Sites

Table 1. List of 1993 Sampling Sites, Locations, and Number and Type of Samples

Sample Site	Location	Number of Composite Samples[1] Whole-fish	Fillet
Walla Walla River	Near mouth	3	2
Mission Creek	Near mouth	0	1
Wenatchee River[2]	Near mouth	2	0
Chehalis River	Below confluence with Skookumchuck River	2	1
Fishtrap Creek	At bridge on River Road	0	1
Nooksack River[2]	Near Ferndale	1	0
Salmon Creek	Near mouth	0	1
Vancouver Lake[2]	Near mouth of Burnt Bridge Creek	1	1
Spokane River	Below Myrtle Point	1	1

[1] - Composite samples include five fish each
[2] - Secondary sampling sites

Composite samples rather than individual samples were collected because composites are the most cost-effective method of estimating average contaminant concentrations (USEPA, 1993). For assessment of sites to be added to the water quality limited list (section 303(d) of the federal Clean Water Act), fish composites must be composed of at least five individuals. Composite samples for the WSPMP included material from five fish. Replicate composites were collected at three sites to evaluate environmental variability.

When possible, all fish collected within a composite were similar in size. Larger (older) individuals are selected when there is a choice, because they have had more time to accumulate contaminants and generally should represent a "worst-case" sample.

Sampling Site Selection

All fish tissue sampling sites, except the Walla Walla and Spokane Rivers, were at or near 1993 surface water sampling sites, which were selected based on pesticide use at the site (Davis and Johnson, 1994b). Fish from the Walla Walla River were also sampled in 1992 for the WSPMP (Davis and Johnson, 1994a). Those results indicated that total DDT (t-DDT) concentrations may be elevated, so additional samples were collected in 1993. Tissue from the Spokane River was analyzed as a matter of opportunity; fish were collected in August of 1993 for a PCB screening survey of the Spokane River (Johnson *et al.*, 1994) and extra tissue was available for pesticide analysis.

Target Analytes

Appendix B lists the fish tissue target pesticides analyzed for the WSPMP in 1993. An initial list of target compounds for fish tissue analysis was compiled from other studies or guidelines on analyzing tissue samples for bioaccumulative pesticides (USEPA, 1993; Schmitt, *et al.*, 1990; Rasmussen and Blethrow, 1991; Crawford and Luoma, 1993). Pesticides recommended for monitoring in tissues in the Puget Sound Basin (Tetra Tech, Inc., 1988) were also included on the list. Endrin aldehyde and endrin ketone were added to the list because they were detected in fish samples from the Yakima River (Johnson, *et al.*, 1986).

A discussion of the characteristics and interrelationships of detected target compounds can be found in Appendix D.

Sampling Procedures, Analytical Methods, QA/QC, and Data Review

Details of sampling procedures are outlined in Appendix E. A brief discussion of analytical methods, quality assurance/quality control, and the data review is in Appendix F.

Results and Discussion

Pesticides Detected

For this report, total DDT refers to the sum of 4,4'- and 2,4'- isomers of DDT, DDD, and DDE. Total chlordane is the sum of cis- and trans-chlordane, cis- and trans-nonachlor, and oxychlordane. Total PCBs is the sum of all Aroclors. These compounds are used in this report for various comparisons because these were the most frequently detected compounds, they comprise a majority of the compounds detected, and in their summed form they simplify comparisons.

A total of 20 pesticides and breakdown products were detected in fish tissue samples collected in 1993 (Table 2). In addition, three PCB mixtures (as Aroclor equivalents) were identified. A minimum of five target analytes were detected per sample site, with a maximum of 19 and an average of 11. At five of the six sites sampled, 63-78% of the compounds detected were DDT, chlordane, and their metabolites. Only three of the detected compounds, DCPA (Dacthal), ethion, and endosulfan sulfate (a breakdown product of endosulfan), are currently registered for use in Washington. For reference, pesticides detected in tissue samples collected for the 1992 WSPMP are included in Appendix N.

Figure 2 shows the frequency of detection for target analytes identified in fish tissue for the 1992 and 1993 WSPMP. The only compound detected in all samples was 4,4'-DDE, a breakdown product of DDT. Other analytes were detected in 2-88% of the 41 samples.

In 1993 samples, two pesticide breakdown products, 4,4'-DDD and trans-nonachlor (products of DDT and chlordane, respectively), and PCB-1260 were detected at five of the six sites, and were found in a minimum of 14 samples. The most commonly detected formulated pesticide was chlordane. Both isomers were found at four sites, and cis-chlordane was identified in 16 samples, while trans-chlordane was detected in 14. Other formulated pesticides frequently identified in fish tissue samples were 4,4'-DDT, hexachlorobenzene, and dieldrin.

Comparisons with Applicable Criteria

Screening Values

As discussed earlier, the WSPMP should be interpreted as a screening survey. Standing alone, data from screening surveys are not adequate for making decisions regarding fish consumption by humans, but USEPA recommends evaluating detected chemical contaminants with screening values to prioritize problem areas. Sites with concentrations exceeding screening values will be

Table 2. Pesticides Detected in Fish Tissue for the 1993 WSPMP (μg/Kg (ppb) wet weight)

Sample Site	Walla Walla River					Nooksack River	Fishtrap Creek	Spokane River	
Fish Species	Suckers[1]	Suckers	Suckers	Carp[1]	Steelhead[1]	Suckers	RB trout	Suckers	RB trout
Tissue Type	Whole-Fish Replicate 1	Whole-Fish Replicate 2	Whole-Fish Replicate 3	Fillets	Fillets	Whole-Fish	Fillets	Whole-Fish	Fillets
% total lipid	4.67	6.41	3.87	3.91	7.01	4.56	3.89	4.73	2.69
2,4'-DDE		1							
4,4'-DDE	305	390	320	600	15	19	7	39	18
2,4'-DDD		8	5	9.8	1				
4,4'-DDD	43	63	40	97	15		2		
2,4'-DDT		1			1				
4,4'-DDT	13	14	17		4	6	2		
total DDT	**361**	**477**	**382**	**707**	**36**	**25**	**11**	**39**	**18**
4,4'-DDMU		10	6	15					
cis-chlordane	3	4	2	8	2	1	1		
trans-chlordane	2	4	2	8.5	1	1	1		
oxychlordane	0.3	1	1	1	1				
cis-nonachlor	2	3	2	5	1		1		
trans-nonachlor	5	7.8		13	3	3	1		1
total chlordane	**12**	**20**	**7**	**36**	**8**	**5**	**4**		**1**
DCPA (dacthal)					5				
dieldrin	4	5.6	4	10	4				
ethion		3		2					
gamma-BHC (lindane)	1	1		1	1	1			
heptachlor epoxide		4	3	8.2	4		1		
hexachlorobenzene	6.2	12	8.3	20	4.8				
PCB-1248								130	150
PCB-1254								950	430
PCB-1260	113		130	300				150	140
total PCBs	**113**		**130**	**300**				**1230**	**720**

[1] - Values are means of duplicate analyses

Table 2 (cont.). Pesticides Detected in Fish Tissue for the 1993 WSPMP (μg/Kg (ppb) wet weight)

Sample Site	Wenatchee River		Mission Creek	Chehalis River			Salmon Creek	Vancouver Lake	
Fish Species	Suckers[1]	Suckers	RB Trout	Suckers	Suckers	M Whitefish	LM Bass	LM Bass	Carp
Tissue Type	Whole-Fish Replicate 1	Whole-Fish Replicate 2	Fillets	Whole-Fish Replicate 1	Whole-Fish Replicate 2	Fillets	Fillets	Fillets	Whole-Fish
% total lipid	4.98	5.18	1.84	4.66	3.30	5.72	2.82	3.85	7.80
2,4'-DDE	2								
4,4'-DDE	380	270	270	14	27	23	11	47	95
2,4'-DDD	8								
4,4'-DDD	68	47	51		3		4	17	45
2,4'-DDT	4					1			
4,4'-DDT	32	26	42						
total DDT	**494**	**343**	**363**	**14**	**30**	**24**	**15**	**64**	**140**
4,4'-DDMU	14	12						5	
cis-chlordane				2	3	2	1	1	5
trans-chlordane				2	2	3	1		
oxychlordane		1			1	1			1
cis-nonachlor					1				2
trans-nonachlor				3	5	5.6		3	
total chlordane		**1**		**7**	**12**	**12**	**2**	**4**	**8**
dieldrin									4
endosulfan sulfate			8						
heptachlor						0.5			
hexachlorobenzene				0.5	0.7	1			
PCB-1248	170								
PCB-1254	250	55		45	55	75		50	120
PCB-1260	48	49		35	34	68		60	160
total PCBs	**468**	**104**		**80**	**89**	**143**		**110**	**280**

[1] - Values are means of duplicate analyses

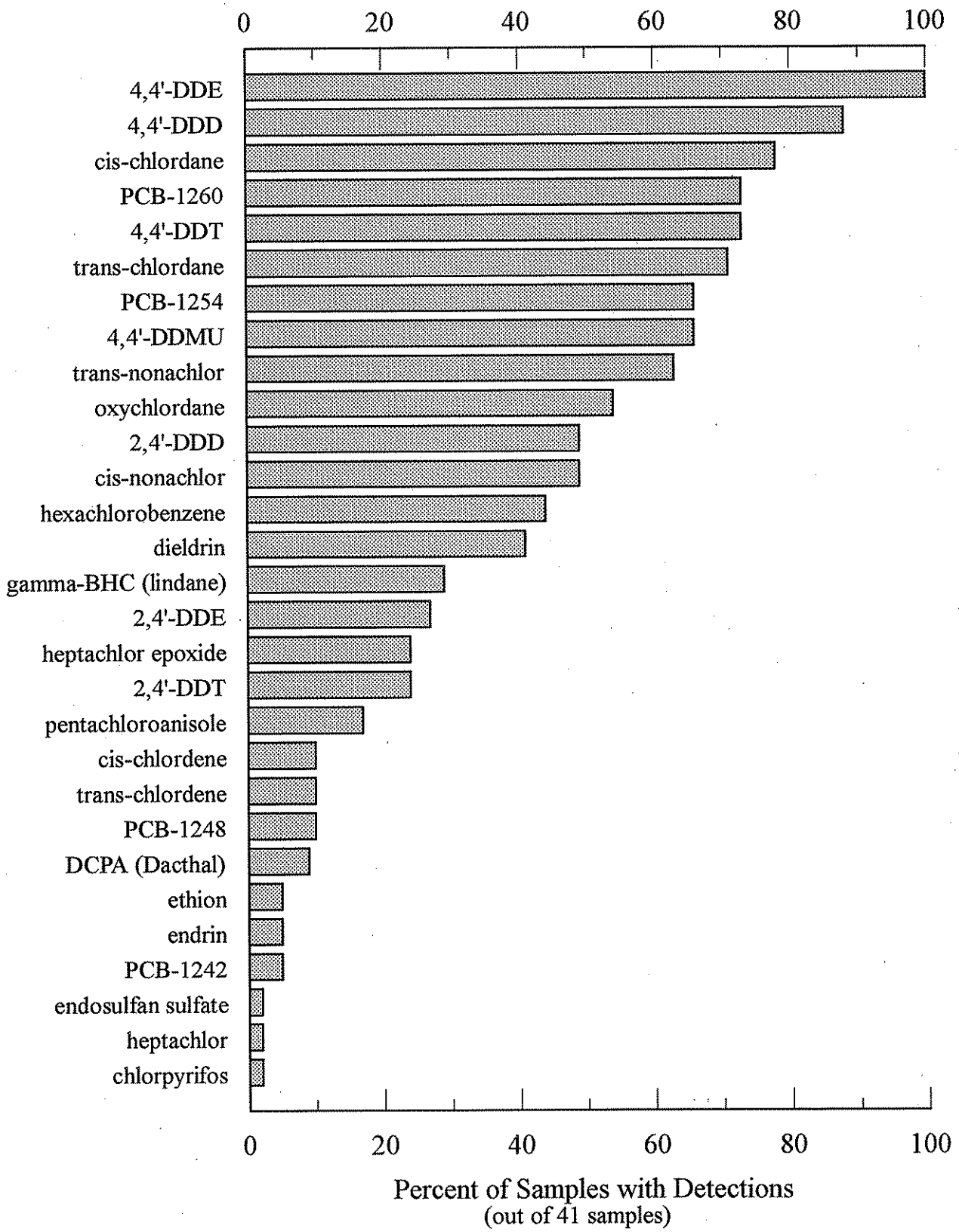

Figure 2. Detection Frequency of Pesticides and PCBs in 1992 and 1993 WSPMP Fish Tissue Samples

evaluated based on a variety of parameters. These parameters include, but are not limited to, the level of exceedance, local fish consumption patterns, and toxicity of the contaminant. If necessary, an intensive survey would be recommended to determine if consumption recommendations or advisories are warranted. The following summarizes the methods recommended by the USEPA (1993) for calculating screening values.

Calculation of Screening Values

Screening values for carcinogenic compounds are calculated using a risk level. A risk level is a value that predicts the increased number of cancer cases caused by a specific or multiple contaminant(s); a risk level of $1x10^{-6}$ is the probability that one person in a million will contract cancer as a result of long-term exposure to the contaminant(s) through consumption of fish tissue. Exposure assumptions include a body weight of 70 kg and a fish tissue consumption rate of 6.5 grams per day. These values represent the mean body weight for all adults and the average consumption rate for the general U.S. population (USEPA, 1993).

Washington State has adopted $1x10^{-6}$ as its risk level under the State Water Quality Standards (173-201A-040 WAC) and the Model Toxics Control Act (173-340-730 WAC). To aid in prioritization, it is useful to compare carcinogenic contaminant concentrations to screening values calculated with a risk level of $1x10^{-5}$.

Screening values for non-carcinogens are calculated using a reference dose that is derived from no observed adverse effects levels (NOAELs) or lowest observed adverse effects levels (LOAELs).

Pesticides detected in the WSPMP are compared to screening values in Table 3. Screening values calculated with a risk level of $1x10^{-6}$ were exceeded for one or more compounds at five of the six sites sampled. At three of those sites, either DDT or chlordane was the only pesticide that exceeded screening values. PCBs were the only compounds above screening values in the sample from the Spokane River. For the Walla Walla River, six screening values were exceeded in carp fillets and three in steelhead.

Using a risk level of $1x10^{-5}$, samples from the same five sites still exceed screening values, but three of those are just for PCBs. Only samples from the Walla Walla River and Mission Creek contained pesticides that exceeded the higher screening level values.

303(d) List

When calculated with a risk level of $1x10^{-6}$, screening values for the carcinogenic compounds listed in Table 3 have the same numerical value as National Toxics Rule (NTR) criteria (40 CFR part 131) that are used to assess sites for possible addition to the water quality limited list

Table 3. Comparison of Pesticides Detected in 1993 Fish Fillets to Screening Values (μg/Kg (ppb) wet weight)

Sample Site	Walla Walla River		Mission Creek	Chehalis River	Fishtrap Creek	Salmon Creek	Vancouver Lake	Spokane River	Screening Values	
Fish Species	Carp*	STLHD*	RBT	MWF	RBT	LMB	LMB	RBT	$1x10^{-6}$ **	$1x10^{-5}$
Carcinogens										
total DDT	**722**	**35**	**363**	24	11	15	**69**	18	32	320
total chlordane	**34**	7		**12**	4	2	4	1	8.3	83
gamma-BHC (lindane)	1	1							8.3	83
dieldrin	**10**	**4**							0.7	7
heptachlor epoxide	**8.2**	**4**			1				1.2	12
hexachlorobenzene	**20**	4.8		1					6.7	67
total PCBs	**383**			**143**			**110**	**720**	1.4	14
Non-Carcinogens										
ethion	3								5400	

Values in bold exceed screening values calculated using a risk level of $1x10^{-6}$

* Values are means of duplicate analyses

** $1x10^{-6}$ is the risk level adopted by Washington State

Fish species key

STLHD=Steelhead Trout
RBT=Rainbow Trout
MWF=Mountain Whitefish
LMB=Largemouth Bass

(section 303(d) of the federal Clean Water Act). The 303(d) list contains state waterbodies that do not meet water quality standards, and is used to help set priorities for addressing water pollution from a variety of sources. WSPMP sites will be added to the list if there are one or more NTR criteria exceeded for a five-fish composite of edible tissue (State Water Quality Policy 1-11, 1993).

Fillet samples from the Walla Walla River, Mission Creek, the Chehalis River, Vancouver Lake, and the Spokane River contained one or more compounds in concentrations above NTR criteria. All of these sites qualify for addition to the water quality limited list.

Wildlife Criteria

There are no Washington State or national pesticide or PCB criteria that have been adopted for protection of wildlife. The WSPMP results are compared to criteria proposed by the state of New York (Newell *et al.*,1987) in Table 4. For more information regarding wildlife criteria, see the discussion in the "Ecological Assessment" section starting on page 21.

Total DDT, DDE and/or PCBs exceeded criteria proposed by Newell *et al.* (1987) at four of the six sites sampled. For samples from Vancouver Lake and the Spokane River, only PCBs were above these criteria. Total DDT and DDE concentrations in samples from the Walla Walla and Wenatchee Rivers exceeded Newell's criteria.

Other Data

Selected data from the 1993 WSPMP are compared to 85th percentile values calculated from other Washington State studies in Table 5. These values were calculated from results of studies in the state that have monitored for pesticides in freshwater fish, including: Davis and Johnson, 1994a; Serdar *et al.*, 1994; Johnson and Norton, 1990; Johnson *et al.*, 1986; Hopkins *et al.*, 1985; Hopkins, 1991; Johnson and Norton, 1988; Schmitt *et al.*, 1990; Rinella *et al.*, 1992; and selected data from Block, 1993. Data collected prior to 1980 were not used. In cases where data have been collected from one site more than once, only the most recent values were used. Samples that were replicated or duplicated were averaged.

Nondetects were included in the percentile calculations, resulting in some 85th percentiles being nondetects. Any detected concentration for these chemicals would therefore be above the 85th percentile. Detection of these compounds by the WSPMP may reflect improved detection limits more than elevated levels.

Percentiles were calculated so that results from the WSPMP sites could be easily compared to levels found at other sites throughout the state. The 85th percentile was selected to indicate when the concentration of a compound is substantially elevated above the median (50th

Table 4. Comparison of Pesticides Detected in 1993 Whole Fish Samples to Recommended Wildlife Criteria (μg/Kg (ppb) wet weight)

Sample Site	Walla Walla River			Wenatchee River		Chehalis River		Nooksack River	Vancouver Lake	Spokane River	Criteria Newell et al., 1987	
	Rep-1[1]	Rep-2	Rep-3	Rep-1[1]	Rep-2	Rep-1	Rep-2				Non-Carcinogens	Carcinogens
DDE	**305**	**391**	**320**	**382**	**270**	14	27	19	95	39	200	270
DDD	43	71	45	76	47		3		45		200	270
DDT	13	15	17	36	26			6			200	270
total DDT	**361**	**477**	**382**	**493**	**343**	14	30	25	140	39	200	270
total chlordane	12	19.8	7			7	12	5	8		500	370
gamma-BHC (lindane)	1	1						1				
dieldrin	4	5.6	4						4		120	22
heptachlor epoxide		4	3								200	210
hexachlorobenzene	6.2	12	8.3			0.5	0.7				330	200
total PCBs	**113**		**130**	**468**	104	80	89		**280**	**1230**	110	110

Values in bold exceed recommended criteria

[1] - Values are means of duplicate analyses

All data are from largescale suckers, except those from Vancouver Lake, which are from carp

Table 5. Comparison of Selected Compounds Detected in 1993 to State-wide 85th Percentiles (μg/Kg (ppb) wet weight)

	t-DDT	t-chlordane	dieldrin	HCB	lindane	heptachlor epoxide	t-PCBs
Whole-Fish							
Walla Walla River	401	13	4	**8**	**1**	2	89
Wenatchee River	456	0.3	u[1]	u	u	u	**347**
Chehalis River	22	10	u	**0.6**	u	u	85
Nooksack River	25	5	u	u	**1**	u	u
Vancouver Lake	140	8	4	u	u	u	**280**
Spokane River	39	u	u	u	u	u	**1230**
State 85th Percentile	650	21	40	u	0.3	3.5	225
Fillets							
Walla Walla River	**722**	**34**	**10**	**19**	**1**	**8.2**	**300**
Walla Walla River	35	**6.5**	4	**4.8**	**0.5**	**4**	u
Mission Creek	363	u	u	u	u	u	u
Chehalis River	24	**12**	u	**1**	u	u	**143**
Fishtrap Creek	11	**4**	u	u	u	**1**	u
Salmon Creek	15	2	u	u	u	u	u
Vancouver Lake	69	**4**	u	u	u	u	110
Spokane River	18	1	u	u	u	u	**720**
State 85th Percentile	500	4	10	1	u	u	120
Lipid Normalized[2]							
Walla Walla River	8900	370	120	**230**	**13**	**84**	3000
Wenatchee River	9100	6	u	u	u	u	**6900**
Mission Creek	19700	u	u	u	u	u	u
Chehalis River	540	240	u	**16**	u	u	2300
Nooksack River	550	110	u	u	**22**	u	u
Fishtrap Creek	280	100	u	u	u	**26**	u
Vancouver Lake	1800	100	26	u	u	u	3200
Salmon Creek	530	71	u	u	u	u	u
Spokane River	750	19	u	u	u	u	**26400**
State 85th Percentile	28300	450	400	15	5	u	4900

Values in bold equal or exceed state-wide 85th percentile

[1] - u=undetected

[2] - Lipid normalized values are means of all whole-fish and fillet samples for each site

Values from duplicate or replicate samples of the same species were averaged for each site

Means were calculated with undetected results set at zero

percentile). These percentiles are likely to be biased to the high side, since sites are generally selected for monitoring based on suspected pesticide contamination. Percentiles are used for relative comparisons, and should not be used as criteria for assessment of potential adverse human health or aquatic wildlife effects.

Selected data are compared to other statewide statistics in Appendix G. In addition, WSPMP results are compared to similar data from the California Toxic Substances Monitoring Program (Rasmussen and Blethrow, 1991), and to national values reported by the USEPA National Study of Chemical Residues in Fish (1992) and the U.S. Fish and Wildlife Service's (USFWS) National Contaminant Biomonitoring Program (Schmitt *et al.*, 1990).

Site Evaluations

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, the Touchet River and several small creeks add to the flow. A wide variety of row crops, in addition to wheat and alfalfa, are grown throughout the Walla Walla Valley. Nearly all of these crops are irrigated from wells or the river. Most of the land that drains into the Touchet River supports dry-land wheat cultivation, but some sections along the river are irrigated.

Largescale sucker and carp samples were collected from the mouth of the Walla Walla where it enters Lake Wallula on the Columbia River to the point where the water became too shallow for boat access, a reach approximately three and one-half miles long. Steelhead were collected from a large pool near the upper end of the reach. The water level in this reach is controlled by the McNary Dam on the Columbia River. Water from Lake Wallula backs up into the lower section of the river and the level changes in the lake.

The Walla Walla River was selected for fish collection in 1993 as a result of moderately high concentrations of DDT and metabolites identified in fish samples collected for the 1992 WSPMP. When lipid normalized, the values found in 1992 were similar to those in samples from the Yakima River, where the Washington State Department of Health has recommended limiting consumption of bottom fish due to DDT contamination. This suggests that the bioavailability of DDT to fish in the Walla Walla River may be as high as in the Yakima River. Samples were collected in 1993 to further evaluate pesticide contamination in the Walla Walla River. Replicate samples of whole-fish were taken to assess variability between composites, and to establish baseline concentrations for future trend analyses.

Relatively high concentrations of DDT and its breakdown products were found in all whole-fish sucker and carp fillet samples. In addition, samples contained elevated levels of chlordane, dieldrin, heptachlor epoxide, hexachlorobenzene, and PCBs. Screening values and NTR criteria were exceeded for all these compounds in carp fillets. Total DDT, DDE, and PCBs in whole-fish samples were above wildlife criteria proposed by Newell *et al.* (1987). Concentrations in steelhead fillets were lower, but total DDT, dieldrin, and heptachlor epoxide still exceeded screening values and NTR criteria.

Similar levels of the same contaminants were found in a whole-fish sample collected for the 1992 WSPMP (Davis and Johnson, 1994a). However, lower concentrations and fewer compounds were detected in a white crappie fillet sample, probably due to the low lipid content of the tissue (0.15%). Fish were also collected from the Walla Walla River for Ecology's 1984 and 1989 Basic Water Monitoring Program (BWMP) surveys (Hopkins *et al.*, 1985; Hopkins, 1991). Concentrations of DDT and its metabolites similar to those for the WSPMP were identified in whole-fish and fillet samples, but no other compounds were detected, possibly because detection limits were higher in the 1980's.

While the total DDT concentration in fish tissue appears to have remained fairly constant, the percentage of DDT compared to its breakdown products, DDE and DDD, has decreased from an average of 17% in 1984 to 11% in 1989, and 5% in 1992 and 1993. This is an indication that DDT and its metabolites are still entering streams in the Walla Walla Valley, but there are no new sources. DDT, which is extremely persistent, remains in the soil from historical uses, and slowly breaks down into DDE and DDD as it is transported into streams from rain and irrigation runoff.

In a statewide perspective, most of the compounds detected in fish from the Walla Walla River are elevated (Table 5). Nearly all detections were above the statewide median and many were above the 85th percentile. Total chlordane and heptachlor epoxide concentrations in the carp fillets were the highest seen in Washington (Appendix G).

In comparison to California and national values (Appendix G), some levels are still elevated. Heptachlor epoxide concentrations in fillets from the Walla Walla River were higher than the California and the national values. DDE and hexachlorobenzene levels were also high.

Figure 3 compares the concentrations of four pesticides commonly detected in fish between all sites sampled for the WSPMP in 1992 and 1993. Levels of all four pesticides in samples from the Walla Walla River were among the highest found, particularly hexachlorobenzene.

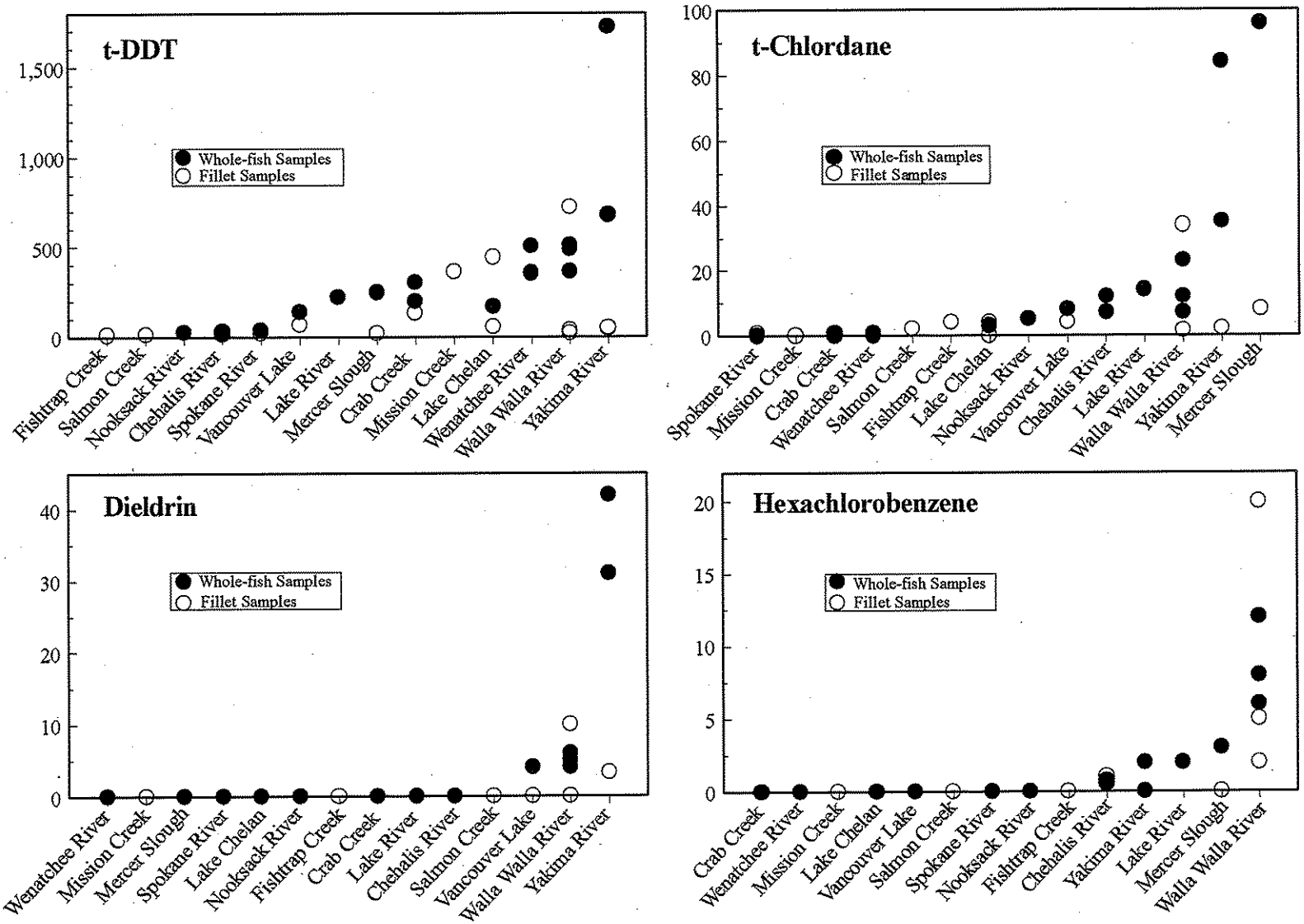

Figure 3. Results for Selected Compounds in Fish Samples Collected for the 1992 and 1993 WSPMP (µg/Kg (ppb) wet weight)

Mission Creek / Wenatchee River

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. Fish were collected above the confluence with Brender Creek, which is near the mouth of Mission Creek. Most of Mission Creek runs through undeveloped land, but the lower section flows directly through several pear and apple orchards, some residential land in the town of Cashmere, and then discharges into the Wenatchee River.

One rainbow trout composite was collected from Mission Creek. No other fish species were seen, so largescale suckers were collected from the Wenatchee River. Two replicate sucker samples were taken from one to two miles upstream of the river's mouth, about six miles downstream from Mission Creek. Land use along the lower Wenatchee River is similar to that of Mission Creek, primarily fruit orchards.

In all three samples, concentrations of DDT and its breakdown products were elevated. However, only two other pesticides were detected. Oxychlordane was identified in one whole-fish sample at a very low concentration and endosulfan sulfate was found in the fillet sample. PCBs were detected in the whole-fish samples, but not in the fillet sample. DDT and PCB concentrations were well above screening values, NTR criteria, and Newell's wildlife guidelines.

Sucker samples were also collected from the lower Wenatchee River for Ecology's 1984 BWMP (Hopkins *et al.*, 1985). Whole-fish samples were not analyzed, but DDT concentrations in edible tissue were similar to those in WSPMP samples. Levels of PCB-1260 were also similar, but no other Aroclors were detected.

DDT contamination in the Wenatchee Valley appears to be similar to that seen in the Walla Walla Valley. While levels of total DDT are remaining constant, the proportion of the parent compound, DDT, has decreased from 17% in 1984 to 9% in 1993. As in the Walla Walla Valley, this indicates that there are no new sources of DDT, but contamination from historical use is an ongoing problem.

Endosulfan sulfate, the primary breakdown product of endosulfan, was detected at a low concentration in the rainbow trout fillet sample from Mission Creek. At the detected concentration, this compound is not a problem. Endosulfan is used on fruit trees around Mission Creek to control aphids in April. This pesticide generally breaks down quickly in water (five weeks at pH 7), and is rapidly degraded and eliminated in most animals, but the sulfate is more persistent (Seyler *et al.*, 1994). Endosulfan was detected in water samples collected in April of 1993 for the WSPMP, but not in subsequent samples taken in June, August, and October (Davis and Johnson, 1994b). The presence of endosulfan sulfate in fish

tissue over five months after use of its parent compound is a concern that deserves further investigation.

In relation to other state data, total DDT concentrations were well above the state median, but below the 85th percentile. Only total PCBs in whole-fish exceeded the 85th percentile. Levels of DDE were similar or higher than most national values, but lower than California's. Total DDT in samples from Mission Creek and the Wenatchee River is among the highest concentrations detected for the WSPMP in 1992 and 1993 (Figure 3).

Chehalis River

The Chehalis River was sampled at a point just below the confluence with the Skookumchuck River, west of Centralia. This section of the river receives runoff from land that is used primarily for forest practices, including logging and subsequent reforestation, and christmas tree farms. Some land along the river and its tributaries supports various agricultural crops. China Creek receives stormwater drainage from Centralia and discharges into the Skookumchuck River just upstream from its confluence with the Chehalis River. Dillenbaugh Creek is adversely impacted by agricultural and industrial activities near the city of Chehalis (Crawford, 1987; Yake, 1987), and discharges to the Chehalis River just south of the Chehalis airport.

Two composite samples of largescale suckers and one of mountain whitefish were collected.

Low concentrations of ten pesticide compounds were detected in the three samples. Eight of these were DDT, chlordane, or their metabolites. Heptachlor and hexachlorobenzene were the remaining two pesticides. Two Aroclors were also found.

Concentrations of total chlordane and total PCBs in the whitefish fillet sample exceeded screening values and the state 85th percentile. The level of total chlordane was also above the state 95th percentile, but similar to or lower than California and national values.

Only DDE and hexachlorobenzene were found in whole-fish samples collected from the Chehalis River near Porter in 1989 (Hopkins, 1991), but detection limits were substantially higher for some of the undetected compounds than WSPMP detection limits.

Fishtrap Creek / Nooksack River

Fishtrap Creek originates in Canada, flows through dairy farms, 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 detected five pesticides in well water samples (Erickson and Norton, 1990). Five different pesticides were detected in surface

water samples collected from Fishtrap Creek for the 1992 WSPMP Reconnaissance Survey (Davis, 1993), and seven pesticides were identified in water samples collected for the 1993 WSPMP (Davis and Johnson, 1994a).

Using a backpack electroshocker, the only fish species that was found in Fishtrap Creek was rainbow trout. To collect largescale suckers, it was necessary to move into the Nooksack River. Sucker collection took place from about one mile downstream of the mouth of Fishtrap Creek to the town of Ferndale. Land use along this reach is similar to that along Fishtrap Creek.

A total of nine pesticide compounds were detected in the two fish species collected, and concentrations were low in both. No screening values, NTR criteria, or wildlife criteria were exceeded for either sample.

Total chlordane, heptachlor epoxide, and hexachlorobenzene concentrations were at or slightly above the state 85th percentiles. Detected levels were all low, but were elevated above other state values which were predominantly nondetects. Detections by the WSPMP may simply be the result of improved detection limits.

Salmon Creek / Vancouver Lake

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. The creek drains into the Lake River about one mile downstream from the river's headwaters at Vancouver Lake.

The only fish that was captured in the creek was largemouth bass. These were collected with an electroshocking boat in about a one mile segment near the creek's mouth. Electroshocking was also tried in the Lake River near the creek, but no fish were caught. To supplement the sample from Salmon Creek, carp and largemouth bass were collected from Vancouver Lake. Both of these species appeared to be extremely abundant in the lake, but no other fish species was found. Vancouver Lake is approximately two miles from the mouth of Salmon Creek, and receives water from similar land use as that along Salmon Creek.

Nine pesticides and two Aroclors were detected in the three samples. Eight of the nine were DDT, chlordane, or their breakdown products. A low concentration of dieldrin, detected only in the carp sample, was the ninth pesticide. Only four pesticides were found in the sample from Salmon Creek; none exceeded criteria. In samples from Vancouver Lake, DDT and PCBs were above screening values and NTR criteria, and PCBs exceeded wildlife criteria

proposed by Newell *et al.* (1987). Only total chlordane in the fillet sample from Vancouver Lake equaled the state 85th percentile.

Thirteen pesticides and two PCBs were identified in whole-fish largescale sucker samples collected from the Lake River in 1992 (Davis and Johnson, 1994a). Eleven of the pesticides were DDT, chlordane, or their metabolites. Hexachlorobenzene and pentachloroanisole were the other two compounds identified in 1992. Concentrations of DDT, chlordane, and PCBs were similar to those found in Vancouver Lake.

Spokane River

Fish from the Spokane River were collected in August of 1993 as a part of the Spokane River PCB reconnaissance survey conducted by the Department of Ecology (Johnson *et al.*, 1994). Samples of rainbow trout and largescale suckers were collected from the river above the Upriver Dam to Myrtle Point. Homogenized tissue from each composite was split into two samples; one was analyzed for the PCB survey and the other was submitted with samples for the WSPMP. Fish collection and processing procedures were the same for both surveys.

The only pesticides detected were DDE and trans-nonachlor, and these were found at low concentrations. Neither exceeded screening values or wildlife criteria. PCB concentrations in trout and suckers were extremely high in both portions of the split samples. The results from the PCB reconnaissance prompted an intensive survey of the Spokane River, performed in August of 1994 by Ecology, to assess the risk to human health and aquatic wildlife from PCB contamination, and to identify possible sources (Ecology, 1995).

Ecological Assessment

Fish

Most of the organochlorine compounds detected in fish tissue are no longer used, and so are unlikely to be found in the water column in concentrations that are acutely toxic to fish or invertebrates. However, many of these compounds bioaccumulate in fatty tissues of aquatic animals even when the concentrations in the water column are very low. Therefore, the body burden of fish can increase over its lifetime, and the older and larger fish may contain the highest concentrations of contaminants (USEPA, 1993).

Adult fish can generally tolerate fairly high concentrations of contaminants that have accumulated in their fat. No adverse effects were observed in rainbow trout when concentrations of t-DDT in the fish reached 4150 μg/Kg (parts per billion) and remained between 2000 and 4000 μg/Kg for 16 months (Bridges *et al.*, 1963). Pesticide levels detected in fish tissue by the WSPMP are probably not adversely affecting adult fish.

The fry stages of several species of fish are much more sensitive to pesticide contamination than other stages (Holden, 1973). Contaminants in eggs can lead to death of fry as the yolk-sac is absorbed. Total DDT exceeding 400 μg/Kg in eggs of speckled rainbow and cutthroat trout caused up to 90% mortality in the resulting fry (Cuerrier *et al.*, 1967). There was no relationship found between fry mortality and the level of PCBs in lake trout from the Great Lakes, but hatching success was negatively correlated with PCB concentrations (Mac *et al.*, 1993).

On a lipid weight basis, pesticide concentrations in fish eggs sampled for the 1992 WSPMP were similar to levels identified in tissues from adult fish (Davis and Johnson, 1994a). If this relationship holds for the fish analyzed for this report, some fry mortality may have resulted from total DDT contamination in eggs of largescale suckers and carp from the Walla Walla River, and in largescale suckers from the Wenatchee River. In addition, hatching success may be reduced for fish in the upper Spokane River due to high PCB concentrations.

Piscivorous Wildlife

The wildlife criteria presented in Table 4 are fish flesh criteria developed by Newell *et al.* (1987) for contaminants found in Niagara River fish to protect piscivorous (fish-eating) wildlife. Criteria were calculated from the no-observed-effect level (NOEL) of the most sensitive species tested to prevent non-carcinogenic effects in fish-eating wildlife. In some cases, the lowest-observed-effect level (LOEL) was used and converted to a NOEL using an application or uncertainty factor. Criteria for carcinogenic compounds were also developed, using experimentally derived cancer risks converted to a risk of 1 in 100 ($1x10^{-2}$) to provide a level of protection for wildlife "to ensure that there will be virtually no reduction in a population from toxic-induced cancer". This methodology was recently selected to develop Canadian tissue residue guidelines for protecting wildlife (Environment Canada, 1994-draft).

DDT and PCBs were the only compounds detected at concentrations exceeding the wildlife criteria. Detected pesticides that were not addressed by Newell *et al.* (1987) include DCPA, ethion, endosulfan sulfate, and heptachlor. Criteria for DDT and PCBs were derived from toxicity tests on piscivorous aquatic wildlife. Brown pelicans and mink were found to be the most sensitive test species to DDT and PCBs, respectively (Blus *et al.*, 1972; Platonow and Karstad, 1973). Pelicans and mink are probably representative of the most sensitive piscivorous wildlife in Washington. Criteria for other pesticides identified by the WSPMP were derived from toxicity tests on typical laboratory animals, such as rats, dogs, pigs, and chickens. Detected concentrations of these compounds were substantially lower than the criteria, so if test animals were less sensitive than some species of wildlife, the error would need to be one or two orders of magnitude lower than the calculated criteria.

The risk to piscivorous wildlife found in Washington from pesticides exceeding wildlife criteria is probably not substantial, but some species may be affected. A review of the literature indicates that numerous studies have been performed to investigate the effects of pesticides on piscivorous species that are found in Washington.

Reduced productivity of California brown pelicans was directly attributed to DDE contamination in anchovies, their major food source, which caused severe eggshell thinning (Anderson *et al.*, 1975). Studies on the eggshell thinning of brown pelicans were used to derive the wildlife criterion for DDT and its metabolites, DDE and DDD (Blus *et al.*, 1971, 1972). Using the information from Blus *et al.* (1972), the USEPA (1976) determined that the NOEL for eggs was 2000 μg/Kg, and then used a biomagnification factor of 10 to estimate a dietary NOEL of 200 μg/Kg for pelicans.

Pelicans feeding exclusively on fish from the Walla Walla or the Wenatchee River would probably experience some eggshell thinning and reduced productivity. Although brown pelicans are rare in Washington, white pelicans are often seen along the Columbia River and other waterbodies in eastern Washington. White pelicans are known to nest within the McNary National Wildlife Refuge (Linehan, 1995), which is only a few miles from the Walla Walla River.

Ospreys are large piscivorous birds that are widely distributed throughout many parts of the world and can be found nesting along rivers and lakes in Washington. Their wide distribution has placed them in areas that have been heavily contaminated with a variety of toxic contaminants, including a number of pesticides and PCBs. The effects of some of these contaminants have been well documented.

Osprey populations in Connecticut and New Jersey were heavily impacted by pesticides in the 1950s and 1960s, and began recovering after many of the bioaccumulative chlorinated pesticides were banned in the 1970s (Ames, 1966; Wiemeyer *et al.*, 1975; Spitzer *et al.*, 1978; Steidl *et al.*, 1991). High concentrations of t-DDT, dieldrin, and PCBs were identified in osprey eggs, fish prey species, and adults. Eggshell thinning and reduced hatching success was primarily attributed to t-DDT. Dieldrin has also caused significant eggshell thinning and reproductive failure (Lehner and Egbert, 1969; Ratcliffe, 1970). PCBs can also cause reproductive problems, but were probably not the cause of reduced hatching success in this case because osprey productivity increased as t-DDT declined and PCB contamination remained high (Spitzer *et al.*, 1978).

Significant eggshell thinning occurred in osprey eggs when levels of t-DDT in the eggs exceeded 3000 μg/Kg (Steidl *et al.*, 1991). Concentrations of t-DDT in fish species eaten by these osprey ranged from 290 to 950 μg/Kg. Total DDT levels in fish from the Walla Walla and Wenatchee Rivers fall within this range.

A few pairs of ospreys probably nest within the Walla Walla and Wenatchee River basins (Johnson, 1995). These birds may be experiencing eggshell thinning and reduced hatching success as a result of t-DDT contamination in their food supply. Concentrations of PCBs found in these two rivers are probably not adversely affecting the ospreys. Levels are much lower than those seen in fish eaten by osprey from Connecticut and New Jersey, that apparently did not significantly affect productivity (Wiemeyer *et al.*, 1975).

Bald eagle diets may consist of up to 90% fish (Newell *et al.*, 1987), but they also commonly eat other birds and small mammals, including carrion. Environmental contaminants, including DDE and PCBs, have been implicated in bald eagle population declines throughout the United States (Wiemeyer *et al.*, 1972, 1984). DDE has been linked to significant eggshell thinning, and PCBs may be responsible for reduced productivity. Most populations have increased since the banning of DDT in 1972 (Anthony *et al.*, 1993).

Most bald eagle populations in Washington are healthy, although reproductive success is low for eagles on the Columbia River estuary (McAllister *et al.*, 1986), and eagles along Hood Canal in Puget Sound appear to be having similar problems (Tacoma News Tribune, 1995). Anthony *et al.* (1993) determined that DDE, and possibly PCBs, have had a negative impact on bald eagle reproduction in the Columbia River estuary. Fish collected from this section of the Columbia River contained moderately high concentrations of DDE and PCBs, comparable to those found in fish from the Wenatchee and Walla Walla Rivers by the WSPMP. However, Anthony *et al.* concluded that the majority of contaminants in the bald eagles probably came from other fish-eating birds that the eagles were consuming.

At least one nesting pair of bald eagles has been observed within the Wenatchee River watershed (unpublished data, Washington State Department of Fish and Wildlife). Depending on the diet of these birds, their reproductivity may be adversely impacted by DDE and PCB contamination from consumption of Wenatchee River fish or other resident fish-eating birds.

Mink and river otters are the only piscivorous mammals that might be found in either the Walla Walla or Wenatchee River systems. However, no mink or river otters have been observed by the Washington State Department of Fish and Wildlife in these rivers (unpublished data, WSDFW).

If present, these animals may be experiencing some degree of reproductive impairment due to consumption of PCB-contaminated fish. As indicated above, mink are the most sensitive animals tested for PCB toxicity (Newell *et al.*, 1987). In experiments performed by Platonow and Karstad (1973), mink suffered reproductive failure with PCB concentrations in their diet similar to those in some fish samples from the Walla Walla and Wenatchee Rivers.

DDT and its metabolites probably do not pose a threat to mink or river otters. Mink fed 100,000 μg/Kg DDT and 50,000 μg/Kg DDD showed no adverse effects to reproduction (Aulerich and Ringer, 1970).

Of the piscivorous wildlife that may be found within the Walla Walla or Wenatchee River basins, nesting ospreys are probably the most at risk due to pesticide contamination of fish in the rivers. PCBs in fish from the Spokane River are certainly high enough to affect reproduction in mink and possibly other wildlife. A discussion of PCBs and their effects on piscivorous wildlife associated with the Spokane River are included in Ecology's (1995) report of the intensive survey performed to investigate PCB contamination in the river. Pesticide and PCB concentrations in fish from the other sites sampled for the 1993 WSPMP are probably too low to adversely affect wildlife.

The discussions above generally address only one or two compounds at a time. Very little is known about the effects due to combinations of chemical contaminants, but they may very well be additive or synergistic, resulting in more environmental damage than expected. In addition, there may be other toxic chemicals present that were not analyzed for the WSPMP. Therefore, fish and piscivorous wildlife at the sites investigated may be experiencing problems that would not be anticipated from the information available.

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Appendices

Appendix A. Sample Site Positions

Site Name	Latitude deg	min	sec	Longitude deg	min	sec	State Plane X	Y
Walla Walla River	46	04	19	118	50	52	2419350	273695
Wenatchee River	47	27	35	120	20	19	2122400	168080
Mission Creek	47	30	44	120	28	19	2006970	794559
Chehalis River	46	37	40	123	03	48	1356091	482458
Nooksack River	48	50	40	122	35	18	1577400	677600
Fishtrap Creek	48	54	52	122	31	12	1513911	1312517
Salmon Creek	45	43	22	122	42	22	1436550	149908
Vancouver Lake	45	40	34	122	41	41	1439000	132800
Spokane River	47	41	36	117	14	08	2803848	877316

Fish were collected near the listed sites, but were also generally collected throughout a reach of the stream as long as 3 or 4 miles.

Appendix B. Target Pesticides and PCBs for 1993 WSPMP Fish Tissue Samples

Compound	Quantitation Limits (ug/Kg, ppb)	Compound	Quantitation Limits (ug/Kg, ppb)
DDT and Analogues		**Benzene Hexachloride**	
4,4'-DDT	10	alpha BHC	5
4,4'-DDE[1]	10	beta BHC	10
4,4'-DDD[2]	15	delta BHC	5
4,4'-DDMU[1]	15	gamma BHC (Lindane)	5
2,4'-DDT	10		
2,4'-DDE[1]	10	**Organophosphates**	
2,4'-DDD[1]	15	diazinon	250
dichlorobenzophenone[1]	70	chlorpyrifos	15
dicofol	65	ethion	35
methoxychlor	30	ethyl parathion	45
		methylparathion	25
Cyclodienes			
aldrin	5	**Phenol**	
dieldrin	15	pentachloroanisole[3]	5
endrin	10		
endrin aldehyde[1]	25	**Misc. Chlorinated Pesticides**	
endrin ketone[1]	120	DCPA (Dacthal)	15
endosulfan I	15	oxadiazon	15
endosulfan II	65	tetradifon	25
endosulfan sulfate[1]	110	hexachlorobenzene	2
cis-chlordane	5	mirex	30
trans-chlordane	5	toxaphene	120
cis-chlordene	5		
trans-chlordene	5	**PCBs**	
cis-nonachlor	10	PCB-1016	60
trans-nonachlor	5	PCB-1221	60
oxychlordane[1]	5	PCB-1232	60
heptachlor	5	PCB-1242	60
heptachlor epoxide[1]	5	PCB-1248	60
		PCB-1254	60
		PCB-1260	60

[1] - Breakdown products

[2] - Insecticide and DDT breakdown product

[3] - Metabolite of pentachlorophenol

Appendix C. Length and Weight Data for the 1993 WSPMP

Location and Species	Collection Date (1993)	Mean Length (mm)	Length Range (mm)	Mean Weight (grams)	Weight Range (grams)	Tissue Type
Walla Walla River	9/14					
largescale sucker (Rep-1)		475	460-493	1065	984-1175	whole
largescale sucker (Rep-2)		495	425-580	1253	930-1880	whole
largescale sucker (Rep-3)		517	485-540	1365	1120-1440	whole
steelhead		702	680-740	2954	2575-3378	fillet
carp		585	525-680	2718	1750-4246	fillet
Wenatchee River	9/13					
largescale sucker (Rep-1)		468	410-507	899	630-1122	whole
largescale sucker (Rep-2)		466	398-545	830	543-1315	whole
Mission Creek						
rainbow trout		241	210-263	179	113-230	fillet
Chehalis River	9/16					
largescale sucker (Rep-1)		426	404-447	778	603-899	whole
largescale sucker (Rep-2)		433	405-460	766	580-882	whole
mountain whitefish		271	242-317	200	140-334	fillet
Nooksack River	9/9					
largescale sucker		443	380-488	865	530-1064	whole
Fishtrap Creek						
rainbow trout		261	209-335	218	113-392	fillet
Salmon Creek	9/7					
largemouth bass		244	209-275	250	169-333	fillet
Vancouver Lake						
largemouth bass		353	286-415	846	452-1319	fillet
carp		469	426-510	1556	1141-2013	whole
Spokane River						
largescale sucker	7/27	434	406-505	837	637-1367	whole
rainbow trout		363	333-386	481	374-541	fillet

Common Name	Scientific Name	Common Name	Scientific Name
largescale sucker	*Catostomus macrocheilus*	steelhead trout	*Oncorhynchus mykiss*
carp	*Cyprinus carpio*	rainbow trout	*Oncorhynchus mykiss*
mountain whitefish	*Prosopium williamsoni*	largemouth bass	*Micropterus salmoides*

Appendix D. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1993

All of the target analytes for the WSPMP were selected because they tend to accumulate in animal tissues. These compounds are lipophilic, i.e. they are chemically attracted to lipids (fats). Once accumulated, these chemicals are either metabolized or excreted by the animal, but the rate can be very different for each compound depending on a variety of factors.

Chlorinated Hydrocarbon Insecticides

All chlorinated hydrocarbon insecticides have a cyclic structure and their molecular weight ranges from about 285 to 545 (Smith, 1991). Most can be divided into five groups: DDT and its analogs, cyclodienes, benzene hexachloride (BHC), toxaphene, and mirex. Thirty-three of the 43 target pesticides are in one of these five groups. These compounds are grouped by structural similarity, but even small differences in structure can result in dramatic differences in toxicity and persistence.

Dicofol, endosulfan, and methoxychlor are currently registered for use in Washington. Dicofol and endosulfan are used primarily as acaricides to control aphids and mites on a variety crops and ornamental plants. Methoxychlor is used on a variety of crops, and is used to control flies and mosquitoes in areas of human habitation (USEPA, 1992).

DDD, DDE, and DDMU are metabolites of DDT. DDD was also marketed as a pesticide (Rhothane). Dicofol and methoxychlor occur as contaminants in commercial formulations of DDT, but have also been used as insecticides. Both are much less toxic and persistent than DDT (Smith, 1991). Dicofol products are often contaminated with DDT and/or PCBs. Dichlorobenzophenone is a metabolite in animals exposed to DDT (Matsumura, 1985).

Cyclodiene pesticides include chlordane, heptachlor, aldrin, dieldrin, endrin, and endosulfan. The structure of this group is characterized by an endomethylene bridge (FCH, 1991). Chlordane has two main isomers, cis- and trans-. Oxychlordane is the major breakdown product of chlordane. The two isomers of nonachlor are found as contaminants of technical chlordane. Heptachlor is more likely to be found as its major breakdown product, heptachlor epoxide. Dieldrin is the metabolite of aldrin, but was also marketed as an insecticide. Endrin is the stereoisomer of dieldrin. Dieldrin is less toxic than endrin, but much more persistent (Smith, 1991). Endosulfan is a mixture of two stereoisomers, I and II. Endosulfan breaks down fairly quickly to endosulfan sulfate, which is more persistent than the parent chemical (Seyler *et al.*, 1994).

Limited use of chlordane is allowed with the requirement that all applications must be done by a licensed applicator (USEPA, 1992). All uses of dieldrin have been voluntarily cancelled by industry. Registration of all endrin products was cancelled in 1984. All uses of heptachlor, except ground insertion for termite control and dipping of roots or tops of nonfood plants, were banned by 1983.

Appendix D. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1993

Benzene hexachloride (BHC) is more properly called hexachlorocyclohexane (HCH), but both are recognized as common names and BHC is used more frequently in the United States (Smith, 1991). BHC has eight isomers, six of which are stable and commonly identified. Four of these are included on the WSPMP target list: alpha, beta, gamma, and delta. The gamma isomer (lindane) was used most extensively as a pesticide and is classified as a probable human carcinogen. Lindane is a restricted use pesticide and application is permitted only under supervision of a certified applicator (USEPA, 1992).

Toxaphene is a complex mixture of as many as 177 compounds; however, only three of the compounds account for most of the toxicity (Smith, 1991). Toxaphene has been classified as a probable human carcinogen, but it is easily metabolized and is not stored to any great extent in tissues (USEPA, 1993). Toxaphene's registration was canceled for most uses in 1982.

Mirex is sometimes referred to as a caged structure. This compound is similar in structure to the cyclodiene insecticides, but does not cause sudden seizures and is very slowly broken down, resulting in bioaccumulation similar to DDT (Smith, 1991). Mirex has been classified as a probable human carcinogen (USEPA, 1993). All registered uses of mirex were cancelled in 1977 (USEPA, 1992).

Organophosphorous Insecticides

Organophosphorous (OP) insecticides are acetylcholinesterase (an enzyme that regulates nerve transmissions) inhibitors, and are generally more toxic than chlorinated insecticides, but usually breakdown much more quickly. Animals that do not receive a fatal dose can typically quickly metabolize OP pesticides and recover completely. Some OPs have the potential to accumulate in tissue, but not to the extent of most chlorinated insecticides.

Five OP pesticides; chlorpyrifos, diazinon, ethion, ethyl parathion, and methyl parathion; are included on the WSPMP target analyte list. All of these compounds are presently registered for use in Washington. Ethion is the only OP insecticide detected in 1993 WSPMP tissue samples. Chlorpyrifos (Dursban, Lorsban) was detected in fish tissue collected in 1992 (Davis and Johnson, 1994a).

Miscellaneous Pesticides

DCPA (Dacthal) is a pre-emergence herbicide that has low toxicity to most animals, but is relatively persistent and accumulates in some tissues (Rasmussen and Blethrow, 1991). DCPA is currently used throughout Washington and has been detected numerous times in surface and ground water samples (Davis and Johnson, 1994; Larson, 1993; Larson and Erickson, 1993).

Appendix D. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1993

Hexachlorobenzene (HCB) is a fungicide that was widely used as a seed protectant until it was banned in 1985 (USEPA, 1993). HCB has low toxicity, but can bioaccumulate to high concentrations and is a known animal carcinogen.

Pentachlorophenol (PCP) has been used on a restricted basis since 1986, primarily as a wood preservative with insecticidal, fungicidal, herbicidal, molluscicidal, and anti-microbial actions (Newell *et al.*, 1987). PCP is extremely toxic to most animals and plants, but is usually not found at concentrations that are lethal (Seyler *et al.*, 1994). PCP is quickly metabolized by animals, but the primary metabolite, pentachloroanisole, is persistent and has a high potential for bioaccumulation (USEPA, 1992). Information on the toxicity of pentachloroanisole is lacking (Newell *et al.*, 1987). Pentachloroanisole was identified in several tissue samples from the 1992 WSPMP, but was not found in 1993.

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are not pesticides, but are typically analyzed for using the same method as chlorinated pesticides and so are usually included in studies monitoring for pesticides. In addition, PCBs are similar to chlorinated pesticides in their chemical and physical properties, and toxicity (USEPA, 1993). There are 209 different PCB compounds (congeners). Mixtures of these congeners were formulated for commercial use under the trade name Aroclor. Different Aroclors were named based on their chlorine content; for example, Aroclor 1260 (PCB-1260) has an average chlorine content of 60%. The first two digits indicate the number of carbon atoms in the parent molecule (except PCB-1016, which was named by the manufacturer).

PCBs were used in a number of applications, primarily as thermal stabilizers in lubricants, hydraulic fluids, and insulating fluids for transformers and capacitors. Although all uses of PCBs in the United States were banned in 1979, there are still many transformers and capacitors in use that contain PCBs.

PCBs are extremely persistent and readily bioaccumulate in fatty tissues. PCBs produce a variety of adverse biological effects in animals including hepatotoxicity, developmental toxicity, immunotoxicity, neurotoxicity, and carcinogenicity (USEPA, 1993). The toxicity of PCBs to humans is poorly understood and is still being investigated.

Appendix E. Sample Collection and Processing Procedures

Sample Collection

Electroshocking equipment and/or gill nets were used to collect fish. When possible, each fish for a composite was taken from a different location within the specified sampling area (space-bulking). This should result in a sample that is more representative of a water body than a sample of fish all taken from the same location. The position of each sampling site was recorded using a Magellan® global positioning system (GPS). As fish were collected, they were placed in clean stainless steel buckets until they could be processed.

Field Processing of Fish Tissue Samples

After collection, all fish samples were rinsed with native water, measured for total length, and weighed. A portable battery powered scale was used to weigh the fish to the nearest gram. Scale samples were taken from sport fish for age determinations, but these samples have not been analyzed.

Fish samples were preserved on ice and transported to the laboratory whole. Each fish was wrapped in aluminum foil with the dull side in contact with the specimen. All specimens forming a composite were placed in a separate polyethylene bag.

Laboratory Processing of Fish Tissue Samples

Fish collected for whole body analysis were cut into chunks small enough to be put through a Hobart® commercial meat grinder. The sex of each fish was recorded during processing. Subsamples of the homogenized whole fish samples were transferred to appropriate containers and refrozen.

Fish collected for muscle tissue (fillets) were processed in the laboratory using the following procedure:

- Clean area of fish to be resected with a cloth.
- Cut a patch through the skin larger than the section of muscle to be taken as the sample.
- Remove skin from the patch.
- Remove a section of muscle from within the skinned area smaller than the original cut.
- Place tissue in an appropriate container.
- Open body cavity to determine sex.
- Repeat process for all specimens to be included in the composite.
- Homogenize tissue and refreeze to -20° C.

Appendix E (cont.). Sample Collection and Processing Procedures

Decontamination Procedures

Fish tissue samples destined for pesticide analysis were stored in glass jars with teflon-lined lids. These containers were precleaned by Eagle-Picher Environmental Services, Miami, Oklahoma using the following process:

- washed in laboratory grade detergent,
- rinsed three times with distilled water,
- rinsed with 1:1 nitric acid,
- rinsed three times with organic-free water,
- oven-dried for one hour,
- rinsed with hexane,
- and oven-dried again for one hour.

Sampling equipment, homogenization equipment and utensils, and resection instruments were stainless steel or glass and were precleaned using the following procedure:

- washed with laboratory grade detergent (Alconox®),
- rinsed with tap water,
- rinsed with deionized water,
- rinsed with pesticide grade acetone, and
- allowed to air dry.

A similar decontamination procedure was used in the field for sampling equipment after each fish composite. Sampling equipment was rinsed with site water before use.

Appendix F. Analytical Methods - QA/QC - Data Review

Analytical Methods

Fish tissue samples were analyzed by the California Department of Fish and Game, Water Pollution Control Laboratory using a method developed by that laboratory. A detailed explanation of the analytical procedure can be found in Rasmussen and Blethrow (1991). Briefly, the tissue is extracted with acetonitrile and the extract is partitioned with petroleum ether and water. The petroleum ether extract is then eluted through a Florisil column in four fractions; fraction one is eluted with petroleum ether, fraction two is eluted with 6% ethyl ether, fraction three is eluted with 15% ethyl ether, and the fourth fraction is eluted with 50% ethyl ether.

Each fraction was analyzed separately with a gas chromatograph using an electron capture detector. A 5 meter J&W DB5 fused silica pre-column was connected to the injector, and the effluent from the pre-column was split into 60 meter J&W DB5 and 60 meter J&W DB17 columns. Pesticide detections in the sample extracts were confirmed with a gas chromatograph/mass spectrometer (GC/MS) using an ion trap detector.

Quality Assurance/Quality Control

Field Quality Control Procedures

Field replicate samples were taken to estimate overall precision and to assess environmental variability. Three replicate largescale sucker samples were collected from the Walla Walla River and two replicate samples were collected from the Wenatchee and Chehalis Rivers.

Duplicate tissue samples (splits) were submitted to evaluate analytical precision. Duplicate samples of largescale suckers, carp, and steelhead were analyzed from the Walla Walla River. Largescale sucker tissue was also analyzed in duplicate from the Wenatchee River.

Fish tissue quality control check material was submitted in duplicate to estimate analytical accuracy and precision.

Laboratory Quality Control Procedures

A portion of one largescale sucker replicate from the Walla Walla River was used for matrix spike and matrix spike duplicate analyses to detect bias due to interferences from the sample matrix. Surrogate standards were added to each sample prior to extraction to evaluate the efficiency of the extractions. Matrix and surrogate spikes performed by the laboratory also provide estimates of accuracy and precision.

Data Review

Fish tissue analysis data packages and quality control results were reviewed and assessed by Karin Feddersen and Stuart Magoon of Ecology's Manchester Environmental Laboratory. No significant problems were encountered for the fish tissue analyses. Minor difficulties required qualification of affected data. All data were considered acceptable as qualified.

The DDT metabolite, 4,4'-DDE, was detected in the method blank at a level less than ten times the concentration found in any of the tissue samples; no qualification of the data was required. Chlorbenside was not recovered from the matrix spikes and so was reported as not analyzed. Detections of dieldrin below 200 μg/Kg could not be confirmed by GC/MS, due to coelution of dieldrin and lipids, and fragmentation of dieldrin.

Detection Limits

The detection limits achieved for fish tissue analyses were a significant improvement over past studies. The values in Appendix C are quantitation limits, which are often different for each sample. Detection limits were not calculated separately, but were generally substantially lower than quantitation limits. In this study, many pesticides were detected below quantitation limits. In most instances, the level of detection was sufficiently low to compare with even the lowest criteria.

Quality Control Samples

No accuracy or precision criteria have been established for any of the analytical methods used, but duplicate quality control check material and matrix and surrogate spike analyses provide estimates of accuracy and precision. Recoveries near 100% indicate good accuracy and low relative percent difference (RPD) values indicate high precision between duplicate analyses.

Fish tissue quality control check material samples were submitted to the laboratory in duplicate. The check material was composed of frozen lake trout from Lake Michigan, obtained from the U.S. Fish and Wildlife Service in Ann Arbor, Michigan. This is not certified reference material, but the USFWS has been analyzing it since 1985 for their studies and have compiled considerable data to establish the expected values.

Appendix H compares check material results to expected values. RPD values between the means of the duplicate analyses and the expected values were better than 40 for all compounds except 4,4'-DDD, which was 76. The average RPD was 21. This same material (essentially a split sample) was analyzed by Ecology's Manchester Laboratory as a part of the 1992 WSPMP fish tissue survey. Their results were similar, with an average RPD of 27. These results suggest good analytical accuracy.

Appendix F (cont.). Analytical Methods - QA/QC - Data Review

Matrix spike and duplicate recoveries and corresponding RPDs are presented in Appendix I. Spiking levels were 3-5 times the quantitation limit for most of the target compounds. Recoveries ranged from 42-150% and averaged 85%, indicating good accuracy. The recoveries for heptachlor (50 and 47%) and methyl parathion (45 and 42%) were the only values below 50%. RPD values averaged 8, indicating that precision was also good.

Surrogate spike recoveries are presented in Appendix J. Recoveries for 4,4'-dibromooctafluorobiphenyl (DBOB) ranged from 52-100% and averaged 70%. Decachlorobiphenyl (DCB) recoveries ranged from 91-151% and averaged 110%. Recoveries of dibutylchlorendate (DBC) ranged from 78-160% with an average of 100%. Surrogate recoveries for the method blank were high (100-200%) and may have been spiked twice; these values were not included in the calculation of average recoveries. With the exception of the method blank, these values are all acceptable.

Results from duplicate analyses (splits) are presented in Appendix K. Four sets of duplicate samples were analyzed, in addition to the matrix spike and duplicate, and the quality control check sample that was analyzed in duplicate. RPDs ranged from 0-67 with an overall average for the four samples of 16. However, the average probably has a bias to the low side because the calculation did not include compounds that were detected in only one of the duplicate samples. Out of 53 detected compounds in the four sets of samples, 10 (19%) were identified in only one of the duplicate samples. All compounds detected in only one sample of a duplicate pair were identified at concentrations below the quantitation limits; therefore, all compounds detected above the quantitation limits were found in both samples and generally at similar concentrations. These results indicate good precision.

Replicate samples were collected to evaluate environmental variability between samples from the same site. Differences between replicate samples were generally small (Appendix L), but were often larger than differences between duplicate analyses. Over 40% of the detected compounds were found in only one of the replicates, but again these compounds were detected below the quantitation limits. Since some of the differences between replicates can be attributed to analytical variability, the relatively small differences observed between replicates indicate that environmental variability is probably low.

In 1992, fish tissue for the WSPMP was analyzed by Ecology's Manchester Environmental Laboratory. Prior to sending the 1993 WSPMP tissue samples to the California Laboratory, a split of a WSPMP sample collected (and frozen) in 1992, that had been analyzed by the Manchester Laboratory, was submitted to the California Laboratory to assess possible differences between the analytical methods used by the two labs. Appendix M compares the results from the two laboratories. Other than two compounds that were detected by the California Lab, but not by the Manchester Lab, identified compounds and concentrations were remarkably similar.

Appendix G. Comparison of Detected Concentrations of Selected Compounds to State-Wide, California, and EPA and USFWS National Results (μg/Kg (ppb) wet weight)

	DDE	t-chlordane	dieldrin	HCB	lindane	heptachlor epoxide	t-PCBs
Whole-Fish							
Walla Walla River	330	13	4	**8**	**1**	2	119
Wenatchee River	343	1	u	u	u	u	**347**
Chehalis River	21	10	u	**0.6**	u	u	85
Nooksack River	19	5	u	u	**1**	u	u
Vancouver Lake	95	8	4	u	u	u	**280**
Spokane River	39	u	u	u	u	u	**1230**
State Mean	301	11	16	1.6	0.7	1.9	103
State Median	91	u	1.9	u	u	u	u
State 85th Percentile	650	21	40	u	0.3	3.5	225
State 95th Percentile	1420	60	80	10	1	10	535
State Maximum	2515	96	100	36	20	20	1600
California[1] 85th Percentile	2428	181	220	7.9	3.9	9.2	294
California 95th Percentile	4270	257	586	11.5	9.3	16.1	572
Fillets							
Walla Walla River	**600**	**34**	**10**	**19**	**1**	**8.2**	**300**
Walla Walla River	15	6.5	4	**4.8**	**1**	**4**	u
Mission Creek	270	u	u	u	u	u	u
Chehalis River	23	**12**	u	**1**	u	u	**143**
Fishtrap Creek	7	4	u	u	u	**1**	u
Salmon Creek	11	2	u	u	u	u	u
Vancouver Lake	47	4	u	u	u	u	110
Spokane River	18	1	u	u	u	u	**720**
State Mean	266	2.2	3.9	0.9	0.1	0.6	67
State Median	39	u	u	u	u	u	u
State 85th Percentile	500	4	10	1	u	u	120
State 95th Percentile	1709	8.3	20	2.1	1	4	330
State Maximum	2406	34	50	20	1.3	8.2	720
California 85th Percentile	690	43.2	11.6	u	u	u	140
California 95th Percentile	2000	115.3	37.2	6.3	3.6	u	397
National Values							
EPA[2] National Mean	295		28.1	5.8	2.7	2.2	1898
EPA National Median	58.3		4.2	u	u	u	209
EPA Background Mean	56.3	5.2	14.3	0.6	0.15	1.6	46.9
EPA Background Median	11.7	u	u	u	u	u	u
EPA Indust./Urban Mean	602	32.8	18.5	31.6	2	1.3	1278
EPA Indust./Urban Median	78.8	11.3	10	0.4	0.3	u	213
EPA Agricultural Mean	1527	17.2	43.9	2.1	1.2	0.6	97.4
EPA Agricultural Median	201	7.9	u	u	0.1	u	8.6
USFWS[3] National Mean	190	110	40	u	u		390

Values in bold exceed the 85th percentile

[1] - Rasmussen and Blethrow, 1991

[2] - USEPA, 1992

[3] - Schmitt et al., 1990

Appendix H. Comparison of Fish Tissue Quality Control Check Material to Expected Values (μg/Kg (ppb) wet weight)

Analyte	Mean Concentration (± ½ duplicate range)	Expected Value	RPD[1]
4,4'-DDE	495 ±5	495	0
4,4'-DDD	145 ±5	65	76
4,4'-DDT	29 ±2	31	7
dieldrin	200 ±0	152	27
heptachlor epoxide	33 ±1	37	11
cis-chlordane	62 ±6	82	28
trans-chlordane	48 ±2	45	6
cis-nonachlor	61 ±1	45	30
trans-nonachlor	140 ±0	94	39
oxychlordane	25 ±0	28	11
total chlordane	335 ±5	294	13
total PCBs	1340 ±0	1333	1

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

Appendix I. Matix Spike Recoveries (%)

Analyte	Matrix Spike	Matrix Spike Duplicate	RPD[1]
2,4'-DDD	90	100	11
4,4'-DDD	100	120	18
2,4'-DDE	73	86	16
4,4'-DDE	*	*	
4,4'-DDMU	86	100	15
2,4'-DDT	80	93	15
4,4'-DDT	100	110	10
aldrin	59	64	8
chlorbenside	0	0	0
cis-chlordane	85	86	1
trans-chlordane	86	84	2
oxychlordane	79	75	5
cis-nonachlor	98	104	6
trans-nonachlor	80	96	18
alpha chlordene	62	67	8
gamma chlordene	64	68	6
chlorpyrifos	78	76	3
dicofol	93	97	4
dichlorobenzophenone	130	150	14
DCPA (dacthal)	110	120	9
diazinon	50	66	28
dieldrin	106	120	12
endosulfan I	90	99	10
endosulfan II	89	94	5
endosulfan sulfate	92	99	7
endrin	84	95	12
ethion	98	100	2
alpha BHC	72	71	1
beta BHC	66	71	7
gamma BHC	76	82	8
delta BHC	58	57	2
heptachlor	50	47	6
heptachlor epoxide	95	100	5
hexachlorobenzene	81	91	12
methoxychlor	96	100	4
oxadiazon	95	98	3
ethyl parathion	65	73	12
methyl parathion	45	42	7
tetradifon	96	97	1
toxaphene	not spiked	not spiked	
mirex	78	94	19
pentachloroanisole	62	64	3
endrin aldehyde	62	66	6
endrin ketone	99	100	1

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

* Spike insignificant compared to concentration in tissue

Appendix J. Surrogate Spike Recoveries (%)

Sample Site	Sample Type	Surrogates DBOB	DCB	DBC
Walla Walla River	WF LSS Rep-1	64	100	78
	Rep-1 Duplicate	97	150	160
	WF LSS Rep-2	72	120	93
	WF LSS Rep-3	77	120	90
	Carp Fillet	100	150	120
	Duplicate	74	120	120
	Stlhd Fillet	60	91	86
	Duplicate	60	92	93
Wenatchee River	WF LSS Rep-1	59	95	92
	Duplicate	74	110	86
	WF LSS Rep-2	52	97	88
Mission Creek	RBT Fillet	71	120	85
Spokane River	WF LSS	65	100	97
	RBT Fillet	82	130	95
Chehalis River	WF LSS Rep-1	69	100	110
	WF LSS Rep-2	67	110	80
	MWF Fillet	88	140	110
Fishtrap Creek	RBT Fillet	66	100	95
Nooksack River	WF LSS	74	110	110
Salmon Creek	LMB Fillet	67	99	99
Vancouver Lake	LMB Fillet	67	96	100
	WF Carp	82	120	95
QC Check Material	WF Lake Trout	62	99	100
	Duplicate	63	100	100
Matrix Spike	WF LSS	53	90	110
Matrix Spike Duplicate		56	100	113
Method Blank		100	130	200

Sample type key WF = Whole Fish
LSS = Largescale Sucker
Stlhd = Steelhead
RBT = Rainbow Trout
MWF = Mountain Whitefish
LMB = Largemouth Bass

Surrogate key DBOB = 4,4'-dibromooctafluorobiphenyl
DCB = decachlorobiphenyl
DBC = dibutylchlorendate

Appendix K. Duplicate Analysis Results (μg/Kg (ppb) wet weight)

Analyte	Sample 1	Sample 2	RPD[1]
Walla Walla River			
largescale sucker			
4,4'-DDE	280	330	18
4,4'-DDD	38	48	23
4,4'-DDT	11	15	31
4,4'-DDMU	ND[2]	8	NC[3]
cis-chlordane	3	3	0
trans-chlordane	2	2	0
oxychlordane	0.6	ND	NC
cis-nonachlor	2	2	0
trans-nonachlor	5	4	22
dieldrin	3	5	57
lindane	ND	1	NC
hexachlorobenzene	5.2	7.1	31
PCB-1260	96	130	30
carp			
4,4'-DDE	620	580	7
2,4'-DDD	10	9.6	4
4,4'-DDD	99	95	4
4,4'-DDMU	16	14	13
cis-chlordane	8	7	13
trans-chlordane	9.3	7.7	19
oxychlordane	ND	1	NC
cis-nonachlor	5	4	22
trans-nonachlor	15	11	31
dieldrin	10	10	0
ethion	3	ND	NC
lindane	1	1	0
heptachlor epoxide	8.7	7.7	12
hexachlorobenzene	21	18	15
PCB-1260	340	260	27

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

Appendix K (cont.). Duplicate Analysis Results (μg/Kg (ppb) wet weight)

Analyte	Sample 1	Sample 2	RPD[1]
Walla Walla River (cont.)			
steelhead			
4,4'-DDE	15	14	7
2,4'-DDD	ND[2]	1	NC[3]
4,4'-DDD	15	15	0
2,4'-DDT	ND	1	NC
4,4'-DDT	4	4	0
cis-chlordane	2	2	0
trans-chlordane	1	1	0
oxychlordane	ND	1	NC
cis-nonachlor	ND	1	NC
trans-nonachlor	3	2	40
DCPA (dacthal)	4	5	22
dieldrin	4	4	0
lindane	1	ND	NC
heptachlor epoxide	4	4	0
hexachlorobenzene	4.5	5.1	13
Wenatchee River			
largescale sucker			
2,4'-DDE	1	2	67
4,4'-DDE	380	380	0
2,4'-DDD	8	8	0
4,4'-DDD	66	69	4
2,4'-DDT	3	4	29
4,4'-DDT	28	36	25
4,4'-DDMU	12	16	29
PCB-1248	150	190	24
PCB-1254	220	280	24
PCB-1260	40	56	33

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

Appendix L. Comparisons between Results from Analysis of Replicate Samples (µg/Kg (ppb) wet weight)

Analyte	Replicate 1	Replicate 2	Replicate 3	Coefficient of Variation[1] (%)
Walla Walla River				
largescale sucker				
4,4'-DDE	280	390	320	17
2,4'-DDD	ND[2]	8	5	33
4,4'-DDD	38	63	40	30
2,4'-DDT	ND	1	ND	NC[3]
4,4'-DDT	11	14	17	21
4,4'-DDMU	ND	10	6	35
cis-chlordane	3	4	2	33
trans-chlordane	2	4	2	43
oxychlordane	0.6	1	1	27
cis-nonachlor	2	3	2	25
trans-nonachlor	5	7.8	ND	31
dieldrin	3	5.6	4	31
ethion	ND	3	ND	NC
lindane	ND	1	ND	NC
heptachlor epoxide	ND	4	3	20
hexachlorobenzene	5.2	12	8.3	40
PCB-1260	96	ND	130	21
Wenatchee River	Rep-1	Rep-2	RPD[4]	
largescale sucker				
2,4'-DDE	1	ND	NC	
4,4'-DDE	380	270	34	
2,4'-DDD	8	ND	NC	
4,4'-DDD	66	47	34	
2,4'-DDT	3	ND	NC	
4,4'-DDT	28	26	7	
4,4'-DDMU	12	12	0	
oxychlordane	ND	1	NC	
PCB-1248	150	ND	NC	
PCB-1254	220	55	120	
PCB-1260	40	49	20	

[1] Coefficient of Variation = (standard deviation/mean) x 100, nondetects not used in calculation
[2] ND = Not Detected
[3] NC = Not Calculated
[4] RPD = Relative Percent Difference, (difference/mean) x 100

Appendix L (cont.). Comparisons between Results from Analysis of Replicate Samples (μg/Kg (ppb) wet weight)

Analyte	Replicate 1	Replicate 2	RPD[1]
Chehalis River			
largescale sucker			
4,4'-DDE	14	27	63
4,4'-DDD	ND[2]	3	NC[3]
cis-chlordane	2	3	40
trans-chlordane	2	2	0
oxychlordane	ND	1	NC
cis-nonachlor	ND	1	NC
trans-nonachlor	3	5	50
hexachlorobenzene	0.5	0.7	33
PCB-1254	45	55	20
PCB-1260	35	34	3

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

Appendix M. Interlaboratory Comparison Results (μg/Kg (ppb) wet weight)

Analyte	Manchester Lab	California Lab[1]	RPD[2]
2,4'-DDD	7.0	7.4	6
4,4'-DDD	51	62	19
2,4'-DDE	2.9	2.8	4
4,4'-DDE	425	405	5
2,4'-DDT	ND[3]	2.0	NC[4]
4,4'-DDT	26	27	2
alpha-BHC	0.5	0.4	22
gamma-BHC	7.9	5.8	31
cis-chlordane	4.6	3.6	26
trans-chlordane	4.9	4.1	19
cis-nonachlor	1.9	2.5	25
trans-nonachlor	10	7.0	36
dieldrin	5	4.8	5
heptachlor epoxide	8.3	8.2	2
hexachlorobenzene	6.9	6.1	12
oxychlordane	2.0	1.7	19
toxaphene	ND	160	NC
PCB-1254	48	47	3
PCB-1260	90	91	1

[1] Values are the mean of duplicate analyses
[2] RPD = Relative Percent Difference, (difference/mean) x 100
[3] ND = Not Detected
[4] NC = Not Calculated

Appendix N. Pesticides and PCBs Detected in 1992 Fish Tissue Samples (µg/Kg (ppb) wet weight)

Sample Site	Lake Chelan				Crab Creek			Walla Walla River		
					Rep1	Rep2				
Fish Species	LSS	RBT	KOK	KOK	LSS	LSS	MWF	LSS	LSS	WCR
Tissue Type	WF	FIL	FIL	EGG	WF	WF	FIL	WF	EGG	FIL
% Total Lipid	1.79	0.13	0.54	2.59	2.54	2.19	2.47	1.94	0.89	0.15
4,4'-DDE	133	53	398	1370	218	162	105	425	57	17
4,4'-DDD	29	2.2 J	17	59	63	26	20	51	7.2 J	1.7 J
4,4'-DDT	5.1 J	1.8 J	19	82	14	7 J	5.2 J	26	3.6 J	
2,4'-DDE	1.7 J		2 J	11				2.9 J		
2,4'-DDD	3 J		2.1 J	12 J	6.5 J	2 J	1.3 J	7.0		
2,4'-DDT			5.1 J	24						
total DDT	172	57	443	1558	302	197	132	512	68	19
DDMU	17 J	6.9 J	14 J	41	18 J	10 J	11 J	16 J	1.9 J	
alpha-BHC	0.5 J			1.5 J				0.5 J		
gamma-BHC (lindane)				0.5 J				7.9	2.3 J	1.3 J
heptachlor epoxide								8.3	2.1 J	3.7 J
dieldrin						3 NJ		5 J		
endrin			2.8 J	13 J						
kelthane			9 NJ	50 NJ						
methoxychlor					1.7 NJ	1.0 NJ				
alpha-chlordene				0.3 NJ						
gamma-chlordene				0.5 NJ						
cis-chlordane (alpha)	1.3 J		0.5 J	2.1 J		0.8 J		4.6 J	0.8 J	0.7 J
trans-chlordane (gamma)	1.3 J		0.6 J	0.8 J				4.9 J	0.7 J	0.7 J
cis-nonachlor			0.1 J	3.8 J				1.9 J		
trans-nonachlor			1.5 J	7.3 J				10 J		
oxychlordane	0.4 J		1.0 J	4.0 J				2.0 J		
total chlordane	3.0		3.7	18.0		0.8		23	1.5	1.4
hexachlorobenzene				2.1 J				6.9 J	2.7 J	2.1 J
pentachloroanisole				0.3 J						
PCB-1242				10 NJ						
PCB-1254	17 J	15 J	12 J	14 J	26 J	19 J	14 J	48 J	10 J	
PCB-1260				16 J	25 J	24 J	16 J	90	22 J	
total PCBs	17	15	12	40	51	43	30	138	32	

Fish species key

LSS = Largescale Sucker
RBT = Rainbow Trout
KOK = Kokanee (land-locked Sockeye Salmon)
MWF = Mountain Whitefish
WCR = White Crappie

Tissue type key

WF = Whole Fish
FIL = Fillet (muscle only)
EGG = Eggs

Data qualifier codes

J = The analyte was positively identified, but the value is an estimate.
NJ = There is evidence that the analyte is present. The value is an estimate.

Appendix N (cont.). Pesticides and PCBs Detected in 1992 Fish Tissue Samples (µg/Kg (ppb) wet weight)

	Yakima River						Mercer Slough		Lake River
	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2			
Fish Species	LSS	LSS	LSS	LSS	SMB	SMB	LSS	RBT	LSS
Tissue Type	WF	WF	EGG	EGG	FIL	FIL	WF	FIL	WF
% Total Lipid	5.90	4.47	1.25	1.11	0.06	0.05	3.66	0.05	4.47
4,4'-DDE	1420	532	107	252	45	43	144	15	157
4,4'-DDD	151 J	76	15	21	3.2 J	2.0 J	75	4.4 J	39
4,4'-DDT	94	45	8.6 J	15	1.3 J	1.0 J	18	3.5 J	17
2,4'-DDE	13	7.1	0.8 J	1.7 J					
2,4'-DDD	26	11	1.6 J	2.4 J			12		5.1 J
2,4'-DDT	13	6.4							2.2 J
total DDT	1717	678	133	292	50	46	249	23	220
DDMU	55	23	6.0 J	13	2.6 J	1.3 J	26 NJ	3 J	13 J
alpha-BHC									0.3 NJ
gamma-BHC (lindane)							1.1 J		0.4 NJ
dieldrin	42	31	11	12	3.3 J	3.3 J			
kelthane								1.4 NJ	
alpha-chlordene	1.7 J	0.7 J					1.7 J		
gamma-chlordene	5.6 J	2.0 J					2.7 J		
cis-chlordane (alpha)	21	7.4 J	1.4 J	2.0 J	0.4 NJ	0.3 NJ	24	2.1 J	3.0 J
trans-chlordane (gamma)	15	6.0 J	0.9 J	1.3 J	0.4 NJ	0.3 NJ	10 J	1.3 J	2.4 J
cis-nonachlor	8.1	3.6 J		0.4 J		0.5 J	17	0.7 J	1.2 J
trans-nonachlor	32	15	2.2 J	4.6 J	0.7 J	0.4 J	43	3.8 J	6.1 J
oxychlordane	7.5	2.9 J	0.8 J	1.5 J	0.5 J	0.5 J	2.3 J	0.4 J	1.0 J
total chlordane	84	35	5.3	9.8	2.0	2.0	96	8.3	13.7
hexachlorobenzene	1.7 J						2.9 J		1.7 J
pentachloroanisole	1.1 NJ	0.5 J		0.2 J			6.2 J	0.6 J	6.1 J
chlorpyrifos	3.37 J								
PCB-1242									21 NJ
PCB-1254	68 J	27 J	6 J	13 J	7 J		104 J	20 J	95
PCB-1260	164	49 J	13 J	27 J	9 J	8 J	275	31 J	83
total PCBs	232	76	19	40	16	8	379	51	199

[1] NAF = Not Analyzed For (insufficient sample volume for analysis)

Fish species key: LSS=Largescale Sucker; RBT=Rainbow Trout; SMB=Smallmouth Bass

Tissue type key: WF=Whole Fish; FIL=Fillet (muscle only); EGG=Eggs

Data qualifier codes: J = The analyte was positively identified, but the value is an estimate.

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