



DEPARTMENT OF
ECOLOGY
State of Washington

**PBTs Analyzed in Bottom Fish from
Four Washington Rivers and Lakes:
Hexabromocyclododecane,
Tetrabromobisphenol A,
Chlorinated Paraffins,
Polybrominated Diphenylethers,
Polychlorinated Naphthalenes,
Perfluorinated Organic Compounds,
Lead, and Cadmium**

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by

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Washington State Department of Ecology
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Waterbody Numbers:

Lake Washington WA-08-9350
Lower Columbia River WA-CR-1010
Lower Yakima River WA-37-1010
Lake Spokane WA-54-9040
(formerly Long Lake, lower Spokane River)

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Abstract

The Washington State Department of Ecology conducted a screening survey to assess the occurrence of persistent, bioaccumulative, and toxic chemicals (PBTs) that have either not previously been analyzed in local fish populations or are a focus of Chemical Action Plans to reduce or eliminate toxic threats. The following chemicals were analyzed in common carp (muscle) and largescale suckers (whole body) collected from Lake Washington, the lower Columbia River, the lower Yakima River, and Lake Spokane (lower Spokane River) in the fall of 2011:

- Hexabromocyclododecane (HBCDD)
- Tetrabromobisphenol A (TBBPA)
- Chlorinated paraffins (CPs)
- Polybrominated diphenyl ethers (PBDEs)
- Polychlorinated naphthalenes (PCNs)
- Perfluorinated organic compounds (PFCs)
- Lead (Pb)
- Cadmium (Cd)

Sampling sites and fish species were selected to maximize the potential for detecting the target chemicals. Flame retardants – HBCDD, TBBPA, PBDEs, and CPs – were a focus of the study.

HBCDD, PCNs, PBDEs, PFCs, CPs, and Pb were detected in all or in most samples. Concentration levels were approximately 100 - 1,000 ng/Kg for HBCDD and PCNs, 2,000 - 100,000 ng/Kg for PBDEs and PFCs, and 300,000 - 1,500,000 ng/Kg for CPs (parts per trillion, wet weight). Pb detections were at 0.10 - 0.50 mg/Kg (parts per million). TBBPA and Cd were not detected in any samples at or above 500 - 900 ng/Kg and 0.10 mg/Kg, respectively. As far as could be determined, this study marks the first time the presence of HBCDD, PCNs, and CPs have been reported in Pacific Northwest freshwater fish.

Recommendations:

- Future studies monitoring PBT residues in Washington State freshwater fish should consider including HBCDD, PCNs, and CPs in addition to other PBTs more routinely analyzed. Preliminary indications are that short- and medium-chain chlorinated paraffins (SCCPs/MCCPs), in particular, may be substantially elevated.
- Some additional investigation into the occurrence of TBBPA is warranted, given the low recoveries encountered in the analyses conducted for the present study.
- Follow-up sampling is recommended to confirm elevated concentrations of HBCDD, PCNs, and CPs detected in Lake Washington suckers, analyzing additional species as appropriate.
- The Washington State Department of Health intends to review the data from this study. Their conclusions about potential human health effects of these compounds may be useful for prioritizing chemicals for follow-up sampling and determining the appropriate level of effort.

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Background

In 2011, the Washington State Department of Ecology (Ecology) Waste 2 Resources Program (W2R) and Environmental Assessment Program (EAP) conducted a screening survey to assess the occurrence of persistent, bioaccumulative, toxic chemicals (PBTs) that have either not previously been analyzed in local fish populations or are a focus of Chemical Action Plans to reduce or eliminate toxic threats. W2R had a particular interest in current-use flame retardants, in view of polybrominated diphenylethers (PBDEs) being phased out of production in the U.S.

W2R and EAP selected the PBTs in Table 1 for analysis, based on high bioaccumulation factors and Ecology's *Multiyear PBT Chemical Action Plan Schedule*

<https://fortress.wa.gov/ecy/publications/summarypages/0707016.html>. Appendix A includes the PBT schedule list from which the target analytes were drawn.

Table 1. Target Chemicals for 2011 Survey of Selected PBTs in Washington Freshwater Fish.

Chemical or Chemical Group	BAF/BCF	Chemical Action Plan	Currently Produced in U.S.?
Hexabromocyclododecane (HBCDD)	18,000	to be determined	yes
Tetrabromobisphenol A (TBBPA)	14,000	"	yes
Short-chain chlorinated paraffins (SCCPs)	40,900	"	yes
Polybrominated diphenyl ethers (PBDEs)	>5,000	Ecology and WDOH (2006)	no (2012)
Polychlorinated naphthalenes (PCNs)	240,000	to be determined	no (1980)
Perfluorinated organic compounds (PFCs)	5,400*	under development	yes
Pb	NA	Ecology and WDOH (2009)	yes
Cd	NA	to be determined	yes

BAF/BCF: bioaccumulation factor/ bioconcentration factor: the ratio of the concentration of a chemical in an aquatic organism to the concentration in the surrounding environment (including food) or to the concentration in water, respectively (from Ecology (2007) except PBDE value from Environment Canada, 2004).

*This value is for perfluorooctane sulfonate (PFOS).

NA: not available

Detailed information on these and other PBTs, including use and release in Washington, regulatory status, bioaccumulation, and toxicity, can be found in the *Chemical Action Plan Schedule* (Gallagher, 2007) and the *PBDE Chemical Action Plan* (Ecology and WDOH, 2006). A brief perspective on each Table 1 chemical or chemical group is provided later in this report. Selected bioaccumulation data for freshwater fish from other areas is also summarized.

HBCDD, TBBPA, PCNs, and SCCPs are infrequently analyzed in environmental samples. As far as could be determined, the present study marks the first effort to assess their presence in Pacific Northwest freshwater fish. The analytical method employed for SCCPs also measured medium- and long-chain chlorinated paraffins (MCCPs and LCCPs).

PBDEs, PFCs, Pb, and Cd have been monitored to varying extents in Washington lakes, rivers, and streams, including in fish tissue samples. Chemical Action Plans have been finalized for PBDEs (Ecology and WDOH, 2006) and Pb (Davies et al., 2009)¹. A Chemical Action Plan for PFCs is anticipated for development. Although Cd is a relatively high-ranking PBT, a schedule has not yet been set for a Chemical Action Plan.

¹ A Chemical Action Plan has also been finalized for mercury (Peele et al., 2003), and one is currently in draft review for polycyclic aromatic hydrocarbons (PAH) (Davies, 2012).

Objectives

The objective of this survey was to assess the occurrence of selected, highly bioaccumulative PBTs in fish from urban/industrial waterbodies in Washington where potential for detection was thought to be greatest. This information was needed to assist Ecology in prioritizing future Chemical Action Plans.

Four fillet and four whole-body samples were analyzed from four rivers and lakes with a history of water quality concerns related to toxic chemical contamination: Lake Washington, lower Columbia River, lower Yakima River, and Lake Spokane (lower Spokane River). The target species were common carp (*Cyprinus carpio*) and largescale suckers (*Catostomus macrocheilus*), both of which have statewide distribution. As a result of their bottom-feeding habit, carp and suckers often have elevated residues of synthetic organic compounds and metals relative to other fish species and thus were considered worst-case samples. Although top predators also qualify as worst-case, they can be difficult to collect and the same species was not available at all four sampling sites.

Filletts were analyzed from carp to obtain data applicable to human health concerns. Suckers were analyzed whole, both as worst-case for fish consumers and for wider ecological concerns. The variability inherent in chemical residues accumulated by individual fish was reduced by using composite samples.

The study was conducted by EAP. Organic compounds were analyzed by AXYS Analytical Services in Sidney B.C. Metals were analyzed by the Ecology Manchester Environmental Laboratory (MEL). Sensitive analytical methods were used to achieve low detection limits for the target chemicals. This study followed a Quality Assurance Project Plan (Johnson, 2011a,b).

Sampling and Analysis

Sample Collection

The field work for this project was conducted during September and October of 2011. Figure 1 shows the approximate locations where fish samples were collected. Detailed maps for each sampling site are provided in Appendix B.



Figure 1. Sites Where Fish Samples were Collected.

Fish sampling followed an EAP standard operating procedure (SOP) (Sandvik, 2006a). Up to five similar-size individuals of each species were collected by electrofishing. Fish selected for analysis were killed by a blow to the head. Each fish was given a unique identifying number and its length and weight recorded (Appendix C). The fish were individually wrapped in aluminum foil, put in plastic bags, and placed on ice for transport to Ecology headquarters, where the samples were frozen pending preparation of the tissue samples.

Tissue Preparation

The fish tissue samples were prepared following an EAP SOP (Sandvik, 2006b). Techniques to minimize potential for contamination were used. People preparing the samples wore non-talc nitrile gloves and worked on heavy-duty aluminum foil or a polyethylene cutting board. The

gloves and foil were changed between samples, and the cutting board was cleaned between samples as described below.

The fish were thawed to remove the foil wrapper and rinsed with tap water to remove any adhering debris, followed by deionized water. The entire fillet from one or both sides of each fish was removed with stainless steel knives, skin removed, and the muscle tissue homogenized in a Kitchen-Aid blender. Whole fish were homogenized in a Hobart blender.

Three to five individual fish were used for each composite sample, except only one carp was obtained from Lake Washington. To the extent possible, the length of the smallest fish in a composite was no less than 75% of the length of the largest fish (EPA, 2000). The composites were prepared using equal weights from each fish. The pooled tissues were homogenized to uniform color and consistency, using three passes through the blender. The homogenates were placed in glass jars with Teflon lid liners, cleaned to EPA (1990) quality assurance/quality control specifications, except high-density polyethylene jars obtained from AXYS were used for PFCs.

Cleaning of resecting instruments, cutting boards, and blender parts was done by washing with Liquinox detergent, followed by sequential rinses with tap water, dilute nitric acid, de-ionized water, and pesticide-grade acetone. The items were then air dried on aluminum foil in a fume hood before use.

The fish tissue samples were refrozen for shipment with chain-of-custody record to the analyzing laboratories. Excess tissue was retained for all samples and archived frozen at Ecology headquarters.

Chemical Analysis

Organic compounds and percent lipids were analyzed by AXYS. Pb and Cd were analyzed by MEL. Table 2 shows the methods used.

Table 2. Analytical Methods.

Analysis	Method	Reference
HBCDD	LC-MS/MS	AXYS MLA-070
TBBPA	LC-MS/MS	AXYS MLA-079 Rev. 03
CPs*	LR-GC/MS	AXYS MLA-020 Rev. 01
PBDEs	HR-GC/MS	EPA 1614
PCNs	HR-GC/MS	AXYS MLA-030
PFCs	LC-MS/MS	AXYS MLA-043
Pb and Cd	ICP/MS	EPA 200.8
Percent lipids	gravimetric	Solvent extraction

*includes short-, medium-, and long-chain chlorinated paraffins (CPs)

LC- MS/MS: liquid chromatography-mass spectrometry/mass spectrometry

HR- GC/MS: high resolution gas chromatography/high resolution mass spectrometry

LR -GC/MS: low resolution gas chromatography/mass spectrometry

ICP/MS: inductively coupled plasma/mass spectrometry

AXYS holds accreditation with the Canadian Association for Laboratory Accreditation (CALA) for PBDEs and PFCs in tissue by HR-GC/MS and LC-MS/MS, respectively. Reciprocity exists between CALA and the Ecology Laboratory Accreditation Program.

No laboratories are currently accredited to analyze HBCDD, TBBPA, CPs, or PCNs. (AXYS' application for accreditation from CALA for HBCDD and TBBPA in serum is currently in progress.) AXYS was the only laboratory that responded to Ecology's request for qualifications and a quote. A waiver to contract with AXYS for HBCDD, TBBPA, CPs, and PCNs was obtained from Ecology's Quality Assurance Officer.

The detection and quantitation limits that AXYS and MEL typically achieved in fish samples for this project are listed in Table 3. Units of ng/Kg (nanogram per kilogram) are equivalent to parts per trillion; mg/Kg (milligram per kilogram) is parts per million.

Table 3. Sensitivity of Analytical Methods (*approximate values*).

Chemical or Chemical Group	Estimated Detection Limit†	Estimated Quantitation Limit†	Units
HBCDD	- -	100	ng/Kg
TBBPA	500	500	ng/Kg
CPs	1,000	- -	ng/Kg
PBDEs*	0.3	6	ng/Kg
PCNs	0.2	2.0	ng/Kg
PFCs	- -	500	ng/Kg
Pb	0.08	0.1	mg/Kg
Cd	0.03	0.1	mg/Kg

*2.9 and 49 ng/Kg for PBDE-209

†Method Detection Limit and Reporting Limit for metals

Data Quality

Data Review and Verification

MEL reviewed and verified all the chemical data for this project. Results of the organic analyses conducted by AXYS were reviewed by MEL's quality assurance coordinator or a MEL chemist experienced with the method. The reviews followed National Functional Guidelines for Superfund Organic Methods Data Review (EPA, 2005a). For the metals results generated by MEL, final review was performed by the unit supervisor or an analyst experienced with the method. Quality assurance and quality control at MEL are described in MEL (2008, 2012).

MEL prepared written case narratives assessing the qualitative and quantitative precision and bias of these data. The reviews include a description of analytical methods and an assessment of holding times, calibration, internal standard recoveries, ion abundance ratios, method blanks, on-going precision and recovery, labeled compound/surrogate recoveries, matrix spike recoveries, laboratory control samples, and laboratory duplicates, as appropriate.

Flags were added by AXYS to draw attention to quality control (QC) conditions that may affect the data. MEL interprets the effect on data quality and adds qualifiers, as appropriate, that are consistent with MEL protocols and Ecology's Environmental Information Management System (EIM) guidelines.

With the exception of TBBPA, discussed below, the results generally met acceptance criteria for these analyses. The reviews and the complete data reports are available from the author on request. Project data can also be accessed through EIM (www.ecy.wa.gov/eim).

Tetrabromobisphenol A (TBBPA)

Percent recovery values for the $^{13}\text{C}^{12}$ -labeled TBBPA surrogate were in the range 10 to 15% in the fish samples. Recoveries were somewhat better in the laboratory blank and laboratory control sample at 19%. These values are below AXYS' interim lower method control limit value of 20%. This resulted in elevated detection limits for native TBBPA in the samples. However, isotope dilution quantification corrects for losses through the analytical procedure. In AXYS' opinion, "any detected concentration and reported detection limits would not be significantly affected by the low recovery values of the $^{13}\text{C}^{12}$ -TBBPA. Given that detection limits provide the method's lower limit, the presence or absence of TBBPA below the detection limit cannot be ascertained." (Devin Mitchell, AXYS, personal communication)

Appendix D has a more detailed assessment by AXYS of their results for TBBPA.

Chlorinated Paraffins (CPs)

CP technical mixtures contain thousands of isomers. There are, for example, roughly 4,200 theoretical isomers and homologues in the SCCP formulations containing 60% chlorine by weight. These compounds have been described “as the most challenging group of substances to analyze and quantify” (Sverko et al., 2012).

AXYS de-archived their Short-Chained Chloroparaffin method (MLA-020 r01) to analyze fish tissue samples for this project. The method provides positive identification of short-, medium-, and long-chain CP components identified in the method description. The method is aligned to methods developed by Environment Canada and Fisheries & Oceans Canada around 2001. The results are suitable for CP reconnaissance (identification of occurrence and levels) and provide information as to whether CPs require further attention in the area studied.

This method has been infrequently run in the past seven years and therefore does not have a wealth of QC statistics to calculate rigid recovery limits and calibration acceptance criteria. Bracketing calibration was used based on technical mixture standards. Analyst discretion was used to determine validity of results vs. preliminary criteria. It is understood that not all CP compounds may be quantifiable in the specific matrices studied. (Devin Mitchell, AXYS, personal communication.)

Method Blanks

Laboratory method blanks were included with each sample batch analyzed. No analytically significant levels of Pb or Cd were detected in the method blanks for metals.

Low levels of some target compounds were detected in blanks for the organics analyses. In cases where the concentration measured in a sample was at least five times greater than the blank, the blank result was considered insignificant relative to the native concentration in the sample and the data were used without further qualification (EPA, 2005). Where the sample concentration was less than five times the blank, the result was flagged as not detected. Results between the estimated quantitation limit (EQL) and estimated detection limit (EDL) were raised to the EQL and flagged as not detected.

Analytical Precision

Estimates of analytical precision were obtained from laboratory duplicates: one homogenized sample split into two separate subsamples. One duplicate was analyzed for fillets and one for whole fish. Lake Spokane samples were used.

The results are summarized in terms of relative percent difference (RPD) in Table 4. RPD is the difference between duplicates expressed as a percent of the mean value. Due to a miscommunication with the laboratory, a duplicate was not analyzed for CPs.

Consistent results were achieved for almost all target chemicals. Duplicate analyses agreed within approximate 20% for alpha-HBCDD (beta and gamma not detected) and better than 10% for the other organic compounds. Cd was not detected in any of the duplicate samples.

Pb showed greater variability, 36% RPD in muscle and 51% RPD in whole fish. These discrepancies could be due to bone fragments in the samples. Pb is primarily sequestered in the bony parts of fish which are difficult to homogenize, especially in a whole fish sample.

Table 4. Agreement between Duplicate Samples.

Organics in ng/Kg, metals in mg/Kg.

Sample Type	Sample No.	alpha-HBCDD	TBBPA	ΣCPs	ΣPBDEs
Carp muscle	-4	128	786 UJ	NA	92,017
	-5	160	1,500 UJ	NA	87,786
	RPD =	22%	ND	- -	5%
Sucker whole	-8	196	529 UJ	NA	103,840
	-10	242	498 UJ	NA	106,848
	RPD =	21%	ND	- -	3%
Sample Type	Sample No. (1112028-)	ΣPCNs	ΣPFCs	Pb	Cd
Carp muscle	-4	139	22,033	0.13	0.098 U
	-5	137	21,035	0.18	0.095 U
	RPD =	1%	5%	36%	ND
Sucker whole	-8	113	39,241	0.35	0.100 U
	-10	105	36,265	0.59	0.100 U
	RPD =	7%	8%	51%	ND

RPD: relative percent difference

U: The analyte was not detected at or above the reported result.

J: Estimated value

ND: Not detected

NA: Not analyzed

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Results and Discussion

Common carp and largescale suckers, collected from four Washington lakes and rivers in 2011, were analyzed for selected PBTs in muscle or as whole-body samples. Results are described for the individual chemicals or chemical groups below, along with a brief perspective on use, environmental behavior, temporal trends, and occurrence in freshwater fish. A summary table follows with the combined chemical data.

Where totals are shown (Σ), these are the summed concentrations for detected compounds only, including estimated values for tentatively identified compounds (NJ qualified data). Results for duplicate samples (Lake Spokane) were averaged (see Table 4). If both results were non-detect, the lower quantitation or reporting limit was used.

Fish Samples Analyzed

The fish samples obtained for this study are described in Table 5.

Table 5. Fish Samples Analyzed.

Waterbody	Collection Date (2011)	Species / Tissue	Number of Individuals	Mean Weight (grams)	Mean Total Length (mm)	Percent Lipids
Lake Washington	10-Oct	Common carp / muscle	1	3,262	592	2.3
Lower Columbia River	29-Sep		5	3,003	571	4.0
Lower Yakima River	27-Oct		4	3,325	606	4.6
Lake Spokane	4-Oct		3	3,674	641	2.4
Lake Washington	10-Oct	Largescale sucker / whole	5	1,426	502	9.9
Lower Columbia River	29-Sep		3	968	449	6.1
Lower Yakima River	27-Oct		5	387	323	8.5
Lake Spokane	4-Oct		5	1,348	505	2.7

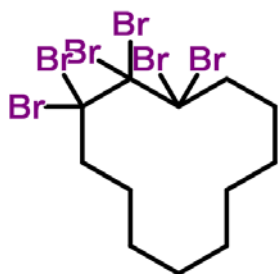
Three to five individuals of each species were collected at most locations, except only a single carp was encountered in Lake Washington. The average weight and length of the fish used in the samples were similar for both species, with the exception of suckers from the Yakima River being smaller fish.

Most of the organic compounds analyzed for this study are lipophilic (fat soluble). Spatial patterns in the data could be influenced by the amount of lipids in the samples because of its effect on chemical uptake across the gills and other membranes. Lipid content was therefore determined to help assess differences in chemical residues among fish collection sites. It should be noted, however, that studies often fail to find a correlation between bioaccumulative organic compounds and lipids, due to chemical uptake from food, the reproductive cycle, and other reasons (Herbert and Keenleyside, 1995; Stow et al., 1997).

Lipids in carp muscle were within a relatively narrow range of 2.3 - 4.6%. Whole suckers exhibited a wider variation of 2.7 - 9.9%, with the highest levels occurring in specimens from Lake Washington and the Yakima River.

Flame Retardants

Hexabromocyclododecane (HBCDD)



*Hexabromocyclododecane*²

HBCDD was first produced in the 1960s and is currently the second most widely used brominated flame retardant (BFR), after tetrabromobisphenol A. Most of the HBCDD is added to polystyrene products for the building and construction industry. Commercial HBCDD is a mixture of three main isomers: alpha (10 - 13%), beta (1 - 12%), and gamma (75 - 89%). Alpha-HBCDD is more persistent and bioaccumulative than the other isomers and biomagnifies in marine and aquatic food webs. HBCDD is an additive – as opposed to reactive – flame retardant not chemically bound to products and thus more readily released to the environment. There is evidence that background levels of HBCDD have been increasing over time in fish and other biota. *References: Covaci et al. (2006), Ecology (2007), Law et al. (2008), CECBP (2008), Arnot et al. (2009), Klecka et al. (2009, 2010), CETOCOEN (2010), Marvin et al. (2011), GLWQA (2011).*

All three HBCDD isomers were analyzed in fish samples for the present study. Only alpha-HBCDD was detected (Table 6). The quantitation limit was approximately 100 ng/Kg (parts per trillion).

Alpha-HBCDD was detected in muscle and/or whole fish from all four waterbodies (Figure 2). Concentrations were in the range of 103 - 234 ng/Kg (parts per trillion), except for a much higher concentration of 1,120 ng/Kg in whole suckers from Lake Washington. The relatively high lipid content of this sample (9.9%) may have been a factor in the result. HBCDD was not similarly elevated in Lake Washington carp muscle (<98 ng/Kg, 2.3% lipids). Overall, however, there was no obvious correlation between HBCDD and percent lipids.

² Chemical structures shown in this report are from www.chemspider.com.

Table 6. Summary of Results for HBCDD (ng/Kg, wet weight).

Sample Type and Collection Site	alpha - HBCDD		beta- HBCDD		gamma- HBCDD	
Common carp / muscle						
Lake Washington	98	U	98	U	98	U
Lower Columbia River	100	U	100	U	100	U
Lower Yakima River	103		99	U	99	U
Lake Spokane	144		98	U	98	U
Largescale sucker / whole						
Lake Washington	1,120		100	U	100	U
Lower Columbia River	234		96	U	96	U
Lower Yakima River	99	U	99	U	99	U
Lake Spokane	219		96	U	96	U

U: The analyte was not detected at or above the reported result.

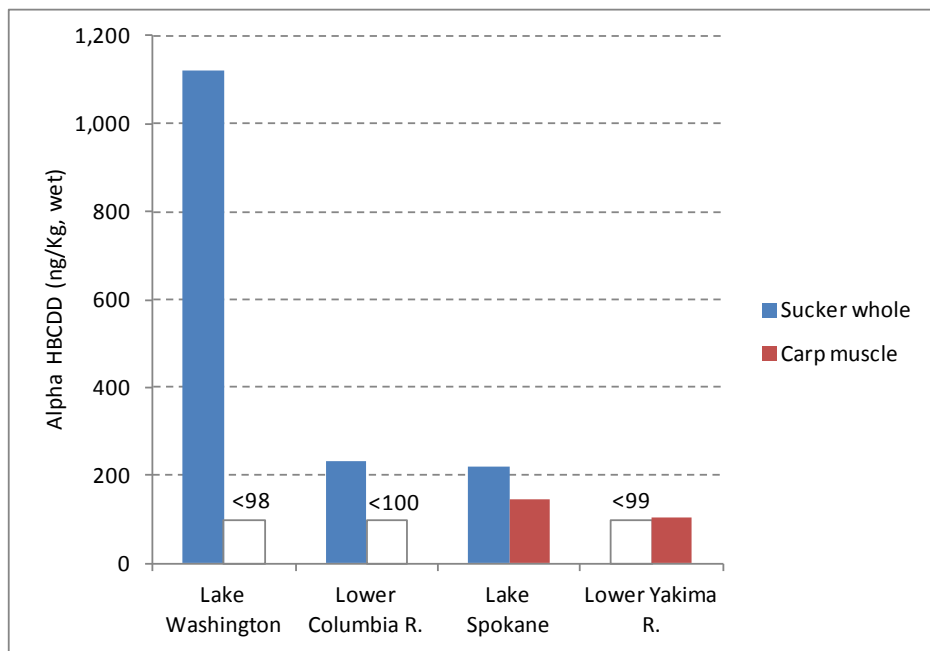


Figure 2. Alpha HBCDD in Fish Tissue Samples.

Unfilled bars not detected at or above value shown.

Several studies have reported HBCDD levels in freshwater fish from other parts of the U.S or in Canada. Table 7 summarizes selected data for species that occur in Washington or related species. Mean concentrations are shown; the Washington means are for detected samples only.

Table 7. HBCDD Concentrations in Freshwater Fish from the U.S. and Canada Compared to Present Study Findings for Washington State.

Mean concentrations in ng/Kg, wet weight.

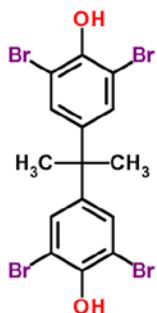
Waterbody	Species	Tissue	Date	N=	alpha-HBCDD	beta-HBCDD	gamma-HBCDD	ΣHBCDD	Ref.
Lake Ontario	Lake trout	whole body	2004	5	2,448	26	228	2,703	1
Lake Winnipeg, Manitoba	Walleye	muscle	2002	5	75	14	48	138	2
	Lake whitefish	"	"	5	14	6	12	32	2
	White sucker	"	"	5	42	6	45	94	2
	Burbot	"	"	5	52	18	146	216	2
Roanoke River, North Carolina	Carp	muscle	2006-07	7	4,180	176	1,540	5,896	3
	Redhorse sucker	muscle	"	8	1,440	24	224	1,688	3
Washington rivers and lakes	Carp	muscle	2011	4	124	<100	<100	124	4
	Largescale sucker	whole body	2011	4	524	<100	<100	524	4

References:

1. Ismail et al., 2009
2. Law et al., 2006
3. Chen et al., 2011
4. Present study

The range of HBCDD concentrations found in Washington fish samples (103 -1,120 ng/Kg) encompasses or approaches most of the concentrations reported for these other waterbodies. The Chen et al. study listed above on the Roanoke River also analyzed fish from the nearby Hyc0 River downstream of known flame retardant-using industrial sites. HBCDD concentrations in these samples were one to two orders of magnitude higher than in the Roanoke.

Tetrabromobisphenol A (TBBPA)



Tetrabromobisphenol A

TBBPA is the highest-volume BFR in the world, representing about 60% of the total market. It is primarily (90%) used as a reactive additive, covalently bound to epoxy and polycarbonate resins in printed circuit boards. Environmental levels of TBBPA are generally low, probably due to its reactive use. TBBPA data for abiotic and biotic matrices are scarce compared to HBCDD and other flame retardants. The available fish tissue data come primarily from European studies. Most samples have been below the limit of quantitation (typically around 1,000 ng/Kg wet weight). TBBPA's relatively high bioconcentration factor may be balanced by rapid excretion. Risks for humans concerning TBBPA exposure may be relatively low. *References: Morris et al. (2004), Ecology (2007), CECBP (2008), Johnson-Restrepo (2008), Covaci et al. (2009), ESFA (2011a), GLWQA (2011).*

Results from analyzing TBBPA in Washington freshwater fish samples are summarized in Table 8. TBBPA was not detected in either fish muscle or whole fish at reporting limits of approximately 500 - 900 ng/Kg.

As previously noted, the TBBPA analysis for this project suffered from low recovery of the radio-labeled TBBPA surrogate, an indication that recovery of native TBBPA from the samples may also have been low (see Data Quality). Reporting limits were comparable to or better than similar studies reported in the literature which have also failed to detect TBBPA. Nevertheless, it is possible that the low-level presence of TBBPA may have been missed in these samples.

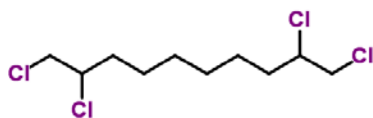
Table 8. Summary of Results for TBBPA (ng/Kg, wet weight).

Sample Type and Collection Site	TBBPA	
Common carp / muscle		
Lake Washington	500	UJ
Lower Columbia River	931	UJ
Lower Yakima River	525	UJ
Lake Spokane	786	UJ
Largescale sucker / whole		
Lake Washington	503	UJ
Lower Columbia River	500	UJ
Lower Yakima River	490	UJ
Lake Spokane	498	UJ

U: The analyte was not detected at or above the reported result.

J: Estimated value

Chlorinated Paraffins (CPs)



Example: Tetrachlorodecane ($C_{10}H_{18}Cl_4$)

Short-chain chlorinated paraffins (SCCPs), first introduced in the 1930s, are complex mixtures mainly used as flame retardants in vinyl plastics and as high-temperature lubricants in metal working machinery. More limited applications include as flame retardants in rubber, paints, adhesives, and sealants. The average chlorine content of SCCPs ranges from approximately 40% to 70% with the limiting molecular formulas set at $C_{10}H_{19}Cl_3$ and $C_{13}H_{16}Cl_{12}$. Medium-chain (C_{14-17}) and long-chain (C_{18-28}) chlorinated paraffins (MCCPs and LCCPs) are alternatives to SCCPs and also have PBT properties. Chlorinated paraffins continue to be manufactured, imported, and used in industrial applications in the U.S. SCCPs and MCCPs have potential for biomagnification. SCCP concentrations in Great Lakes fish and sediments increased in the 1970s and have decreased since then. *References: Tomy et al. (1997), Ecology (2007), Tomy et al. (2007), Environment Canada (2008), Houde et al. (2008), EPA (2009a), Ismail et al. (2009), Klecka et al. (2009, 2010), GLWQA (2011).*

Table 9 summarizes the results of analyzing short-, medium-, and long-chain chlorinated paraffins in Washington fish tissue samples.

Table 9. Summary of Results for Chlorinated Paraffins (ng/Kg, wet weight).

Sample Type and Collection Site	SCCPs	MCCPs	LCCPs	Σ CPs
Common carp / muscle				
Lake Washington	194,000	107,000	18,200	320,000
Lower Columbia River	242,000	132,000	30,700	404,000
Lower Yakima River	459,000	190,000	39,200	687,000
Lake Spokane	340,000	208,000	28,900	577,000
Largescale sucker / whole				
Lake Washington	895,000	663,000	108,000	1,670,000
Lower Columbia River	391,000	259,000	53,200	703,000
Lower Yakima River	541,000	480,000	89,900	1,110,000
Lake Spokane	353,000	245,000	66,000	665,000

Short-, medium-, and long-chain chlorinated paraffins were detected in all samples. The highest concentrations were recorded for Lake Washington and the Yakima River. SCCPs ranged from 194,000 to 459,000 ng/Kg in carp muscle and 353,000 to 895,000 ng/Kg in whole suckers. Figure 3 plots the SCCP data by location and sample type.

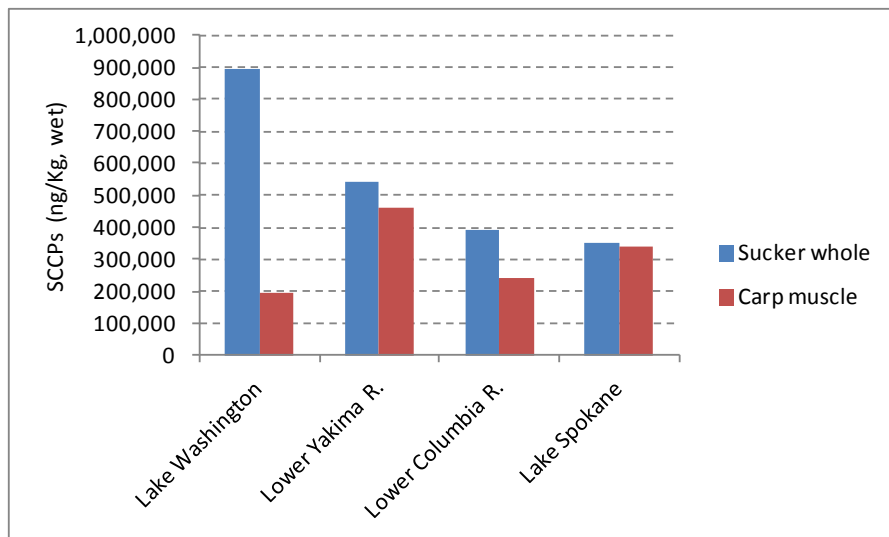


Figure 3. SCCPs in Fish Tissue Samples.

Total CPs reached 1,670,000 ng/Kg, almost 2 parts per million. On average, SCCPs and MCCPs comprised 57% and 32% of the total, respectively (Figure 4). LCCPs were found at much lower levels, about 7% of total CPs. The relative amounts of each group were fairly consistent among sampling sites, as illustrated for whole suckers in Figure 5.

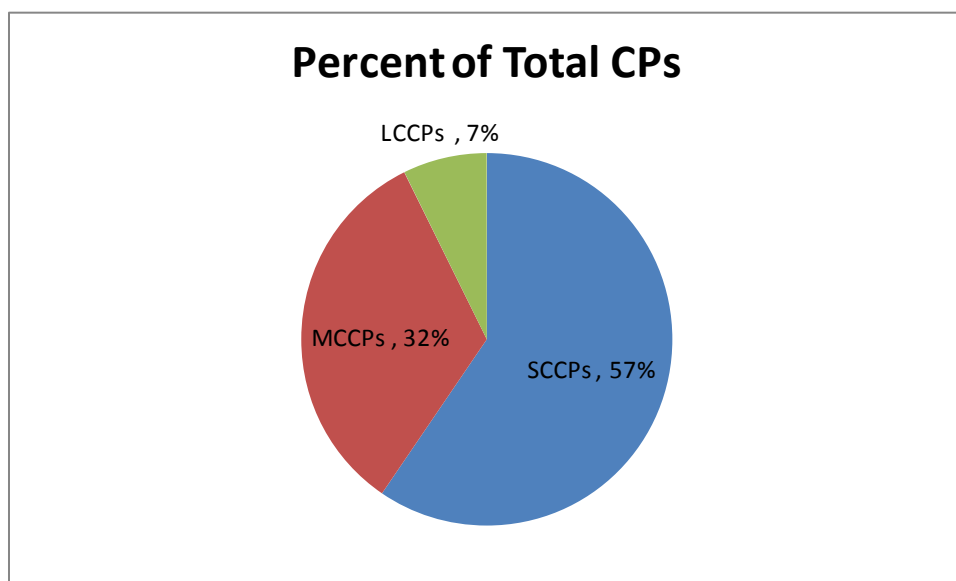


Figure 4. Relative Contribution of Short-, Medium-, and Long-Chain CPs to Total CPs in Fish Tissue Samples from Four Washington Rivers and Lakes (*average*).

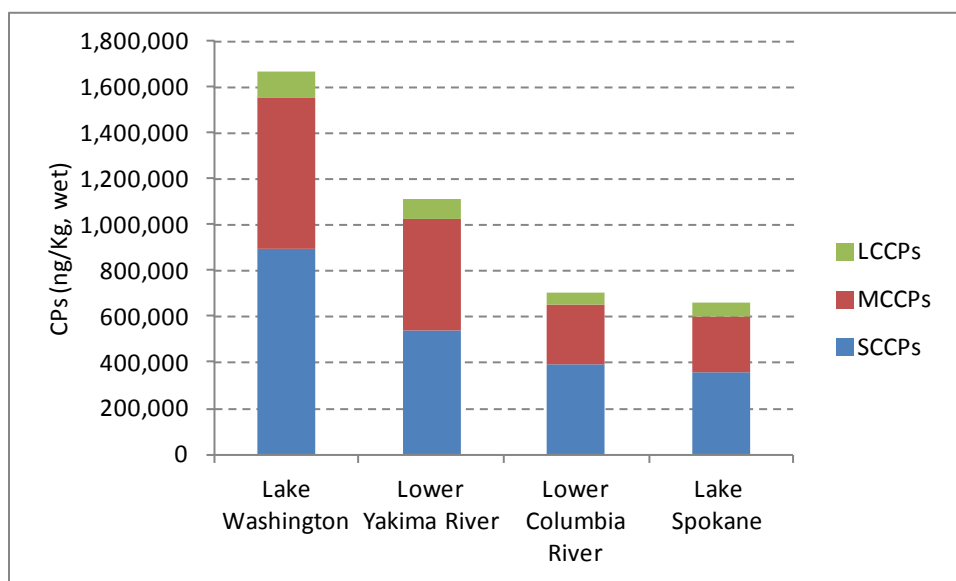


Figure 5. Relative Concentrations of Short-, Medium-, and Long-Chain CPs in Whole Sucker Samples.

Monitoring data for chlorinated paraffins are rather limited. Several investigators have measured SCCPs and MCCPs in fish from the Great Lakes and vicinity (Table 10). These studies did not report any results for LCCPs.

Table 10. SCCP and MCCP Concentrations Measured in Freshwater Fish from the U.S. and Canada Compared to Present Study Findings for Washington State.

Mean concentrations in ng/Kg, wet weight.

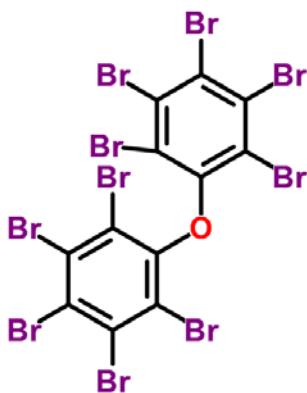
Waterbody	Species	Tissue	Date	N=	ΣSCCPs	ΣMCCPs	Ref.
Detroit River, Michigan	Yellow perch	muscle	1995	1	1,148,000	NA	1
	Carp			1	305,000	NA	1
Lake Michigan	Sculpin	whole body	2001	2	69,000	2,900	2
	Lake Trout			7	123,000	5,600	2
Lake Ontario	Sculpin			2	25,000	108,000	2
	Lake Trout			7	34,000	24,000	2
Lake Ontario	Carp	whole body	1996	3	2,630,000	NA	3
	Lake Trout			10	66,000	NA	3
Lake Ontario	Lake Trout	whole body	2004	5	17,440	8,150	4
Washington lakes and rivers	Carp	muscle	2011	4	308,750	114,250	5
	Largescale sucker	whole body		4	545,000	411,750	5

1. Tomy et al. (1997)
2. Houde et al. (2008)
3. Muir et al. (2001)

4. Ismail et al. (2009)
5. Present study
- NA: not analyzed

As described earlier in this report, chlorinated paraffins are exceedingly complex mixtures that are difficult to analyze. Interlaboratory comparisons have shown poor agreement on SCCP measurements, sometimes differing by more than an order of magnitude (Sverko et al., 2012). Although the results for Washington look reasonable, the apparent elevations compared to some other waterbodies may or may not be significant. These findings do, however, appear to warrant further investigation.

Polybrominated Diphenyl Ethers (PBDEs)



Example: Decabromodiphenyl ether (PBDE-209)

Until recently, PBDEs were the most widely used BFRs in the U.S. and Canada, followed by TBBPA, and then HBCDD. Three main types of PBDEs are used in consumer products: Penta-BDE, Octa-BDE, and Deca-BDE. U.S. manufacturers of Penta-BDE and Octa-BDE agreed to voluntarily stop producing these two forms by the end of 2004. Washington's PBDE Law ([RCW 70.76](#)) placed several restrictions on the use of PBDEs in products sold in Washington State, including a prohibition on Deca-BDE effective in 2011. In 2009, three major producers reached an agreement with EPA to stop producing, importing, and selling Deca-BDE by the end of 2012. The highest levels of PBDEs have been found in North America, more than 10 times above those reported from Europe. PBDEs have shown dramatic increases in environmental samples, including Pacific Northwest freshwater fish beginning in the 1990s – a trend that appears to be on the decline. *References: Rayne et al. (2003), Ecology and WDOH (2006), Environment Canada (2006), EPA (2009b), Ismail et al. (2009), Klecka et al. (2009, 2010), Furl and Meredith (2010a), EFSA (2011b), GLWQA (2011).*

Table 11 and Figure 6 show the total PBDE concentrations measured in Washington fish samples from the present study.

Total PBDEs ranged over two orders of magnitude, from 5,285 ng/Kg in Lake Washington carp muscle to 105,344 ng/Kg in whole suckers from Lake Spokane. Muscle tissue from Lake Spokane carp was also high in PBDEs (89,902 ng/Kg).

The Lake Spokane samples had the lowest lipid levels in the study. Lipid-normalized concentrations of total PBDEs in these samples were elevated to an even greater extent compared to fish from other locations, 3,809 and 3,872 ug/Kg lipid for muscle and whole fish, respectively,

vs. 113 - 901 ug/Kg lipid in fish from Lake Washington, the lower Columbia River, and the lower Yakima River (parts per billion).

Table 11. Summary of Results for Total PBDEs (*ng/Kg, wet weight*).

Sample Type and Collection Site	ΣPBDEs
Common carp / muscle	
Lake Washington	5,285
Lower Columbia River	26,965
Lower Yakima River	41,202
Lake Spokane	89,902
Largescale sucker / whole	
Lake Washington	64,710
Lower Columbia River	44,136
Lower Yakima River	9,625
Lake Spokane	105,344

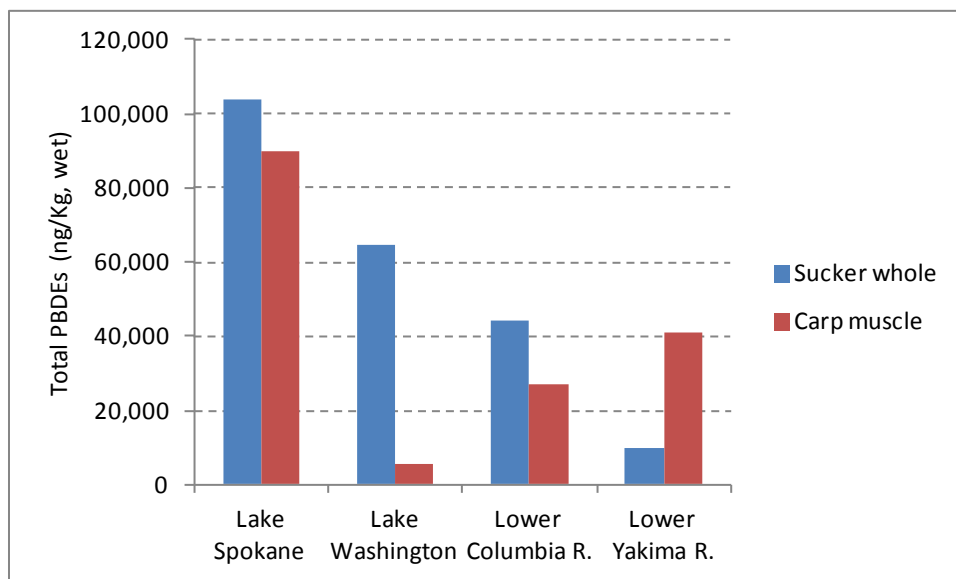


Figure 6. Total PBDEs in Fish Tissue Samples.

Of the 47 individual PBDE congeners³ analyzed, 29 were routinely detected (Figure 7). Congeners 47, 100, 28/33, 49, and 154, in that order, contributed most of the PBDE residues, 97% of total PBDEs, on average (Figure 8). These tri-, tetra-, penta-, and hexa-BDEs are

³ One of many variants or configurations of a common chemical structure.

typically encountered in the highest concentrations in fish tissue samples, both locally and nationally (Hites, 2004; Johnson et al., 2006).

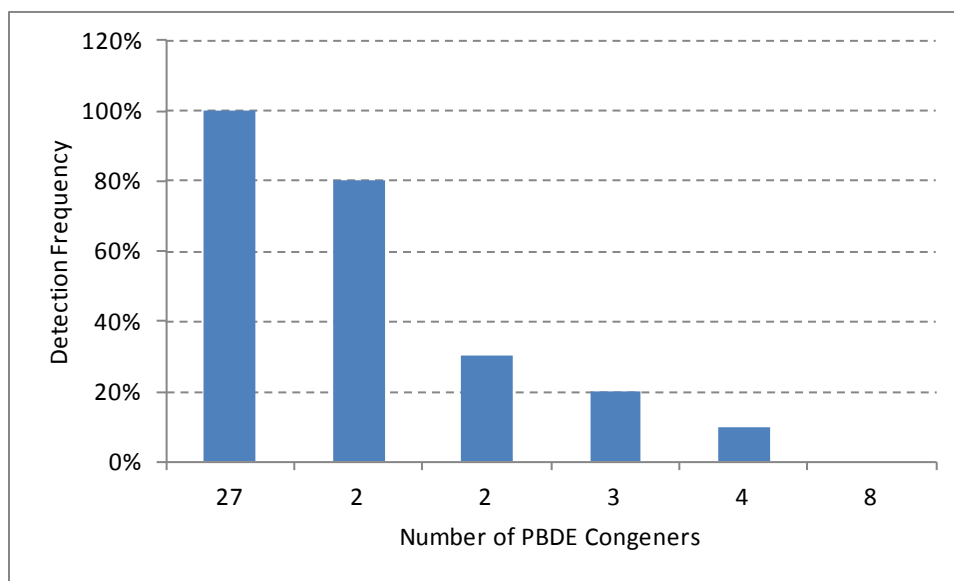


Figure 7. Detection Frequency of PBDE Congeners in Fish Tissue Samples from Four Washington Rivers and Lakes.

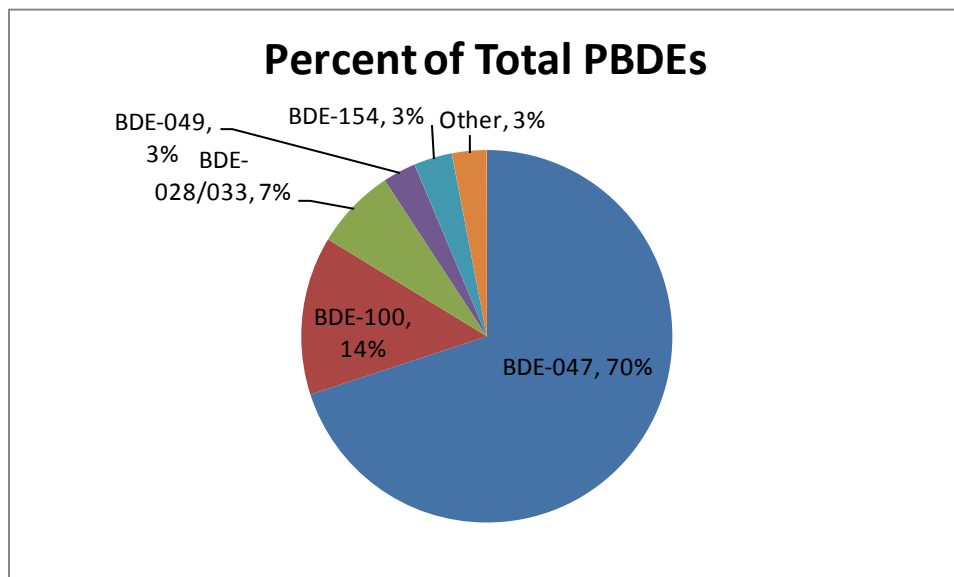


Figure 8. Relative Contribution of PBDE Congeners to Total PBDEs in Fish Tissue Samples from Four Washington Rivers and Lakes (*average*).

Currently produced Deca-BDE (PBDE-209) was detected in all samples, but at relatively low levels. Mean concentrations were 22 ng/Kg in muscle and 18 ng/Kg in whole fish. Due to the large size of the molecule, PBDE-209 is poorly accumulated by fish (Dodder et al., 2002). However, PBDE-209 has been shown to degrade to lower PBDE species that do bioaccumulate (Ecology and WDOH, 2006).

PBDE concentrations in Washington freshwater fish have been documented in several studies (e.g., Seiders and Deligeannis, 2009; Johnson et al., 2006; WDOH, 2005). Special attention has focused on the Spokane River due to the unusually high levels first discovered in 1999 (Johnson and Olson, 2001). Furl and Meredith (2010) analyzed more recent PBDE data on Spokane River fish. They concluded that concentrations had declined between 2005 and 2009.

Figure 9 compares the 2005/2009 data from Furl and Meredith on whole suckers from Lake Spokane with the sample collected at this same site in 2011. The result for 2011 suggests that PBDE levels are continuing to decline in this part of the river. However, the small sample size for 2011 limits the ability to conclude that PBDE levels are still dropping. Ecology will be collecting a new set of data on PBDEs in Spokane River fish this fall (2012).

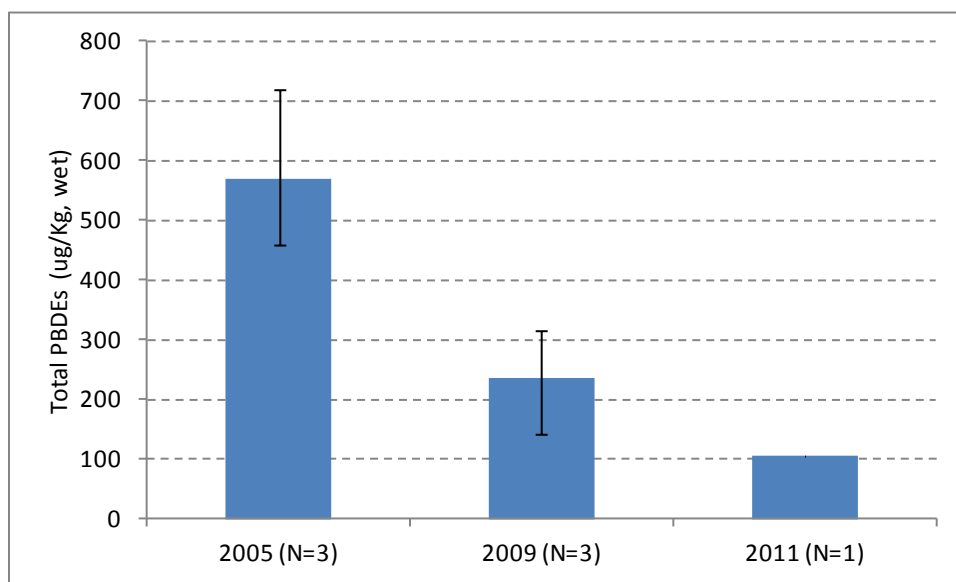


Figure 9. Total PBDEs in Whole Suckers Collected from Upper Lake Spokane (Spokane River) in 2005 - 2011.

ug/Kg, wet; parts per billion; min and max error bars.

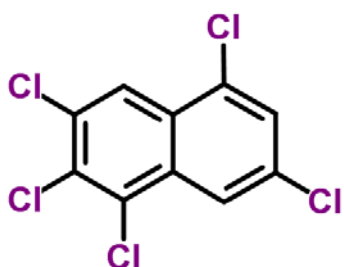
Waterbodies and sample types for the present survey were selected to maximize the potential for detecting target PBTs. A comparison of the PBDE concentrations measured in carp muscle with results on fish samples from other Washington lakes and rivers gives a perspective on PBDE levels grading from background to urban-industrial (Table 12). The waterbodies sampled for the present study are clearly elevated in PBDEs compared to other parts of the state. Similar data are not available for the other chemicals analyzed or for whole fish.

Table 12. Summary of Total PBDE Data on Fish Muscle Samples from Washington Rivers and Lakes (ng/Kg, wet weight).

Data Set	N=	Median	90th percentile
Northeast Washington Background*	23	765	3,810
Statewide Background*	32	1,560	1,731
Statewide Non-Background*	187	3,210	22,340
Present study	4	34,084	75,292

*from Johnson et al. (2011c)

Polychlorinated Naphthalenes (PCNs)



Example: 1,2,3,5,7 -Pentachloronaphthalene

PCNs are structurally similar to polychlorinated biphenyls (PCBs) and share many of the same properties. Until the 1970s, PCNs were high-volume industrial chemicals, about 10% of PCB usage. U.S. production stopped in 1980. The use and application of PCNs is diverse: as capacitor dielectrics, cutting oils, engine oil additives, electroplating stop-off compounds, die casting, wood, paper, and fabric preservatives, and wire insulation. Other sources include as an additive to flame retardants, from municipal waste incineration, and as contaminants in commercial PCB mixtures. The pattern of PCN toxicity resembles TCDD (dioxin). Two studies in the Great Lakes, conducted in 1996-2003, calculated that PCNs contributed as much as half the combined TCDD toxicity equivalents⁴ (TEQs) from dioxin-like PCNs and PCBs in food chain samples. *References: Jakobsson and Asplund (2000), Van de Plassche and Schwegler (2002), Ecology (2007), Helm et al. (2008), Fernandez et al. (2011), Environment Canada (2011), Kannan et al. (2011).*

Seventy-five individual PCN congeners are theoretically possible, ranging from mono- to octa-chlorinated. Seventy congeners were analyzed in fish samples for the current project. Thirty-six of these co-elute with other congeners and cannot be differentiated by this method. Table 13 and Figure 10 summarize the results in terms of the summed concentrations of the PCNs detected.

⁴ EPA and the World Health Organization have not yet recommended TCDD toxicity equivalency factors (TEFs) for PCNs, but agree they should be considered for inclusion in the TEF concept (EPA, 2010; Van den Berg et al., 2006).

Table 13. Summary of Results for Total PCNs (ng/Kg, wet weight).

Sample Type and Collection Site	ΣPCNs
Common carp / muscle	
Lake Washington	184
Lower Columbia River	89
Lower Yakima River	156
Lake Spokane	138
Largescale sucker / whole	
Lake Washington	1,145
Lower Columbia River	257
Lower Yakima River	75
Lake Spokane	109

PCNs were detected in all samples. In most instances, concentrations were in a relatively narrow range of 75 -257 ng/Kg. A much higher concentration, 1,145 ng/Kg, was found in whole suckers from Lake Washington, similar to findings for HBCDD. Here again, the elevated lipid content in this sample would favor PCN accumulation.

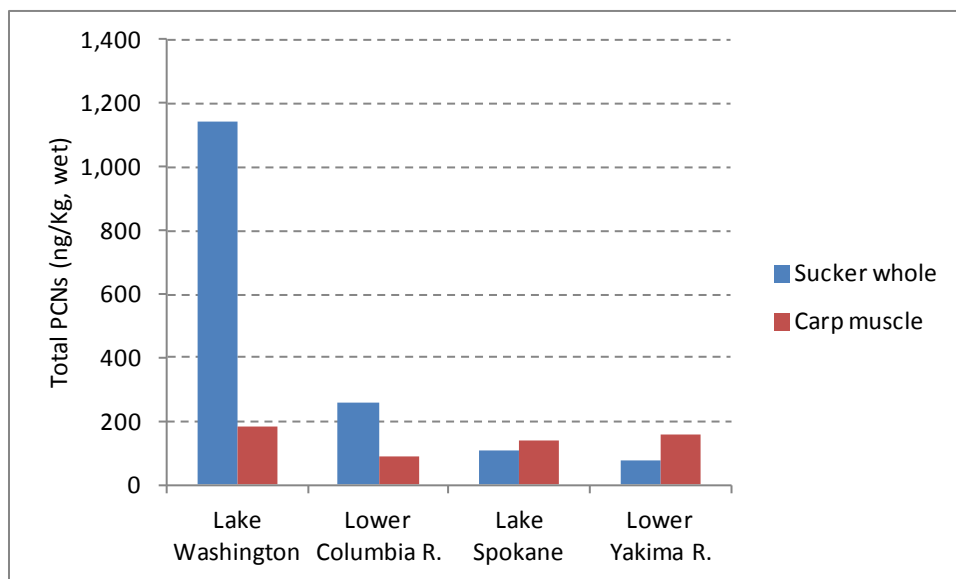


Figure 10. Total PCNs in Fish Tissue Samples.

Of the 70 congeners analyzed, 50 were quantified in 80% or more of the samples, although a number of these co-elute and were reported as single values by the laboratory (Figure 11).

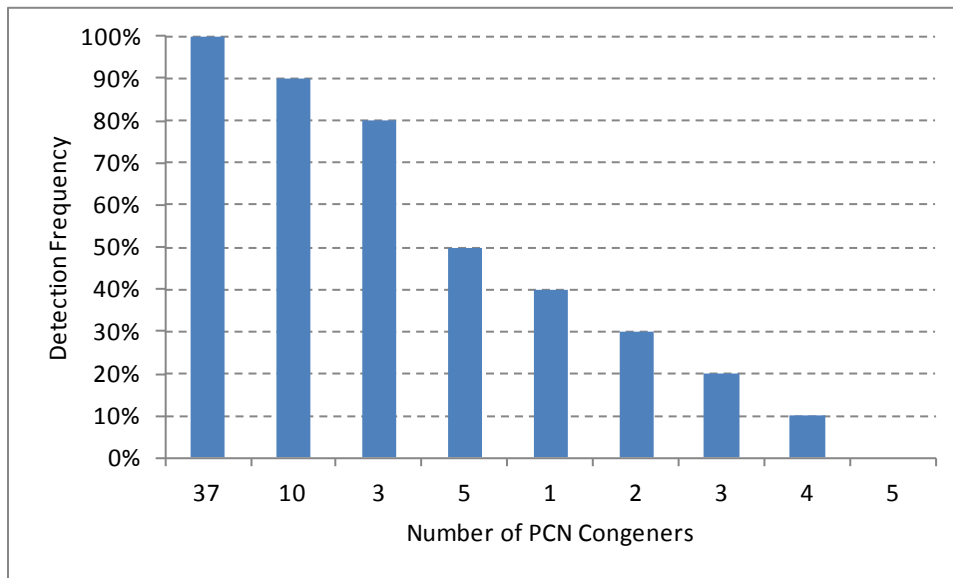


Figure 11. Detection Frequency of PCN Congeners in Fish Tissue Samples from Four Washington Rivers and Lakes.

Six PCNs contributed more than half (57%) of the total PCN concentration, on average (Figure 12). The congeners present at the highest levels were 1,2,3,5,7-pentaCN, 1,2,4,6,8-pentaCN, and 1,3,5,7-tetraCN. These same penta and tetra congeners are commonly reported to be among those that dominate in fish and wildlife (Jakobsson and Asplund, 2000; Fernandez et al., 2011; Helm et al., 2008).

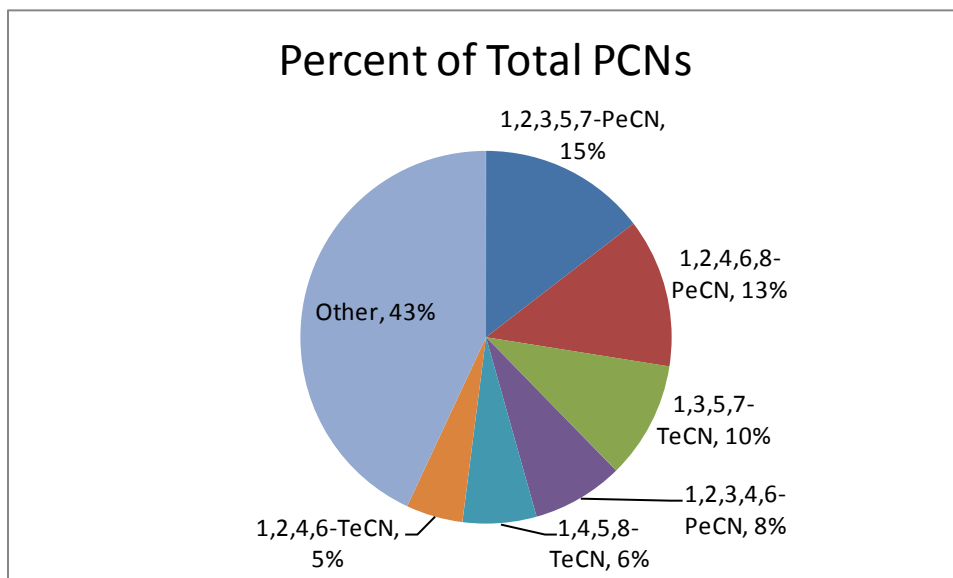


Figure 12. Relative Contribution of PCN Congeners to Total PCNs in Fish Tissue Samples from Four Washington Rivers and Lakes (*average*).

Table 14 compares the PCN results with concentrations reported for selected freshwater fish species from other parts of North America. Concentrations similar to the Washington samples have been found in some rivers and lakes. Much higher levels have been reported in fish from waterbodies with known sources (Detroit River) or in top predator species (lake trout).

Table 14. Total PCN Concentrations Measured in Freshwater Fish from the U.S. and Canada Compared to Present Study Findings for Washington State.

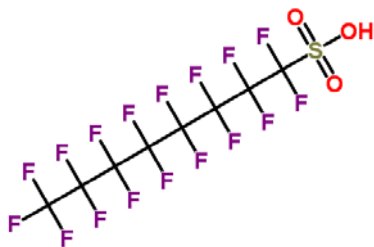
Mean concentrations in ng/Kg, wet weight.

Waterbody	Species	Tissue	Date	N=	Σ PCNs	Ref.
Detroit River, Michigan	Carp	whole body	1996	2	13,900	1
Pine River, Michigan		muscle	1997	1	110	1
Muskegon River, Michigan	Redhorse sucker		1996	1	160	1
Great Lakes	Lake trout			4	660	1
Raisin River, Michigan	Smallmouth bass		1998-99	3	18	2
	Largemouth bass			1	223	2
Lake Ontario	Lake trout	whole body	2002	5	3,500	3
Washington rivers and lakes	Carp	muscle	2011	4	142	4
	Largescale sucker	whole body		4	396	4

References:

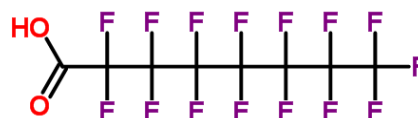
1. Kannan et al. (2000)
2. Hanari et al. (2004)
3. Helm et al. (2008)
4. Present study

Perfluorinated Organic Compounds (PFCs)



Examples:

Perfluorooctane sulfonate (PFOS)



Perfluorooctanoic acid (PFOA)

PFCs are a family of chemicals that impart fire resistance and oil, stain, grease, and water repellency. The most noteworthy representatives are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). PFOS is used in metal plating, the semiconductor industry, and in hydraulic fluids for the aviation industry. PFOA is used to make Teflon®. Other applications for PFOS/PFOA are in the fabrication of water- and stain-resistant materials (e.g., Gore-Tex®) and in fire-fighting foams.

PFCs have been in widespread use over the past 50 years. EPA (2009c) reports the highest PFC levels in U.S. freshwater fish have been found near the 3M® Cottage Grove site in Minnesota. PFOS in liver samples from bass, walleye, and carp ranged up to 6,350,000 ng/Kg wet weight. Since 3M® phased out production of PFOS in 2002, PFOA is now the most common PFC in commerce. As PFOS-based products became more strictly regulated in developed countries, production shifted elsewhere. China began large scale production in 2003. In 2006, EPA initiated a PFOA stewardship program in which eight major producers committed to reducing the manufacture of PFOA by 95% no later than 2010.

PFCs were first reported in biota in 2001. Unlike organic compounds that partition into lipids, PFCs persist in protein-rich compartments of fish, birds, and marine mammals such as carcass, blood, and liver. PFOS appears to have potential for biomagnification.

References: Ecology (2007), EPA (2009c), Furdui et al. (2008), Klecka et al. (2009, 2010), Delinsky et al. (2010), Furl and Meredith (2010b), Giesy and Kannan (2010), GLWQA (2011), Environment Canada (2012).

Present study results for PFCs are summarized for detected compounds in Table 15 and Figure 13. As noted in the table, five out of the 14 PFCs analyzed were not detected at or above 240 - 510 ng/Kg. The complete chemical names for all PFCs analyzed are in Appendix D.

Table 15. Summary of Results for PFCs (*ng/Kg, wet weight*).

Sample Type and Collection Site	PFOS		PFUnA		PFDA		PFDnA		PFOSA		PFNA		PFOA		PFHpA		ΣPFCs
Common carp / muscle																	
Lake Washington	15,700		1,310		1,170		1,750		341	U	244	U	244	U	244	U	19,930
Lower Columbia River	3,920		280		248		262		340	U	243	U	243	U	243	U	4,710
Lower Yakima River	2,130		250	U	250	U	250	U	350	U	250	U	250	U	250	U	2,130
Lake Spokane	19,800		295		1,110		330		340	U	250	U	243	U	243	U	21,534
Largescale sucker / whole																	
Lake Washington	45,700		20,300		10,000		9,540		3,430		1,590		790		558		91,908
Lower Columbia River	5,300		602		423		478		605		250	U	250	U	250	UJ	7,408
Lower Yakima River	2,930		240	U	339		240	U	337	U	240	U	240	U	240	UJ	3,269
Lake Spokane	34,650		485		1,595		399		404		463		243	U	243	UJ	37,996

PFCs not detected: PFBA, PFBS, PFPeA, PFHxA, and PFHxS (< 240 - < 510 ng/Kg).

U: The analyte was not detected at or above the reported result.

J: Estimated value

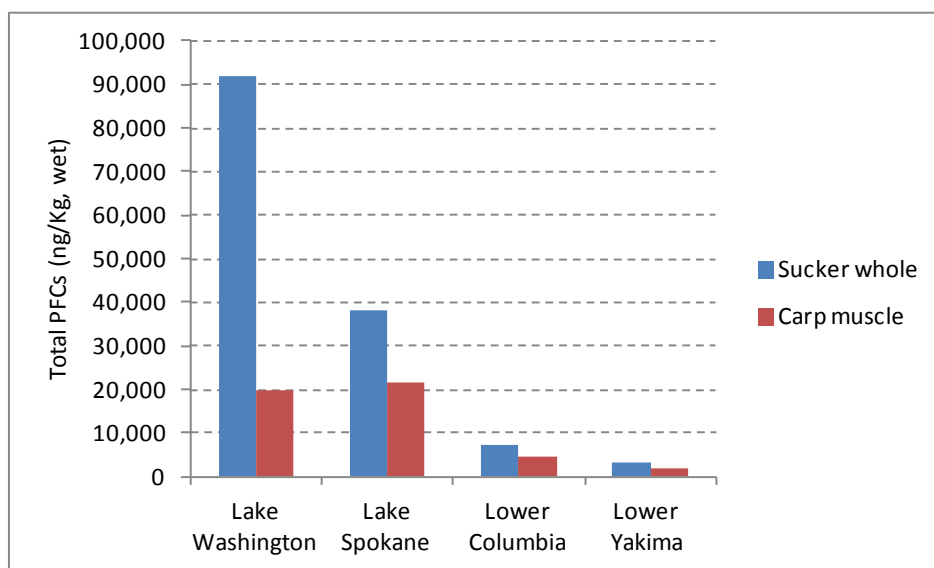


Figure 13. Total PFCs in Fish Tissue Samples.

Total PFC levels followed a decreasing trend in both fish muscle and whole fish going from Lake Washington to Lake Spokane to the Lower Columbia River to the Lower Yakima River. The maximum and minimum concentrations observed were 91,908 ng/Kg (whole suckers) and 2,130 ng/Kg (carp muscle). PFOS was detected in all samples, PFDA, PFUnA, and PFDoA in approximately 80% of the samples, and PFOSA, PFNA, PFOA and PFHPA in approximately 40-10% of samples (Figure 14). Eighty-two percent of the total PFC residues was due to PFOS, on average (Figure 15). The predominance of PFOS is consistent with previous analyses of PFCs in Washington freshwater fish (Furl and Meredith, 2010b). PFOA is generally concluded to have a much lower bioaccumulation potential than PFOS (Klecka et al., 2010).

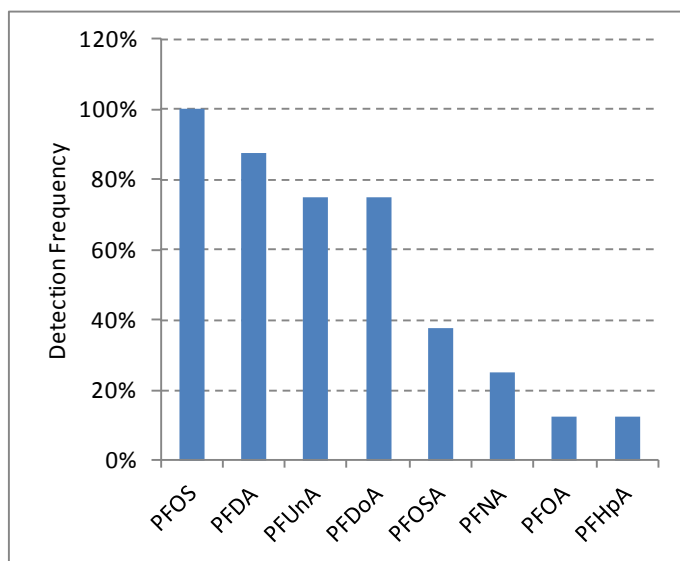


Figure 14. Detection Frequency of PFC Compounds in Fish Tissue Samples from Four Washington Rivers and Lakes.

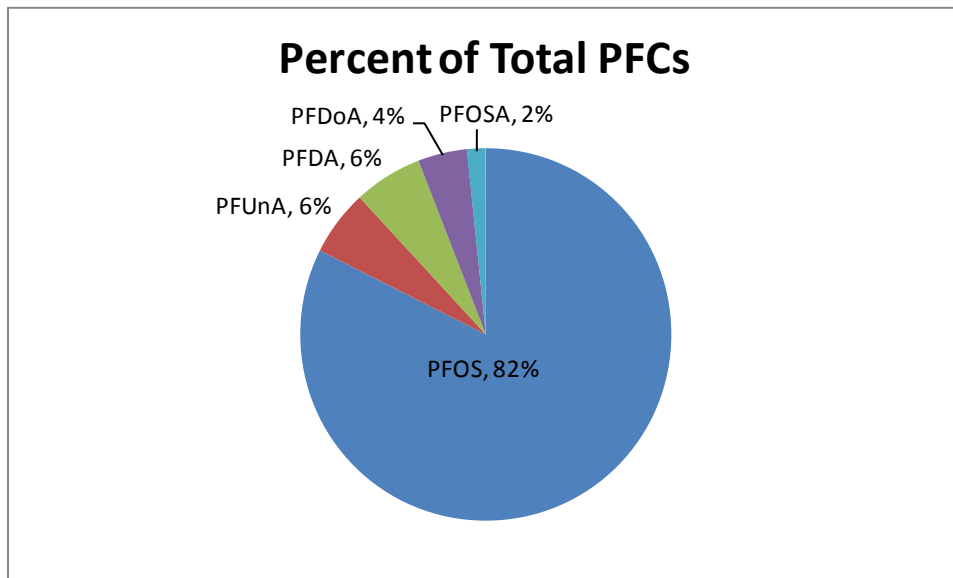


Figure 15. Relative Contribution of PFC Compounds to Total PFCs in Fish Tissue Samples from Four Washington Rivers and Lakes (*average*).

In 2008, Furl and Meredith (2010b) analyzed PFCs in surface water, treatment plant effluents, fish tissue, and osprey eggs collected across Washington State. Detection limits for fish tissue were considerably higher than in the present study: 10,000 ng/Kg vs. approximately 500 ng/Kg. PFOS was the primary contaminant detected in fish. Concentrations in fish muscle were < 10,000 - 75,000 ng/Kg, comparable to the range of PFOS concentrations measured in the present study. PFOS levels in fish liver reached 527,000 ng/Kg. PFDA, PFUnA, and PFDaA were each detected once in both fillet and liver samples at concentrations lower than PFOS. PFCs were not detected at two background locations (<10,000 ng/Kg, Entiat and Quinault Rivers).

Table 16 compares the PFOS concentrations measured in fish muscle samples from the same sites sampled by Furl and Meredith in 2008 and the present study in 2011. PFOS levels for Lake Washington are in reasonable agreement. Differences in detection limits make it difficult to compare findings for the lower Columbia and Spokane Rivers.

Table 11 in Furl and Meredith (2010b) summarizes data on PFOS in fish samples from various U.S. rivers and lakes. They conclude that “Washington fillet values were within or lower than the expected range based on previous studies.” On the other hand, the maximum osprey egg PFOS concentration from the Furl and Meredith study (910,000 ng/Kg) was the second highest value recorded for osprey eggs nationwide.

Table 16. PFOS Concentrations in Fish Muscle Samples from Washington Waterbodies Sampled in 2008 (Furl and Meredith, 2010b) and 2011 (present study) (*ng/Kg, wet weight*).

Waterbody	Species	Date	PFOS
Lake Washington	Smallmouth bass	2008	33,580
	Largescale sucker		11,140
	Peamouth chub		51,210
	Yellow perch		22,450
	Carp	2011	15,700
Lower Columbia River	Largemouth bass	2008	75,540
	Largescale sucker		<10,000
	Carp	2011	3,920
Spokane River	Largescale sucker	2008	<10,000
	Carp	2011	19,800

Lead (Pb) and Cadmium (Cd)

Pb and Cd are naturally occurring in rocks and soils. The major use of Pb is in lead-acid storage batteries and, historically, in leaded gasoline and lead-based paints. Historical sources in Washington State also include smelter emissions and lead-arsenate insecticide applications to orchards. Most (~ 99%) of the Pb currently being cycled through the environment is due to man-made inputs. Cd has many uses, including batteries, pigments, metal coatings, and plastics. In Washington freshwater and marine areas, concentrations of Pb have decreased since the ban on tetraethyl lead gasoline in the 1970s and other restrictions. Efforts to reduce or recycle Cd in consumer products have been more limited. The evidence for temporal trends in Cd levels is inconclusive in Washington.

Uptake of Pb and Cd by fish and other aquatic organisms is fundamentally different than lipophilic organic compounds. Most Pb is bound to the skeleton, especially in areas of active bone formation. Cd tends to concentrate in the viscera of vertebrates, particularly the liver and kidneys. As a result, fish muscle tends to be low in both Pb and Cd. Elevated levels have been reported in fish organs or whole fish samples, but almost always associated with industrial or urbanized areas or point-source discharges of metals-containing waste.

References: Eisler (1985, 1988), Lefkovitz et al. (1997), Ecology (2007, 2009), Hallock (2009), Furl and Roberts (2011), Mathieu and Friese (2012).

Table 17 shows the Pb and Cd concentrations measured in the carp and sucker samples. In most cases, Pb was near or below reporting limits (<0.10 - 0.23 mg/Kg) both in muscle and in whole fish. Cd was not detected in any samples at or above 0.10 mg/Kg.

Table 17. Summary of Results for Pb and Cd.
mg/Kg, parts per million, wet weight.

Sample Type and Collection Site	Pb		Cd	
Common carp / muscle				
Lake Washington	0.32		0.10	U
Lower Columbia River	0.10		0.10	U
Lower Yakima River	0.10	U	0.10	U
Lake Spokane	0.15		0.10	U
Largescale sucker / whole				
Lake Washington	0.10	U	0.10	U
Lower Columbia River	0.23		0.10	U
Lower Yakima River	0.10	U	0.10	U
Lake Spokane	0.47		0.10	U

U: The analyte was not detected at or above the reported result.

For the most part, these Pb and Cd levels are comparable to fish tissue samples analyzed from background lakes and rivers in Washington (Johnson et al., 2011c; Seiders, 2010). Somewhat elevated Pb concentrations were found in the Lake Spokane sucker and Lake Washington carp samples, 0.47 and 0.32 mg/Kg, respectively.

The Spokane River is contaminated with Pb, Cd, and other metals due to historic mining and milling operations in Idaho (Hopkins et al, 1985; Pelletier, 1998; Kadlec, 2000). Serdar and Johnson (2006) reported Pb concentrations of approximately 3 - 7 mg/Kg in whole sucker samples from the upper Spokane River in Washington in 2005, decreasing to about 1 mg/Kg or less further downstream in Lake Spokane, comparable to the result for 2011. Cd concentrations in whole suckers also decreased moving downstream, from approximately 0.15 - .25 mg/Kg to less than 0.10 mg/Kg (not detected) in Lake Spokane, the same result obtained in 2011.

Elevated Pb in the Lake Washington carp muscle sample may be associated with the surrounding dense urban/industrial land use. As noted earlier in this report, the presence of bone fragments in fish muscle samples can cause an elevated result for Pb.

Summary of Results

Results for all of the PBTs analyzed in fish tissue samples for this study are compiled in Table 18. PCNs, PFCs, PBDEs, and CPs were detected in all samples. HBCDD and Pb were found in about half the samples and at least once for every waterbody. TBBPA and Cd were not detected.

Table 18. Summary of Results for Selected PBTs Analyzed in Fish Tissue Samples Collected from Four Washington Rivers and Lakes in 2011.

ng/Kg for organics, mg/Kg for metals; wet weight.

Sample Type and Collection Site	Lipids (%)	TBBPA		HBCDD		ΣPCNs	ΣPFCs	ΣPBDEs	ΣCPs	Pb		Cd	
Common carp / muscle													
Lake Washington	2.3	500	UJ	98	U	184	19,930	5,285	320,000	0.32		0.10	U
Lower Columbia River	4.0	931	UJ	100	U	89	4,710	26,965	404,000	0.10		0.10	U
Lower Yakima River	4.6	525	UJ	103		156	2,130	41,202	687,000	0.10	U	0.10	U
Lake Spokane	2.4	786	UJ	144		138	21,534	89,902	577,000	0.15		0.10	U
Largescale sucker / whole													
Lake Washington	9.9	503	UJ	1,120		1,145	91,908	64,710	1,670,000	0.10	U	0.10	U
Lower Columbia River	6.1	500	UJ	234		257	7,408	44,136	703,000	0.23		0.10	U
Lower Yakima River	8.5	490	UJ	99	U	75	3,269	9,625	1,110,000	0.10	U	0.10	U
Lake Spokane	2.7	498	UJ	219		109	37,753	105,344	665,000	0.47		0.10	U

U: The analyte was not detected at or above the reported result.

J: Estimated value

Figure 16 gives a perspective on the relative concentrations of the organic compounds analyzed. Concentration levels were approximately 100 - 1,000 ng/Kg for HBCDD and PCNs, 2,000 - 100,000 ng/Kg for PBDEs and PFCs, and 300,000 - 1,500,000 ng/Kg for CPs. TBBPA was not detected at or above approximately 500 - 900 ng/Kg.

Table 19 highlights the waterbodies where the highest contaminant concentrations were found, using the lowest concentration sample of that type as a point of reference. For most chemicals, the highest levels tended to occur in Lake Washington or Lake Spokane. Within the context of this data set, the occurrence of elevated concentrations in the Lower Columbia and Lower Yakima was limited to PBDEs in carp muscle.

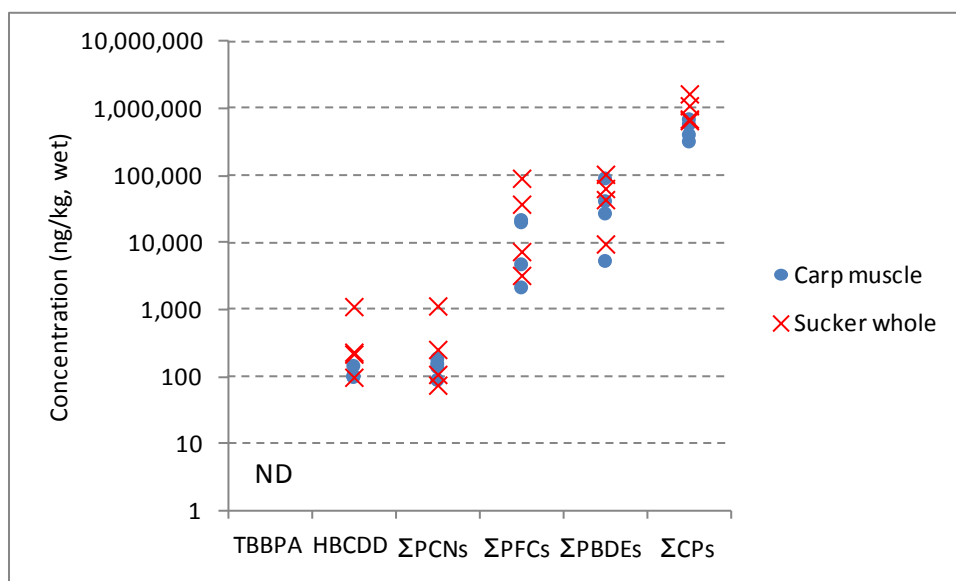


Figure 16. Relative Concentrations of the Organic Compounds Analyzed in Fish Tissue Samples Collected from Four Washington Rivers and Lakes in 2011 (ND = not detected).

Log scale, three HBCDD results plotted at the reporting limit.

Table 19. Fish Tissue Samples Elevated by a Factor of 10 or More Compared to Lowest Concentration for Same Sample Type in Present Study.

Pb minimum assumed equal to half the reporting limit.

Chemical	Lake Washington	Lower Columbia River	Lower Yakima River	Lake Spokane
TBBPA				
HBCDD	○			
ΣPCNs	○			
ΣPFCs	○●			○●
ΣPBDEs		●	●	○●
ΣCPs	○			
Pb				○
Cd				

○= whole suckers elevated by $\geq 10X$

●= carp muscle elevated by $\geq 10X$

Environmental Significance

Ecological Risk

A brief literature search was conducted to locate fish tissue criteria that could be used to assess ecological risk for the chemical concentrations measured in the present study. Only limited information was found.

Environment Canada has conducted ecological screening assessments for HBCDD, PFOS, PBDEs, and CPs that include developing critical tissue values (lowest or no observable effect levels) for wildlife diets (Environment Canada 2006a,b; 2008; 2011a). The U.S. Geological Survey determined risk to piscivorous fish and wildlife by comparing results of a national fish tissue monitoring program for U.S. river basins to published toxicity thresholds for metals, chlorinated pesticides, PCBs, and dioxins (Hinck et al., 2009). Similar information was not found on TBBPA or PCNs⁵.

Critical tissue values and toxicity thresholds (benchmarks) from these sources are compared to present study findings for whole fish samples in Table 20; note that the units are parts per million. A risk quotient (RQ) was calculated by dividing the maximum whole fish concentration by the benchmark value. RQs greater than 1.0 suggest potential for ecological harm. MCCPs (Lake Washington) and Pb (Spokane River) have RQs greater than 1.0, 1.7 and 1.2, respectively. SCCPs and PFOS have a lower RQ of 0.1. The RQs for HBCDD and PBDEs are extremely low, 0.01 or less.

Due to the many assumptions and extrapolations underlying these benchmark values, any conclusions about risk are preliminary at best. Environment Canada cautioned that “Because of limitations in available exposure and effects data, the absence of RQs above 1 cannot be considered proof that these persistent and bioaccumulative substances do not cause ecological harm.”

⁵ Environment Canada (2011b) conducted an ecological screening assessment of PCNs but did not develop critical tissue values. Based largely on persistence and bioaccumulation concerns, it was concluded that PCNs have the potential to cause environmental harm in Canada. An ecological screening assessment for TBBPA is reportedly underway. (<http://www.bfr2010.com/abstract-download/2007/O-27.pdf>).

Table 20. Benchmarks for Effects on Fish and Wildlife (*parts per million*).

Chemical	Present Study (mg/Kg)	Benchmark (mg/Kg in diet)				Maximum Risk Quotient
	Maximum	Conc.	Type	Organism	Ref.	
TBBPA	0.001 UJ	-----not available-----				--
HBCDD	0.001	40	critical tissue value	wildlife	1	<0.001
PCNs	0.001	-----not available-----				--
PFOS	0.05	0.4	critical tissue value	wildlife	2	0.1
PBDEs	0.10	8.4			3	0.01
SCCPs	0.9	10		fish and wildlife	4	0.1
MCCPs	0.7	0.4			4	1.7
Pb	0.5	0.4 - 8.8	toxicity threshold	fish and wildlife	5	1.2
Cd	0.1 U	0.2 - 16			5	<0.5

U: The analyte was not detected at or above the reported result.

J: Estimated value

References:

- 1: Environment Canada (2011a)
- 2: Environment Canada (2006a)
- 3: Environment Canada (2006b)
- 4: Environment Canada (2008)
- 5: Hinck et al. (2009)

Fish Consumption Advisories

The organic compounds analyzed in this study were identified relatively recently as emerging chemicals of concern. Only two states have set advisory levels for fish consumers. The Minnesota Department of Health (2008) has published meal frequency advice for PFOS. The California Office of Environmental Health Hazard Assessment (2011) has developed advisory tissue levels for PBDEs. These guidelines are shown in Table 21 and compared to the maximum concentration found in fish samples during the present study (parts per billion).

Table 21. Fish Consumption Advisory Levels for PFOS and PBDEs (*parts per billion*).

Chemical and Advisory Level (ug/Kg, wet)	Meal Frequency
PFOS (Minnesota Meal Advice)	
≥ 40	Unrestricted
> 40 - 200	One meal per week
> 200 - 800	One meal per month
> 800	Do not eat
Maximum fish muscle concentration present study = 20	
Maximum whole fish concentration present study = 46	
PBDEs (California Fish Contaminant Goals)	
≤ 100	Three 8-ounce servings per week
> 100 - 210	Two 8-ounce servings per week
> 210 - 630	One 8-ounce serving a week
> 630	No consumption
Maximum fish muscle concentration present study = 90	
Maximum whole fish concentration present study = 105	

The maximum PFOS and PBDE concentrations (Lake Washington and Lake Spokane whole fish, respectively) fall into the lower end of the restricted consumption category. The maximum PBDE concentration observed in fish muscle (Lake Spokane) also approaches the minimally restricted consumption category.

EPA (2000) recommends a Cd screening value of 0.49 mg/Kg for subsistence fishers. Screening values are used to identify chemical concentrations in fish or shellfish tissue that are of potential public health concern. All Cd concentrations in the present study were less than 0.10 mg/Kg (not detected). EPA (2000) does not have screening values for Pb.

There is currently a Washington State Department of Health (WDOH) fish consumption advisory for the Spokane River that includes PBDEs and Pb (WDOH, 2011). The area of greatest concern is upstream of the Lake Spokane site sampled in the present study. In issuing the advisory, WDOH did not set fish consumption advisory levels similar to what Minnesota and California did for PFOS and PBDEs.

Any further assessment of human health implications of study findings is beyond the scope of this report. The data have been provided to the WDOH Office of Environmental Health Assessment. At a later date, they intend to conduct a literature review regarding potential human health effects on some of the compounds and see what other states are doing in terms of screening or regulatory values (Dave McBride, personal communication).

Conclusions and Recommendations

Conclusions

Based on the detection frequency and concentration levels observed in fish muscle and whole fish from four urban/industrial rivers and lakes, HBCDD, SCCPs, MCCPs, and PCNs appear to warrant further investigation as potentially significant PBT contaminants not previously analyzed in Washington State freshwater fish. TBBPA, on the other hand, was not found at readily detectable levels in any fish tissue samples, consistent with findings of similar investigations done elsewhere.

This study further characterized several other PBTs more frequently monitored in local fish populations. PBDEs continue to be elevated in Spokane River fish, although the levels appear to be declining. PFOS was the major PFC detected, consistent with a recent statewide assessment of PFCs in Washington. Both PBDEs and PFOS were substantially elevated over local background levels for freshwater fish.

Most Pb and all Cd concentrations were near or below detection limits. This reflects their known low accumulation rate in fish muscle and, for whole fish, implies distance from significant sources.

A limited comparison with information on ecological risk and fish consumption advisories shows that MCCPs, PFOS, PBDEs, and Pb approached or exceeded levels of concern in some samples.

Recommendations

- Future studies monitoring PBT residues in Washington State freshwater fish should consider including HBCDD, PCNs, and CPs in addition to other PBTs more routinely analyzed. Preliminary indications are that SCCPs and MCCPs, in particular, may be substantially elevated.
- Some additional investigation into the occurrence of TBBPA is warranted, given the low recoveries encountered in the analyses conducted for the present study.
- Follow-up sampling is recommended to confirm elevated concentrations of HBCDD, PCNs, and CPs detected in Lake Washington suckers, analyzing additional fish species as appropriate.
- The Washington State Department of Health, Office of Environmental Health Assessment intends to review the data from the present study. Their conclusions about potential human health effects of these compounds may be useful for prioritizing chemicals for follow-up sampling and determining the appropriate level of effort.

References

- Arnot, J., L. McCarty, J. Armitage, L. Toose-Reid, F. Wania, and I. Cousins. 2009. An Evaluation of Hexabromocyclododecane (HBCD) for Persistent Organic Pollutant (POP) Properties and the Potential for Adverse Effects in the Environment. Submitted to the European Brominated Flame Retardant Industry Panel. University of Toronto Scarborough.
- CECBP. 2008. Brominated and Chlorinated Organic Chemical Compounds Used as Flame Retardants. Materials for the December 4-5, 2008 Meeting of the California Environmental Contaminant Biomonitoring Group (CECBP) Scientific Guidance Panel (SGP). <http://oehha.ca.gov/multimedia/biomon/pdf/120408flamedoc.pdf>
- CETOCOEN. 2010. Hexabromocyclododecane (HBCDD) – a brominated flame retardant of “very high concern” Center for Research on Toxic Substances in the Environment, Masaryk University, Kamenice, Czech Republic. www.recetox.muni.cz/res/file/pdf/HBCDD.pdf
- Chen, D., M.J. La Guardia, D.R. Luellen, E. Harvey, T. Mainor, and R.C. Hale. 2011. Do Temporal and geographical patterns of HBCD and PBDE flame retardants in U.S. fish reflect evolving industrial usage? *Environmental Science and Technology* 45: 8254-8261.
- Covaci, A., A.C. Gerecke, R.J. Law, S. Voorspoels, M. Kohler, N.B. Heeb, H. Lesli, C.R. Allchin, and J. DeBoer. 2006. Hexabromocyclododecanes (HBCDs) in the Environment and Humans: A Review. *Environmental Science and Technology* 40(12): 3679-3688.
- Covaci, A., S. Voorspoels, M.A.-E Abdallah, T. Geens, S. Harrad, and R.J. Law. 2009. Analytical and environmental aspects of the flame retardant tetrabromobisphenol-A and its derivatives. *Journal of Chromatography A* 1216, 346–363.
- Davies, H. et al., 2009. Washington State Lead Chemical Action Plan. Washington State Department of Ecology, Olympia, WA. Publication No. 09-07-008. <https://fortress.wa.gov/ecy/publications/summarypages/0907008.html>
- Davies, H., 2012. Draft Polycyclic Aromatic Hydrocarbon (PAH) Chemical Action Plan. Washington State Department of Ecology, Olympia, WA. Publication No. 12-07-038. <https://fortress.wa.gov/ecy/publications/summarypages/1207038.html>
- Delinsky, A.D., M.J. Strynar, P.J. McCann, J.L. Varns, L. McMillan, S. Nakayama, and A.B. Lindstrom. 2010. Geographical distribution of perfluorinated compounds in fish from Minnesota lakes and rivers. *Environmental Science and Technology* 44:2549-2554.
- Dodder, N.G., B. Strandberg, and R.A. Hites, 2002. Concentrations and spatial variation of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the Northeastern United States. *Environmental Science and Technology* 36(2):146-151.

Ecology. 2007. Multiyear PBT Chemical Action Plan Schedule: Final. Washington State Department of Ecology, Olympia, WA. Publication No. 07-07-016.
<https://fortress.wa.gov/ecy/publications/summarypages/0707016.html>

Ecology and WDOH. 2006. Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: Final Plan. Washington State Department of Ecology and Washington State Department of Health. Publication Nos. 05-07-048 and 334-079, respectively.
<https://fortress.wa.gov/ecy/publications/summarypages/0507048.html>

Ecology and WDOH. 2009. Washington State Lead Chemical Action Plan. Washington State Department of Ecology and Washington State Department of Health. Publication No. 09-07-008. <https://fortress.wa.gov/ecy/publications/summarypages/0907008.html>

Eisler, R. 1985. Cadmium Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Survey, Patuxent Wildlife Research Center, Laurel, MD. Biological Report 85(1.2).

Eisler, R. 1988. Lead Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Survey, Patuxent Wildlife Research Center, Laurel, MD. Biological Report 85(1.15).

Environment Canada. 2004. Environmental Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs).

Environment Canada. 2006a. Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C₈F₁₇SO₂ or C₈F₁₇SO₃, or C₈F₁₇SO₂N Moiety. www.ec.gc.ca/lcpe-cepa

Environment Canada. 2006b. Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). www.ec.gc.ca/lcpe-cepa

Environment Canada. 2008. Chlorinated Paraffins. www.ec.gc.ca/lcpe-cepa

Environment Canada. 2011a. Environment Canada Screening Assessment Report on Hexabromocyclododecane. www.ec.gc.ca/ese-ees

Environment Canada. 2011b. Ecological Screening Assessment Report, Chlorinated Naphthalenes. www.ec.gc.ca/ese-ees

Environment Canada. 2012. Ecological Screening Assessment Report on Perfluorooctane Sulfonate, Its Salts and Its Precursors that Contain the C₈F₁₇SO₂ or C₈F₁₇SO₃, or C₈F₁₇SO₂N Moiety. www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=98B1954A-1&offset=3&toc=show

EPA. 1990. Specifications and Guidance for Obtaining Contaminant-Free Sample Containers. U.S. Environmental Protection Agency. OSWER Directive #93240.0-05.

EPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories: Volume 1 Fish Sampling and Analysis. EPA 823-B-00-007.
http://water.epa.gov/scitech/swguidance/fishshellfish/techguidance/risk/upload/2009_04_23_fish_advice_volume1_vlcover.pdf

EPA. 2005. National Functional Guideline for Superfund Organic Methods Data Review. OSWER 9240.1-46. U.S. Environmental Protection Agency. EPA-540-R-04-009.

EPA. 2009a. Short-Chain Chlorinated Paraffins (SCCPs) and Other Chlorinated Paraffins: Action Plans. U.S. Environmental Protection Agency.
www.epa.gov/oppt/existingchemicals/pubs/actionplans/sccps.html

EPA. 2009b. Columbia River Basin: State of the River Report for Toxics. U.S. Environmental Protection Agency, Region 10.

EPA. 2009c. Long-Chain Perfluorinated Chemicals (PFCs): Action Plans. U.S. Environmental Protection Agency. www.epa.gov/oppt/existingchemicals/pubs/actionplans/pfcs.html

EPA. 2010. Recommended Toxicity Equivalence Factors (TEFs) for Human Health Risk Assessments of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and Dioxin-Like Compounds. U.S. Environmental Protection Agency. EPA/100/R 10/005.
www.epa.gov/raf/files/tefs-for-dioxin-epa-00-r-10-005-final.pdf

EFSA. 2011a. Scientific opinion on trabromobisphenol A (TBBPA) and its derivatives in food. EFSA Panel on Contaminants in the Food Chain. EFSA Journal 2011;9(12):2477.
www.efsa.europa.eu/efsajournal

EFSA. 2011b. Scientific opinion on polybrominated diphenyl ethers (PBDEs) in food. EFSA Panel on Contaminants in the Food Chain. EFSA Journal 9(5):2156.
www.efsa.europa.eu/efsajournal

Fernandez, A.R., C. Tlustos, M. Rose, F. Smith, M. Carr, and S. Panton. 2011. Polychlorinated naphthalenes (PCNs) in Irish foods: Occurrence and human dietary exposure. *Chemosphere* 85(3):322-8.

Furdui, V.I., P.A. Helm, P.W. Crozier, C. Lucaciu, E.J. Reiner, C.H. Marvin, D.M. Whittle, S.A. Mabury, and G.T. Tomy. 2008. Temporal trends of perfluoroalkyl compounds with isomer analysis in lake trout from Lake Ontario (1979-2004). *Environmental Science and Technology* 42:4739-4744.

Furl, C. and C. Meredith. 2010a. PBT Monitoring: PBDE Flame Retardants in Spokane River Fish, 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 10-03-015. <https://fortress.wa.gov/ecy/publications/summarypages/1003015.html>

Furl, C. and C. Meredith. 2010b. Perfluorinated Compounds in Washington Lakes and Rivers. Washington State Department of Ecology, Olympia, WA. Publication No. 10-03-034. <https://fortress.wa.gov/ecy/publications/summarypages/1003034.html>

Furl, C. and T. Roberts. 2011. PBT Chemical Trends in Washington State Determined from Age-Dated Lake Sediment Cores, 2010 Sampling Results. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-045.

<https://fortress.wa.gov/ecy/publications/summarypages/1103045.html>

Gallagher, M. 2007. Multiyear PBT Chemical Action Plan Schedule - Draft. Washington State Department of Ecology, Olympia, WA. Publication No. 06-07-025.

<https://fortress.wa.gov/ecy/publications/SummaryPages/0607025.html>

Giesy, J.P. and K. Kannan. 2001. Global distribution of perfluorooctane sulfonate in wildlife. *Environmental Science and Technology* 25:1339-1342.

GLWQA. 2011. Chemicals of Emerging Concern. Great Lakes Water Quality Agreement, 2009-2011 Priority Cycle Report, International Joint Commission.

Hallock, D., 2009. River and Stream Water Quality Monitoring Report, Water Year 2008. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-041.

<https://fortress.wa.gov/ecy/publications/summarypages/0903041.html>

Hanari N, K. Kannan, Y. Horii, S. Taniyasu, N. Yamashita, D.J. Jude, and M.B. Berg. 2004. Polychlorinated naphthalenes in benthic organisms of a Great Lakes food chain. *Archives of Environmental Contamination and Toxicology* 47:84-93.

Helm, P.A., S.B. Gewurtz, D.M. Whittle, C.H. Marvin, A.T. Fisk, and G. Tomy. 2008. Occurrence and biomagnification of polychlorinated naphthalenes and non- and mono-ortho PCBs in Lake Ontario sediment and biota. *Environmental Science and Technology* 42(4): 1024-1031.

Herbert, C.E. and K.A. Keenleyside, 1995. To normalize or not to normalize: fat is the question. *Environmental Toxicology and Chemistry* 14(5):801-807.

Hinck, J.E., C.J. Schmitt, K.A. Chopjnacki, and D.E. Tillitt. 2009. Environmental contaminants in freshwater fish and their risk to piscivorous wildlife based on a national monitoring program. *Environmental Monitoring and Assessment* 152:469-494.

Hites, R.A., 2004. Polybrominated diphenyl ethers in the environment and people: a meta-analysis of concentrations. *Environmental Science and Technology* 38(4): 945-956.

Hopkins, B.S., D.K. Clark, M. Schlender, and M. Stinson, 1985. Basic Water Monitoring Program Fish Tissue and Sediment Sampling for 1984. Washington State Department of Ecology, Olympia, WA. Publication No. 85-7.

<https://fortress.wa.gov/ecy/publications/summarypages/857.html>

Houde, M., D.C.G. Muir, G.T. Tomy, D.M. Whittle, C. Teixeira, and S. Moore. 2008. Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environmental Science and Technology* 42(10):3893-3899.

Ismail, N., S.B. Gewurtz, K. Pleskach, D.M. Whittle, P.A. Helm, C.H. Marvin, and G.T. Tomy. 2009. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) between 1979 and 2004 and possible influences of food-web changes. *Environmental Toxicology and Chemistry* 28(5):910-920.

Johnson, A. 2011a. Quality Assurance Project Plan: Analyzing Chlorinated Pesticide Residues in Fish from Washington Background Lakes. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-108.

<https://fortress.wa.gov/ecy/publications/summarypages/1103108.html>

Johnson, A. 2011b. Addendum to Quality Assurance Project Plan for Analyzing Chlorinated Pesticide Residues in Fish from Washington Background Lakes: Analysis of Supplemental PBTs in Non-Background Waterbodies. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-108-Addendum-1.

<https://fortress.wa.gov/ecy/publications/summarypages/1103108.html>

Johnson, A., M. Friese, J. Roland, C. Gruenenfelder, B. Dowling, A. Fernandez, and T. Hamlin. 2011c. Background Levels of Metals and Organic Compounds in Northeast Washington Lakes, Part 2: Fish Tissue. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-54. <https://fortress.wa.gov/ecy/publications/summarypages/1103054.html>

Johnson, A. and N. Olson. 2001. Analysis and occurrence of polybrominated diphenyl ethers in Washington State freshwater fish. *Archives of Environmental Contamination and Toxicology* 41:339-344.

Johnson, A., K. Seiders, C. Deligeannis, K. Kinney, P. Sandvik, B. Era-Miller, and D. Alkire. 2006. PBDE Flame Retardants in Washington Rivers and Lakes: Concentrations in Fish and Water, 2005-06. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-027. <https://fortress.wa.gov/ecy/publications/summarypages/0603027.html>

Johnson-Restrepo, B., Adams, D.H., Kannan, K., 2008. Tetrabromobisphenol A (TBBPA) and hexabromocyclododecanes (HBCD) in tissues of humans, dolphins, and sharks from the United States. *Chemosphere* 70, 1935–1944.

Kadlec, M., 2000. Ecological Risk Analysis of Elevated Metal Concentrations in the Spokane River, Washington. Prep. for the Washington State Department of Ecology, Toxics Cleanup Program, Spokane, WA.

Kannan K., T. Imagawa, A.L. Blankenship, and J.P. Giesy. 1998. Isomer-specific analysis and toxic evaluation of polychlorinated naphthalenes in soil, sediment and biota collected near the site of a former chlor-alkali plant. *Environmental Science and Technology* 32:2507–2514.

Kannan K., N. Yamashita, T. Imagawa, W. Decoen, Y.S. Khim, R.M. Day, C.L. Summer, and J.P. Giesy. 2000. Polychlorinated naphthalenes and polychlorinated biphenyls in fishes from Michigan waters including the Great Lakes. *Environmental Science and Technology* 34:566–572.

Klasing, S. and R. Brodberg. 2011. Development of Fish Contaminant Goals and Advisory Levels for Common Contaminants in California Sport Fish: Polybrominated Diphenyl Ethers (PBDEs). Pesticide and Environmental Toxicology Branch, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.
<http://oehha.ca.gov/fish/gtlsx/pdf/PBDEs052311.pdf>

Klecka, G., C. Persoon, and R. Currie. 2009. Review of Chemicals of Emerging Concern and Analysis of Environmental Exposures in the Great Lakes Basin. IJC Workgroup on Chemicals of Emerging Concern. Dow Chemical Co. and University of Iowa.

Klecka, G., C. Persoon, and R. Currie. 2010. Chemicals of Emerging Concern in the Great Lakes Basin: An Analysis of Environmental Exposures. Chapter 1 in Reviews of Environmental Contamination and Toxicology Volume 207.

Law, R.J., D. Herzke, S. Harrad, S. Morris, P. Bersuder, and C.R. Allchin. 2008. Levels and trends of HCD and BDEs in the European and Asian environments, with some information on other BFRs. *Chemosphere* 73:233-241.

Law, K., T. Halldorson, R. Danell, G. Stern, S. Gewurtz, M. Alaei, C. Marvin, M. Whittle, and G. Tomy. 2006. Bioaccumulation and trophic transfer of some brominated flame retardants in a Lake Winnipeg (Canada) food web. *Environmental Toxicology and Chemistry* 25(8):2177-2186.

Lefkowitz, L.F., V.I. Cullinan, and E.A. Creclius. 1997. Historical Trends in the Accumulation of Chemicals in Puget Sound. National Oceanic and Atmospheric Administration, Silver Springs, MD. NOAA Technical Memorandum NOS ORCA 111. 60 pp. + appendices.

Marvin, C.H., G.T. Tomy, J.M. Armitage, J.A. Arnot, L. McCarty, A. Covaci, and V. Palace. 2011. Hexabromocyclododecane: current understanding of chemistry, environmental fate and toxicology and implications for global management. *Environmental Science and Technology* 45: 8613-8623.

Mathieu, C. and M. Friese, 2012. PBT Trend Monitoring: Measuring Lead in Suspended Particulate Matter from Washington State Rivers and Lakes, 2011 Results. Washington State Department of Ecology, Olympia WA. Publication Number 12-03-031.
<https://fortress.wa.gov/ecy/publications/summarypages/1203031.html>

MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

MEL, 2012. Manchester Environmental Laboratory Quality Assurance Manual. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Minnesota Department of Health. 2008. Meal Advice Categories Based on Levels of PFOS in Fish Tissue. Fish Consumption Advisory Program.
www.health.state.mn.us/divs/eh/fish/eating/sitespecific.html

Morris, S., C.R. Allchin, B.N. Zefers, J.J.H. Haftka, J.P. Boon, C. Belpaire, P.E.G. Leomards, S.P.J. van Leeuwen, and J. de Boer. 2004. Distribution and fate of HBCD and TBBPA brominated flame retardants in North Sea estuaries and aquatic food webs. *Environmental Science and Technology* 38, 5497–5504.

Muir, D.C.G., D. Bennie, C. Teixeira, A. Fisk, G. Tomy, G. Stern, and M. Whittle. 2001. Short chain chlorinated paraffins: Are they persistent and bioaccumulative? In *Persistent, Bioaccumulative and Toxic Chemicals II, Assessment and New Chemicals*; Lipnick, R.L., Jansson, B., Mackay, D., Petreas, M., Eds.; ACS symposium Series 773; American Chemical Society: Washington, DC.

Peele, C. et al. 2003. Washington State Mercury Chemical Action Plan. Washington State Department of Ecology, Publication No. 03-03-001. Washington State Department of Health, Olympia, WA. Publication No. 333-051.
<https://fortress.wa.gov/ecy/publications/summarypages/0303001.html>

Pelletier, G.J., 1998. Cadmium, Lead, and Zinc in the Spokane River: Recommendations for TMDL and Waste Load Allocations. Washington State Department of Ecology, Olympia, WA. Publication No. 98-329. <https://fortress.wa.gov/ecy/publications/summarypages/98329.html>

Rayne, S., M.G. Ikonou, and I.H. Rogers. 2003. Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. *Environmental Science and Technology* 37(13):2847-2854.

Sandvik, P., 2006a. Standard Operating Procedure for Field Collection, Processing, and Preservation of Finfish Samples at the Time of Collection in the Field. Version 1.0. Washington State Department of Ecology, Olympia, WA.

Sandvik, P., 2006b. Standard Operating Procedure for Resecting Finfish Whole Body, Body Parts, or Tissue Samples. Version 1.0. Washington State Department of Ecology, Olympia, WA.

Seiders, K. and C. Deligeannis. 2009. Washington State Toxics Monitoring Program: Freshwater Fish Tissue Component, 2008. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-055.
<https://fortress.wa.gov/ecy/publications/summarypages/0903055.html>

Seiders, K. 2010. Unpublished fish tissue data for Leo Lake and Pierre Lake collected by the Washington State Toxics Monitoring Program. 7/21/10 email to Art Johnson, Washington State Department of Ecology, Olympia, WA.

Stow, C.A., L.J. Jackson, and J.F. Amrhein, 1997. An examination of the PCB: lipid relationship among individual fish. *Canadian Journal of Fish and Aquatic Science* 54:1031-1038.

Sverko, D., G.T. Tomy, C.H. Marvin, and D.C.G. Muir. 2012. Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environmental Science and Technology* 46:4697-4698.

Tomy, G.T., K. Pleskach, N. Ismail, D.M. Whittle, P.A. Helm, E. Sverko, D. Zaruk, and C.H. Marvin. 2007. Isomers of Dechlorane Plus in Lake Winnipeg and Lake Ontario food webs. *Environmental Science and Technology* 41(7):2249-2254.

Tomy, G.T., G.A. Stern, D.C.G. Muir, A.T. Fisk, C.D. Cymbalisky, and J.B. Westmore. 1997. Quantifying C10-C13 polychloroalkanes in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry. *Analytical Chemistry* 69: 2762–2771.

Van den Berg et al. 2006. The 2005 World Health Organization Reevaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-Like Compounds. *Toxicological Sciences* 93(2): 223–241.

Van de Plassche, E. and A. Schwegler. 2002. Polychlorinated Naphthalenes. Ministry of VROM/DGM, The Netherlands.

WDOH. 2005. Unpublished data on PBDEs in Lake Washington fish tissue samples. Washington State Department of Health, Office of Environmental Health, Safety, and Toxicology, Olympia, WA.

WDOH. 2007. Evaluation of PCBs, PBDEs and Selected Metals in the Spokane River, Including Long Lake, Spokane, Washington. Prepared by the Washington State Department of Health Under a Cooperative Agreement with the Agency for Toxic Substances and Disease Registry. DOH Publication No. 334-147.

Appendices

Appendix A. PBT Lists from Ecology's Multiyear PBT Chemical Action Plan Schedule

<https://fortress.wa.gov/ecy/publications/summarypages/0707016.html>

Target chemicals for the present 2011 study are highlighted in bold font, except PBDEs are addressed separately from this schedule in Ecology and WDOH (2006).

Table A-1 (Table 4 in Ecology and DOH, 2006). Persistence(P), Bioaccumulation(B), and Human Health Toxicity(T) for PBTs and Metals of Concern.

Chemicals	CAS Number	P: Regional Half Life (Days)	P: Source	P: Ranking Score	B: BAF/BCF Value	B: Source	B: Ranking Score	T: RfD (mg/kg/day) Non-cancer	T: CPF (mg/kg/day)-1 cancer	T: Human Health Rank (Table 3)	TOTAL: P+B+ Human Health T
Cadmium	7440-43-9	NA	NA	NA	NA	NA	NA	0.0002	.38 (B1) *	2	2
Hexabromocyclododecane (HBCD)	25637-99-4	540	PBT Profiler	1	18,000	KemI	2	0.2	NA	1	4
Hexachlorobenzene (HCB)	118-74-1	7300	EPA 1999	2	18,620	EPA 1998	2	0.00005	1.8 (B2)	3	7
Hexachlorobutadiene (HCBD)	87-68-3	284	Howard	1	6918	EPA 1998	1	0.0002	.078 (C)	2	4
Lead	7439-92-1	NA	NA	NA	NA	NA	NA	0.0005	NA (B2)	2	2
Pentachlorobenzene	608-93-5	7800	EPA 1999	2	8314	EPA 1998	1	0.0008	NA (D)	2	5
Perfluorooctane sulfonates (PFOS) Ammonium Salt	29081-56-9	14,965	Env Can	3	5400	OECD	1	NA	NA	3	7
Polybrominated dibenzodioxins and furans (PBDD/PBDFs) (2,3,7,8 tetrabromodibenzo-p-dioxin)	50585-41-6	1600	PBT Profiler	2	3800	PBT Profiler	1	NA	156000 (B2)	3	6
Polychlorinated biphenyls (PCBs) (3,3',4,4',5,5' hexachlorobiphenyl)	32774-16-1	1600	PBT Profiler	2	74,000	PBT Profiler	3	0.00002	1560 (B2)	3	8
Polychlorinated dibenzofurans (2,3,4,7,8 pentachlorodibenzofuran) (PCDFs)	57117-31-4	7300	EPA 1999	2	42,500	PBT Profiler	3	0.00000003	75300 (B2)	3	8
Polychlorinated dibenzo-p-dioxins (2,3,7,8 tetrachlorodibenzo-p-dioxin) (PCDDS)	1746-01-6	1600	PBT Profiler	2	34,000	PBT Profiler	2	0.000000001	156000 (B2)	3	7
Polychlorinated naphthalenes (hexachloronaphthalene) (PCNs)	1335-87-1	1600	PBT Profiler	2	240,000	PBT Profiler	3	NA	624	2	7
Polycyclic aromatic hydrocarbons (PAHs) (Fluoranthene) (PAHs)	206-44-0	540	PBT Profiler	1	1900	PBT Profiler	1	0.04	120 (2B)	2	4
Chlorinated paraffins (CPs)	85535-84-8	365	OSPAR	1	40,900	OSPAR	3	NA	.089 (2B)	1	5
Tetrabromobisphenol A (TBBPA))	79-94-7	1600	PBT Profiler	2	14,000	PBT Profiler	2	0.2	NA (B2)	1	5
Tetrachlorobenzene, 1,2,4,5 (1,2,4,5 TCB)	95-94-3	730	Mackay et al.	1	4830	OSPAR	1	0.0003	NA	2	4

BAF/BCF Value: BAF: Bioaccumulation factor, the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment (including food).

BCF: Bioconcentration factor, the ratio of the concentration of a chemical in an aquatic organism to the concentration of the chemical in water.

RfD: Reference Dose

CPF: Cancer Potency Factors. The EPA weight of evidence classification appears in parentheses after "NA," when available.

mg/L: Milligrams per Liter

NA: (Data) Not Available. For human health toxicity, the EPA weight of evidence classification appears in parentheses after "NA," when available.

Table A-2 (Table 6 in Ecology and DOH, 2006). Persistence(P), Bioaccumulation(B), and Ecological Toxicity(T) for PBTs and Metals of Concern.

Chemicals	CAS Number	P: Regional Half Life (Days)	P: Source	P: Ranking Score	B: BAF/BCF Value	B: Source	B: Ranking Score	T: Ecological Toxicity Value (mg/L) (Table 5)	T: Ranking Score	T: Source	TOTAL: P+B+ Ecological T
Cadmium	7440-43-9	NA	NA	NA	NA	NA	NA	0.0007	3	ECOTOX	3
Hexabromocyclododecane (HBCD)	25637-99-4	540	PBT Profiler	1	18000	KemI	2	0.00062	3	PBT Profiler	6
Hexachlorobenzene (HCB)	118-74-1	7300	EPA 1999	2	18620	EPA 1998	2	0.012	1	PBT Profiler	5
Hexachlorobutadiene (HCBd)	87-68-3	284	Howard	1	6918	EPA 1998	1	0.0065	2	ECOTOX	4
Lead	7439-92-1	NA	NA	NA	NA	NA	NA	0.004	2	ECOTOX	2
Pentachlorobenzene	608-93-5	7800	EPA 1999	2	8314	EPA 1998	1	0.038	1	PBT Profiler	4
Perfluorooctane sulfonates (PFOS): Ammonium Salt	29081-56-9	14965	Env Can	3	5400	OECD	1	0.002	2	PBT Profiler	6
Polychlorinated biphenyls (PCB): 2,3',4,4',5,5' Hexachlorobiphenyl	52663-72-6	1600	PBT Profiler	2	56,000	PBT Profiler	3	0.00044	3	PBT Profiler	8
Polychlorinated dibenzofurans (PCDFs) (1,2,3,6,7,8 hexachlorodibenzofuran)	57117-44-9	7300	TRI	2	3600	PBT Profiler	1	0.00025	3	PBT Profiler	6
Polybrominated dibenzodioxins and furans (2,3,7,8 tetrabromodibenzo-p-dioxin) (PBDD/PBDFs)	50585-41-6	1600	PBT Profiler	2	3800	PBT Profiler	1	0.00035	3	PBT Profiler	6
Polychlorinated dibenzo-p-dioxins (1,2,3,7,8 pentachlorodibenzo-p- dioxin) (PCDDs)	40321-76-4	7300	EPA 1999	2	26000	PBT Profiler	2	0.0005	3	PBT Profiler	7
Polychlorinated naphthalenes (hexachloronaphthalene) (PCNs)	1335-87-1	1600	PBT Profiler	2	240000	PBT Profiler	3	0.0013	2	PBT Profiler	7
Polycyclic aromatic hydrocarbons (PAHs): Dibenzo(a,h)pyrene	189-64-0	1600	PBT Profiler	2	26000	PBT Profiler	2	0.00074	3	PBT Profiler	7
Short-chain chlorinated paraffins (SCCPs)	85535-84-8	365	OSPAR	1	40900	OSPAR	3	0.04	1	EU Risk Assess	5
Tetrabromobisphenol A (TBBPA)	79-94-7	1600	PBT Profiler	2	14000	PBT Profiler	2	0.003	2	PBT Profiler	6
Tetrachlorobenzene, 1,2,4,5- (1,2,4,5 TCB)	95-94-3	730	Mackay, et al.	1	4830	OSPAR	1	0.12	1	PBT Profiler	3

BAF/BCF Value: BAF: Bioaccumulation factor, the ratio of the concentration of a chemical in an organism to the concentration of the chemical in the surrounding environment (including food).

BCF: Bioconcentration factor, the ratio of the concentration of a chemical in an aquatic organism to the concentration of the chemical in water.

RfD: Reference Dose

CPF: Cancer Potency Factors. The EPA weight of evidence classification appears in parentheses after "NA," when available.

mg/L: Milligrams per Liter

NA: (Data) Not Available. For human health toxicity, the EPA weight of evidence classification appears in parentheses after "NA," when available.

Appendix B. Areas Where Fish Samples Were Collected in 2011

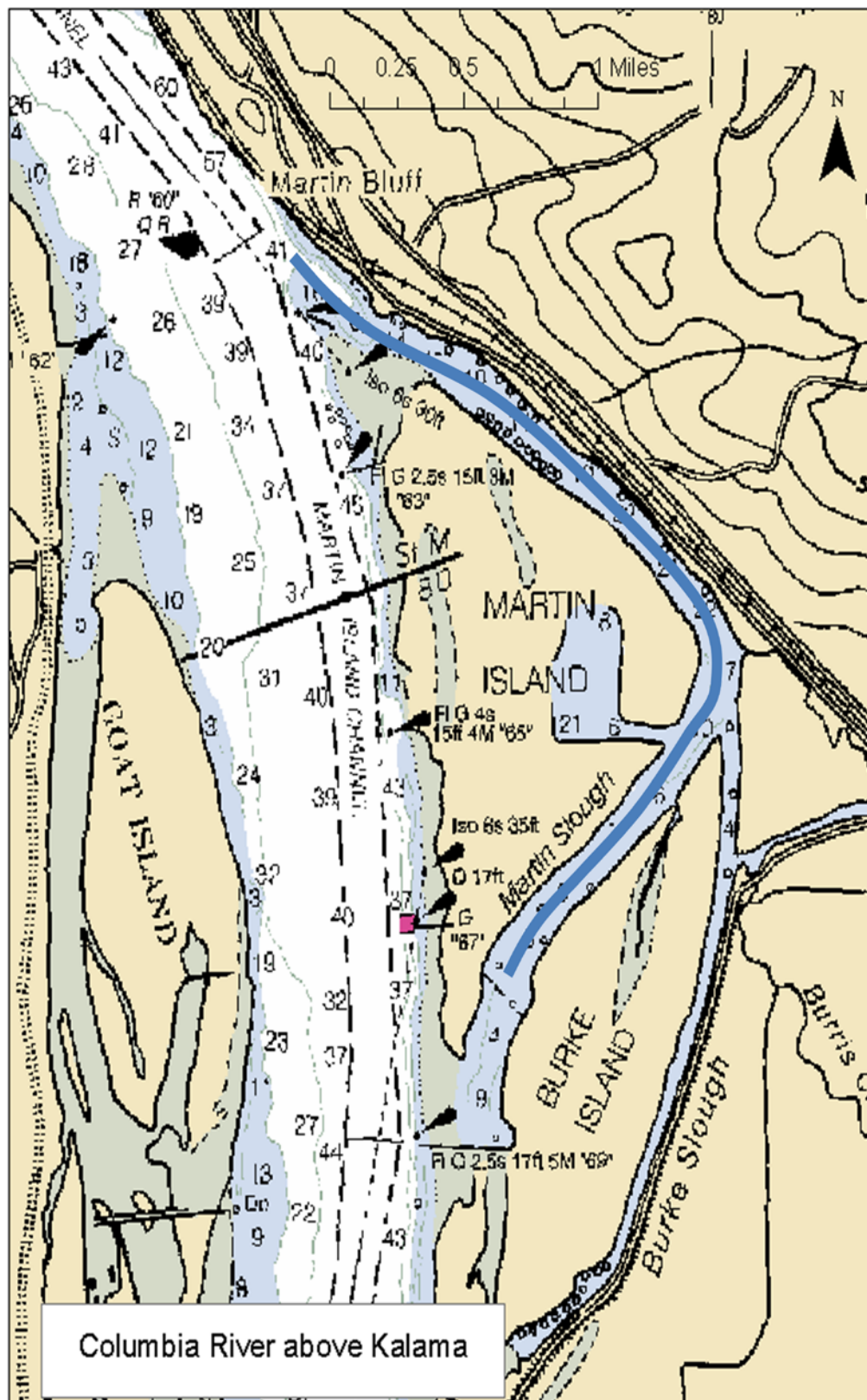


Figure B-1. Fish Collection Reach, Columbia River above Kalama, 9/29/2011.



Figure B-2. Fish Collection Reach, Lake Washington at Seward Park, 10/10/2011.

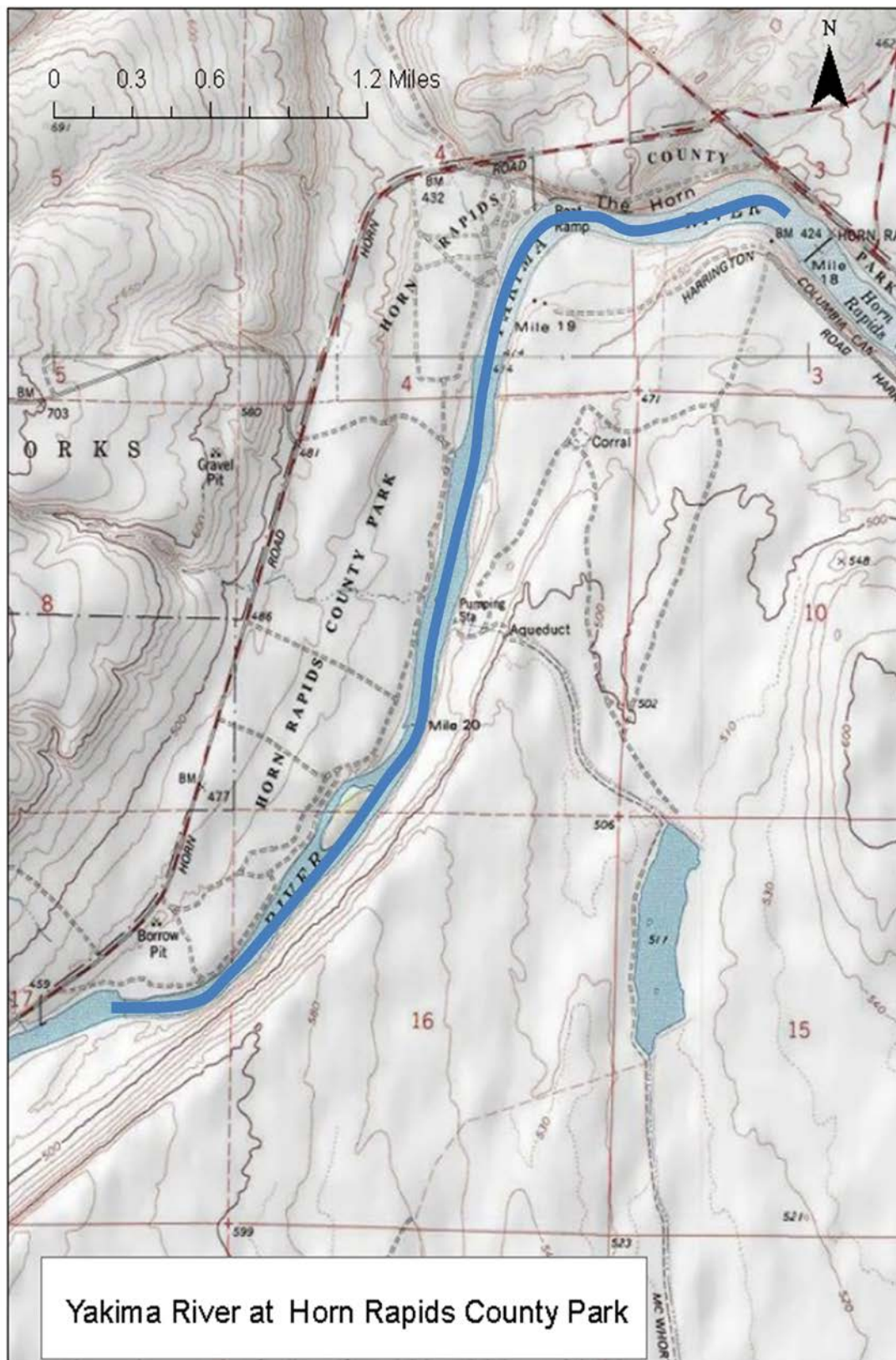


Figure B-3. Fish Collection Reach, Yakima River at Horn Rapids County Park, 10/27/2011.

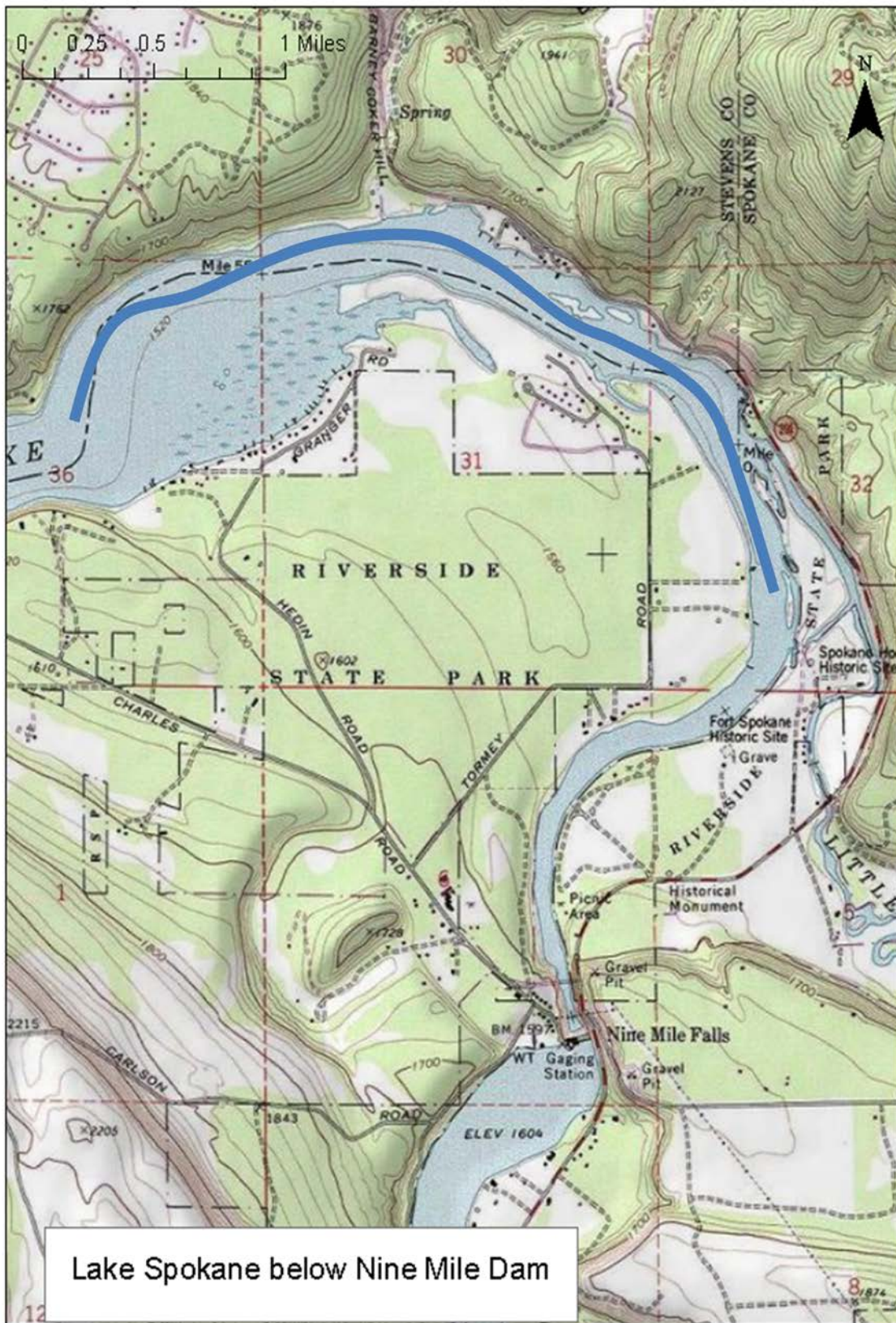


Figure B-4. Fish Collection Reach, Lake Spokane below Nine-Mile Dam, 10/4/2011.

Appendix C. Fish Samples Analyzed

Site	Collection Date	Species / Tissue	Sample No. 1112028-	Weight (grams)	Length (mm)
Lake Washington	10/10/2011	Common carp* / muscle	1	3,262	592
Lower Columbia River	9/29/2011		2	2,948	565
				3,024	580
				4,500	650
				2,240	515
				2,305	545
Lower Yakima River	10/27/2011		3	4,202	703
				4,968	690
				2,745	620
				1,386	409
Lake Spokane	10/4/2011		4 & 5	3,144	602
				3,665	650
				4,214	670
Lake Washington	10/10/2011	Largescale sucker [†] / whole	6	1,476	514
				1,692	554
				1,525	517
				1,295	492
				1,143	431
Lower Columbia River	9/29/2011		7	1,109	442
				963	470
				832	436
Lower Yakima River	10/27/2011		9	419	338
				526	350
				320	310
				325	306
				343	312
Lake Spokane	10/4/2011		8 & 10	1,377	512
				1,670	557
				1,340	506
				1,138	469
				1,217	479

**Cyprinus carpio*

[†]*Catostomus macrocheilus*

Appendix D. AXYS Assessment of Low Recoveries in the TBBPA Analysis

(Devin Mitchell 5/22/2012 email to Art Johnson, Washington State Department of Ecology)

Low surrogate recovery in TBBPA analysis can be caused by the loss of the analyte during analytical process and ion suppression from sample matrix. In this batch, a dilution and instrumental re-analysis was conducted and the dilution data are provided in the data package under “Unvalidated Data” section in the data package. Surrogate recoveries in the dilution data are similar to that of the original. This suggests that ion suppression of the surrogate was minimal and the low surrogate recovery was mainly due to the loss of the analyte during analytical processes.

Although the surrogate recovery (10% to 20%) appeared to be low compared to no analyte loss of 100%, the surrogate instrumental responses are at least 5300 and S:N ratio is at least 90, the surrogate is sufficient for accurate quantification of the analyte. The low surrogate recovery is not considered to have affected the data as the data is recovery corrected by isotope dilution quantification method. This is demonstrated by the fact that the percent recovery of the analyte TBBPA is 114% in the Ongoing Precision and Recovery (AXYS ID WG38755-102) although the surrogate recovery is 19.2%. The surrogate recoveries in samples are slightly lower than the QC samples OPR and lab blank (AXYS ID WG38755-102 and -101, respectively), suggesting that the individual sample matrix difference from the QC samples be an additional factor besides the regular variables causing the surrogate recovery being lower than method nominal lower limit of 20%.

The low surrogate recovery does cause the increase in the sample detection limit (SDL) and the SDL becomes greater than the lowest method calibration limit (LCML) for samples 112028-2,-3,-10,-4 and its duplicate (AXYS ID L17327-2, -3, -10,-4 and WG38755-104, respectively). This has been reflected in analysis report forms. Since the sample detection limit in samples in the analysis batch WG38755 is similar to the Method Detection Limit (MDL) provided in the data package, the data quality are not compromised by the low surrogate recovery and the data is considered to be appropriately reported.

Appendix E. Acronyms and Abbreviations

AXYS	AXYS Analytical Services LTD
BFR	brominated flame retardant
Cd	cadmium
CPs	chlorinated paraffins
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
HBCDD	hexabromocyclododecane
LCCPs	long-chain chlorinated paraffins
MCCPs	medium-chain chlorinated paraffins
MEL	Manchester Environmental Laboratory
Pb	lead
PBDEs	polybrominated diphenyl ethers
PBTs	persistent, bioaccumulative, toxic chemicals
PCB	polychlorinated biphenyl
PCNs	polychlorinated naphthalenes
PFBA	perfluorobutanoate
PFBS	perfluorobutanes sulfonate
PFCs	perfluorinated compounds
PFDA	perfluorodecanoate
PFDoA	perfluorododecanoate
PFHpA	perfluoroheptanoate
PFHxA	perfluorohexanoate
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoate
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	perfluorooctane sulfonamide
PFPeA	perfluoropentanoate
PFUnA	perfluoroundecanoate
RPD	relative percent difference
SCCPs	short-chain chlorinated paraffins
SOP	standard operating procedures
TBBPA	tetrabromobisphenol A
W2R	Waste 2 Resources

Units of Measurement

Σ	sum
mg/Kg	milligrams per kilogram (parts per million)
mm	millimeter
ng/Kg	nanograms per kilogram (parts per trillion)
ug/Kg	micrograms per kilogram (parts per billion)