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Washington State Pesticide Monitoring Program

1994 Fish Tissue and Sediment Sampling Report

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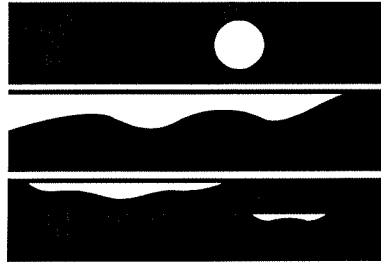
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1994 Fish Tissue and Sediment Sampling Report

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

December 1996

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Abstract

Fourteen fish tissue samples and five sediment samples were collected from six sites in September 1994 for the Washington State Pesticide Monitoring Program (WSPMP). Tissue samples were analyzed for 43 target pesticides and breakdown products, as well as seven polychlorinated biphenyls (PCBs). Sediment samples were analyzed for 140 pesticides and breakdown products, and four PCBs. Total lipid content was also determined for each tissue sample; and grain size, total organic carbon, and total solids were determined for sediment samples.

A total of 20 pesticides and breakdown products, as well as two PCBs (Aroclor equivalents), were detected in fish tissue samples. DDT, chlordane, and their metabolites comprised 56-89% of the detections. Four of the detected compounds -- DCPA (Dacthal), ethion, lindane, and methoxychlor -- are currently registered for use in Washington, but actual frequency and quantity of use is not known. Other frequently detected compounds were hexachlorobenzene and PCB-1254 and -1260. Only four pesticides or breakdown products -- 4,4'-DDE, 4,4'-DDD, bromoxynil, and pentachlorophenol -- were found in sediment samples.

Results were compared to USEPA human health screening values, proposed wildlife criteria, and to 85th percentiles calculated from statewide data. Screening values for total DDT and PCBs were exceeded in fillet samples from Lakes Chelan and Sacajawea, and the Palouse and Okanogan Rivers. Total DDT in carp from the Okanogan River was two orders of magnitude higher than the screening value, and one order of magnitude higher in smallmouth bass from Lake Chelan and in channel catfish from Lake Sacajawea. Proposed wildlife criteria for the protection of fish-eating wildlife were exceeded for total DDT in whole largescale sucker samples from all sites except the Soleduck River. Total DDT concentrations in suckers from Lake Chelan and the Entiat and Okanogan Rivers were substantially higher than the proposed criteria, and were well above the state 85th percentile. Total chlordane, hexachlorobenzene, and heptachlor epoxide in fillet and whole fish samples from the Palouse River, and total chlordane and hexachlorobenzene in fillet samples from Lake Sacajawea, also exceeded state 85th percentiles.

Comparisons to data from the U.S. Fish and Wildlife Service indicate that concentrations of contaminants in suckers from Lake Sacajawea have essentially remained the same for 23 years. Differences observed between samples collected by the WSPMP from Lake Chelan in 1992 and 1994 are probably due to differences in average fish size. Chronic contamination problems may be associated with disturbance of contaminated soils, which are carried into streams and lakes by storm-water runoff, and eventually accumulated by fish. It is likely that chlorinated pesticide contamination in fish tissue will continue to be a problem for many years.

Recommendations include an intensive survey for Lake Chelan to evaluate potential human health risks and fisheries impacts, additional sampling for the Entiat River to confirm high concentrations of DDT and to evaluate human health risks, an intensive survey of sport fish in the lower Okanogan River to assess the extent and range of DDT contamination, a study to determine if piscivorous wildlife within the Wenatchee, Okanogan, and Lower Snake watersheds are being adversely impacted by total DDT contamination, and collection of additional sport fish from Lake Sacajawea to assess the impact to human health from multiple contaminants. Development of guidelines for disturbance of soils contaminated with chlorinated pesticides is also recommended.

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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 and sediment monitoring results for 1994. Tissue and sediment samples were also collected in 1992 (Davis and Johnson, 1994), and fish were sampled in 1993 (Davis *et al.*, 1995).

Fish were collected from Lakes Chelan and Sacajawea, as well as the Entiat, Okanogan, Palouse, and Soleduck Rivers. 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 kokanee, rainbow trout, mountain whitefish, smallmouth bass, channel catfish, northern squawfish, 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).

Bottom sediments were collected at all of the above sites except the Palouse River. Composite samples of at least five grabs using a petite ponar sampler were collected at each site. Samples were analyzed for 140 pesticides and breakdown products, and four PCB mixtures.

A total of 20 pesticides and breakdown products, and two PCBs, were detected in fish tissue samples. No pesticides or PCBs were detected in fish from the reference site, the Soleduck River. A maximum of 18 target analytes were detected per sample; these were in largescale suckers from Lake Sacajawea. At the five sites with detections, 56-89% of the compounds detected were DDT, chlordane, and their metabolites. Only four of the detected compounds -- DCPA (Dacthal), ethion, lindane, and methoxychlor -- are currently registered for use in Washington. Actual quantity and frequency of use is not known.

Only four pesticides -- DDE, DDD, bromoxynil, and pentachlorophenol (PCP) -- were detected in sediment samples. Fewer target analytes were found in sediments as compared to fish tissue from the same water bodies, and concentrations were much lower. PCP and bromoxynil were detected in sediment samples, but not in tissue from the same sites. Bromoxynil is not thought to be persistent in the environment, so its detection was not expected.

Results were compared to USEPA human health screening values, proposed wildlife criteria, and to 85th percentiles calculated from statewide data. Screening values for total DDT and PCBs were exceeded in fillet samples from Lakes Chelan and Sacajawea, and the Palouse and Okanogan Rivers. Total DDT in carp from the Okanogan River was two orders of magnitude higher than the screening value, and one order of magnitude higher in smallmouth bass from Lake Chelan and in channel catfish from Lake Sacajawea.

Proposed wildlife criteria for the protection of fish-eating wildlife were exceeded for total DDT in whole largescale sucker samples from all sites except the Soleduck River. Total DDT concentrations in samples from Lake Chelan and the Entiat and Okanogan Rivers were substantially higher than the proposed criteria. Total DDT levels in samples from Lake Chelan and the Entiat and Okanogan Rivers were well above the state 85th percentile. Total chlordane, hexachlorobenzene, and heptachlor epoxide in fillet and whole fish samples from the Palouse River, and total chlordane and hexachlorobenzene in fillet samples from Lake Sacajawea, also exceeded state 85th percentiles.

Freshwater sediment criteria have not been adopted by Washington State. Provincial sediment quality guidelines developed by the Ontario Ministry of the Environment were used to compare detected concentrations to values that would be expected to produce severe effects on sediment-dwelling organisms that are chronically exposed. Of the compounds detected in sediment samples, guidelines were available for DDE and DDD. In this study, concentrations of these metabolites of DDT were well below guidelines.

Piscivorous wildlife in Washington that may be sensitive to high concentrations of DDE and total DDT include white pelicans, osprey, and bald eagles. White pelicans are frequently seen in many parts of eastern Washington and are known to nest within the McNary National Wildlife Refuge. Osprey are commonly seen nesting along rivers and lakes throughout Washington. In Washington, nesting bald eagles are found predominantly west of the Cascade Mountains, but nesting pairs have also been observed east of the Cascades. Concentrations of total DDT in whole fish from Lakes Chelan and Sacajawea, and the Entiat and Okanogan Rivers, are similar to levels in fish that have been linked to eggshell thinning and low reproductive success in piscivorous birds. Reproductive success of piscivorous mammals, such as mink and river otters, is probably not affected by the concentrations of total DDT identified in this study.

Comparisons to data from the U.S. Fish and Wildlife Service indicate that concentrations of contaminants in largescale suckers from Lake Sacajawea have essentially remained the same for 23 years. The proportion of DDE, a breakdown product of DDT, in all samples is much higher than DDT, suggesting that the contaminants are well-aged and that there are no new sources. However, total DDT concentrations appear to remain high for over two decades. Chronic contamination problems may be associated with disturbance of contaminated soils, which are carried into streams and lakes by storm-water runoff, and eventually accumulated by fish. It is likely that chlorinated pesticide contamination in fish tissue will continue to be a problem for many years. Developing guidelines for disturbance of contaminated soils may help to reduce ongoing contamination of water bodies.

Recommendations

Lake Chelan

Available data, including results from the 1992 WSPMP, indicate that some age classes and species of fish from this site have a high potential for causing adverse human health and fisheries effects.

- Perform an intensive survey in conjunction with the Washington State Department of Fish and Wildlife to evaluate potential human health risks and the impact on fisheries.
- Sample a variety of sport fish species and size classes to determine the range of contamination, and which would pose the most risk for human consumption.

Entiat River

Concentrations of total DDT in whole suckers were an order of magnitude higher than proposed wildlife criteria. No sport fish were collected, but levels in whole fish suggest that total DDT in fillets would exceed the human health screening value.

- Collect additional whole fish samples to confirm the level of DDT contamination.
- Collect fillet samples to evaluate potential human health risks.

Okanogan River

Concentration of total DDT in carp fillets was nearly two orders of magnitude higher than the human health screening value, and the level in whole suckers was well above the recommended wildlife criterion. These concentrations were substantially higher than levels found in fish from Lake Osoyoos, upstream at the U.S.-Canada border.

- Perform an intensive survey of sport fish in the Okanogan River from the Columbia River to Lake Osoyoos to assess the extent and range of contamination, and to evaluate potential human health risks.

Wenatchee and Okanogan Watersheds

Total DDT concentrations in whole fish samples from lakes and streams in these watersheds are typically five to ten times higher than the recommended wildlife criterion for protection of fish-eating wildlife. Wildlife in these watersheds, birds in particular, may be at an increased risk compared to other areas in the state because a higher proportion of the water bodies they feed from are contaminated.

- Conduct a joint study with the Washington State Department of Fish and Wildlife to determine if fish-eating wildlife in these watersheds are being adversely affected by total DDT contamination.

Lake Sacajawea

Concentrations of contaminants in catfish from Lake Sacajawea were not excessively high, but total DDT, t-chlordane, dieldrin, and t-PCBs all exceeded screening values. DCPA, ethion, heptachlor epoxide, hexachlorobenzene, and methoxychlor were also found in catfish fillets, but at levels below screening values. The same is true for whole-fish sucker samples; only DDT exceeded wildlife criteria, but several other contaminants were identified.

Although little is known about the effects of combinations of contaminants, it is generally assumed that at a minimum the effects are additive. If this is true, then the combination of contaminants in fish from Lake Sacajawea may be impacting human health and wildlife more than would be expected when the contaminants are assessed individually.

- Collect additional sportfish to assess impact to human health.
- Include the Lower Snake Watershed in the study described above to evaluate the effects of pesticide contamination on fish-eating wildlife.

Contaminated Soils

When soils contaminated with long-lived chlorinated pesticides are disturbed, storm-water runoff can carry the contaminants into nearby streams and lakes, where they are accumulated by resident fish. Wind can also transport contaminated dust into water bodies. The following steps are recommended for reduction of contaminated soils transport:

- Identify areas where soils are likely to be contaminated by historical chlorinated pesticides use.
- Analyze soil samples to confirm contamination in each area.
- In areas with known contamination, any disturbance of soils should require analysis of soil samples from the site that will be disturbed.
- Best Management Practices (BMPs) should be developed for disturbance of contaminated soils that minimize transport of contaminants from the site.
- Transfer of ownership of property in areas with known contamination should require analysis of soil samples from the property.

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. 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 State.
- 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, 1995) 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, 1994). Fish tissue was collected again in 1993, but not sediments (Davis *et al.*, 1995). This report addresses fish tissue and sediment sampling for 1994. Surface water samples were also collected in April, June, and October of 1994, and results have been summarized in a report by Davis (1996).

Methods

Sampling Design

Fish tissue samples were collected for the WSPMP at six sites and sediment from five (Figure 1) in September 1994. 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.

Tissue samples were analyzed for 43 pesticides and breakdown products, as well as seven polychlorinated biphenyl mixtures (PCBs) (Appendix B-1). Tissue was also analyzed for percent total lipids. The length and weight of each fish was recorded in the field and is summarized in Appendix C. Scientific names for each species collected are also listed in Appendix C.

Sediments were analyzed for 140 pesticides and breakdown products, and four PCBs (Appendix B-2). Grain size, total organic carbon (TOC), and total solids were also determined for sediment samples; results are listed in Appendix D.

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 and allowing particulates to settle out.

For a screening survey, the USEPA recommends collecting one composite for each of two species at each sample site (USEPA, 1995). 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:

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

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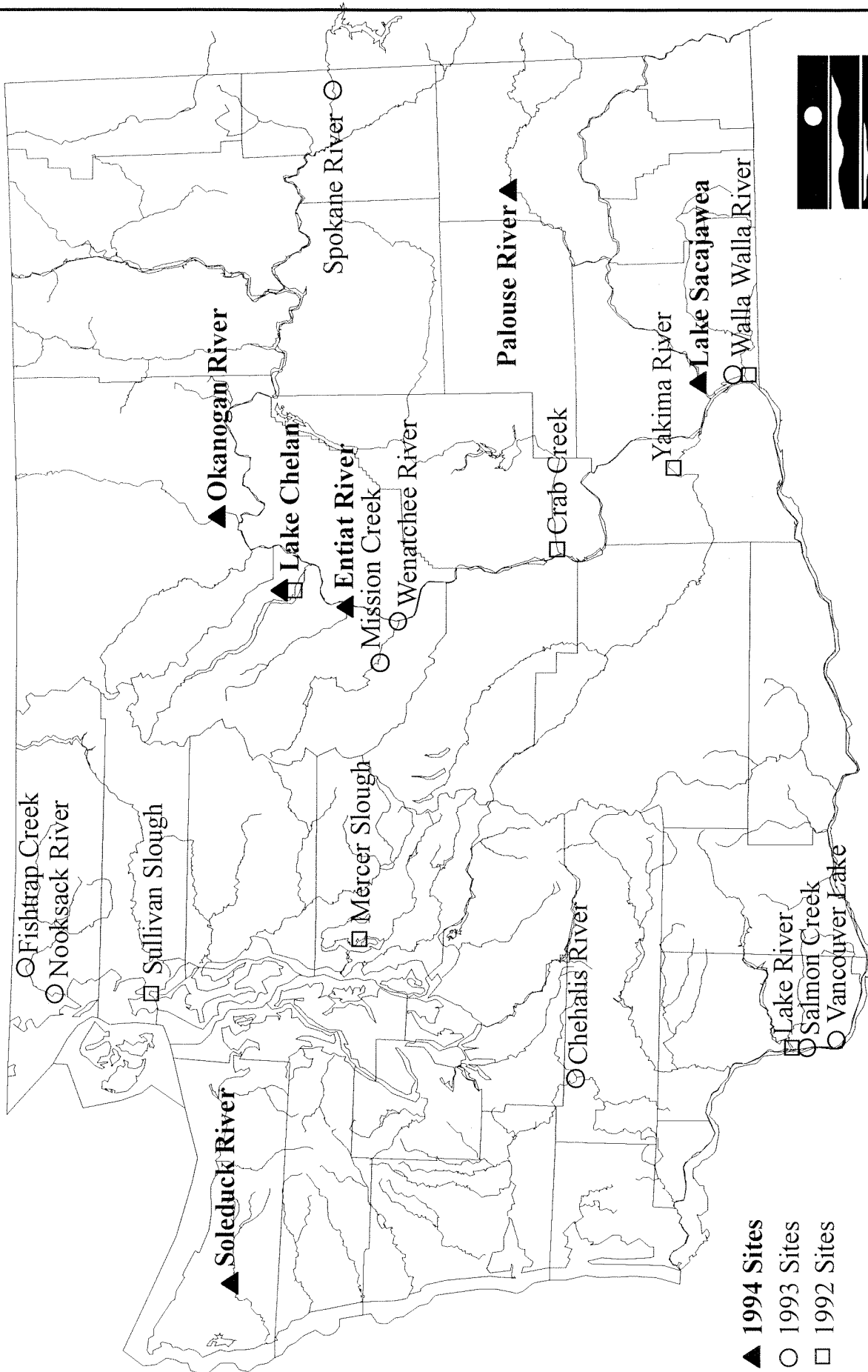


Figure 1. 1992, 1993, and 1994 WSPMP Fish Tissue and Sediment Sampling Sites
 (Sediment was not collected at any of the sites in 1993, from Lake Chelan in 1992, and the Palouse River in 1994)

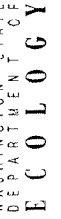


Table 1. List of Sampling Sites, Locations, and Number and Type of Samples

Sample Site	Location	Number of Composite Samples		
		Whole Fish	Fillet	Sediment
Wenatchee Watershed				
Lake Chelan	Near Wapato Point Chelan County	1	3	1
Entiat River	Near Entiat Chelan County	2	0	1
Upper and Lower Snake Watershed				
Lake Sacajawea	Near Ice Harbor Dam Walla Walla/Franklin Counties	1	1	1
Palouse River	Near Winona Whitman County	1	1	0
Western Olympic Watershed				
Soleduck River	Near Sappho Clallam County	0	1	1
Okanogan Watershed				
Okanogan River	Above Brewster Okanogan County	2	1	1
Totals		7	7	5

Largescale suckers were chosen as the bottom feeding species because they possess nearly 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 trout, kokanee, mountain whitefish, smallmouth bass, channel catfish, northern squawfish, and carp.

Composite samples, rather than individual samples, were analyzed because composites are the most cost-effective method of estimating average contaminant concentrations (USEPA, 1995). For assessment of water bodies to be added to Ecology's 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 or sediment grabs. Fish for replicate tissue composites were collected at two sites, the Entiat and Okanogan Rivers, to evaluate variability between composites.

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

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

The sampling emphasis for the 1994 WSPMP was within the Wenatchee, Western Olympic, and Upper and Lower Snake River watersheds. The Nooksack/San Juan watershed was also included in this cycle, but higher priority sites were identified in the other watersheds. In addition, sites within the Nooksack watershed were sampled in 1993 (Davis *et al.*, 1995).

Lake Chelan and the Entiat River are in the Wenatchee watershed. Lake Chelan was resampled in 1994 to verify high pesticide concentrations identified in fish by the 1992 WSPMP (Davis and Johnson, 1994). The Soleduck River is in the Western Olympic watershed, and was sampled as a reference site. The Palouse River is in the Upper Snake watershed and Lake Sacajawea is in the Lower Snake. The Okanogan River is not in this group of watersheds, but high concentrations of total DDT found in fish sampled in 1984 by the Ecology Basic Water Monitoring Program (Hopkins *et al.*, 1985) identified this river as a priority. If WSPMP sampling for the Okanogan watershed had followed the schedule for the watershed cycle, it would not have taken place until 1998.

Target Analytes

Appendix B-1 lists the fish tissue target pesticides analyzed for the WSPMP in 1994. 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, 1995; 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, 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).

The target analyte list for sediments (Appendix B-2) is a reduced version of the list for water (Davis, 1996; Appendix B). All pesticides that were designated by Tetra Tech (1988) as being of primary or secondary concern in sediments are included in the list. Sediment samples were not analyzed for carbamates or pyrethroids due to poor detection limits.

A discussion of the characteristics and interrelationships of target compounds, including current registration status, can be found in Appendix E.

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

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

Results and Discussion

Pesticides Detected

Fish Tissue

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 (1) these were the most frequently detected compounds, (2) they comprise a majority of the compounds detected, and (3) in their summed form they simplify comparisons.

A total of 20 pesticides and breakdown products were detected in fish tissue samples collected in 1994 (Table 2). In addition, two PCB mixtures (as Aroclor equivalents) were identified. No pesticides or PCBs were detected in fish from the reference site, the Soleduck River. A maximum of 18 target analytes were detected per sample; these were in largescale suckers from Lake Sacajawea. The average detection rate per sample was nine analytes. At the five sites with detections, 56-89% of the compounds detected were DDT, chlordane, and their metabolites. Four of the detected compounds -- DCPA (Dacthal), ethion, lindane, and methoxychlor -- are currently registered for use in Washington. Actual quantity and frequency of use is not known. For reference, pesticides detected in tissue samples collected for the 1992 and 1993 WSPMP are included in Appendix H.

Figure 2 shows the frequency of detection for target analytes identified in fish tissue for the 1992, 1993 and 1994 WSPMP. DDT, chlordane, and their breakdown products have consistently been the most frequently detected pesticides. PCBs-1254 and -1260 were also commonly found in fish tissue. In addition to the four currently used pesticides found in 1994 samples, endosulfan sulfate, a breakdown product of endosulfan, and chlorpyrifos are currently used pesticides that were detected by the WSPMP in 1992 or 1993. Frequency of detection for these six compounds ranges from 2-24%. Other analytes were detected in 2-43 % of the 51 samples.

A similar pattern of detection is seen in 1994 fish tissue samples. DDT and its breakdown products, DDE, DDD, and DDMU, were the most frequently detected compounds. These compounds were found at five of the six sites and in at least ten of the 14 samples. Cis- and trans-chlordane and their metabolites, cis- and trans-nonachlor, and oxychlordane, were also commonly detected. PCBs-1254 and -1260 were among this group of frequently identified analytes. Dieldrin, hexachlorobenzene (HCB), and heptachlor epoxide were found at two to four sites and in three to seven samples.

**Table 2. Pesticides and PCBs Detected in 1994 Fish Tissue Samples
(µg/Kg (ppb) wet weight)**

Sample Site Fish Species Tissue Type	Lake Sacajawea		Palouse River		Okanogan River		
	LS Sucker Whole-fish	Catfish Fillet	LS Sucker Whole-fish	Squawfish Fillet	LS Sucker Whole-fish Replicate 1	LS Sucker Whole-fish Replicate 2	Carp Fillet ¹
% Total Lipid	26.8	4.9	2.6	1.5	8.4	6.1	9.1
2,4'-DDE	0.91 J	1.4 J			1.4 J	2.2 J	12
4,4'-DDE	270	360	170	73	760	1100	1650
2,4'-DDD	5.6 J	2.9 J	2.8 J		13 J	18	135
4,4'-DDD	43	44	18		120	180	1050
2,4'-DDT						1.2 J	
4,4'-DDT	15	21	12 J		21	39	5.6 J
total DDT	335	429	203	73	915	1340	2853
4,4'-DDMU	7.0 J	5.8 J	2.7 J		19	28	125
cis-chlordane	2.9 J	4.0 J	5.7	1.2 J			
trans-chlordane	3.0 J	5.8	14				
oxychlordane	1.4 J		7.2	2.4 J			
cis-nonachlor	2.3 J	3.2 J	1.7 J	0.75 J	0.38 NJ	0.42 J	
trans-nonachlor	5.1 J	6.5 J	4.7 J	2.1 J		0.81 NJ	
total chlordane	14.7	19.5	33	6.5	0.38	1.23	
DCPA (Dacthal)	25	9.5					
dieldrin	7.5	4.0 J	13	7 NJ			
ethion	4.5 J	5.4 J					
alpha-BHC							
gamma-BHC (Lindane)			0.27 NJ	0.44 J			
heptachlor epoxide	1.0 J	0.45 J	14	6.3			
hexachlorobenzene	6.9	4.7	10	3.6	0.66 J	0.78 NJ	0.89 J
methoxychlor	1.2 J					0.70 NJ	
PCB-1254	29 NJ	26 NJ	13 J		22 J	24 NJ	25 J
PCB-1260	33	35 J	18 J	11 J	34 J	48 J	20 NJ
total PCBs	62	61	31	11	56	72	45

¹ - Values are means of duplicate analyses

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

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

A blank indicates that the target analyte was not detected.

**Table 2 (cont.). Pesticides and PCBs Detected in 1994 Fish Tissue Samples
($\mu\text{g}/\text{Kg}$ (ppb) wet weight)**

Sample Site	Lake Chelan				Entiat River		Soleduck River
	LS Sucker	Kokanee	RB Trout	SM Bass	LS Sucker	LS Sucker	M Whitefish
Fish Species	Whole-fish	Fillet	Fillet	Fillet	Whole-fish	Whole-fish	Fillet
Tissue Type					Replicate 1	Replicate 2	
% Total Lipid	4.7	1.6	1.5	3.9	4.9	4.5	6.5
2,4'-DDE	1.6 J				4.0 J	1.6 J	
4,4'-DDE	800	140	56	330	1700	1100	
2,4'-DDD	9.7 NJ	2.5 J		4.8 J	28	11 J	
4,4'-DDD	93	12 NJ		34	130	120	
2,4'-DDT					2.0 J		
4,4'-DDT	53	12 J		28	160	130	
total DDT	957	167	56	397	2024	1363	
4,4'-DDMU	34	3.7 J	5.0	12	47	26	
cis-chlordane				0.5 J			
trans-chlordane	0.45 NJ						
oxychlordane		0.47 J		0.48 NJ			
cis-nonachlor	0.95 J	1.1 NJ	0.29 J	0.61 NJ	0.28 NJ		
trans-nonachlor	2.3 J	1.2 NJ	0.31 NJ	0.86 J	2.2 NJ	1.0 NJ	
total chlordane	3.7	2.8	0.60	2.4	2.5	1.0	
DCPA (Dacthal)							
dieldrin							
ethion							
alpha-BHC	0.38 J			0.38 J			
gamma-BHC (Lindane)							
heptachlor epoxide							
hexachlorobenzene					0.63 J		
methoxychlor							
PCB-1254	34 J	84	65	16 J	28 NJ	20 NJ	
PCB-1260	35 J	15 J	15 NJ		36 J	40 J	
total PCBs	69	99	80	16	64	60	

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

NJ - There is evidence that the analyte is present. The associated numerical result is an estimate.

A blank indicates that the target analyte was not detected.

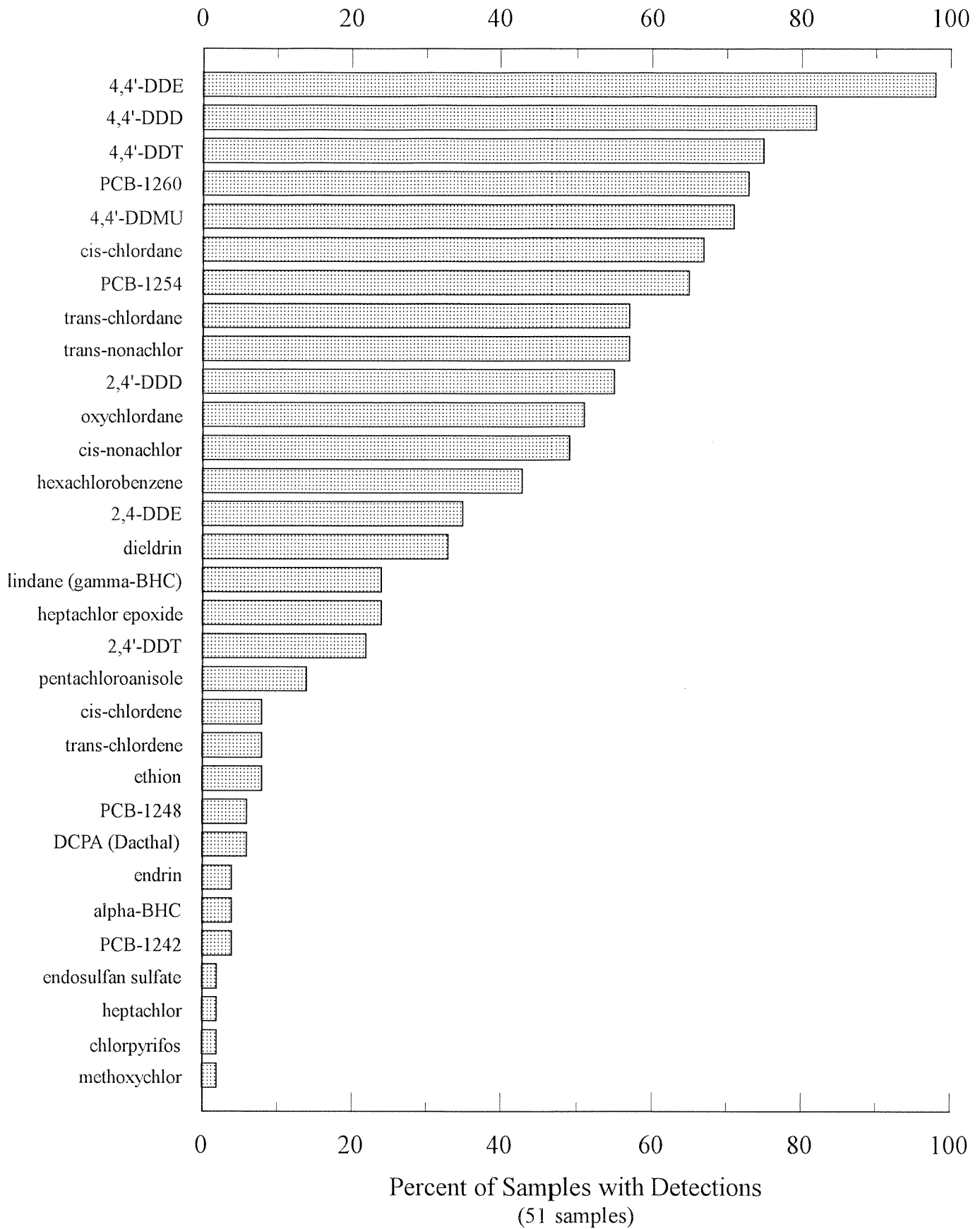


Figure 2. Detection Frequency of Pesticides and PCBs in 1992, 1993, and 1994 WSPMP Fish Tissue Samples

Sediment

Pesticides detected in sediments are listed in Table 3. Far fewer target analytes were found in sediments as compared to fish tissue from the same water bodies, and concentrations were much lower. In addition, levels detected in sediments were not proportional to the concentrations observed in tissue samples. DDE in fish tissue from the Entiat River was higher than in samples from Lake Chelan, but DDE concentration in sediment from these two sites was nearly the same.

Pentachlorophenol (PCP) and bromoxynil were detected in sediment samples, but not in tissue, from the same sites. PCP was also found at all sites in 1992 (Davis and Johnson, 1994), and is apparently present in low concentrations in most sediments, as evidenced by its presence in all samples collected by the USEPA in 1988 (Crecelius *et al.*, 1989) and in 1989-90 (PTI, 1991). Bromoxynil is not thought to be persistent in the environment, so its detection at four sites was not expected. For more information, see Appendix E.

Sample Site	Lake Sacajawea	Okanogan River	Lake Chelan	Entiat River	Soleduck River
% Fines	27	73	80	7	5
% TOC	1.0	2.0	1.6	1.0	0.6
4,4'-DDE	2.7 J	6.4 J	7.5	7.0	
4,4'-DDD		5.8 J	12		
bromoxynil	35 NJ	29 NJ	10 NJ	11 NJ	
pentachlorophenol	13 NJ	36 NJ	27 NJ	49	21 NJ
<small>J - The analyte was positively identified, but the value is an estimate. NJ - There is evidence that the analyte is present, but its presence is not confirmed.</small>					

Comparisons with Applicable Criteria

Human Health 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 the USEPA recommends evaluating detected chemical contaminants with screening values to prioritize problem areas. Sites with concentrations exceeding screening values will be 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 factors that were used to calculate screening values as outlined by the USEPA (1995).

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 1×10^{-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. Washington State has adopted 1×10^{-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 also useful to compare carcinogenic contaminant concentrations to screening values calculated with a risk level of 1×10^{-5} .

Exposure assumptions used to calculate screening values 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, 1995).

Screening values for non-carcinogens were 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 1994 WSPMP fish tissue samples are compared to screening values in Table 4. Screening values calculated with a risk level of 1×10^{-6} were exceeded for one or more compounds at four sites. Total DDT and PCBs were above screening values in all samples from the four sites. Total chlordane and dieldrin were also above screening values in channel catfish fillets from Lake Sacajawea, and heptachlor epoxide exceeded screening values in the squawfish sample from the Palouse River. The total DDT concentration in carp from the Okanogan River was approximately two orders of magnitude above the screening value. Total DDT and PCBs in samples from Lake Chelan, Lake Sacajawea, and the Okanogan River were higher than screening values calculated with a risk level of 1×10^{-5} . No sport fish fillets were analyzed from the Entiat River for screening value comparisons, but levels of total DDT and PCBs in fillets would likely exceed screening values based on whole fish results.

Water Quality Limited List

When calculated with a risk level of 1×10^{-6} , screening levels for the carcinogenic compounds listed in Table 4 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 (section 303(d) of the federal Clean Water Act). The 303(d) list contains state water bodies 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

Table 4. Comparison of Pesticides Detected in 1994 Fish Fillets to Screening Values ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

Sample Site Fish Species	Lake Chelan		Lake Sacajawea Catfish	Palouse River N Squawfish	Okanogan River Carp ¹	Soleduck River M Whitefish	Screening Values	
	Kokanee	RB Trout					1×10^{-6} *	1×10^{-5}
Carcinogens								
total DDT	167	56	429	73	2853		32	320
total chlordane	2.8	0.60	19.5	6.5			8.3	83
gamma-BHC (Lindane)				0.44			8.3	83
dieldrin			4.0				0.7	7
heptachlor epoxide			0.45	6.3			1.2	12
hexachlorobenzene			4.7	3.6	0.89		6.7	67
total PCBs	99	80	61	11	45		1.4	14
Non-Carcinogens								
DCPA (Dacthal)			9.5				5400	
ethion			5.4				5400	

Values in bold exceed screening values calculated using a risk level of 1×10^{-6}

¹ - Values are means of duplicate analyses

* - 1×10^{-6} is the risk level adopted by Washington State

A blank indicates that the target analyte was not detected.

be added to the list if there is one or more NTR criterion exceeded for a five fish composite of edible tissue (Washington State Water Quality Policy 1-11, 1993).

Fillet samples from Lakes Chelan and Sacajawea, and the Palouse and Okanogan Rivers, 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 whole fish results are compared to criteria proposed by the state of New York for protection of fish-eating wildlife (Newell *et al.*, 1987) in Table 5. For more information regarding wildlife criteria, see the discussion in the "Ecological Assessment" section starting on page 22.

Total DDT exceeded criteria proposed by Newell *et al.* (1987) at five of the six sites sampled, and levels of DDE were above criteria at four sites. No other target analytes were found above the wildlife criteria. Concentrations of DDT in samples from Lake Sacajawea and the Palouse River were only marginally higher than the criteria, but samples from the Okanogan and Entiat Rivers and Lake Chelan contained DDT levels substantially above the recommended criteria.

Other Data

Selected fish tissue data from the 1994 WSPMP are compared to 85th percentile values calculated from other Washington State studies in Table 6. These values were calculated from results of studies that have monitored for pesticides in freshwater fish, including: Davis *et al.*, 1995; Davis and Johnson, 1994; Serdar *et al.*, 1994; Johnson and Norton, 1988,1990; Johnson *et al.*, 1986; Hopkins *et al.*, 1985; Hopkins, 1991; 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 a 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 percentile). These percentiles are likely to be biased to the high side, since sites are generally selected for monitoring based on suspected pesticide

Table 5. Comparison of Pesticides Detected in 1994 Whole Fish Samples to Recommended Wildlife Criteria (µg/Kg (ppb) wet weight)

	Lake Sacajawea	Palouse River	Okanogan River		Lake Chelan	Entiat River		Criteria	
			Rep-1	Rep-2		Rep-1	Rep-2	Newell <i>et al.</i> , 1987 as Non-Carcinogens	Carcinogens
DDE	271	170	761	1102	802	1704	1102	200	270
DDD	49	21	133	198	103	158	131	200	
DDT	15	12	21	40	53	162	130	200	
total DDT	335	203	915	1340	958	2024	1363	200	
total chlordane	14.7	33	0.38	1.23	3.7			500	370
dieldrin	7.5	13						120	22
heptachlor epoxide	1.0	14						200	210
hexachlorobenzene	6.9	10	0.66	0.78		0.63		330	200
total PCBs	62	31	56	72	69	64	60	100	110

Values in bold exceed recommended criteria

All data are from Largescale suckers

A blank indicates that the target analyte was not detected

Table 6. Comparison of Selected Compounds Detected in 1994 Fish Tissue Samples to State-wide 85th Percentiles ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

	t-DDT	t-chlordane	dieldrin	HCB	lindane	heptachlor epoxide	t-PCBs
Whole Fish							
Lake Sacajawea	335	14.7	7.5	6.9	u ¹	1.0	62
Palouse River	203	33	13	10	0.3	14	31
Okanogan River	1128	0.8	u	0.66	u	u	64
Lake Chelan	957	4	u	u	u	u	69
Entiat River	1694	1.8	u	0.63	u	u	64
State 85th Percentile	650	21	40	u	0.3	3.5	225
Fillets							
Lake Sacajawea	429	19.5	4.0	4.7	u	0.45	61
Palouse River	73	6.5	7	3.6	0.44	6.3	11
Okanogan River	2853	u	u	0.89	u	u	45
Lake Chelan	167	2.8	u	u	u	u	99
Lake Chelan	56	0.6	u	u	u	u	80
Lake Chelan	397	2.4	u	u	u	u	16
Soleduck River	u	u	u	u	u	u	u
State 85th Percentile	500	4	10	1	u	u	120
Lipid Normalized²							
Lake Sacajawea	5000	230	55	61	u	6.5	420
Palouse River	6300	860	250	310	15	480	960
Okanogan River	21400	2	u	6	u	u	580
Lake Chelan	10950	39	u	u	u	u	3100
Entiat River	35800	u	u	7	u	u	810
Soleduck River	u	u	u	u	u	u	u
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

Means were calculated with undetected results set at zero

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 I. 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).

Sediment Guidelines

Freshwater sediment criteria have not been adopted by Washington State. Provincial sediment quality guidelines developed by the Ontario Ministry of the Environment (Persaud *et al.*, 1991) can be used to compare detected concentrations to values that would be expected to produce severe effects on sediment-dwelling organisms that are chronically exposed. These values are organic carbon normalized to reflect the bioavailability of the contaminants.

Of the compounds detected in sediment samples, guidelines are available for DDE and DDD. In this study concentrations of these metabolites of DDT were well below guidelines.

Site Evaluations

Lake Sacajawea

Lake Sacajawea is the Snake River impoundment from behind the Ice Harbor Dam to the Lower Monumental Dam. The Ice Harbor Dam is located about nine miles upstream from the confluence of the Snake River with the Columbia River. The lake is in the Lower Snake watershed, but little of the water originates from this area. The headwaters of the Snake River are in northwestern Wyoming, near the Grand Teton National Park. The river flows through southern Idaho, northward to form the border between Idaho and Oregon and then Idaho and Washington for a short distance before moving west to southwest in Washington where it flows into the Columbia River just southeast of Pasco. Numerous streams contribute to the flow before it enters Washington.

Largescale sucker and channel catfish samples were collected from Lake Sacajawea along the northern shoreline near the boat ramp at Ice Harbor Dam. The sediment sample was collected at the end of the dock at the boat ramp.

Among the six sites sampled in 1994, the largest number of target compounds were detected in samples from Lake Sacajawea. Eighteen were found in whole suckers and 16 in catfish filets. Levels of total DDT, t-chlordane, dieldrin, and t-PCBs in catfish filets

exceeded screening values and NTR criteria. At 19.5 $\mu\text{g}/\text{Kg}$, the concentration of t-chlordane was the highest of the seven fillet samples collected in 1994. This level is also substantially higher than the state 85th percentile of 4 $\mu\text{g}/\text{Kg}$. Although the concentration of total DDT (429 $\mu\text{g}/\text{Kg}$) was an order of magnitude higher than the screening value, it was below the state 85th percentile of 500 $\mu\text{g}/\text{Kg}$. Total DDT in whole suckers exceeded wildlife criteria, but again was lower than the 85th percentile. What this indicates is that total DDT levels in fish from Lake Sacajawea are elevated enough to be of concern, but are lower as compared to other sites in the state.

Fish tissue has been collected at the Ice Harbor Dam site by the U.S. Fish and Wildlife Service (USFWS) since 1971 (Lowe *et al.*, 1985; Schmitt *et al.*, 1981, 1983, 1985, 1990), and samples were collected farther upstream in Idaho as far back as 1967 (Henderson *et al.*, 1971). The last reported set of samples was collected at the Ice Harbor Dam site by the USFWS in 1984-85 (Schmitt *et al.*, 1990). Target analytes for the USFWS are similar to those of the WSPMP, which facilitates data comparisons.

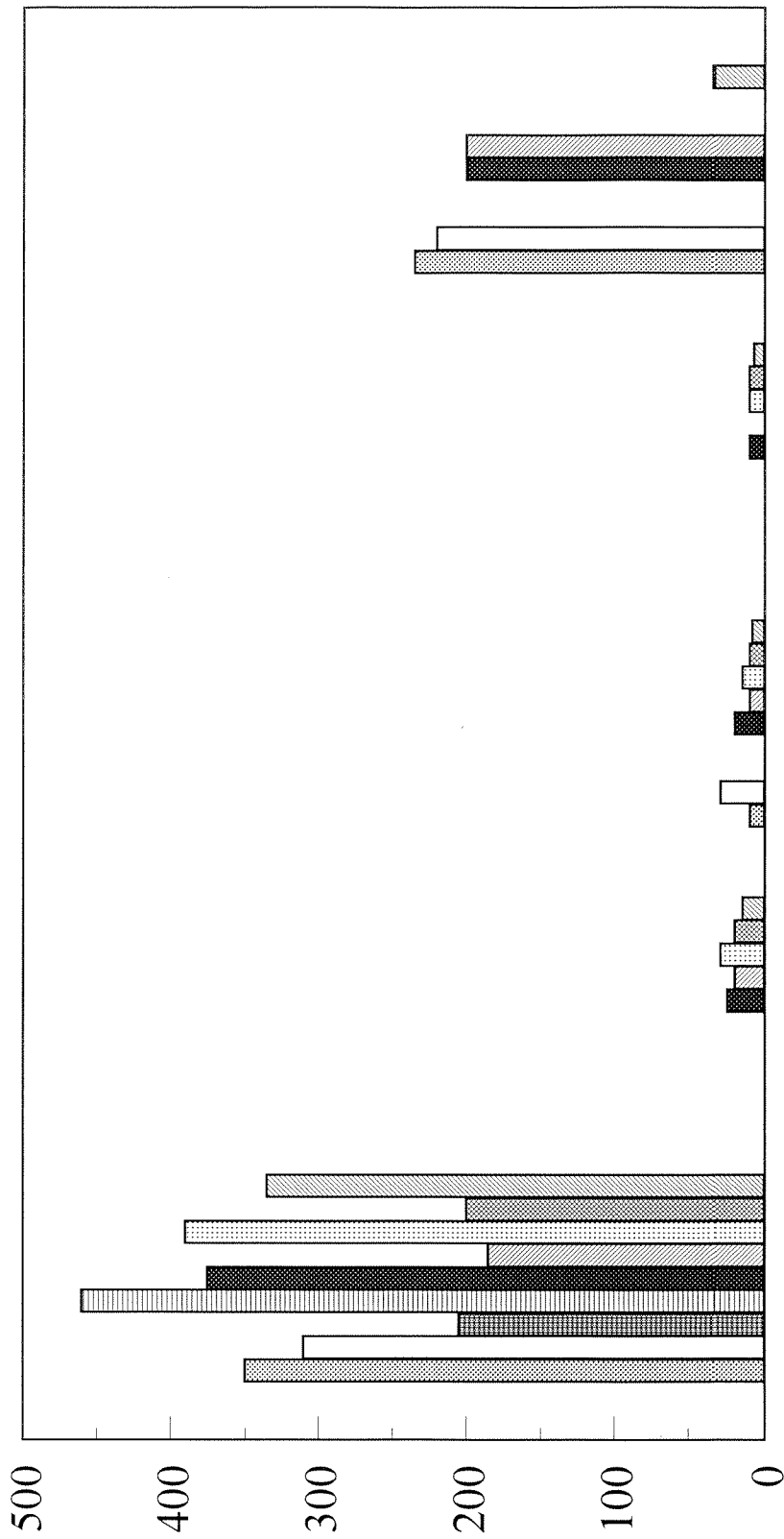
Pesticide concentrations in whole largescale suckers from Ice Harbor Dam have essentially remained the same for 23 years (Figure 3). Differences between years can easily be explained by sample variability. The apparent increase in levels of total chlordane and hexachlorobenzene are probably due to improved detection limits. DCPA (Dacthal) was not measured until 1980, but appears to have dropped by about half from 60 $\mu\text{g}/\text{Kg}$ in 1980 to 25 $\mu\text{g}/\text{Kg}$ in 1994. PCBs are the only contaminants that seem to have dropped significantly, from 235 $\mu\text{g}/\text{Kg}$ in 1971 to 33 $\mu\text{g}/\text{Kg}$ in 1994.

Possible sources of these contaminants within Washington are the croplands along the river, and along tributaries including the Palouse River. The majority of the water in the Snake River originates outside of Washington, and probably contributes a majority of the contaminants. Largescale suckers collected from the Snake River in Idaho in 1969 contained concentrations of contaminants similar to the WSPMP sucker sample from Lake Sacajawea (Henderson *et al.*, 1971). More information is needed to identify specific sources.

Palouse River

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

Largescale sucker and northern squawfish samples were collected at Winona, upstream of the confluence with Rebel Flat Creek. No sediment sample was collected. The Palouse River was chosen to represent dry-land agriculture pesticide use within the Upper Snake watershed, which is the predominant land use upstream from Winona. Downstream from



	t-DDT	t-chlordane	dieldrin	hexachlorobenzene	t-PCBs
1971	350	u	10	u	235
1972	310	u	30	u	220
1973	205	u	u	u	u
1974	460	u	u	u	u
1976	375	25	20	10	200
1978	185	20	10	u	200
1980	390	30	15	10	u
1984	200	20	10	10	u
1994	335	15	8	7	33

Figure 3. Comparison of Pesticide Concentrations Detected in Whole Largescale Suckers from Lake Sacajawea (Snake River at Ice Harbor Dam) - 1971 through 1994 ($\mu\text{g}/\text{Kg}$, wet weight)

1971 to 1984 data are from U.S. Fish and Wildlife Service, 1994 data are from the WSPMP

Winona the river receives water from streams that are not primarily representative of dry-land agriculture.

Fifteen compounds were detected in whole suckers and nine in squawfish fillets. Levels of total DDT, heptachlor epoxide, and t-PCBs in fillets were above screening values and NTR criteria, but not substantially. At 203 $\mu\text{g}/\text{Kg}$, the concentration of total DDT in whole suckers was essentially at the wildlife criterion of 200 $\mu\text{g}/\text{Kg}$. Levels of total DDT and t-PCBs were well below state 85th percentiles, but t-chlordane, HCB, and heptachlor epoxide exceeded the 85th percentiles in whole fish and fillets from the Palouse River. Although concentrations of the analytes detected in fish from the Palouse River were generally fairly low, four exceeded criteria and another three were above state 85th percentiles. While the levels of individual compounds were only moderately elevated, the toxicity of these contaminants may be additive or synergistic, which could result in adverse effects more significant than expected.

Okanogan River

The Okanogan River begins in Canada as Okanogan Lake, flows into Lake Osoyoos at the U.S./Canada border, and then continues almost directly south to its confluence with the Columbia River near Brewster. Most of the river valley on both banks is dedicated to fruit orchards, primarily apples. This is the case in Canada as well. River water is used to irrigate the orchards, and several small streams return runoff to the river. Some of these streams carry fairly high concentrations of DDT and its metabolites (Johnson *et al.*, 1995).

Largescale suckers and carp were collected from a reach of the Okanogan River extending from the boat ramp near Monse to the railroad trestle about five miles upstream. Most of the river, from Lake Osoyoos to its confluence with the Columbia River, is slow moving. Sediments entering the river settle out quickly, resulting in numerous depositional areas. The sediment sample was collected from one such depositional area about two miles upstream from the boat ramp.

DDT appears to be the only significant pesticide contaminating the Okanogan River. High concentrations of total DDT were found in whole suckers and carp fillets, and were well above screening values and wildlife criteria. PCBs also exceeded screening values. Levels of total DDT were higher than whole fish and fillet 85th percentiles, but not the lipid normalized 85th percentile. Concentration of DDE in carp was higher than any of the national values, and DDE in suckers was higher than all national values except the EPA agricultural mean (Appendix I).

Concentrations of total DDT in WSPMP samples from the lower portion of the river were substantially higher than levels in fish from Lake Osoyoos (Serdar *et al.*, 1996). In particular, concentrations in carp fillets were two to three times higher in fish from the river than from the lake. This suggests that the contributions of total DDT from irrigation return tributaries downstream of Lake Osoyoos result in a substantial increase in body burdens for fish in the lower Okanogan River.

Lake Chelan

Lake Chelan lies along the northeastern border of Chelan County, and is the largest and deepest natural lake in the state. Fish and sediment have been analyzed for pesticides as a part of Ecology's now discontinued Basic Water Monitoring Program (BWMP) (Hopkins *et al.*, 1985), the Lake Chelan Water Quality Assessment (Patmont *et al.*, 1989), and the 1992 WSPMP (Davis and Johnson, 1994). Elevated levels of total DDT were detected in all three studies, and numerous other compounds were identified in fish tissue by the 1992 WSPMP.

Samples for the 1994 WSPMP were collected in the Wapato basin near Wapato Point, where the highest pesticide levels have been found. Collected were (1) one whole largescale sucker sample, (2) fillets from kokanee, rainbow trout, and smallmouth bass, and (3) sediment.

Concentrations of total DDT and t-PCBs in fillets were relatively low (below the 85th percentiles), but levels in all three samples exceeded screening values. Total DDT in whole suckers was higher, exceeding wildlife criteria and the state 85th percentile. Other pesticides detected included chlordane and its breakdown products, and alpha-BHC, all at low concentrations.

Compared to concentrations detected in 1992, 1994 values were variable. The level of total DDT in rainbow trout fillets was about the same, but the concentration was higher in whole suckers and lower in kokanee fillets in 1994. The differences may be explained by the sizes of fish collected. The suckers in 1992 were smaller than in 1994, average of 255 mm long and 173 grams, compared to 306 mm and 383 grams. Kokanee in 1992 were larger, 345 mm long and 427 grams, compared to 286 mm and 250 grams. All but one of the kokanee collected in 1994 were juveniles, while the kokanee caught in 1992 were adults preparing to spawn. Kokanee and rainbow trout are both planted in Lake Chelan, and the lower concentrations of total DDT in these fish may be due to their residence in the lake for only a few months.

Entiat River

The Entiat River flows to the southeast through the Entiat Valley midway between Lake Chelan and the Wenatchee River, picking up water that drains from the Chelan Mountains to the east and from the Entiat Mountains to the west, and then discharges to the Columbia River just south of the town of Entiat. Land along the southern portion of the river and some of its tributaries is used primarily for tree fruit production.

Two replicate samples of largescale suckers were collected from an area about one-half mile upstream from the mouth. No sport fish were captured for fillet analysis. The current in the river is fast enough, even near the mouth, so that fine depositional sediment could not be found. Sediment that was collected was very sandy, but probably represented the finest grain material that is retained on the river bottom.

DDT and its breakdown products were the main contaminants found in whole suckers from the Entiat River. Low concentrations of HCB and PCBs were also found. Levels of total DDT were well above the state 95th percentile and were about an order of magnitude higher than recommended wildlife criteria. These levels are similar to the highest concentrations of total DDT found in suckers from the Yakima River (Davis and Johnson, 1994; Rinella *et al.*, 1992; Johnson *et al.*, 1986). In 1993, the Washington State Department of Health issued a consumption recommendation for bottom fish from the Yakima River. The recommendation suggests limiting consumption of bottom fish such as suckers due to high concentrations of total DDT in fish tissue.

Soleduck River

The Soleduck River begins in the Olympic Mountains in the Western Olympic watershed south of Lake Crescent and flows through the Soleduck Valley, eventually discharging into the Quillayute River about four miles from the Pacific Ocean. This river was chosen as a reference site, where no pesticides were expected to be found. The Soleduck is isolated from most commercial development, and even residential property is well dispersed. Other than a few scattered Christmas tree farms and other forest practices along the river, pesticides are probably rarely used.

Mountain whitefish were collected near the boat ramp at the Solduc salmon hatchery. No suckers could be found for whole-fish analysis. Sediment was collected from shallow water near the boat ramp. Little fine-grained sediment could be found.

No contaminants were detected in fish or sediment. The whitefish had a high lipid content of 6.5%, so if any fat soluble contaminants were present it is likely that these fish would have accumulated them.

Ecological Assessment

A detailed assessment of the effects of detected pesticides on fish and fish-eating wildlife was presented in the 1993 WSPMP fish tissue sampling report (Davis *et al.*, 1995). Most of that information is applicable to this report, but will not be repeated in full here. Instead, specific information from the 1993 report will be used to evaluate possible toxic effects on fish and wildlife from compounds detected in 1994.

Adult fish are known to tolerate high accumulated concentrations of some contaminants in their tissues with no adverse effects (Bridges *et al.*, 1963). However, many species of fish are much more sensitive to pesticide contamination in the fry stages of development (Holden, 1973). Total DDT concentrations in eggs higher than 400 µg/Kg (parts per billion) may result in up to 90% mortality in the resulting fry (Cuerrier *et al.*, 1967). Some fry mortality may have resulted from total DDT contamination in eggs of largescale suckers from Lake Chelan and the Okanogan and Entiat Rivers.

Wildlife criteria previously presented in Table 5 are fish flesh criteria developed by Newell *et al.* (1987) for contaminants found in Niagara River fish to protect piscivorous (fish-eating) wildlife. The methodology used by Newell *et al.* to calculate criteria has been selected to develop Canadian tissue residue guidelines for protecting wildlife (Environment Canada, 1994-draft).

Only DDE and total DDT were detected in 1994 fish tissue samples at concentrations exceeding wildlife criteria. Detected pesticides that were not addressed by Newell *et al.* (1987) include DCPA, ethion, and methoxychlor. Concentrations of these three pesticides were low.

Piscivorous wildlife in Washington that may be sensitive to high concentrations of DDE and total DDT include white pelicans, osprey, and bald eagles. Wildlife criteria for DDT and its metabolites, DDE and DDD, were derived from the dietary no-observed-effect level (NOEL) established by the USEPA (1976) for brown pelicans, which was determined to be the most sensitive species. White pelicans are frequently seen in many parts of eastern Washington and are known to nest within the McNary National Wildlife Refuge (Linehan, 1995). Osprey are large, exclusively piscivorous birds that are commonly seen nesting along rivers and lakes throughout Washington. Bald eagle diets consist of up to 90% fish, but they also eat other birds and small mammals, including carrion. In Washington, nesting bald eagles are found predominantly west of the Cascade Mountains, but nesting pairs have also been observed east of the Cascades (McAllister *et al.*, 1986; unpublished data, Washington State Department of Fish and Wildlife).

Concentrations of total DDT over 300 $\mu\text{g}/\text{Kg}$ in fish eaten by osprey can accumulate in the bird's tissues, resulting in total DDT levels in their eggs over 3000 $\mu\text{g}/\text{Kg}$ and significant eggshell thinning (Steidl *et al.*, 1991). Similar concentrations of DDE in fish consumed by bald eagles has been linked to eggshell thinning and low reproductive success (Wiemeyer *et al.*, 1972, 1984).

Other piscivorous birds in Washington that have been studied for their sensitivity to total DDT are double-crested cormorants, black-crowned night-herons, and great blue herons (Henny *et al.*, 1984, 1989; Blus *et al.*, 1980). Cormorants are seabirds that breed in the northern coastal areas of Washington and would not be exposed to contaminants in eastern Washington water bodies. Both species of herons are found in eastern Washington. Assuming that the bioaccumulation rate for herons is the same as for osprey (a factor of ten from food to eggs), black-crowned night-heron productivity may be adversely affected by concentrations of DDE as low as 800 $\mu\text{g}/\text{Kg}$ in their food supply (Henny *et al.*, 1989). Eggshell thickness of great blue herons can be significantly reduced by DDE levels over 1600 $\mu\text{g}/\text{Kg}$ in fish they consume, but reproductive success is apparently not affected because the birds lay replacement clutches (Blus *et al.*, 1980).

Reproductive success of piscivorous mammals, such as mink and river otters, is probably not affected by the concentrations of total DDT identified in this study. Mink fed

100,000 µg/Kg DDT and 50,000 µg/Kg DDD showed no adverse effects to reproduction (Aulerich and Ringer, 1970).

All whole-fish samples collected in 1994 contained total DDT concentrations above the wildlife criterion. Levels in fish from the Palouse River and Lake Sacajawea were only slightly elevated above the criterion, and are probably not a threat to piscivorous wildlife unless they are consuming these fish exclusively. DDE and total DDT concentrations in whole suckers from Lake Chelan and the Entiat and Okanogan Rivers were substantially higher than the criteria, and have the potential to cause adverse effects in sensitive species. White pelicans, osprey, bald eagles, and black-crowned night-herons are likely to experience significant eggshell thinning and reduced hatching success if a high proportion of their diet consists of fish from these three water bodies.

Effects of total DDT contamination in fish from Lake Chelan, and the Entiat and Okanogan Rivers on piscivorous birds may be compounded by the close proximity of these three water bodies. In addition, fish collected from the Wenatchee River for the 1993 WSPMP (Davis *et al.*, 1995) had elevated levels of total DDT. A large proportion of the fish consumed by piscivorous birds feeding from water bodies in Chelan and Okanogan Counties would be contaminated with total DDT, and the birds may be accumulating total DDT faster and to higher concentrations than birds that live where the contamination is more isolated.

The specific effects of these chemical contaminants on local bird populations are unknown, and would be very difficult to determine. The number of nesting pairs of black-crowned night-herons often varies substantially from year to year for a variety of reasons (Henny *et al.*, 1984). Much more population data would be necessary to separate chemical contaminant effects from other factors.

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. These chemicals may also cause sublethal effects, such as endocrine disruption, that can result in subtle adverse changes in the population without increased mortality (Colborn *et al.*, 1996). 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. Fish Tissue and Sediment Sampling Site Positions for the 1994 WSPMP

Site Name	Latitude			Longitude			State Plane	
	deg	min	sec	deg	min	sec	X	Y
Lake Sacajawea at Ice Harbor Dam	46	15	13	118	52	51	2409573	339793
Palouse River at Winona	46	56	44	117	48	13	2673351	599435
Okanogan River above Brewster	48	10	21	119	40	27	2201580	1036565
Lake Chelan near Wapato Point	47	52	57	120	8	58	2074799	927507
Entiat River near Entiat	47	39	50	120	14	10	2065035	850047
Soleduck River near Sappho	48	3	26	124	18	30	1068727	1015931

Appendix B-1. Target Pesticides List for Tissue Analyses

Analyte	Quantitation Limit ¹ (µg/Kg, ppb wet)	Analyte	Quantitation Limit (µg/Kg, ppb wet)
2,4'-DDD	10	endosulfan I	5
4,4'-DDD	10	endosulfan II	7
2,4'-DDE	10	endosulfan sulfate	10
4,4'-DDE	5	endrin	15
4,4'-DDMU	15	endrin aldehyde	5
2,4'-DDT	10	endrin ketone	5
4,4'-DDT	10	ethion	20
aldrin	5	heptachlor	5
alpha-BHC	2	heptachlor epoxide	5
beta-BHC	10	hexachlorobenzene	2
delta-BHC	5	methoxychlor	15
gamma-BHC (Lindane)	2	mirex	5
cis-chlordane	5	oxadiazon	5
trans-chlordane	5	ethyl-parathion	10
oxychlordane	5	methyl-parathion	10
cis-nonachlor	5	pentachloroanisole	5
trans-nonachlor	5	tetradifon	10
alpha-chlordene	5	toxaphene	100
gamma-chlordene	5	PCB-1016	50
chlorpyrifos	10	PCB-1221	50
DCPA (Dacthal)	5	PCB-1232	50
diazinon	50	PCB-1242	50
dichlorobenzophenone	30	PCB-1248	50
dicofol (Kelthane)	100	PCB-1254	50
dieldrin	5	PCB-1260	50

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

Appendix B-2. Target Pesticides List for Sediment Analyses

EPA METHOD 1618

Chlorinated Pesticides

Analyte	Quantitation Limit ¹ (µg/Kg, ppb dry)	Analyte	Quantitation Limit (µg/Kg, ppb dry)
4,4'-DDT	7	oxychlordane	12
4,4'-DDE	7	dicofol (kelthane)	47
4,4'-DDD	7	dieldrin	7
2,4'-DDT	12	endrin	7
2,4'-DDE	12	endrin aldehyde	7
2,4'-DDD	12	endrin ketone	7
DDMU	12	endosulfan I	7
aldrin	7	endosulfan II	7
alpha-BHC	7	endosulfan sulfate	7
beta-BHC	7	heptachlor	7
delta-BHC	7	heptachlor epoxide	7
gamma-BHC (Lindane)	7	hexachlorobenzene (HCB)	12
captan	35	methoxychlor	7
captafol	59	mirex	12
cis-chlordane	12	pentachloroanisole	12
trans-chlordane	7	toxaphene	140
alpha-chlordene	12	PCB-1242	47
gamma-chlordene	12	PCB-1248	47
cis-nonachlor	12	PCB-1254	47
trans-nonachlor	12	PCB-1260	47

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

Appendix B-2 (cont.). Target Pesticides List for Sediment Analyses

EPA METHOD 1618

Nitrogen-Containing Pesticides

Analyte	Quantitation Limit ¹ (µg/Kg, ppb dry)	Analyte	Quantitation Limit (µg/Kg, ppb dry)
alachlor	30	metolachlor	180
ametryn	60	metribuzin	12
atraton	180	MGK-264	420
atrazine	60	molinate	32
benefin	19	napropamide	37
bromacil	74	norflurazon	19
butachlor	43	oxyfluorfen	32
butylate	19	pebulate	30
carboxin	140	pendimethalin	19
chlorothalonil	30	profluralin	30
chlorpropham	62	prometon	60
cyanazine	19	prometryn	60
cycloate	19	pronamide	37
diallate	47	propachlor	25
dichlobenil	15	propazine	60
diphenamid	37	simazine	60
diuron	74	tebuthiuron	60
eptam	19	terbacil	62
ethalfluralin	19	terbutryn	60
fenarimol	37	triadimefon	32
fluridone	99	triallate	32
hexazinone	19	trifluralin	19
metalaxyl	84	vernolate	19

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

Appendix B-2 (cont.). Target Pesticides List for Sediment Analyses

EPA METHOD 1618

Organophosphorus Pesticides

Analyte	Quantitation Limit ¹ (µg/Kg, ppb dry)	Analyte	Quantitation Limit (µg/Kg, ppb dry)
azinphos-ethyl	17	fenitrothion	8
azinphos-methyl	20	fensulfothion	11
carbophenothion	11	fenthion	8
chlorpyrifos	8	fonofos	7
chlorpyrifos-methyl	8	imidan	12
coumaphos	13	malathion	9
DEF	15	mevinphos	11
demeton-O	8	paraoxon-methyl	20
demeton-S	8	parathion	9
diazinon	9	parathion-methyl	8
dichlorvos	9	phorate	8
dimethoate	9	phosphamidan	26
dioxathion	18	propetamphos	22
disulfoton	7	ronnel	8
EPN	11	sulfotepp	7
ethion	8	sulprofos	8
ethoprop	9	temephos	98
fenamiphos	16	tetrachlorvinphos	22

EPA METHOD 8150

Chlorinated Herbicides

2,3,4,5-tetrachlorophenol	33	D CPA (Dacthal)	48
2,4-D	61	dicamba	60
2,4-DB	73	dichlorprop	66
2,4,5-T	48	diclofop-methyl	90
2,4,5-TB	54	ioxynil	62
2,4,5-TP	48	M CPA	120
2,4,5-trichlorophenol	36	M CPP	120
2,4,6-trichlorophenol	36	pentachlorophenol	60
3,5-dichlorobenzoic acid	60	picloram	61
bentazon	90	trichlopyr	48
bromoxynil	60		

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

Appendix C. 1994 Fish Length (Total) and Weight Data

Location and Species	Collection Date (1994)	Mean Length (mm)	Length Range (mm)	Mean Weight (grams)	Weight Range (grams)	Tissue Type
<u>Soleduck River</u> Mountain Whitefish	9/7	348	328-377	393	334-459	Fillet
<u>Entiat River</u> Largescale Sucker (Rep-1)	9/12	502	454-556	1097	899-1343	Whole
Largescale Sucker (Rep-2)		477	461-505	1006	909-1118	Whole
<u>Lake Chelan</u> Largescale Sucker	9/12	306	229-419	383	115-787	Whole
Kokanee		286	247-332	250	157-393	Fillet
Rainbow Trout		259	238-297	173	134-242	Fillet
Smallmouth Bass		288	255-326	479	312-675	Fillet
<u>Okanogan River</u> Largescale Sucker (Rep-1)	9/13	478	443-522	1141	912-1522	Whole
Largescale Sucker (Rep-2)		486	443-555	1129	866-1622	Whole
Carp		602	520-680	3766	2325-5758	Fillet
<u>Palouse River</u> Largescale Sucker	9/14	389	229-473	855	333-1347	Whole
Northern Squawfish		344	332-376	366	260-540	Fillet
<u>Lake Sacajawea</u> Largescale Sucker	9/14	490	459-525	1392	1157-1579	Whole
Channel Catfish		452	386-500	927	627-1221	Fillet

<u>Common Name</u>	<u>Scientific Name</u>
Mountain Whitefish	<i>Prosopium williamsoni</i>
Largescale Sucker	<i>Catostomus macrocheilus</i>
Kokanee (landlocked Sockeye Salmon)	<i>Oncorhynchus nerka</i>
Rainbow Trout	<i>Oncorhynchus mykiss</i>
Smallmouth Bass	<i>Micropterus dolomieu</i>
Carp	<i>Cyprinus carpio</i>
Northern Squawfish	<i>Ptychocheilus oregonensis</i>
Channel Catfish	<i>Ictalurus punctatus</i>

Appendix D. Sediment Conventional Parameters for the 1994 WSPMP

Sample Site	Collection Date	Percent Solids	Percent Total Organic Carbon	Grain Size (percent of total weight)			
				Gravel >2.0 mm	Sand 2.0-0.063 mm	Silt 0.063-0.004 mm	Clay <0.004 mm
Lake Sacajawea	14-Sep	64.5	1.0	1	72	24	3
Okanogan River	13-Sep	42.5	2.0	0	27	67	6
Lake Chelan (Rep-1)	12-Sep	33.2	1.6	0	20	72	8
(Rep-2)				0	18	74	8
(Rep-3)				0	21	71	8
Entiat River	12-Sep	63.2	1.0	12	81	6	1
Soleduck River	7-Sep	71.9	0.6	6	89	4	1
Duplicate 1			0.6				
Duplicate 2			0.7				

Appendix E. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1994

The tissue 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 of 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 can occur as contaminants in commercial formulations of DDT. 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 E. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1994

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, 1995). 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, 1995). 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 usually 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, 1994).

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 E. Characteristics and Interrelationships of Pesticides/PCBs Detected in 1994

Hexachlorobenzene (HCB) is a fungicide that was widely used as a seed protectant until it was banned in 1985 (USEPA, 1995). 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 or 1994.

Bromoxynil is a selective herbicide that is used for postemergent control of weeds in grain crops. Little is known about the environmental fate of bromoxynil (Seyler *et al.*, 1994). The half-life in various soils ranges from ten days to two weeks. Bromoxynil is moderately soluble in water (130 mg/L), so its apparent accumulation in sediments was not expected. Bromoxynil has been detected in about eight percent of the water samples collected for the WSPMP, but always at low concentrations (Davis, 1996).

Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are not pesticides, but are typically analyzed 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, 1995). There are 209 different PCB compounds (congeners). In the United States, 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, 1995). The toxicity of PCBs to humans is poorly understood and is still being investigated.

Appendix F. Sample Collection and Processing Procedures

Fish 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). When possible, whole fish samples were a mixture of males and females. 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 each 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. At the laboratory, all fish were kept frozen until processed.

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. Fillet samples were homogenized with a grinding attachment for a Kitchen-Aid® food mixer. All fish were processed frozen.

Fish collected for fillets (skin on) were processed in the laboratory using the following procedure:

- Clean and remove scales (skin of catfish and carp was removed).
- Remove entire fillet on left side of fish from the gill arch to the caudal peduncle.
- Place fillet in an appropriate container.
- Open body cavity to determine sex.
- Repeat process for all specimens to be included in the composite.
- Homogenize fillets and refreeze to -20° C.

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

Sediment Collection

Sediment samples were collected with a stainless steel 0.05m² Ponar grab sampler. Sampling positions were located in depositional areas as close as possible to the positions where fish samples were collected and were recorded using GPS. After collection, samples were judged for acceptability using the following criteria:

- Partial samples - grabs filling only a portion of the sampler were discarded.
- Washed samples - grabs that were washed excessively from a door staying open or from sloshing were discarded.
- Under- or over-filled sampler - sampler penetration of less than 5cm or a sample touching the top of the sampler was unacceptable.
- Leaves, sticks, and rocks - samples that consisted primarily of leaves, sticks, rocks, or other unrepresentative debris were discarded.

Overlying water was removed by siphoning with a short piece of tubing, being careful not to disturb the surface of the sediment. The top 2cm of sediment was removed with a precleaned stainless steel spatula and placed in a precleaned stainless steel bowl. Only sediment that did not touch the edge of the sampler was removed. The completed composite sample was homogenized to a uniform color and consistency. Enough of the sample was transferred to fill two 8 oz. jars 3/4 full. In addition, aliquots of sediment were taken for total organic carbon, percent solids, and grain size analysis.

Decontamination Procedures

Fish tissue and sediment samples destined for pesticide analysis were contained 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.

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

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

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

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

Appendix G-1. 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 five 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.

Sediment samples were analyzed by Ecology's Manchester Environmental Laboratory. Chlorinated, organophosphorus, and nitrogen-containing pesticides were analyzed using EPA Method 1618, modified to include non-standard target compounds (modifications are summarized in Huntamer *et al.*, 1992). This method allows the use of alternate detectors. The Atomic Emission Detector (AED) was selected because it has a high degree of specificity for the elements of interest (Cl, P, N) and non-target compounds can be identified and quantified. Chlorinated herbicides were analyzed using EPA Method 8150. These methods were developed for the surface water analyses and have been extended for analysis of sediments.

Sediment grain size samples were analyzed using the procedure outlined by the Puget Sound Protocols (Puget Sound Estuary Program, 1986). Total organic carbon in sediment was determined using EPA Method 415.1. Percent lipid in tissue samples is determined using the method described in the USEPA document "Manual of Analytical Methods for the Analyses of Pesticides in Humans and Environmental Samples", EPA-600 18-80-038, June 1980.

Quality Assurance/Quality Control

Field Quality Control Procedures

Field replicate samples were taken to estimate overall precision and to assess environmental variability. Two replicate largescale sucker samples were collected from the Entiat and Okanogan Rivers.

Duplicate tissue samples (splits) were submitted to evaluate analytical precision. Duplicate samples of carp were analyzed from the Okanogan River. Fish tissue quality control check material was submitted in duplicate to estimate analytical accuracy and precision.

Appendix G-1 (cont.). Analytical Methods - QA/QC - Data Review

Laboratory Quality Control Procedures

A portion of the whitefish sample collected from the Soleduck River was used for matrix spike and matrix spike duplicate analyses to detect bias due to interferences from the sample matrix. Sediment samples for matrix spike and spike duplicate analyses were selected by the laboratory, and included samples from the Soleduck River (chlorinated pesticides and chlorinated herbicides) and the Entiat River (organophosphorus pesticides and nitrogen pesticides). 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 of Ecology's Manchester Environmental Laboratory. Sediment results were reviewed by Dickey Huntamer, also with the Manchester Laboratory. No significant problems were encountered for the fish tissue analyses. Matrix spike recoveries for the nitrogen pesticides sediment analyses were low due to degradation after extraction, but before analysis. The samples sat for an extended period of time after extraction while waiting for a new shipment of drying agent. Results for compounds with zero percent recovery were rejected. Results with recoveries of less than 40% were "J" qualified. Other minor difficulties required qualification of affected data. All data were considered acceptable as qualified.

Detection Limits

The detection limits achieved for fish tissue analyses were a significant improvement over past studies. The values in Appendix B-1 are quantitation limits, which are often different for each sample. Detection limits were not calculated separately, but were generally substantially lower than quantitation limits. A quantitation limit is the smallest concentration of a compound that the laboratory can quantify with a specified degree of confidence. When compounds are detected below the quantitation limit, these chemicals can often be positively identified, but the degree of confidence for the concentration of these compounds is lower than for those above the quantitation limit, and reported concentrations are qualified as estimates. In most instances, the level of detection was sufficiently low to compare with even the lowest criteria. However, comparison of qualified results to criteria should be made with caution.

While there is some uncertainty associated with the concentration of compounds detected below the quantitation limit, the probability of a false positive is still low in most cases. In a screening survey, such as the WSPMP, the consequences of a false positive are generally not serious. Detected compounds of interest would simply require additional sampling to verify their presence. False negatives would be more serious, indicating that there is no problem when one may be present.

Appendix G-1 (cont.). Analytical Methods - QA/QC - Data Review

Quality Control Samples

No accuracy or precision criteria have been established for any of the analytical methods used, but duplicate samples 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 G-2 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, cis-nonachlor, and trans-nonachlor, which were 79, 64, and 52 respectively. The average RPD was 31. This same material (essentially a split sample) was also analyzed in 1993. Results from 1993 and 1994 are compared in Appendix H. RPD values ranged from 3 to 56, with an average of 20. This material 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 and precision.

Matrix spike and duplicate recoveries and corresponding RPDs are presented in Appendix G-3a for fish tissue analyses and Appendix G-3b for sediment analyses. Spiking levels were 3-5 times the quantitation limit for most of the target compounds. Recoveries for fish tissue ranged from 32-130% and averaged 89%, indicating good accuracy. The recoveries for heptachlor (39 and 32%) were the only values below 40%. RPD values averaged 7, indicating that precision was also good.

Recoveries for sediment analyses were variable. Spike recoveries for chlorinated and organophosphorus pesticides were excellent ranging from 0-143% with averages of 95 and 82%, respectively, and RPDs of 3 and 19. Only the recoveries for merphos were below 40%; both were zero. These results indicate that the accuracy and precision of the chlorinated and organophosphorus analyses was good. Recoveries for the chlorinated herbicides matrix spike were also good, with an average of 86%, but the duplicate was consistently lower, with an average of 60%, resulting in a relatively high average RPD of 38. These results are still considered to be good.

As discussed above, in the "Data Review" section, analytical difficulties resulted in poor recoveries for the nitrogen-containing pesticides analyses. Seven of the compounds in the matrix spikes had zero percent recovery, and another four were below 40%. RPDs were low with an average of 16, suggesting that all samples were equally affected.

Appendix G-1 (cont.). Analytical Methods - QA/QC - Data Review

Surrogate spike recoveries for fish analyses are presented in Appendix G-4a. Recoveries ranged from 54-131%, with an overall average of 103%. Appendix G-4b lists surrogate recoveries for Sediment analyses. Recoveries ranged from 21-177% with an overall average of 82%. Some of the chlorinated herbicide recoveries for the sediment analyses were low, but only the sample from Lake Chelan was below 40%. These values are all acceptable.

Results from duplicate analyses (splits) are presented in Appendix G-5. One set of duplicate samples was analyzed, in addition to the quality control check sample that was analyzed in duplicate. RPDs ranged from 0-25 with an overall average of 7. 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 G-6), but with an average RPD of 43, were larger than differences between duplicate analyses. However, 30% of the detected compounds were found in only one of the replicates, and were not included in the average. All of the compounds found in only one replicate were detected at concentrations near the limits of detection, below the quantitation limits. Since some of the differences between replicates can be attributed to analytical variability, the 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 G-7 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-2. 1994 Fish Tissue Quality Control Check Material Results
(µg/Kg (ppb) wet weight)**

Analyte	Mean Concentration (± ½ duplicate range)	Expected Value	RPD ¹
4,4'-DDE	610 ±10	495	21
4,4'-DDD	150 ±0	65	79
4,4'-DDT	43 ±0	31	32
dieldrin	205 ±5	152	30
heptachlor epoxide	39 ±1	37	5
cis-chlordane	110 ±10	82	29
trans-chlordane	53 ±1	45	16
cis-nonachlor	87 ±2	45	64
trans-nonachlor	160 ±0	94	52
oxychlordane	28 ±0	28	0
total chlordane	438 ±10	294	39
total PCBs	1300 ±40	1333	3

Analyte	1994 Results Mean Concentration (± ½ duplicate range)	1993 Results Mean Concentration (± ½ duplicate range)	RPD
4,4'-DDE	610 ±10	495 ±5	21
4,4'-DDD	150 ±0	145 ±5	3
4,4'-DDT	43 ±0	29 ±2	39
dieldrin	205 ±5	200 ±0	3
heptachlor epoxide	39 ±1	33 ±1	17
cis-chlordane	110 ±10	62 ±6	56
trans-chlordane	53 ±1	48 ±2	10
cis-nonachlor	87 ±2	61 ±1	35
trans-nonachlor	160 ±0	140 ±0	13
oxychlordane	28 ±0	25 ±0	11
total chlordane	438 ±10	335 ±5	27
total PCBs	1300 ±40	1340 ±0	3

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

Appendix G-3a. Matix Spike Recoveries for 1994 Fish Tissue Analyses (%)

Analyte	Matrix Spike	Matrix Spike Duplicate	RPD ¹
2,4'-DDD	110	100	9.5
4,4'-DDD	120	110	8.7
2,4'-DDE	80	73	9.2
4,4'-DDE	85	80	6.1
4,4'-DDMU	79	73	7.9
2,4'-DDT	80	69	15
4,4'-DDT	110	110	0
aldrin	63	59	6.6
cis-chlordane	100	99	1.0
trans-chlordane	100	98	2.0
oxychlordane	96	91	5.4
cis-nonachlor	110	110	0
trans-nonachlor	81	76	6.4
alpha chlordene	67	62	7.8
gamma chlordene	64	58	9.8
chlorpyrifos	77	74	4.0
dicofol	94	84	11
dichlorobenzophenone	120	120	0
DCPA (dacthal)	130	130	0
diazinon	100	100	0
dieldrin	130	120	8.0
endosulfan I	130	118	9.7
endosulfan II	70	74	5.6
endosulfan sulfate	48	54	12
endrin	120	110	8.7
ethion	84	89	5.8
alpha BHC	76	65	16
beta BHC	67	60	11
gamma BHC	79	69	14
delta BHC	60	53	12.4
heptachlor	39	32	20
heptachlor epoxide	100	99	1.0
hexachlorobenzene	66	61	7.9
methoxychlor	120	120	0
oxadiazon	120	120	0
ethyl parathion	120	120	0
methyl parathion	100	99	1.0
tetradifon	120	120	0
toxaphene	not spiked	not spiked	--
mirex	97	88	9.7
pentachloroanisole	71	64	10
endrin aldehyde	50	47	6.2
endrin ketone	110	100	9.5

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

Appendix G-3b. Matrix Spike Recoveries for 1994 Sediment Analyses (%)

Analyte	Matrix Spike	Matrix Spike Duplicate	RPD ¹
Chlorinated Pesticides			
4,4'-DDD	100	99	1
4,4'-DDE	102	98	4
4,4'-DDT	96	98	2
aldrin	91	90	1
trans-chlordane	94	99	5
dieldrin	91	95	4
endosulfan I	93	92	1
endosulfan II	100	99	1
endosulfan sulfate	102	101	1
endrin	109	107	2
endrin aldehyde	50	53	6
endrin ketone	95	90	5
alpha BHC	95	90	5
beta BHC	101	98	3
delta BHC	91	93	2
gamma BHC (Lindane)	98	94	4
heptachlor	98	93	5
heptachlor epoxide	100	97	3
methoxychlor	101	108	7
Organophosphorus Pesticides			
azinphos ethyl	93	80	15
carbophenothion	115	104	10
chlorpyrifos	71	64	10
chlorpyrifos methyl	108	97	11
demeton-O	63	40	45
demeton-S	96	78	21
disulfoton	106	80	28
EPN	128	108	17
ethion	143	109	27
fenitrothion	77	67	14
fonofos	81	65	22
malathion	62	53	16
merphos (1&2)	0	0	--
sulfotepp	115	99	15

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

Appendix G-3b (cont.). Matrix Spike Recoveries for 1994 Sediment Analyses (%)

Analyte	Matrix Spike	Matrix Spike Duplicate	RPD ¹
Nitrogen Containing Pesticides			
alachlor	60	51	16
atraton	0	0	--
atrazine	0	0	--
bromacil	32	24	29
butachlor	80	53	41
carboxin	31	28	11
chlorpropham	77	66	15
dichlobenil	74	73	1
diphenamid	69	53	26
ethalfluralin	63	60	5
fenarimol	80	88	10
fluridone	30	27	11
metolachlor	0	0	--
metribuzin	28	22	24
MGK-264	0	0	--
molinate	81	59	31
napropamide	79	55	36
norflurazon	68	72	6
oxyflurazon	97	93	4
pebulate	79	67	16
pendimethalin	87	71	20
prometryn	0	0	--
pronamide	66	60	10
propachlor	60	61	2
simazine	0	0	--
tebuthiuron	0	0	--
terbacil	60	51	16
trifluralin	62	62	0
Chlorinated Herbicides			
2,4-D	97	61	46
2,4-DB	97	65	40
2,4,5-T	96	65	39
2,4,5-TB	96	73	27
2,4,5-TP (Silvex)	89	66	30
2,4,5-trichlorophenol	80	59	30
2,4,6-trichlorophenol	75	48	44
2,3,4,5-tetrachlorophenol	77	62	22
3,5-dichlorobenzoic acid	89	66	30
bentazon	83	57	37
bromoxynil	62	30	70
DCPA (Dacthal)	98	69	35
dicamba	97	67	37
dichlorprop	95	69	32
diclofop methyl	87	61	35
ioxynil	41	20	69
MCPA	94	67	34
MCPP	99	75	28
pentachlorophenol	80	68	16
picloram	85	42	68
trichlopyr	87	63	32

Appendix G-4a. Surrogate Recoveries for 1994 Fish Tissue Analyses (%)

Sample Site	Sample Type	DBOB	Surrogates DCB	DBCE
Soleduck River	M Whitefish Fillet	68	104	110
Entiat River	Whole LS Sucker, Rep-1	72	120	123
	Whole LS Sucker, Rep-2	73	119	113
Lake Chelan	Whole LS Sucker	79	124	123
	Kokanee Fillet	77	118	123
	Rainbow Trout Fillet	79	122	131
	Smallmouth Bass Fillet	80	120	124
Okanogan River	Whole LS Sucker, Rep-1	75	117	120
	Whole LS Sucker, Rep-2	84	139	126
	Carp Fillet	86	119	125
	Carp Fillet Duplicate	75	113	119
Palouse River	Whole LS Sucker	74	121	126
	Squawfish Fillet	71	107	114
Lake Sacajawea	Whole LS Sucker	77	116	113
	Catfish Fillet	70	106	108
Matrix Spike		57	109	124
Matrix Spike Duplicate		54	101	117
Method Blank		77	118	115
Quality Control Check Material		75	115	107
QC Check Duplicate		72	118	108
Range		54-86	101-131	107-131
Mean		74	116	118
Standard Deviation		7.7	8.3	7.1

Surrogate key DBOB = 4,4'-dibromooctafluorobiphenyl
 DCB = decachlorobiphenyl
 DBCE = dibutylchloroendate

Appendix G-4b. Surrogate Recoveries for 1994 Sediment Analyses (%)

Sample Site	DBOB	TCX	DCB	TPP	DMNB	TBP
Soleduck River	92	82	85	135	76	43
Entiat River	100	87	75	131	77	63
Lake Chelan	70	73	21	177	77	30
Okanogan River	80	77	36	152	74	48
Lake Sacajawea	78	71	47	136	68	42
Matrix Spike	96	88	96	113	74	64
Matrix Spike Duplicate	83	80	92	92	54	52
Method Blank 1	89	82	91	96	72	42
Method Blank 2	92	94	104	136	78	74
Range	70-100	71-94	21-104	92-177	54-78	30-74
Mean	87	82	72	130	72	51
Standard Deviation	9.6	7.4	29.7	26.6	7.5	13.8

Surrogate Key DBOB = 4,4-dibromooctafluorobiphenyl (chlorinated pesticides)
 TCX = tetrachloro-m-xylene (chlorinated pesticides)
 DCB = decachlorobiphenyl (chlorinated pesticides)
 TPP = triphenyl phosphate (organophosphorus pesticides)
 DMNB = 1,3-dimethyl-2-nitrobenzene (nitrogen-containing pesticides)
 TBP = 2,4,6-tribromophenol (chlorinated herbicides)

Appendix G-5. 1994 Fish Tissue Duplicate Analysis Results ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

Analyte	Sample 1	Sample 2	RPD ¹
<u>Okanogan River Carp</u>			
2,4'-DDD	140	130	7.4
4,4'-DDD	1100	1000	9.5
2,4'-DDE	13	11	17
4,4'-DDE	1800	1500	18
4,4'-DDT	6.3	4.9	25
4,4'-DDMU	130	120	8.0
hexachlorobenzene	0.88	0.89	1.1
PCB-1254	23	27	16
PCB-1260	20	19	5
<u>QC Check Material</u>			
2,4'-DDD	31	31	0
4,4'-DDD	150	150	0
2,4'-DDE	8.6	7.4	15
4,4'-DDE	620	600	3.3
4,4'-DDT	43	43	0
4,4'-DDMU	17	16	6.1
cis-chlordane	120	100	18
trans-chlordane	54	52	3.8
oxychlordane	28	28	0
cis-nonachlor	85	88	3.5
trans-nonachlor	160	160	0
DCPA (Dacthal)	7.5	8.0	6.5
dieldrin	200	210	4.9
endrin	11	11	0
alpha-BHC	11	12	8.7
gamma-BHC	1.5	1.5	0
heptachlor epoxide	39	38	2.6
hexachlorobenzene	9.7	10	3.0
PCB-1254	590	510	15
PCB-1260	750	750	0

¹ - RPD = Relative Percent Difference, $(\text{difference}/\text{mean}) \times 100$

Appendix G-6. 1994 Fish Tissue Replicate Analysis Results ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

Analyte	Replicate 1	Replicate 2	RPD ¹
<u>Entiat River Largescale Sucker</u>			
2,4'-DDD	28	11	87
4,4'-DDD	130	120	8.0
2,4'-DDE	4.0	1.6	86
4,4'-DDE	1700	1100	43
2,4'-DDT	2.0	ND ²	NC ³
4,4'-DDT	160	130	21
4,4'-DDMU	47	26	58
cis-nonachlor	0.28	ND	NC
trans-nonachlor	2.2	1.0	75
hexachlorobenzene	0.63	ND	NC
PCB-1254	28	20	33
PCB-1260	36	40	11
<u>Okanogan River Largescale Sucker</u>			
2,4'-DDD	13	18	32
4,4'-DDD	120	180	40
2,4'-DDE	1.4	2.2	44
4,4'-DDE	760	1100	37
2,4'-DDT	ND	1.2	NC
4,4'-DDT	21	39	60
4,4'-DDMU	19	28	38
cis-nonachlor	0.38	0.42	10
trans-nonachlor	ND	0.81	NC
hexachlorobenzene	0.66	0.78	17
PCB-1254	22	24	9
PCB-1260	34	48	34

¹ - RPD = Relative Percent Difference, $(\text{difference}/\text{mean}) \times 100$

² - ND = Not Detected

³ - NC = Not Calculated

Appendix G-7. Interlaboratory Comparison Results ($\mu\text{g}/\text{Kg}$ (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, $(\text{difference}/\text{mean}) \times 100$

³ ND = Not Detected

⁴ NC = Not Calculated

**Appendix H-1. Pesticides Detected in Fish Tissue Samples for the 1992 WSPMP
(µg/Kg (ppb) wet weight)**

Sample Site	Lake Chelan				Crab Creek			Walla Walla River		
	LSS	RBT	KOK	KOK	Rep1	Rep2		LSS	LSS	WCR
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 H-1 (cont.). Pesticides Detected in Fish Tissue Samples for the 1992 WSPMP
(µg/Kg (ppb) wet weight)**

Fish Species Tissue Type	Yakima River						Mercer Slough		Lake River
	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2	LSS	RBT	LSS
	LSS	LSS	LSS	LSS	SMB	SMB	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

Fish species key

LSS=Largescale Sucker

Tissue type key

WF=Whole Fish

RBT=Rainbow Trout

FIL=Fillet (muscle only)

SMB=Smallmouth Bass

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 H-2. Pesticides Detected in Fish Tissue for the 1993 WSPMP ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

Sample Site	Walla Walla River				Nooksack River		Fishtrap Creek		Spokane River	
	Suckers' Whole-Fish Replicate 1	Suckers' Whole-Fish Replicate 2	Suckers' Whole-Fish Replicate 3	Carp' Fillets	Steelhead' Fillets	Suckers Whole-Fish	RB trout Fillets	Suckers Whole-Fish	RB trout 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	1					
4,4'-DDD	43	63	40	97	15		2			
2,4'-DDT	1	1	1	1	1					
4,4'-DDT	13	14	17	4	4	6	2			
total DDT	361	477	382	707	36	25	11	39	18	
4,4'-DDMU	10	6	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	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

Appendix H-2 (cont.). Pesticides Detected in Fish Tissue for the 1993 WSPMP ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

Sample Site	Wenatchee River		Mission Creek		Chehalis River		Salmon Creek		Vancouver Lake	
	Suckers' Whole-Fish Replicate 1	Suckers' Whole-Fish Replicate 2	Suckers' Whole-Fish Replicate 1	Suckers' Whole-Fish Replicate 2	Suckers' Whole-Fish	M Whitefish Fillets	LM Bass Fillets	LM Bass Fillets	LM Bass Fillets	Carp Whole-Fish
% total lipid	4.98	5.18	4.66	3.30	5.72	2.82	3.85	7.80		
2,4'-DDE	2									
4,4'-DDE	380	270	14	27	23	11	47	95		
2,4'-DDD	8									
4,4'-DDD	68	47		3		4	17	45		
2,4'-DDT	4				1					
4,4'-DDT	32	26								
total DDT	494	343	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	1	7	12	12	2	4	8		
dieldrin										4
endosulfan sulfate										
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

Appendix I. Comparison of Detected Concentrations of Selected Compounds to State-Wide, California, and EPA and USFWS National Results ($\mu\text{g}/\text{Kg}$ (ppb) wet weight)

	DDE	t-chlordane	dieldrin	HCB	lindane	heptachlor epoxide	t-PCBs
Whole-Fish							
Lake Sacajawea	270	15	8	7	u	1	33
Palouse River	170	33	13	10	u	14	31
Okanogan River	930	0.4	u	0.7	u	u	56
Lake Chelan	800	3	u	u	u	u	69
Entiat River	1400	u	u	0.6	u	u	36
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
Filletts							
Lake Sacajawea	360	20	4	5	u	0.5	35
Palouse River	73	7	u	4	0.4	6	11
Okanogan River	1650	u	u	1	u	u	27
Lake Chelan	140	0.5	u	u	u	u	99
Lake Chelan	56	0.3	u	u	u	u	65
Lake Chelan	330	1	u	u	u	u	16
Soleduck River	u	u	u	u	u	u	u
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 Bléthrow, 1991

² - USEPA, 1992

³ - Schmitt *et al.*, 1990