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Little Spokane River PCBs Screening Survey of Water, Sediment, and Fish Tissue

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Little Spokane River
PCBs

Screening Survey of
Water, Sediment, and Fish Tissue

by

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Water Resource Inventory Area (WRIA) and 8-digit Hydrologic Unit Code (HUC) numbers for the study area:

WRIA
- 55 - Little Spokane

HUC numbers
- 17010308 - Little Spokane
- 17010307 - Lower Spokane

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Abstract

Previous studies by the Washington State Department of Ecology have identified elevated levels of polychlorinated biphenyls (PCBs) in fish tissue fillets from the Little Spokane River. As a result, the lower section of the river has been listed in Category 5 of the 303(d) list as being water quality-impaired for PCBs in fish tissue. Recent efforts by the Spokane River Regional Toxics Task Force to characterize and reduce PCB concentrations in the Spokane River have raised questions about PCB levels in Spokane River tributaries.

The objectives of this 2014-2015 study were to verify the level of PCB contamination in fish tissue fillets and attempt to spatially characterize the extent of potential PCB contamination in the Little Spokane River.

This study determined the following PCB levels in fish, sediment, and water in the Little Spokane River.

- Three fish species – rainbow trout, mountain whitefish, and northern pikeminnow – were analyzed as fillet composites at three sites. PCB concentrations in fish tissue ranged from 3.85 to 62.4 ug/kg. Although PCB levels were lower than those measured in 1994 and 1996, most fish tissue samples still exceeded the National Toxics Rule human health criteria (NTR=5.3 ug/kg).
- Sediment PCB concentrations ranged from 0.46 to 3.95 ug/kg. Total PCBs in sediments were much lower than the sediment cleanup objective (110 ug/kg) described in WAC 173-204.
- During fall and spring, water samples were collected from an upstream site and a downstream site. PCB concentrations in water were estimated to be well below chronic (0.014 ug/L) and acute (2 ug/L) aquatic life criteria.

Acknowledgements

The authors of this report thank the following Department of Ecology staff for their contributions to this study:

- Scott Tarbutton for assistance with site selection, landowner contact, and reconnaissance.
- Casey Deligeannis, Brandee Era-Miller, and Will Hobbs for assistance with fieldwork.
- Dale Norton and Will Hobbs for reviewing the report.

Introduction

Background

Study

Previous studies by the Washington State Department of Ecology (Ecology) collected fish from the Little Spokane River as a result of investigations of sources and concentrations of polychlorinated biphenyls (PCB) in the Spokane River drainage. Fish tissue PCB concentrations resulted in 303(d) listings under Category 5 for the Little Spokane River as being water quality impaired for PCBs.

Ecology's Water Quality Program, Eastern Regional Office, requested that Ecology's Environmental Assessment Program conduct a study to evaluate current PCB levels in Little Spokane River fish. This study was designed to verify current PCB concentrations in fish tissue. Sediment and water samples were collected in order to spatially categorize the extent of any PCB contamination in the river basin.

Polychlorinated Biphenyls (PCBs)

PCBs are a family of chemical compounds that were commonly used in insulating and hydraulic fluids, inks and carbonless copy paper, caulk and paint, and plasticizers. PCBs have been determined to be carcinogens in laboratory tests on animals and are believed to be human carcinogens (EPA, 2013). Production of these persistent and toxic chemicals was banned by the U.S. Environmental Protection Agency (EPA) in 1979. Inadvertent production of these compounds are still allowed at concentrations of less than 50 parts per million under the Toxic Substances Control Act (CFR, 2015). Small amounts are still intentionally produced for research purposes.

Due to the stability of these persistent organic pollutants, PCBs are widely present in sediments, biological organisms, and a global atmospheric pool. Since PCBs are bioaccumulative, higher PCB levels would be expected to be found in organisms than in their environments.

Study Area

The Little Spokane River drains 700 square miles of Spokane, Pend Oreille, and Stevens Counties in northeast Washington, as well as Bonner County in the state of Idaho. The river is one of two major tributaries to the Spokane River (Hangman (also known as Latah) Creek being the other). The Little Spokane discharges into the Spokane River at River Mile (RM) 56.3 (Figure 1). This section of the Spokane River is called Lake Spokane, previously known as Long Lake.

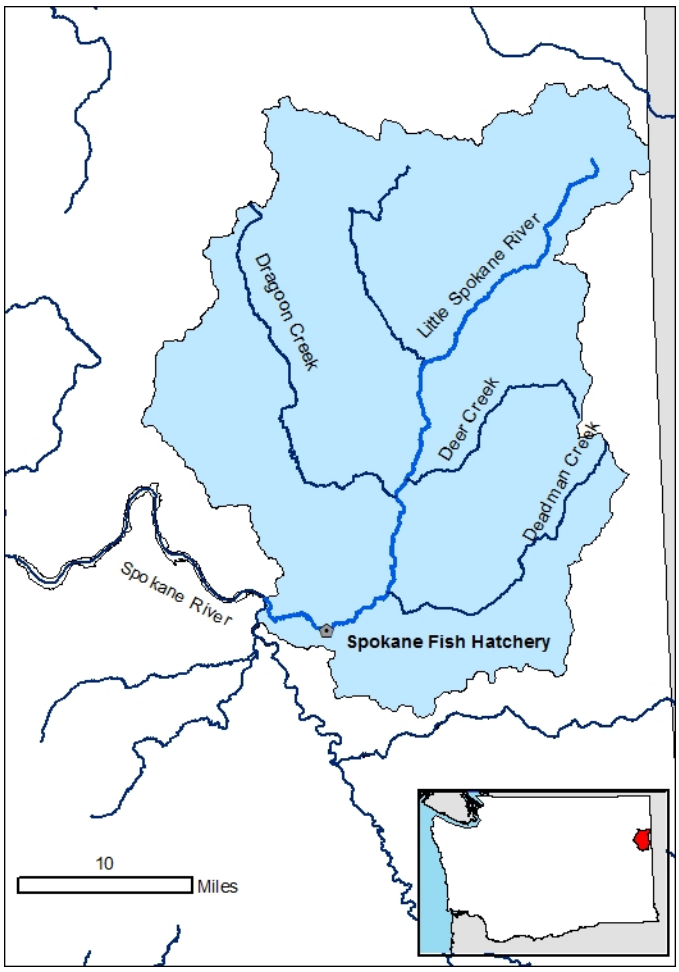


Figure 1. Study Area for Little Spokane River PCB Verification

The study area consists of forest, rangeland, agriculture, and urban development (Ecology, 1995). Urban areas within the watershed are the cities of Spokane and Deer Park, and the town of Mead. The lower 8 miles of the river were designated a State Scenic River corridor in 1991 by the Washington State Legislature. The upstream section of the river between Highway 2 and 395 is within the Spokane Urban Growth Area. Upstream of Highway 2, land use is rural residential, agricultural, and forest. Groundwater contributes significantly to Little Spokane River flow (Ecology, 2015).

Three permitted facilities have historically discharged or currently discharge water into the Little Spokane River. The Colbert Landfill discharged treated groundwater that was contaminated with organic solvents from 1975 to 1980 (EPA, 2009) and the Washington Department of Wildlife (WDFW) Spokane Fish Hatchery on the Little Spokane River discharges water from the hatchery. The former Kaiser Aluminum Plant in Mead is currently inactive. NMC Mead LLC purchased the facility from Kaiser and sold it to Spokane Recycling Company, LLC in the fall of 2014 (pers. comm., Pat Hallinan). This facility is currently inactive but still discharges stormwater under their NPDES permit. Ecology has documented groundwater from this facility contaminated with fluoride and cyanide flowing into the Little Spokane River (Ecology Agreed Order, 2001).

Goal and Objectives

Goal

The goal of this study was to evaluate current PCB levels in fish tissue, water, and sediments in the Little Spokane River relative to water quality standards and sediment cleanup standards.

Objectives

The objectives of the 2015 study were as follows:

- Collect fish samples to evaluate if PCB levels are still elevated compared to 303(d) listing criteria.
- Collect water and sediment samples to assess if PCB concentrations in fish tissue are representative of the Little Spokane River.
- Spatially characterize PCB contamination using sediment concentrations.

PCB concentrations in fish, water and sediment will be compared to regulatory criteria to evaluate the extent of PCB contamination. See Table 1 for regulatory criteria.

The National Toxics Rule (NTR) criterion is sometimes evaluated as a Fish Tissue Equivalency Concentration (FTEC). Washington uses FTECs to evaluate water quality criteria for contaminants that have criteria lower than can be reliably quantified by current analytical methods. This is a numeric criteria established by multiplying the Washington State water quality criteria by the EPA bioconcentration factor (BCF) to calculate the corresponding PCB concentration in fish tissue.

Table 1. Regulatory Criteria for Different Matrices.

Analyte	Matrix	Regulatory Criteria	Concentration
PCB congeners	fish	human health criterion (NTR as FTEC)	5.3 ug/kg
PCB congeners	sediment	sediment cleanup objective[1]	110 ug/kg
PCB congeners	water	human health criterion (NTR)	0.00017 ug/L
PCB congeners	water	aquatic life criterion[2] (acute)	2.0 ug/L
PCB congeners	water	aquatic life criterion[2] (chronic)	0.014 ug/L

[1] WAC 173-204-563
[2] WAC 173-201A-240 (24-hour average)

Methods

Field Methods

The Ecology field crew was not able to use electrofishing techniques to selectively collect fish due to equipment failure. Hook and line methods were used to collect fish from the shore. Fish were collected from 3 river locations. Fish collection and preservation followed procedures described in the Standard Operating Procedure (SOP) for Field Collection, Processing and Preservation of Finfish Samples at the Time of Collection in the Field (Sandvik, 2010a). Location information and matrices sampled are shown in Table 2. The most upstream location was at the Deer Park/Milan Road crossing of the Little Spokane River. Fish were also collected at the Colbert Road crossing. Downstream fish samples were collected just below the WDFW Spokane Fish Hatchery. See Figure 2 for a map of sample locations. Fish were weighed and measured in the field, then wrapped in foil, labeled and stored on ice for transport to Headquarters (SOP EAP009). After processing at Headquarters, fish tissue composites were analyzed for PCB congeners.

Table 2. Site Location and Matrices Sampled.

Site	Latitude	Longitude	Matrices Sampled
Eloika	48.0068	-117.3627	Sediment
Deer/Milan	47.9695	-117.3339	Fish, Sediment, Water
Colbert	47.8239	-117.3741	Fish, Sediment
Little Deep	47.7957	-117.3799	Sediment
Deadman	47.7955	-117.3799	Sediment
Below Hatchery	47.7689	-117.4645	Fish, Sediment
Painted Rocks	47.7809	-117.4959	Fish, Sediment

Sediments were sampled so as to spatially represent the Little Spokane River (Figure 2). The upstream sections of the mainstem of the river contained sand and gravel, sediments not suitable for organics analysis. As a result, no samples were collected from the mainstem upstream from Deer Park/Milan Road. The Eloika sample, collected from the west fork of the Little Spokane River had sediments suitable for organics analysis.

Sediment samples were collected by hand scooping fine sediments from the top 5 cm of depositional areas of the river. Pre-cleaned stainless scoops were used to collect and homogenize composite sediment samples. Samples were placed in certified clean sample jars (EPA 1992), cooled on ice in the field and frozen for shipping to the lab. Sediment samples were analyzed for PCB congeners.

Water samples were collected using submersible pumps which concentrate contaminants on a solid phase extraction (SPE) disc. These samplers are called Continuous Low-level Aquatic Monitors (CLAMs). The CLAM samplers collect a high volume sample in the field, eliminating the need to transport large volumes of water to the lab (Friese and Coots, 2014). The samples extracted from the SPE discs were analyzed at a contract laboratory for PCB congeners. Water

samples were collected from an upstream reference site (Deer/Milan) and a site that includes the influences of tributaries and groundwater (Painted Rocks). Figure 2 shows sample sites and matrices sampled at each site.

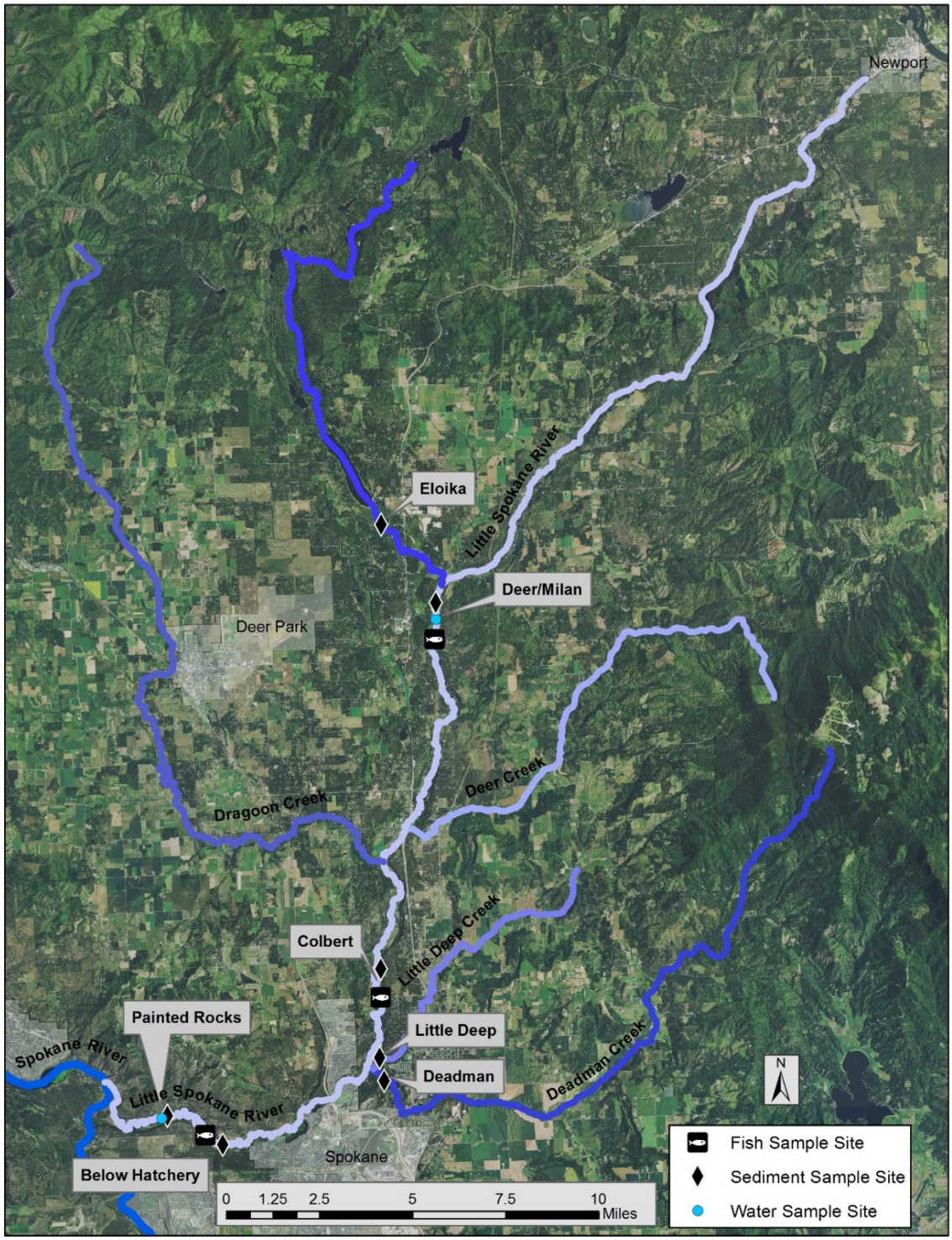


Figure 2. Map of Sampling Sites.

Laboratory Methods

Fish, sediment, and water samples were all analyzed for PCB congeners using EPA method 1668C. All samples were analyzed using gas chromatography on a high resolution mass spectrometer (HRGC/MS). Calibration was verified at the beginning and end of each run with a single point 209 congener standard. Reporting limits were set at 2.5 times signal to noise ratio. Method blanks were run with extraction and clean up procedures, sample results less than 10 times (10x) blank results were qualified "U" as non-detect.

EPA's National Functional Guidelines for Organic Data Review recommends using 10x the amount in the blank as a threshold for positively identifying target analytes that are common laboratory contaminants (EPA, 1999).

Fish Processing

Samples were processed at Ecology's Headquarters by staff familiar with protocols before being shipped to the contract laboratory for analysis. Fish were rinsed with tap water and the scales were removed. After a rinse with de-ionized water, fillets were removed, cut into smaller pieces and ground in a Kitchen Aid® food grinder. Tissue samples were ground once, then equal aliquots from each fish in the composite were combined and ground twice more with the Kitchen Aid®. Composite samples were mixed with stainless steel utensils to a uniform color and texture. All equipment was cleaned with soap and solvents prior to use, adhering to SOPs (Friese and Coots, 2014).

SOPs were followed for all fish processing. For more detail, consult SOP EAP007, *Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples*: http://www.ecy.wa.gov/programs/eap/quality.html (Sandvik, 2010b).

Results

Quality Assessment

Results were reviewed for qualitative and quantitative accuracy following the National Functional Guidelines for Organic Data Review under the Contract Laboratory Program (CLP). Written case narratives assessing the quality of the data reports were provided by Ecology's Manchester Environmental Laboratory (MEL). These narratives included descriptions of the analytical methods, a review of sample holding times, instrument calibration checks, blank results, surrogate recoveries, matrix spike recoveries, and laboratory control samples. The case narratives and complete data reports can be obtained from the report author, by request.

The quality assurance (QA) review verified laboratory performance met most quality control (QC) specifications outlined in the analytical methods. Exceptions are noted below. After reviewing the data to assure EPA Method 1668C criteria and data quality objectives outlined in the QAPP (Friese and Coots, 2014) were met, this data was considered acceptable as qualified for the purposes of this project. All quality assurance data can be found in Appendix B.

Sample Holding

All study samples were maintained and transferred to Ecology under chain-of-custody from the time of collection. Study samples were sent by courier to MEL and most arrived in coolers on ice within the proper holding temperature of <6° C for water and <-10° C for sediment. As an exception, CLAM disc samples (water) arrived at the laboratory above holding temperature. CLAM samples were immediately cooled to 4° C and the lab felt this did not interfere with the analysis. All samples were prepared and analyzed within method holding time limits.

PCB Congeners

PCB data often have large numbers of non-detected or qualified results. Depending on the end use of the data, PCB totals may be summed differently. For this study, PCB totals are the sum of all detected congeners, and "J" qualified values per sample. Results qualified with a "J" were positively identified but reflect an approximate concentration. The "NJ" flag qualifies data that meets all identification criteria except the isotope abundance ratio. Since these data do not meet EPA Method 1668C's criteria for positive identification, they are unusable for regulatory purposes. Data qualified as "NJ" (approximate concentration, tentatively identified) were not included in any PCB totals. Non-detected PCB values ("U" and "UJ") were also excluded from totals. When PCB congeners or homologs are summed, the totals are J qualified if 10% or more of the concentration to be totaled is J qualified.

Results less than 10 times the laboratory blank concentration are qualified with a "U" as non-detects at the *Estimated Quantitation Level* (EQL). When congener concentrations were more than 10 times the blank concentration, no qualification was applied.

EQL is defined as the lowest validated non-zero standard in the calibration curve, adjusted for sample volume, weight and any dilutions. It is equivalent to the "Minimum Level" described in EPA method 1668. *Estimated Detection Limit* (EDL) **i**s an estimate of the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the signal background level. The estimate is sample-specific and analyte-specific and may vary with sample size and dilution.

At times the EDL is reported at a higher concentration than the EQL. This is a result of the use of different types of samples to generate the data and how EDLs and EQLs are calculated. The EDL is calculated as 2.5 times the "sample" average signal-to-noise ratio. When sample matrix interference pushes the signal-to-noise ratio upwards, the EDL is increased proportionally. The EQL is calculated from a clean matrix or ideal sample like a low level laboratory standard. When EQLs and EDLs were applied to sample data, the higher result of the two is used as a detection limit.

Laboratory results from this study will be entered into Ecology's Environmental Information Management (EIM) database with the exception of data generated by samples collected by CLAM samplers. Because SOP development has not yet occurred for the CLAM samplers, it is considered an evolving technology, results are currently considered estimates. As the volume of water sampled by the CLAMs is uncertain, the calculated concentration is considered an estimate.

Fish Tissue Data Quality

Acceptance criteria for internal standards were recoveries within a range of 25% and 150%. A range of 15% to 150% was used to evaluate monochlorobiphenyl congeners (PCB-1L and PCB-3L). All samples with low monochlorobiphenyl recoveries were re-extracted and re-analyzed with the exception of the lab duplicate which was inadvertently not re-analyzed. As a result of the low monochlorobiphenyl recoveries, affected data were "J" qualified for detected analytes and "UJ" for non-detects. Any recoveries below 5% were rejected. After excluding low PCB-1L and PCB-3L values, recoveries ranged from 20% to 140% with a mean of 80%.

Congener results from fish data that did not meet isotopic abundance ratio criteria were qualified "NJ" (tentatively identified, concentration is approximate) and not included in totals.

One fish sample, the Northern pikeminnow (sample # 1502050-05) from downstream of the hatchery was split as a lab duplicate. As a means to evaluate variability, Relative Percent Difference (RPD) was calculated from PCB congener results for detected and "J" qualified field replicate data. Average RPD for congener pairs was 12% and ranged from 0% to 57%. Most of the RPDs for congener pairs were within the MQOs (≤50%) established in the QAPP (Friese and Coots, 2014).

Sediment Data Quality

Internal standard recoveries were within QC limits with the exception of monochlorobiphenyls from the field replicate sample collected from Eloika (1410050-10). As a result, PCB-001, PCB-002, and PCB-003 concentrations were not included in PCB totals for this sample. Labeled congener recovery rates for sediment samples ranged from 13% to 102% with a mean of 64%. Internal standard and labeled congener recoveries for EPA 1668C are congener-specific. The complete data set for sediment-labeled congeners is available in Appendix B.

Sediment congener results that did not meet isotopic abundance ratio criteria were qualified "NJ" as tentatively identified. Since these results did not meet the criteria for EPA Method 1668C, "NJ" qualified results are not included in any PCB or homolog totals.

A field replicate was collected from the Eloika sample site (1410050-08 and 1410050-10). The replicate was collected immediately following the initial sample at the same location, using the same method as the original sample. The average RPD was 34% and RPDs ranged from 0% to 75%. Acceptance criteria for sediment RPDs was ≤50%. The RPDs were calculated using only results that were considered detections. Sediment RPDs met MQOs from the QAPP in 84% of the detected results. Variability shown in RPDs >50% is likely due to natural variability in PCB concentrations.

CLAM (Water) Data Quality

Water samples collected with CLAM pumps and solid phase extraction (SPE) discs had problems with blank contamination. The field blank from 2014 had more contamination than the fall lab blank while the spring 2015 lab blank had more contamination (Figure 3.) The fall 2014 lab and field blanks each had 35 detections of PCB congeners and co-eluted congeners. The spring 2015 lab blank had 66 detections and the field blank had 21 detections. This resulted in a large amount of the CLAM data being qualified as non-detected ("U" or "UJ") above the reported EQL. As a result of the concern about blank contamination, the contract lab ran an additional series of experiments with new SPE discs and housings. The results suggest the source of the PCB contamination may be coming from the SPE disc housing. The dominant congener detected in lab blank samples was PCB-007 (Appendix B). Other congeners detected in blank samples were PCBs 047/048, 018, 005/008, 028, 011, and 017, in descending order of concentration. The high level of blank contamination makes it difficult to quantify with confidence the PCB data from water samples.

Recoveries of labeled congeners from the fall samples ranged from 21% to 86% with a mean of 62%. The spring CLAM samples produced labeled congener recoveries from 17% to 118% with a mean of 72%.

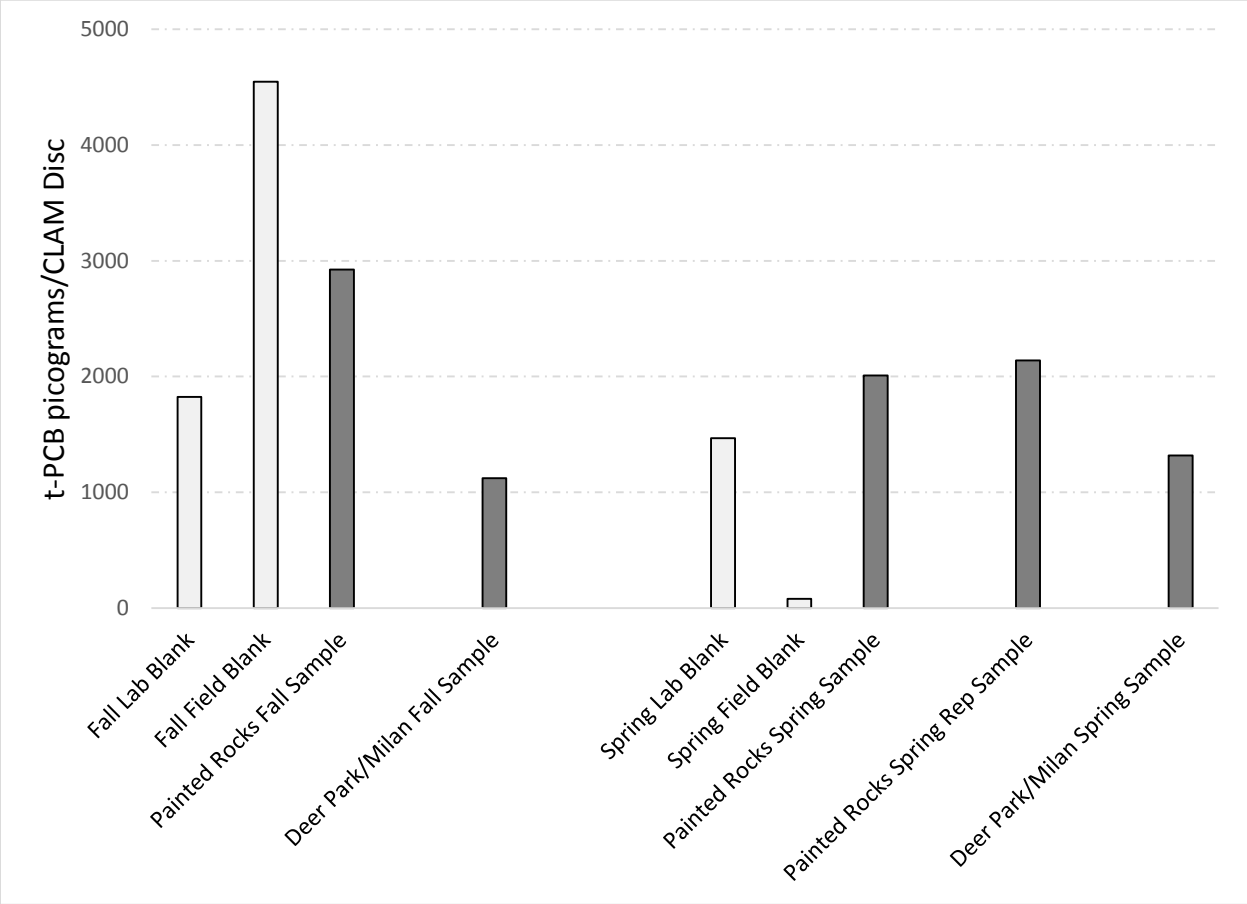


Figure 3. Absolute Values of CLAM Water Samples and Blanks.

Fish

Fish samples were composites of 3 fish, with the exception of individual rainbow trout and mountain whitefish fillets from the site below the Spokane fish hatchery. Rainbow trout were not adipose clipped, indicating they were most likely naturally reproducing fish, not of hatchery origin. Mountain whitefish and northern pikeminnow are not reared in hatcheries, so it is certain that those fish are naturally reproducing.

The range of total PCB concentrations in Little Spokane River fish was 3.8 - 62.4 ug/kg, wet weight. Total PCB concentrations in fish tissue are displayed in Figure 4. The highest PCB levels were found in northern pikeminnow collected below the Spokane Fish Hatchery, followed by the mountain whitefish collected from the same site. All fish samples for this project were analyzed as fillets. Age data are also presented in Figure 4. Age data were not available for the rainbow trout collected below the hatchery because the scales were regenerated and age could not be determined. All of the other fish from this study were of a comparable age, 2-3 years, with the exception of northern pikeminnow that were significantly older, with an average age of 8 years.

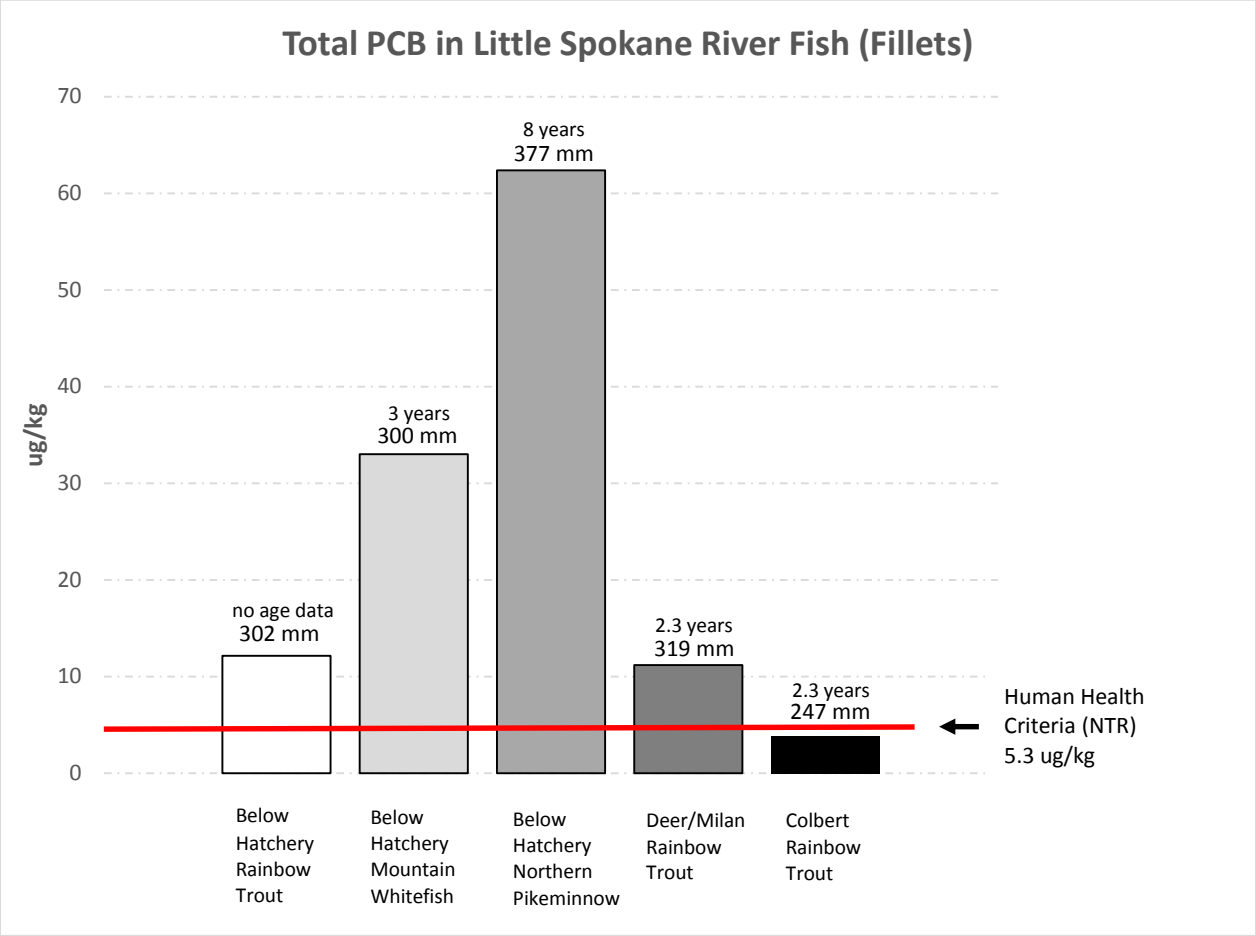


Figure 4. Total PCB in Little Spokane River Fish.
Average length and age displayed above bars.

A previous Ecology study investigated concentrations of persistent organic pollutants in fish from Washington State hatcheries (Serdar, 2006). PCB concentrations in rainbow trout fillets from the Troutlodge and Spokane hatcheries, which supply fish for stocking Lake Spokane, were estimated to be 14.4 ug/kg and 6.5 ug/kg, respectively. With the exception of rainbow trout collected at the Colbert Road crossing, rainbow trout analyzed for the present study had higher PCB concentrations than fish analyzed from Troutlodge and Spokane Fish Hatcheries.

As previously mentioned, Washington State uses a fish tissue equivalent concentration (FTEC) as the 303(d) listing criteria that corresponds to the human health criteria in the NTR. The FTEC is calculated by multiplying an analyte specific bioconcentration factor with the water quality standard criterion for that analyte. Fish tissue PCB concentrations were generally higher than the FTEC.

Sediment

Sediment samples were collected from 7 locations throughout the Little Spokane River. From upstream moving downstream, the sediment sites are named Eloika, Deer Park/Milan, Colbert, Deadman, Little Deep, Painted Rocks, and Below Hatchery. A map with sediment sample sites is shown in Figure 2. Total PCB concentrations in sediment ranged from 0.46 to 3.85 ug/kg. PCB concentrations in sediment were well below the sediment cleanup objective of 110 ug/kg. Currently this is the only Washington State regulatory criteria for PCBs in sediment (WAC 173-204). Figure 5 displays the total PCB concentration in Little Spokane River sediment. PCB concentrations in sediments increased moving downstream. Sediment results were not normalized as regression analysis determined that there was no relationship between total organic carbon (TOC) or % fines and PCB concentrations. TOC and % fines results are shown in Appendix B.

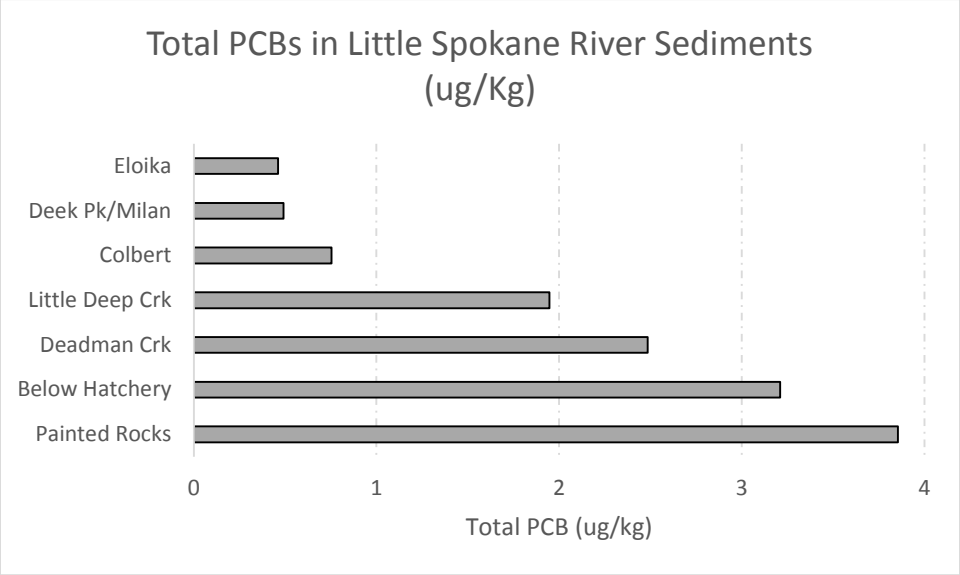


Figure 5. Total PCBs in Little Spokane River Sediment.

PCB Homologs are groups of PCB congeners grouped by the number of chlorine atoms attached to a biphenyl molecule. For example, pentachlorobiphenyls are all congeners with five chlorine atoms attached to biphenyl (a molecule made up of two benzene rings). Comparing the distribution of homologs can be useful when evaluating spatial distribution of PCB contamination. Similar homolog distributions may indicate that contamination originates from a similar source. The sediment from the three upstream sites all show a similar distribution of homolog groups, with the exception of slightly elevated di-chlorinated biphenyls in the Eloika field replicate sample. The downstream sites' distributions are dominated by higher chlorinated homologs. Deadman and Little Deep, tributaries to the Little Spokane River have nearly identical homolog patterns, suggesting a different PCB source from that part of the watershed. The two farthest downstream sites show a similar pattern to the tributaries with a difference in the magnitude of concentrations.

See Figure 6 for PCB homolog concentrations from sediment samples.

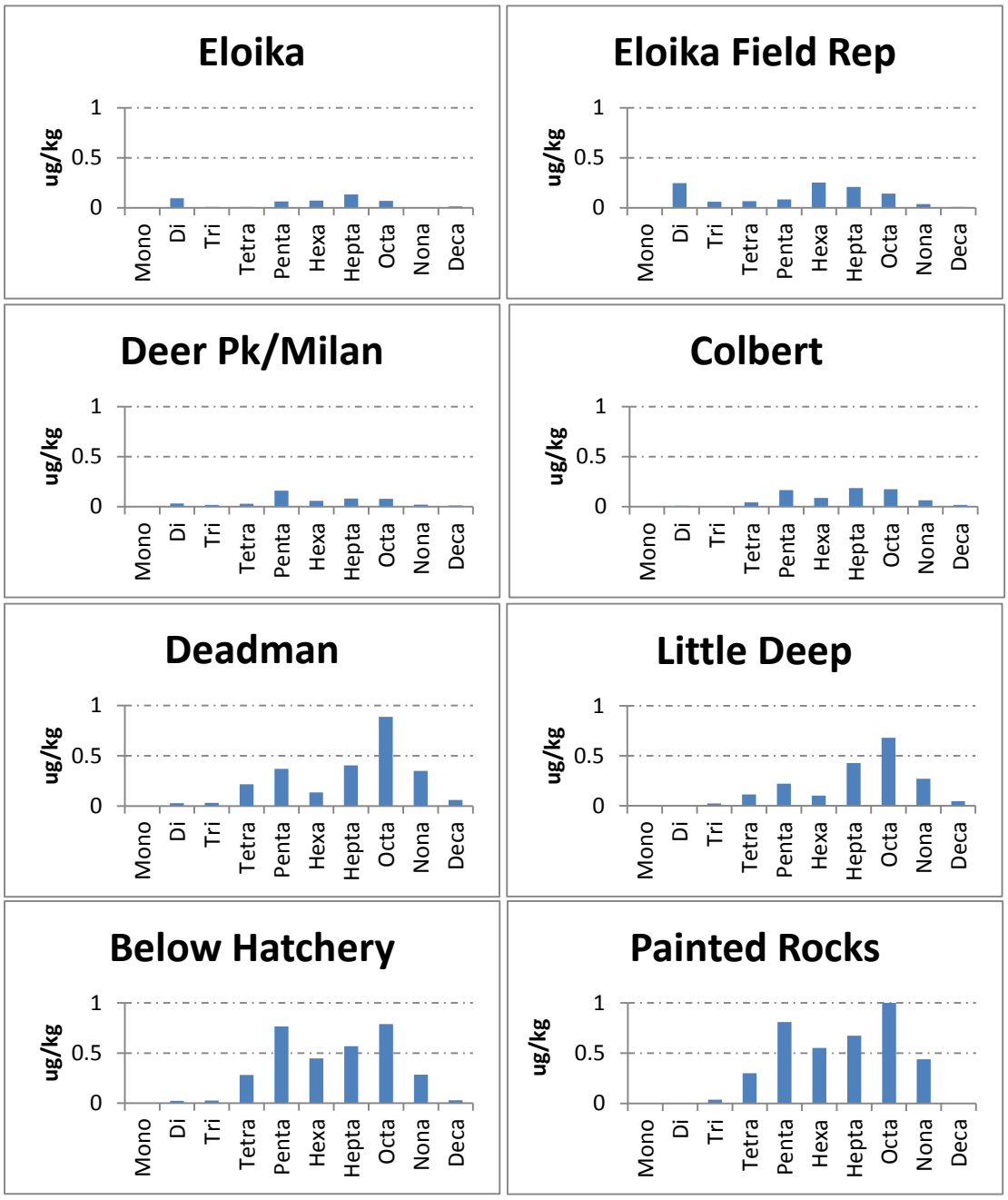
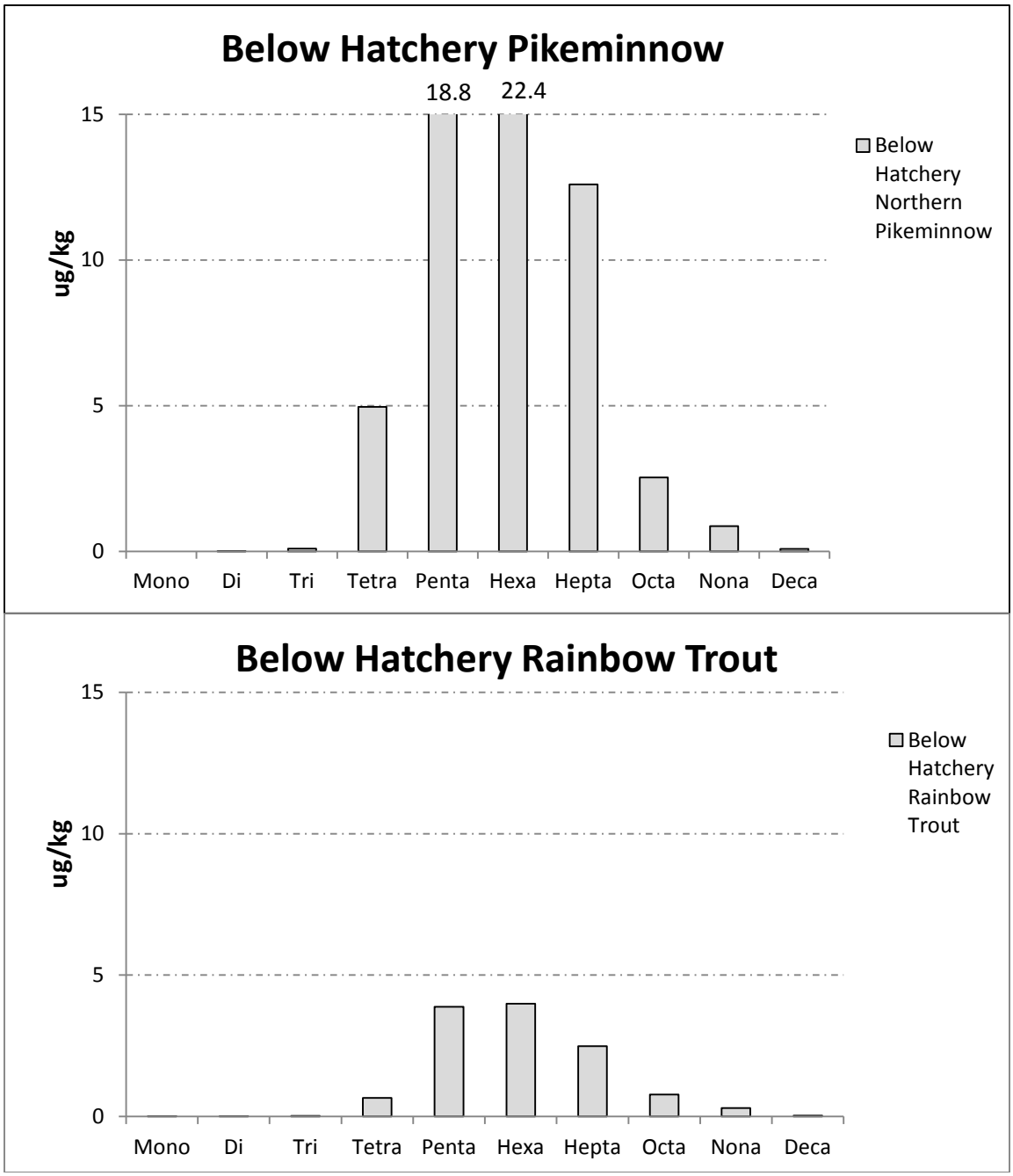


Figure 6. PCB Homolog Concentrations in Little Spokane River Sediments.

Fish PCB Homolog Concentrations

Figure 7 shows PCB homolog concentrations detected in fish fillets from the Little Spokane River.



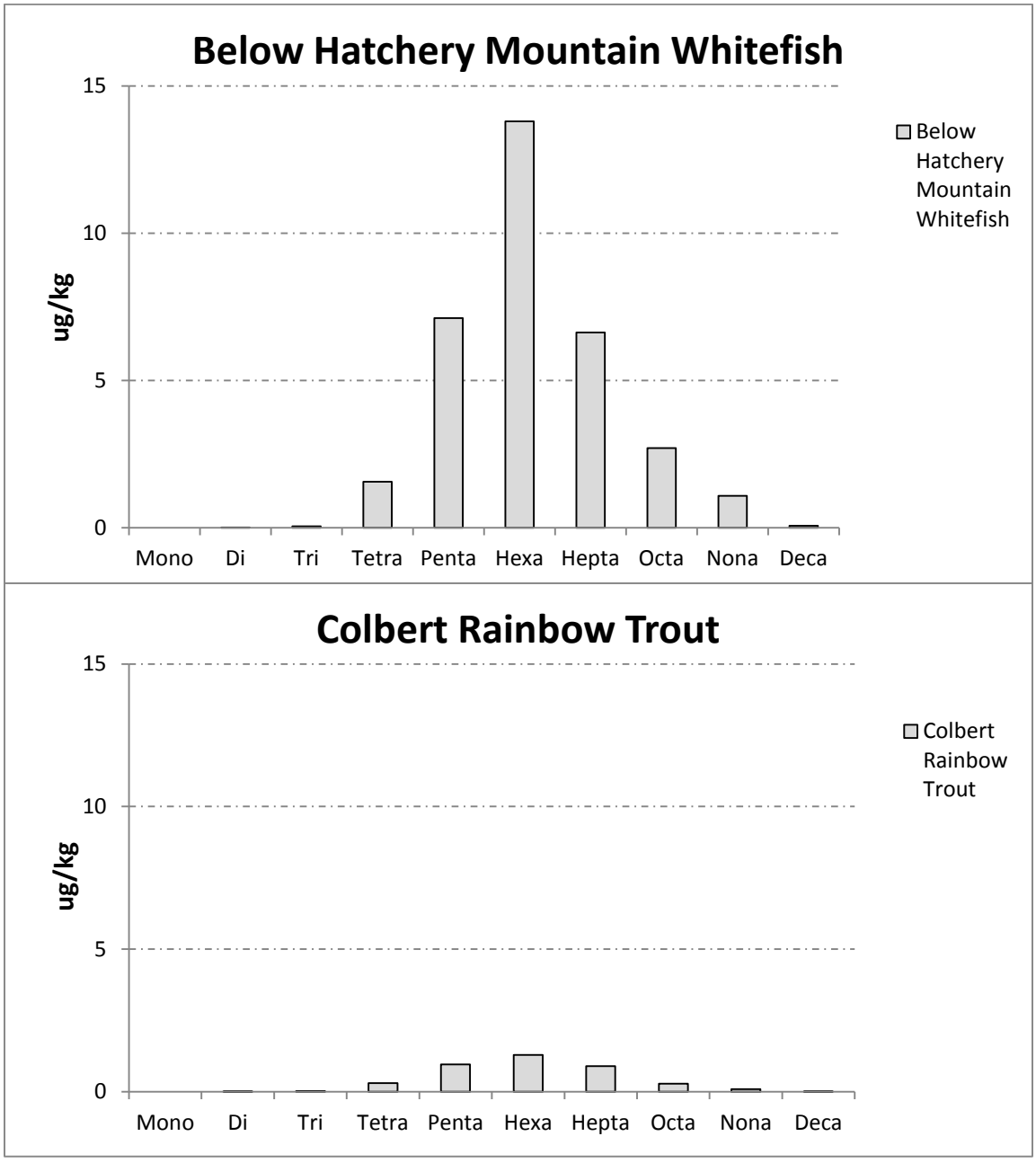
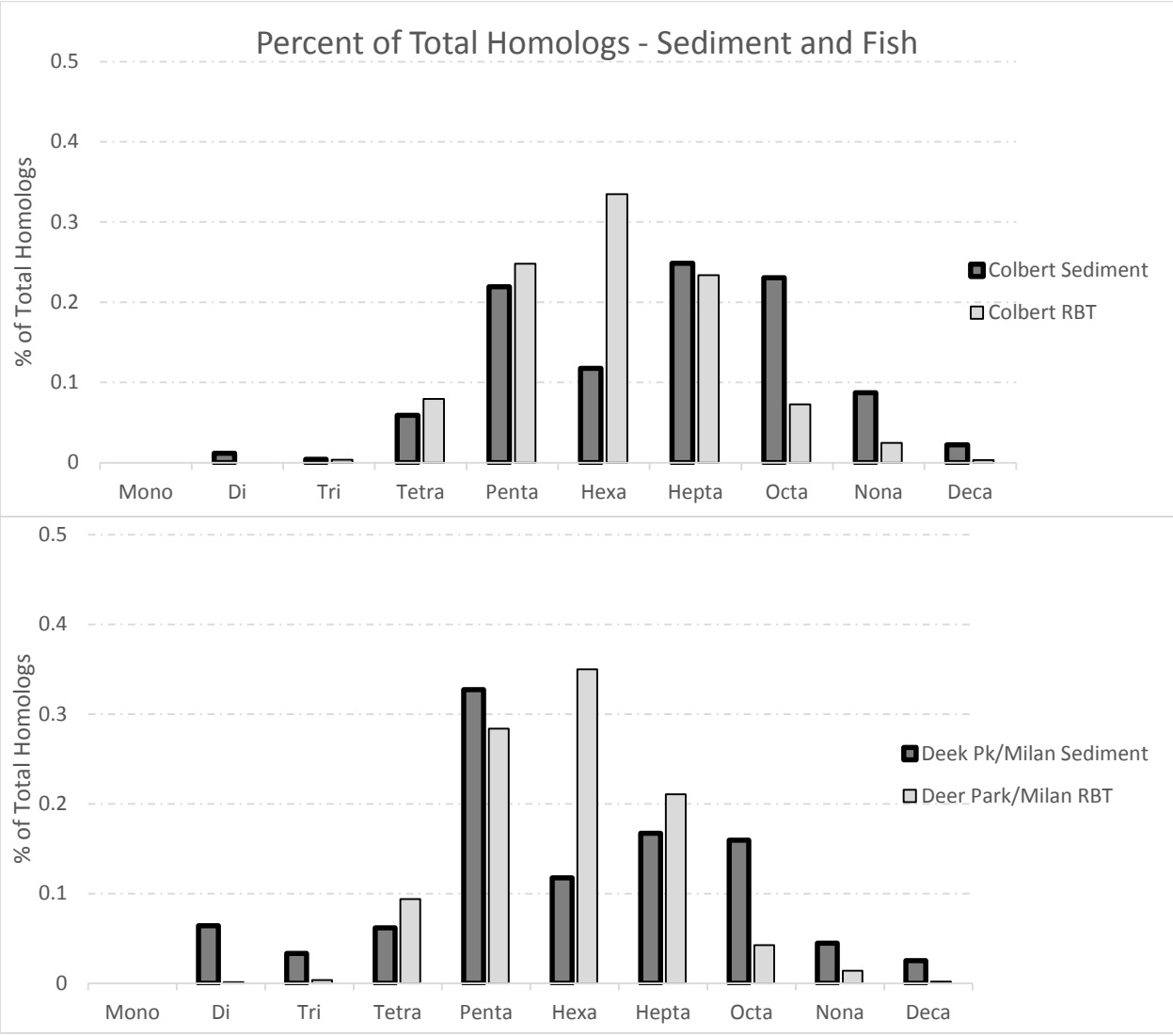


Figure 7. PCB Homolog Distribution in Fish Fillets.

Percent of Total PCB Homolog Concentrations in Sediment and Fish

Percent of total PCB homologs can be a useful tool for comparing PCB concentrations in different matrices. When % of total homologs in Little Spokane River sediments are compared to homolog percentages in fish tissue, no distinct relationship is apparent. It is important to consider that when PCB concentrations are low, as they are in these samples, a small difference in concentration can make a big difference in the percentage of total PCBs. Sediment and fish homolog percentages are compared in Figure 8.



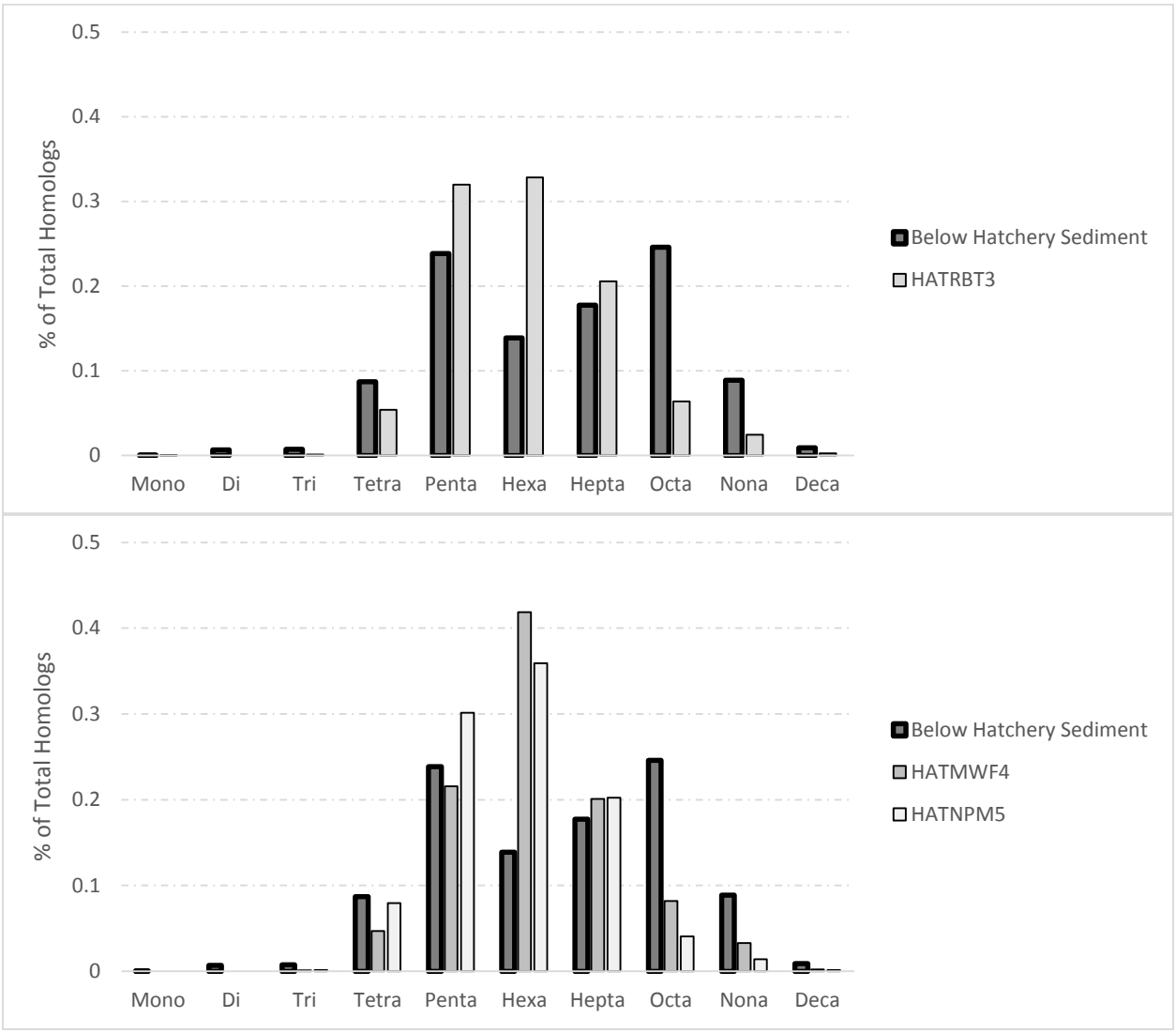


Figure 8. Percent of Total Homologs in Sediment and Fish.

CLAM Sample Volume Estimates

CLAM samplers work by pumping a volume of water through a SPE disc, concentrating contaminants from the water onto the disc. This is a new technology and Ecology has been experimenting with different methods of measuring or estimating the volume of water sampled. Sample volume must be determined to calculate an estimate of PCB concentration in the water. The manufacturer suggested measuring the volume of water pumped in a minute period at the beginning and end of the sample period. These volumes can be used with a linear regression equation to estimate sample volume. Ecology has found that the linear calculation provides a volume estimate that is likely biased high (Ecology, unpublished data).

Recently the manufacturer provided Ecology with a "totalizer" to measure the volume of sampled water. This device uses optics to continuously measure the volume of water sampled by the CLAM. Totalizers were used for this study on the second round of water sampling during the spring of 2015. Field staff deploying CLAMs found discrepancies between the volumes measured by the totalizer and volumes measured manually with a graduated cylinder. Totalizer volumes were mostly higher than volumes measured with a graduated cylinder.

Though the totalizers were not found to be accurate, they were still considered a useful tool to evaluate if the volume estimate was reasonable. Volume estimates using linear regression were biased high when compared to the totalizer volume. See Table 3 for results of the three methods of calculating an estimated sample volume. Fitting an exponential model to estimate sample volume was found to be closer to the totalizer volume than the linear regression method.

It is likely that previous studies using CLAMs have overestimated sample volume by using linear regression equations. A sample volume that was biased high would result in a sample concentration estimate that was biased low. Ecology now recommends that future studies using CLAMs should collect the volume of water being sampled. This will eliminate the need for an optic volume measurement (totalizer) or a calculated volume estimate.

CLAM samples collected for this project used the exponential method of estimating sample volume.

Table 3. CLAM Sample Volume Methods.

Linear Model	Exponential Model	Totalizer
41.61 L†	27.97 L†	23.81L††

† volume estimate
†† optic volume measurement

Water

CLAM samplers were used to collect a large volume water sample for PCB congener analysis. A large volume sample was used to allow for lower detection limits because PCBs are normally found at such low concentrations in water. The sample volumes are displayed above the bars in Figure 9. Water samples were collected in fall of 2014 and spring of 2015. Fall and spring sampling was conducted to account for seasonal variability of the PCB concentrations in the river. CLAM samples were collected in the Little Spokane River at 2 locations. The downstream location was in a section of Riverside State Park known as Painted Rocks, at an Ecology gaging station just downstream of the Rutter Parkway Bridge. The upstream location was under the bridge crossing on Deer Park-Milan Road. Sample locations are shown in Figure 2.

All water samples were found to have lower PCB concentrations than found in the blank samples when using volume to calculate concentration. When absolute values are considered (Figure 3), the fall field blank contained more total PCB than either fall sample. The spring field blank had very little PCB contamination while the spring lab blank was 68-73% of the Painted Rocks sample and replicate, respectively. The spring lab blank had more PCB than the Deer Park/Milan sample.

As mentioned in the Quality Assurance section of this report, there were PCB contamination issues in the CLAM blanks, possibly originating from the SPE disc housing. PCB data from water samples were heavily qualified as a result of the blank contamination issues. Water sample data are presented here for informational purposes only. The blank contamination creates more of an issue for this study as water concentrations are so low. If water concentrations were at or above criteria (170 pg/L), the results could be more easily distinguished from the blank contamination. Even with the blank contamination issues, the results show that PCB concentrations in the Little Spokane River are low−well below the freshwater NTR criterion.

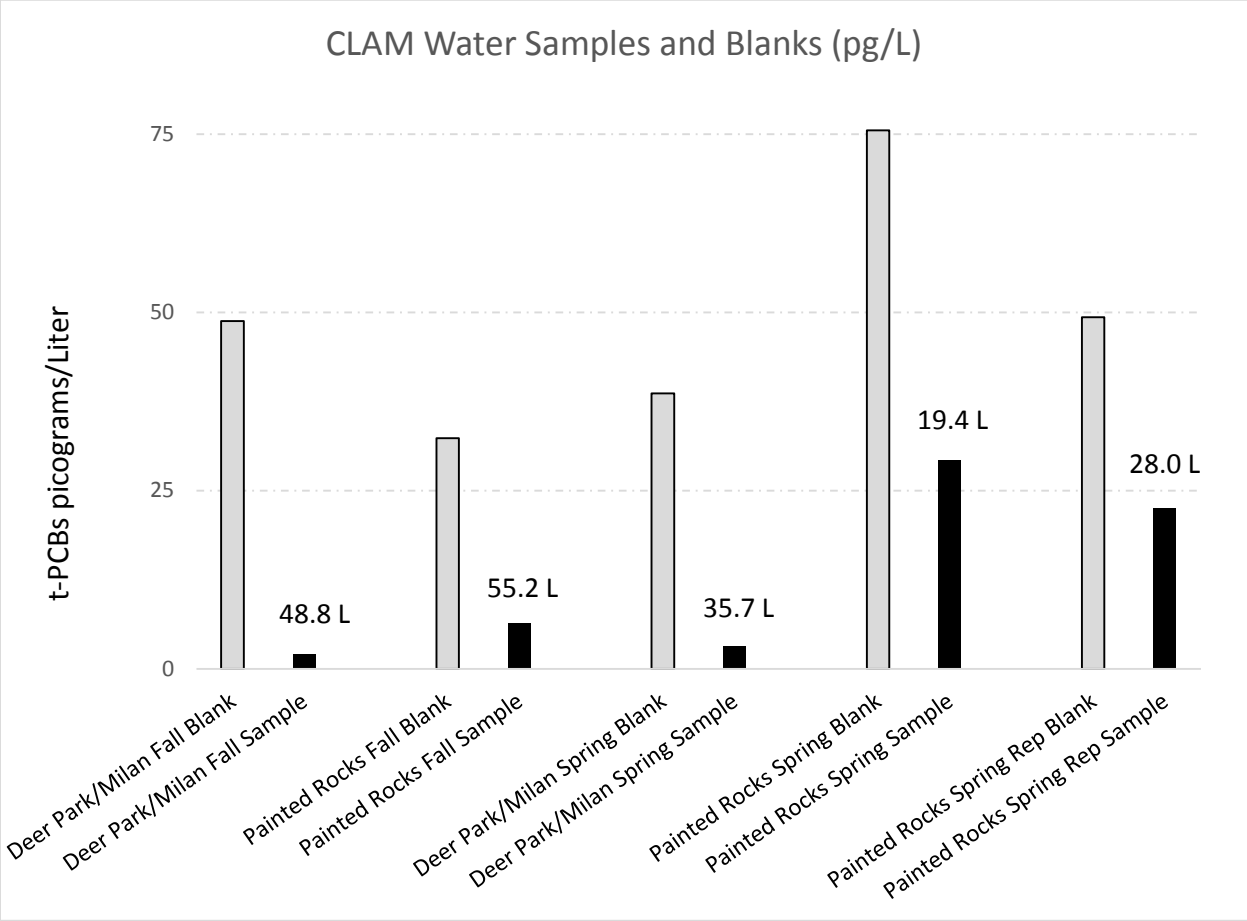


Figure 9. Total PCB Concentration in Samples and Blanks.

Sample volume estimates are above bars.

Blank concentrations were calculated using site-specific sample volumes.

Discussion

Fish Tissue Verification

A goal of this project was to determine if elevated PCB levels are still present in Little Spokane River fish (Friese and Coots, 2014). All but one of the fish composites were above the human health criteria as FTEC (Table 4). These fish tissue PCB concentrations suggest the Little Spokane River should remain on Category 5 of the 303(d) list as water quality-impaired for PCBs. PCB concentrations in fish tissue in the Little Spokane River are lower than those observed in previous studies, though still above the human health criteria of 5.3 ug/kg (Table 4). The highest PCB concentrations measured in this study were at the low end of previously measured fish tissue samples. The small sample size from previous studies and the present study precludes determining any statistically significant trends in PCB concentrations. Differences in species, size, and age further complicate the comparison between previous and present PCB concentrations. Though the data do suggest decreasing PCB concentrations, further study would be necessary to establish and verify a trend.

Table 4. Previous and Current PCB Concentrations in Little Spokane River Fish Fillets.

Species	Concentration (ug/kg)	Year Collected	Number in Composite	Data Source
Mountain whitefish	145	1994	8	Ecology, 1995
Mountain whitefish	235	1994	8	Ecology, 1995
Mountain whitefish	285	1994	8	Ecology, 1995
Cutthroat trout	188	1994	1	Ecology, 1995
Mountain whitefish	164	1996	8	Johnson, 1997
Mountain whitefish	130	1996	8	Johnson, 1997
Mountain whitefish	53	1996	8	Johnson, 1997
Rainbow trout	4	2014	3	Present Study
Rainbow trout	11	2014	3	Present Study
Northern pikeminnow	62	2014	3	Present Study
Mountain whitefish	33	2014	1	Present Study
Rainbow trout	12	2014	1	Present Study

FTEC = 5.3 ug/kg

There is no hatchery production of northern pikeminnow or mountain whitefish, so these fish are known to be of natural origin. What is not known is whether the PCB loads in these fish have originated from the Little Spokane River. There are no fish passage barriers between the Spokane River (Lake Spokane at the confluence) and the Little Spokane River. It is possible that a portion of the PCB body burden in these fish originated within the Spokane River watershed instead of the Little Spokane River watershed. Without telemetry studies or some other kind of fish migration study, it is impossible to connect the PCB loads in the fish to one particular reach of the Spokane River system. Food web analysis, including evaluation of PCB concentrations in fish prey would likely help to narrow down the origin of PCB burdens in fish tissue. PCB

concentrations are low in ambient water and sediment; therefore, the PCB body burdens in the sampled fish likely originated outside the Little Spokane River drainage.

Hatchery rainbow trout are planted annually into Lake Spokane by the Washington Department of Fish and Wildlife (WDFW). The adipose fins of hatchery-planted trout are clipped by WDFW to distinguish these hatchery fish from naturally reproducing rainbow trout. Though these fish can migrate in and out of the Little Spokane River without obstruction, they are bred to live a lacustrine life cycle, preferring a lake habitat to a fluvial or riverine system. As a result, these hatchery trout are unlikely to move in and out of the Little Spokane River. It is more likely that naturally reproducing, "wild" fish would migrate in and out of the Little Spokane River (pers. comm, Chris Donley). All of the rainbow trout used in this study had their adipose fins intact, indicating they are most likely naturally reproducing fish.

The total PCB concentrations in 3 out of 4 of the fish samples used for this study were above the NTR human health criterion (as FTEC) of 5.3 ug/kg. When PCB concentrations in the fish used for this study are compared to other fish tissue PCB concentrations around Washington State (Seiders, et. al., 2015), Little Spokane River fish rank between the 22nd to 76th percentiles. When compared to only Spokane River fish, Little Spokane River fish rank in the 0 to 23% percentiles. See Figure 10 for a cumulative frequency distribution chart. This shows rank of the fish used for this study, as compared to rank of fish analyzed from the Spokane River and other Washington State fish previously analyzed from 2001 - 2014. Note the logarithmic scale on the y-axis.

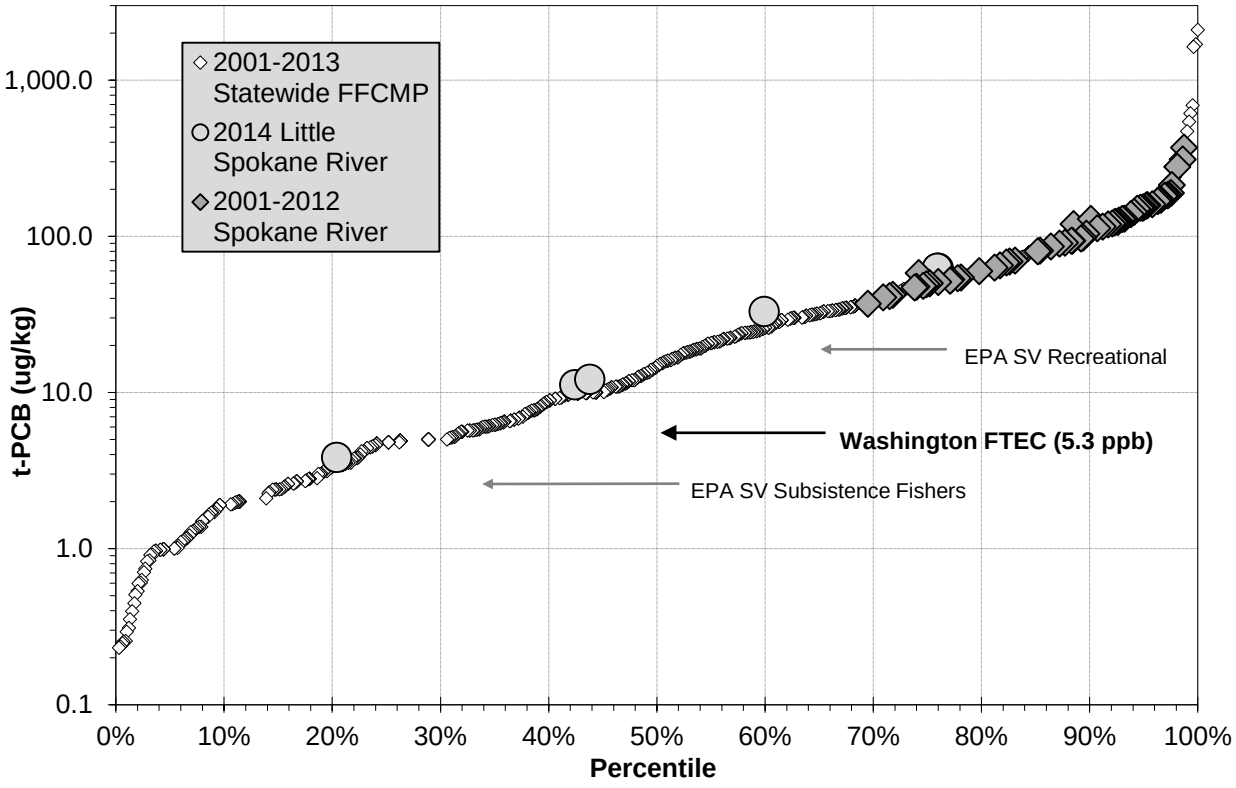


Figure 10. Total PCB Distribution of Little Spokane River Fish Tissue Compared to Statewide and Spokane River Results.

Different species of fish accumulate, metabolize, and store environmental contaminants at different rates. Trophic level, feeding regime, and metabolic rates all contribute to the differences in how environmental contaminants build up in individual fish species. When compared to fish of the same species collected from Washington State and analyzed for PCBs, the percent ranking is very different than the ranking within the distribution of all fish species (Table 5). Northern pikeminnow were the highest ranked (i.e., NPM from the Little Spokane have higher PCB concentrations than 80% of the NPM measured throughout the state), rainbow trout were above average and mountain whitefish were relatively low. PCB concentration percentiles compared to the same species are displayed in Table 5.

Table 5. Percentiles of PCB in Little Spokane River Fish Compared to Statewide Fish of the Same Species.

Site	Fish Species	Percentiles
Colbert	RBT	35%
Deer/Milan	RBT	60%
Below Hatchery	RBT	63%
Below Hatchery	MWF	38%
Below Hatchery	NPM	80%

Study Results Compared to Background PCB Concentrations

Previous studies have identified elevated PCB concentrations in fish from waterbodies with minimal human influence (Johnson et al., 2010). For the purpose of this study, background waterbodies have been defined as those with little or minimal human influence. PCB concentrations in fish tissue from 24 waterbodies sampled during 2007-08 ranged from 0.04 to 88 ug/kg. Fish collected from the Little Spokane River in 2014 were within the range of background PCB concentrations established in the 2007-08 Ecology study. Fish tissue concentrations from the present study ranged from 3.8 to 62.4 ug/kg. According to previous Ecology investigation of PCB concentrations in fish tissue from background sites (Johnson et al., 2010) the Little Spokane River should be viewed as low to medium priority for TMDL investigations.

Dioxin-Like PCB Congeners in Fish Tissue

There are 12 PCB congeners that exhibit dioxin-like properties and are known as *dioxin-like PCBs*. Out of the 209 PCB congeners, the 12 dioxin-like congeners are especially toxic. The most toxic of the dioxin-like congeners is PCB 126 which was only detected in one Mountain Whitefish sample collected from the Below Hatchery site with a concentration of 0.0071 ug/kg. The distribution of dioxin-like PCB congeners in fish tissue is shown in Figure 11.

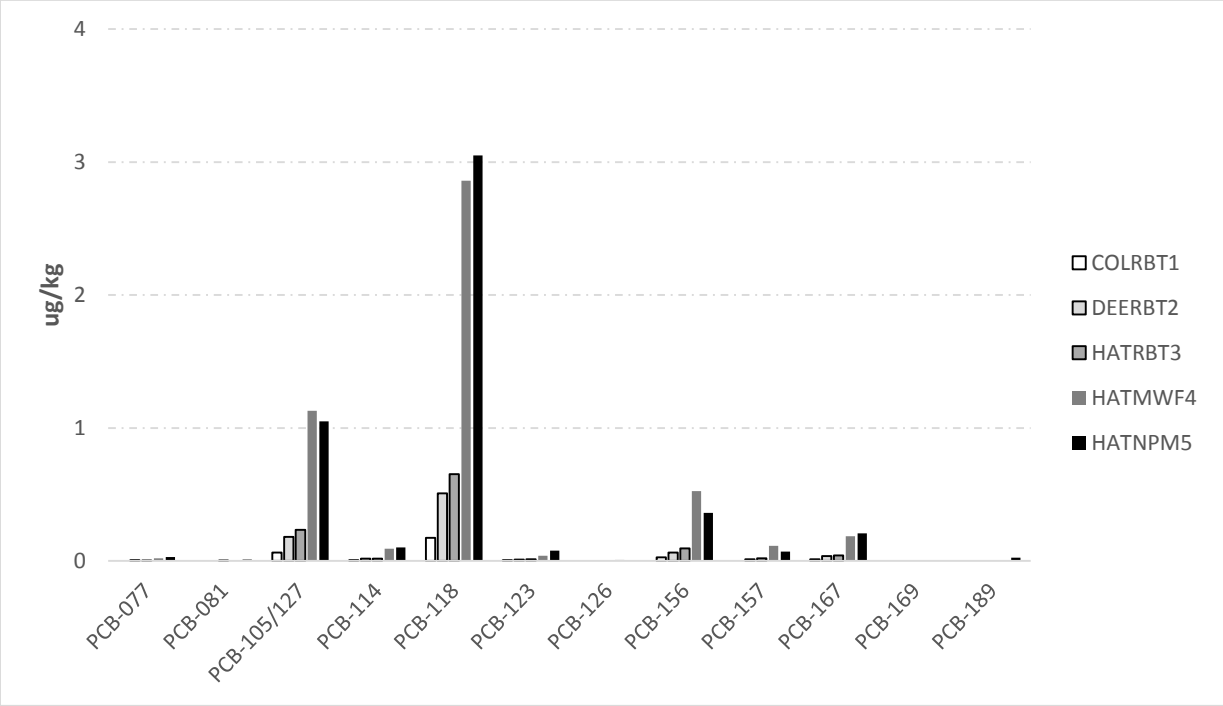


Figure 11. Distribution of Dioxin-Like PCB Congeners in Fish Tissue.

Dioxin-Like PCB Congeners in Sediment

The dioxin-like PCB congeners in Little Spokane River sediment are displayed in Figure 12. Note the difference in the scale of the Y-axis compared to Figure 11. The distributions of dioxin-like congeners in sediment are similar to the patterns observed in fish tissue data.

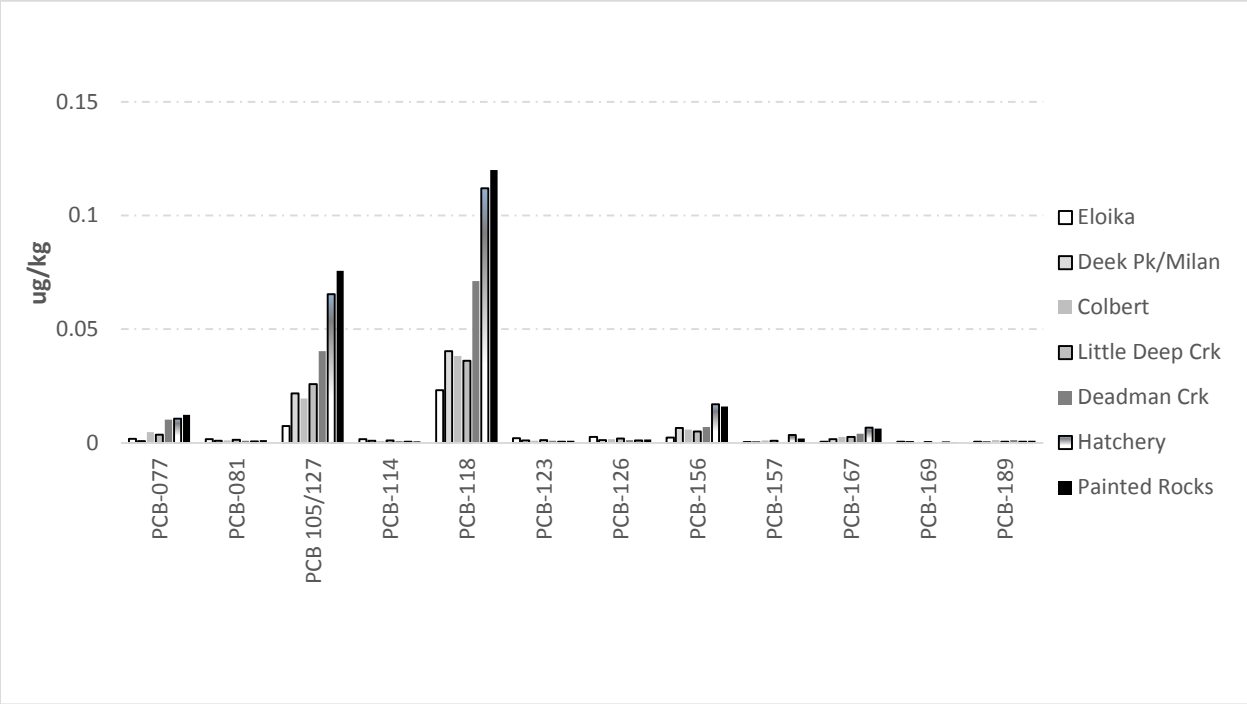


Figure 12. Distribution of Dioxin-Like PCBs in Sediment.

Conclusions and Recommendations

Results of this 2014-2015 study support the following conclusions and recommendations.

Conclusions

- Three of four fish composite samples exceeded the Human Health Criteria (as FTEC= 5.3 ug/kg) for total PCBs. Species sampled included rainbow trout, northern pikeminnow, and mountain whitefish.
- Despite the fact that fish tissue PCB concentrations exceed the FTEC used for listing, compared to statewide data, they are within the range of background levels established during Ecology's 2010 study (Johnson et al., 2010). The 2010 study established background levels of 0.04 - 88 ug/kg. The range of PCB concentrations detected in the current study was 3.8 - 62.4 ug/kg. According to the recommendations for prioritization established in the 2010 Ecology study, the Little Spokane River is considered low to medium priority for TMDL.
- Rainbow trout collected for this study had adipose fins intact (indicating naturally reproducing fish). These fish have a higher potential to migrate in and out of lacustrine systems like the Spokane River (Lake Spokane) to the Little Spokane River. PCB concentrations in fish tissue may reflect contamination originating within the Spokane River basin, because there are no fish passage barriers to prevent fish migrations in and out of the Spokane River (Lake Spokane).
- PCB concentrations in sediment increased moving downstream. Concentrations ranged from 0.5 to 3.9 ug/kg throughout the drainage, well below the sediment clean-up objective of 110 ug/Kg.
- Despite the blank contamination issues, samples collected with CLAM samplers indicate low PCB concentrations in water.

Recommendations

- Based on PCB concentrations in three fish tissue samples, the Little Spokane River should remain on Category 5 of the 303(d) list.
- A larger sample size of specific fish species would be needed to statistically evaluate trends in tissue concentrations.
- Food web analysis would be useful to track PCBs through the food web. Determining the concentrations at different trophic levels may explain the dramatic differences between water, sediment, and fish tissue PCB concentrations. Establishing that prey organisms of the study fish in the Little Spokane River are not contaminated with PCBs would further suggest that accumulation of PCB is occurring in the Spokane River mainstem outside the Little Spokane River basin.
- Consider looking for PCB sources in the Spokane River that might have contributed to PCB loads in Little Spokane River fish.
- Results from low-level PCB sampling using CLAM samplers should be used cautiously until sampling system contamination issues have been resolved.

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Appendices

Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

Bioconcentration factor: The ratio of a contaminant concentration in a plant or animal relative to its surrounding media.

Congener: Any one of the 209 total possible PCB combinations, defined by the number and location of the chlorine atoms attached to the biphenyl rings. PCB congeners have different levels of toxicity. Toxicologists consider a dozen of the 209 congeners dioxin-like.

Estimated Detection Limit (EDL): Minimum concentration required to produce a specified signal to noise ratio.

Estimated Quantification Limit (EQL): The lowest concentration that can be reliably quantified within specified limits of precision and accuracy.

Fish Tissue Equivalent Concentration (FTEC): The concentration of a contaminant in fish tissue that equates to Washington's water quality standard for toxic substances for the protection of human health. Washington uses the National Toxics Rule Water Quality Criteria for the protection of human health. The FTEC is calculated by multiplying the contaminant-specific Bioconcentration Factor (BCF) times the contaminant-specific National Toxics Rule Water Quality Criterion for water.

Homolog: Homologs are subcategories of PCB congeners having equal numbers of chlorine substituents. For example, the tetrachlorobiphenyls are all PCB congeners with exactly 4 chlorine substituents that may be in any arrangement.

Lacustrine: A lake environment or originating from within a lake.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Relative Percent Difference: A comparison between two numbers expressed as a ratio. In the context of this report, RPD is used to evaluate the accuracy and precision of replicate and/or duplicate samples.

Telemetry: A process in which measurements or data are transmitted to receiving equipment for monitoring.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

303(d) list: Section 303(d) of the federal Clean Water Act requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

Acronyms and Abbreviations

BCF	Bio-Concentration Factor
CLAM	Continuous Low-level Aquatic Monitoring
CLP	Contract Laboratory Program
DW	Dry weight
EAP	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EDL	(See Glossary above)
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EQL	(See Glossary above)
FTEC	(See Glossary above)
HRGC/HRMS	High Resolution Gas Chromatography/ High Resolution Mass Spectrometry
MEL	Manchester Environmental Laboratory
NPDES	(See Glossary above)
NTR	National Toxics Rule
PCB	Polychlorinated biphenyls
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WW	Wet weight

Units of Measurement

°C	degrees Celsius
L	Liter
pg/L	pictograms per liter (parts per quadrillion)
ug/Kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)

Appendix B. Complete Project Data

Appendix B data are available via a zip file on the web, linked to this report at https://fortress.wa.gov/ecy/publications/SummaryPages/1603001.html