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Wenatchee River PCB and DDT Source Assessment

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Quality Assurance Project Plan

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EAP: Environmental Assessment Program
EIM: Environmental Information Management database

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2.0 Abstract

Over the last 10 years, some of the highest concentrations of PCBs in fish tissue within Washington State have been found in the resident fish of the Wenatchee River (mainly mountain whitefish). Fish advisories have been in place for much of this time. The Wenatchee River is also listed as impaired under the USEPA 303(d) list for DDT and DDT metabolites. The main source of DDT to the river is suspected to be agricultural lands in the Mission Creek sub-basin, a tributary in the Lower Wenatchee Valley. The source of PCBs to the Wenatchee River is more ambiguous.

A significant amount of background data on fish tissue has been collected within the Wenatchee River Basin. There is a lack of data on contaminant burdens in other biotic media and PCBs in the river. The basin has a long history of electric rail, logging, and orchard operations, which potentially represent numerous contaminant sources.

The goal of this study is to assess, identify, and prioritize the sources of PCB and DDT contamination to the Wenatchee River. A two-phase sampling plan is proposed which will (1) conduct a synoptic survey in the Wenatchee River mainstem to assess the concentrations of PCBs, DDT, DDD, and DDE, and (2) focus on identifying and characterizing the sources of these compounds to the Wenatchee River, based on the results of the synoptic survey. This project will rely on the involvement of many stakeholders vested in the quality and management of the Wenatchee Watershed.

3.0 Background

3.1 Study area and surroundings

The Wenatchee River Basin is situated in central Washington, on the east side of the Cascade Mountains. The basin covers approximately 1310 square miles (3400 km^2) and is bound by the Entiat Mountains to the north, Cascades to the east and the Wenatchee Range to the south. The Wenatchee River flows from headwater tributaries in the mountains to Lake Wenatchee, where it becomes the Wenatchee River at the outlet and flows 53 miles (85 km) to the confluence with the Columbia River. The river meanders on a gentle gradient from Lake Wenatchee until it flows through a deeply incised valley (Tumwater Canyon) to the town of Leavenworth. There the gradient lowers and the valley opens up. The river traverses a number of biogeoclimatic zones, with the major transition taking place near Leavenworth when the topography becomes lower relief (Fig. 2). Much of the upper forested regions of the basin are part of the Wenatchee National Forest, managed by US Forest Service.

The geology of the basin is variable, comprising a number of different landforms ranging from the alpine and sub-alpine peaks of the Cascades to the low-lying Columbia plateau. The upper basin is underlain by metamorphic, sedimentary, and intrusive and extrusive igneous rock. Basalts and volcanic rock are present in the southwestern portion of the basin (Icicle Creek sub-watershed) and parts of the northern basin (Nason and Chiwawa Creeks). The Lower portion of the basin below Wenatchee Lake to the west of Wenatchee River is composed of sedimentary

rock of the Chumstick Formation. The Quaternary geology of the basin is dominated by three alpine glaciations, eroding the Wenatchee Valley and depositing moraines and outwash terraces with soil development during the intervening periods (Waitt Jr., 1977). The pro-glacial material of the Lower Wenatchee also contains lacustrine sediments and signs that glacial floods have eroded much of the deposits. The tributary valleys contain alluvial material, and eroded alpine glacial drift is sporadically deposited throughout the upper and lower basin.

The climate of the Wenatchee Basin is continental with hot, dry summers and cold, wet winters. Precipitation across the basin is variable, mostly falling in the winter as snow in the Cascade Mountain headwaters. Annual precipitation ranges from 82 inches at Stevens Pass (4,070 ft above sea level) to 9 inches at the city of Wenatchee (640 ft above sea level). Temperatures in Leavenworth range from 25 °F in the winter to 70 °F in the summer.

3.1.1 Logistical problems

Discharge
Sampling for this project will be conducted during low and high flow periods. The size of tributaries to the Wenatchee range from ephemeral streams to perennial rivers. The approximate percentages of contribution from the major creeks and rivers are: White River (25%), Icicle Creek (20%), Nason Creek (18%), Little Wenatchee River (15%), Chiwawa River (15%), Chumstick and Peshastin Creeks (3%), and Mission Creek (1%), with a remaining 3% from minor streams (Berry and Kelly, 1982). 205 lakes in the mountainous headwater regions of the watershed help to mediate low-flow conditions during the mid- to late-summer. Groundwater influence on the Wenatchee River is more prominent in the lower region of the river valley, where alluvial deposits (sands and gravels) are more common.

The discharge of the Wenatchee River and tributaries are snow-dominated and peak with the snowmelt in the spring and early summer months (Fig. 3). There are a number of withdrawals from the river and tributaries. The major ones are from (1) Icicle Creek (for Leavenworth National Fish Hatchery, the City of Leavenworth drinking water, and irrigation water for the Lower Wenatchee Valley), (2) Lower Wenatchee Valley tributaries, Mission, Chumstick, Chiwawa and Peshastin, for irrigation withdrawals and drinking water withdrawals for the towns of Cashmere and Peshastin if groundwater supplies require supplementing.

Site Access
There are no foreseeable issues with access to proposed sample sites. Collaboration with Chelan County and communication with private landowners will insure the security and access of the sites. Safe deployment of sampling gear will be a priority in this non-wadeable river.

3.1.2 Parameters of concern

The primary contaminants of concern in the Wenatchee River Basin are polychlorinated biphenyls (PCBs). The secondary contaminant of concern is dichloro-diphenyl-trichloroethane (DDT) and metabolites, dichloro-diphenyl-dichloroethylene (DDD) and dichloro-diphenyl-dichloroethane (DDE).

3.1.1.1 Polychlorinated biphenyls (PCBs)

History

Polychlorinated biphenyls (PCBs) are a class of 209 compounds or congeners which contain 1 to 10 chlorine atoms attached to two rings of biphenyl. There are a number of congener groups which are defined by the degree of chlorination, ranging from monochlorobiphenyls (1 Cl atom) to decachlorobiphenyls (10 Cl atoms), and referred to as *homolog* groups. Commercial and industrial applications of PCBs in the US relied on formulations of PCB mixtures under the trade name Aroclor (Table 1). Each Aroclor is identified by a four-digit number, where the last two digits describe the % chlorine by weight (e.g., Aroclor 1254 contained 54% chlorine by weight).

PCBs were manufactured in the US from 1929-1977 and banned in 1979. However, they continue to be inadvertently and intentionally produced, because limited amounts are allowable under the 1976 Toxic Substances Control Act (Erikson and Kaley II, 2011). Their primary use was as an electrical insulating fluid, and also as hydraulic, heat transfer, and lubricating fluids (Table 1). The bulk of PCBs were incorporated into capacitors (~50% by mass) and transformers (~25%) (Erikson and Kaley II, 2011). Additional minor applications were blends of PCBs and other chemicals as carbonless copy paper (~4%), plasticizers, and fire retardants. These blends have been used in many products, such as sealants, caulks, and adhesives and cumulatively represent ~ 9% of the PCBs produced. The numerous applications of PCBs as plasticizers and additives represent a much smaller PCB pool, but they do have a much greater circulation in the environment.

Environmental transport and fate

PCBs were created to resist degradation and persist, which has made them a ubiquitous environmental contaminant, despite many of their uses being in so-called *closed systems*. They are particularly soluble in lipids, leading to the accumulation of PCBs in biological systems. PCBs have been released into the environment mainly through volatilization into the atmosphere and spilling into waterways and onto land. In aquatic systems, sediments are an important environmental sink, while volatilization from water can be a significant loss from an aquatic system. Atmospheric losses of PCBs from lakes have received more attention in the scientific literature than losses from rivers (Honrath et al., 1997; Salamova et al., 2013); however, the loss of lighter PCBs from turbulent rivers could be significant.

The biodegradation of PCBs in sediments and soils is very slow (tens of years) and realistically does not represent a significant loss of PCBs in the environment (Sinkkonen and Paasivirta, 2000). In reality, PCBs are more likely to be redistributed and diluted within environmental media. The Aroclor PCB mixtures have different weathering rates because of the variable physical properties of the mixture of congeners, leading to an Aroclor mixture in the environment that does not resemble the original source. This clearly impacts our ability to identify specific historical PCB sources based on the analysis for Aroclor mixtures.

Bioaccumulation and toxicity

The bioaccumulation of fat-loving or lipophilic chemicals in aquatic organisms is dependent on the physical characteristics of the chemical and the exposure pathway. The factor by which PCBs

bioaccumulate will therefore vary among locations and with congener composition. However, the factor can be quantified by the ratio of PCB concentration in the organism to total bioavailable (dissolved) concentration in the water. Similar to the way in which PCB congeners move between air, water, and soils; there is preferential biotic assimilation of heavier congeners (penta- and hexachlorobiphenyls), owing to lighter congeners being expelled during metabolism and heavier congeners binding more effectively to lipids (Fisk et al., 1998). PCBs are carcinogenic and can also affect the immune system, endocrine system, nervous system, and reproductive system. The most toxic have similar molecular structure to polychlorinated dibenzo-*p*-dioxins and are referred to as *dioxin-like*. To quantify the relative toxicity of these dioxin-like PCBs, the concentrations are often adjusted in terms of the toxic equivalence (TEQ), which is relative to the most toxic dioxin congener (2,3,7,8-tetrachlorodibenzo-*p*-dioxin).

Dichloro-diphenyl-trichloroethane (DDT)

History

DDT is an organochlorine insecticide that breaks down or is metabolized aerobically to dichloro-diphenyl-dichloroethylene (DDE) and anaerobically to dichloro-diphenyl-dichloroethane (DDD). Total DDT (t-DDT) refers to the sum of DDT and metabolites. DDT was developed in 1874 and applied widely beginning in the mid-1940s when its insecticidal properties were discovered. It was used to help eradicate malaria and reduce insect damage on food crops. It has been used broadly in orchards to control codling moth populations. By the late 1950s and 1960s, concerns over its persistence and toxicity to non-target organisms led to the start of phasing it out. The EPA banned the compound in 1972; however, the chemical is currently applied in some developing countries.

Environmental transport and fate

DDT is highly hydrophobic but is highly soluble in oils, fats, and organic solvents. The stability of DDT and metabolites and the affinity for solids high in organic carbon have led to large sinks or deposits in agricultural soils that persist today. Bound DDT slowly redistributes mainly through the erosion of soils but also through volatilization and bioaccumulation. The half-life for DDT in soils can range from 2 to 15 years, but in the aquatic environment (sediments) can be around 150 years (Callahan et al., 1979).

Bioaccumulation and toxicity

DDT is poorly absorbed through mammalian skin (bioconcentration) but is easily absorbed through an insect's exoskeleton. In aquatic ecosystems, algae and sediments containing DDT provide the bioavailable mass of the contaminant to the upper trophic levels. DDT becomes concentrated in the fatty tissues of the predators. Bioconcentration factors vary among fish species and affect their tissue burden of DDT (Arnot and Gobas, 2006). DDT can be excreted and does get metabolized in the organism to DDD and DDE. For organisms with DDT in fat stores that undergo periods of starvation, DDT metabolites are released into the blood where they can be toxic to the liver and nervous system. DDT is carcinogenic, can affect reproduction, and can be acutely toxic to aquatic organisms.

3.1.3 History of study area

The possible sources of PCBs and DDT within the Wenatchee River Basin in relation to historical activities are summarized in Tables 2 and 3 and described in the subsequent sections.

Potential PCB Sources

Localized sources

Railway

The section of the Great Northern Railway (GNR) within the Wenatchee River Basin finished construction in 1892 and ran from Wenatchee, up Tumwater Canyon, and over the Cascade Mountains. The first tunnel was finished in 1900 and the line was electrified in 1909, due to the hazards of diesel fumes in the tunnel. At this time, a hydroelectric dam and powerhouse were built in Tumwater Canyon. From the dam, water was delivered through a wooden pipeline (penstock) to the powerhouse which had 3 large turbines and 3, 2000 kW generators (Fig. 4).

The City of Leavenworth was a rail hub in the early 1900s and the GNR built a roundhouse, switchyard, and division headquarters in Leavenworth. In 1922 GNR moved its operations to Wenatchee but maintained the rail line through Leavenworth. In 1928, the Tumwater Canyon section of the rail line was moved to its present location in Chumstick Canyon. Today's tunnel through the Cascades was constructed and opened in 1929. The powerhouse and dam remained in operation until 1956. Many of the historical operations for GNR in Leavenworth were at their peak before PCBs were first manufactured in 1929. A small station and substation in Leavenworth continued to operate after the line moved to Chumstick Canyon. Further clarification on the location and magnitude of GNR operations in Leavenworth could yield an additional potential PCB source.

Transformer in river bed

While surveying the riverbed for steelhead spawning in April 2009, Washington Department of Fish and Wildlife noted a suspected transformer (or possibly two) embedded in the mid-channel near the town of Cashmere. On subsequent reconnaissance trips, the transformer has not been seen, due to higher flow. Only 5-10% of transformers were manufactured with PCBs during the regulated PCB production period due to cost restrictions. The most common transformer askarels (mixtures) were 60% Aroclor 1260 / 40% trichlorobenzene (Type A) and 70% Aroclor 1254 / 30% Trichlorobenzene (Type D) (Erikson and Kaley II, 2011). Electric rail locomotives contained PCB transformers on board (approximately 300-1100 kg of askarel per transformer) (Durfee et al., 1976).

If there is a transformer discharging PCBs into the river, the physical properties of the chemicals suggest that most should bind with sediments or evaporate from the river (MacKay et al, 1992). Further investigation of the suspected transformer location is necessary at low flow. Walking or paddling the Lower Wenatchee at low flow would determine whether the reported transformer is present. Washington Department of Fish and Wildlife personnel, who originally noted the transformer, will be available to assist with the survey (A. Murdoch, personal communication).

Leavenworth National Fish Hatchery

The Leavenworth National Fish Hatchery (LFH) of the US Fish and Wildlife Service was constructed in the early 1940s as a mitigation response to anticipated diminished fish stocks from the construction of the Grand Coulee Dam. The hatchery is situated on Icicle Creek near the confluence with the Wenatchee River. Water for the hatchery comes mainly from a diversion 1.5 miles upstream in Icicle Creek; however, during low-flow conditions there is insufficient supply for the hatchery and an irrigation allotment. At low-flow, supply is therefore supplemented by groundwater wells on the hatchery site and water from Snow and Nada Lakes, located in the Alpine Lakes Wilderness (Wurster, 2006). There are 5 permitted discharge points from LFH.

Historical land use and contaminated sites

The Washington State Department of Ecology maintains the Integrated Site Information System (ISIS) that the Toxics Cleanup Program uses to prioritize and track the remediation of contaminated sites. This database identifies sites along the Wenatchee River where possible or confirmed PCB contamination was present (Table 4). The landfill sites in Cashmere and Dryden have been capped and decommissioned, and it is unlikely that industrial waste was dumped in them. The Dryden landfill does have some groundwater sample results for t-PCBs, which showed concentrations less than method detection limits (P. Shanley, personal communication). This list of identified properties is not comprehensive and may not include additional contaminated sites that have not been identified or investigated.

Publicly Owned Treatment Works (POTWs) and stormwater

Urban areas might contribute PCBs through the storm and water treatment collection systems to adjacent receiving waters at a significant enough concentration to impact aquatic life, e.g., Spokane River (Serdar et al., 2011). Possible sources in an urban environment are old transformers and capacitors, inks (e.g., paper recycling facilities), and sealants and caulking in buildings and piping. There are 7 active National Pollutant Discharge Elimination System (NPDES) permits for municipal treatment works. These wastewater treatment plants (WWTPs) discharge to the Wenatchee River (Table 5). There are also a number of industrial stormwater permits and industrial to POTW permits, where the permittee discharges to a WWTP.

Irrigation returns

The Lower Wenatchee Valley is heavily agricultural and orchards have been in operation since the early incorporation and settlement of the valley. While PCBs are not a suspected contaminant in the application of pesticides or insecticides on agricultural land, the irrigation returns which drain these lands and discharge to the Wenatchee River can act as conduits for various pollutants which may be associated with historical practices, dump sites, or atmospheric deposition. No major agricultural drains discharge to the Wenatchee River. Minor irrigation returns will be identified during the first phase of the project.

Diffuse sources

Atmospheric deposition of PCBs

Cold condensation or cold-trapping dynamics predict that higher concentrations and heavier PCBs (K_{WA} between 3.5 and 6) should be preferentially scavenged at higher altitudes with high precipitation and cold temperatures (Grimalt et al., 2001; Gallego et al., 2007; Wania and

Westgate, 2008). This translates into the prevalence of congeners in the hexa – to heptachlorobiphenyl range and is counter to cold-trapping at high latitudes where lighter congeners are preferentially trapped. Lighter PCBs are subject to further atmospheric advection from the mid-latitudes and transport to higher latitudes; this process is known as the grasshopper effect (Wania and Westgate, 2008). In the case of the Wenatchee basin, it is more likely that the deposition of atmospheric PCBs emanating from the Puget Sound region would take place on the western side of the Cascades. This is supported by empirical data from the Canadian Rockies (Daly et al., 2007).

Salmon-derived PCBs

The idea that anadromous salmon can be vectors for organic contaminants into freshwater ecosystems has been studied in river and lake populations (Krummel et al., 2005; O'Neill and West, 2009). Returning hatchery Chinook salmon (*Oncorhynchus tshawytscha*) are the most abundant anadromous fish in the Wenatchee River. The percentage of spawners that are left to decompose in the Wenatchee is currently not known and it is unknown whether this is a significant PCB contribution to the river.

Potential DDT Sources

Localized sources

Irrigation returns

DDT was used extensively in the lower Wenatchee Basin on orchard lands as a potent insecticide, according to the Total Maximum Daily Load Study on DDT contamination and transport (Serdar and Era-Miller, 2004). Historical knowledge of the area was gathered through Washington State Department of Agriculture waste pesticide collection events (J. Hoffman, personal communication). Irrigation returns from orchard lands can act as a localized source of DDT to the Wenatchee River from orchard soil inputs or former dump sites for legacy pesticides. The Lower Wenatchee Valley does not contain any major irrigation returns or wasteways from agricultural lands, but there are minor irrigation returns that discharge to the Wenatchee River. These minor returns were documented and sampled by Carroll et al. (2006) during an investigation of the dissolved oxygen, pH, and total phosphorus of the Wenatchee River Basin. There are 6 minor irrigation returns identified by Carroll et al. (2006); however, site reconnaissance may reveal further returns.

Publicly Owned Treatment Works (POTWs) and stormwater

Typically, the discharge from POTWs or WWTPs serving urban areas would not contain DDT; however, many fruit packaging operations within the towns along the Wenatchee River discharge to the WWTP. While DDT is no longer used in fruit growing, there is small possibility of entrainment of contaminated soils from the orchard to the processing facility.

Historical land use and contaminated sites

Localized dumping of unwanted pesticides was not an uncommon practice historically. Small dump sites are also not registered on Ecology's ISIS and therefore could represent an underreported source of DDT. The landfill sites mentioned previously in the PCB source section, also could contribute DDT to the Wenatchee River (Table 4). Other than those sites highlighted in Table 4, no sites would be a potential source of DDT.

Diffuse sources

Orchard lands

Diffuse inputs of DDT from orchard lands can occur as overland flow and wind erosion of soils (Serdar and Era-Miller, 2004). It is likely that the main source of DDT to the Wenatchee River is the Mission Creek sub-basin and the upland orchard soils within this sub-basin. We will be conducting our study under the working hypothesis that the *Mission Creek watershed is the main contributor of DDT to the Wenatchee River*.

3.1.4 Results of previous studies

PCBs in the Wenatchee River Basin

All former sampling sites within the Wenatchee Basin are shown on Fig. 6 and detailed below.

PCBs in fish

PCB concentrations in fish tissue samples from the Wenatchee River have been among the highest in Washington for many years (Seiders et al., 2012). A complete overview of t-PCBs in fish tissue from the Wenatchee River is found in Table 6. Early sampling by Hopkins et al. (1985) reported levels in Mountain Whitefish (MWF) from the Lower Wenatchee near the Columbia with PCB Aroclor 1260 concentration of 46 ppb, exceeding the current human health criteria. Since this initial sampling, concentrations have not decreased in MWF. Instead, locations with concentrations two orders of magnitude greater have been identified (Era-Miller, 2004; Seiders et al., 2012a). While MWF have not been the only fish species sampled, they are a species of particular interest because they are resident, important to the local sport fishery, and lipid-rich, which generally results in higher PCB concentrations.

Spatially, the concentrations of t-PCBs in fish tissue appear higher in the Lower Wenatchee River and Leavenworth area (Fig. 7). Seiders et al. (2012a) sampling in 2010 of the Upper Wenatchee tributaries (Nason Creek) and Lake Wenatchee showed some of lowest concentrations (2.4 -12.7 ppb t-PCBs). However, the Johnson et al. (2010) statewide survey shows that the Upper Wenatchee samples can still be considered greater than the median and 90th percentile of background t-PCB concentrations and in excess of the National Toxics Rule criteria for human health (Fig. 7). Fish Lake, which is above Lake Wenatchee, has been sampled in the past as part of the previously mentioned survey on background concentrations of PCBs in fish tissue throughout the state. The authors showed that Fish Lake exhibited the highest concentrations of t-PCBs out of the 24 sites across the state chosen as *background*. Five resident fish species were sampled, and a brown trout composite showed the highest concentrations (88 ppb).

There is no clear lipid:PCB relationship in MWF of the Wenatchee River. PCBs are lipophilic, however it is not a given that there is a positive linear relationship between lipid content and PCB concentrations in individual fish (Stow et al. 1997; Johnson et al., 2010a). The lack of a relationship could be due to differences in congener composition across the basin, sex of the fish and spawning, and exposure pathways. There is also no relationship between the age or total length of the MWF and the t-PCB concentrations. There does appear to be a PCB:lipid relationship in the Lower Wenatchee River.

In 1999, the EPA analyzed five composites of spring Chinook supplied by the Leavenworth National Hatchery (USEPA, 2002). Chinook composites showed little variability and ranged from 13 to 19 ppb t-PCBs (composed almost entirely of Aroclor 1254). These results can be used to calculate a back-of-the-envelope PCB burden from anadromous salmon to the Wenatchee, *assuming that all carcasses are left to decompose in the river*. Based on a simple calculation of mean PCB burden (17 ppb t-PCB), body mass at the time of spawning (5.4 Kg, n = 1300 fish) (Murdoch et al., 2005) and the range of Chinook returns to the hatchery, a conservative estimate of PCB mass contributed annually by anadromous salmon would be 0.04 to 1.38 g t-PCB.

In 2004, Ecology collected fish food and paint samples from the rearing tanks (raceways) at LFH. The results from these analyses showed no detectable PCBs (measured using EPA 8081, Aroclor method) in the feed and a large range of concentrations in the paint (75 to 610 ppb of Aroclor 1245). As a follow-up, sampling of juvenile Chinook salmon was undertaken. Chinook fry tissue samples from the painted and fiberglass raceways showed higher detectable Aroclors in the painted raceways, however t-PCBs were not significantly different. The larger pre-smolt Chinook had significantly higher t-PCB concentrations (mean of 31.7 ppb), indicating the continued uptake of PCBs during hatchery life history. An estimated 57% of the smolts survive the migration down to the Columbia River (McNary Dam), meaning there is a PCB contribution to the Wenatchee River from unsuccessful smolts not including those lost to bird predation. However, the measured pre-smolt concentrations would not be considered a direct risk to piscivorous wildlife (Table 7; Newell et al., 1987).

PCBs in water

The US Geological Survey (USGS) used semi-permeable membrane devices (SPMDs) to sample the Columbia River and a number of tributaries at their confluence during a low-flow period in 1997 (MacCarthy and Gale, 1999). Wenatchee River had some of the highest estimated PCB concentrations relative to the other sites, where data were presented based on weight of PCBs per SPMD, not absolute PCB concentrations in the water column. In the Wenatchee River sample, the total PCBs were 50% greater than the sum of dissolved PCBs, due mainly to the abundance of lower weight PCB congeners and low total organic carbon (TOC) in the water. This was unusual across the survey sites, where total was usually 300% greater than dissolved. In the follow-up sampling in 1998 at high flow, concentrations in the SPMDs were detected but too low to reliably quantify.

Ecology assessed the dissolved and total t-PCB concentrations using SPMDs during high (April/May) and low (August/September) flow in 2007 (Sandvik, 2009). The estimated dissolved t-PCB concentrations in water of the Lower Wenatchee River at Monitor, WA were 54 pg L^{-1} and 45 pg L^{-1} at low and high flow respectively. The estimated concentrations in the Wenatchee River are below the state criteria of 170 pg L^{-1} for the protection of human health. During the same sampling event, concentrations from the Columbia River at the Rock Island Dam downstream of the Wenatchee River confluence were 9.8 pg L^{-1} and 27 pg L^{-1} at low and high flow respectively. Similar to the USGS results, lighter PCB congeners seemed to dominate the water column samples.

In a recent study by Morace (2012), the City of Wenatchee WWTP and one stormwater outfall that discharge to the Columbia River were sampled in December 2009. The WWTP effluent contained measurable concentrations of PCBs, but the stormwater did not.

PCBs in river and lake sediments

A small number of sediment samples have been taken from the Wenatchee River over the years. In 2005, the US Fish and Wildlife Service sampled Icicle Creek, a tributary near Leavenworth, as part of a targeted study to investigate the possibility of PCB contributions from the paint on the tanks within the Leavenworth Hatchery facility. (See *Project Description - Potential PCB Sources* section.) Samples were collected above and below the hatchery in Icicle Creek and from the on-site settling pond. Sediments from the river bottom were composed of fine to coarse sands with some silt and had low organic carbon concentrations (0.46% and 0.43%). Sediments from the settling pond were composed of fish waste and silts and had a TOC concentration of 3.2 %. Concentrations in sediments from Icicle Creek were below method reporting limits for all Aroclor mixtures, while the settling pond sediments had a mean t-PCB concentration of 24.8 ppb (where ~80% was similar to Aroclor 1260 and ~20% was similar to Aroclor 1242). The concentrations found in the settling pond are below the state sediment cleanup objectives of 110 ppb (WAC 173-204).

In 2010, Ridolfi Consulting (2011a) conducted a pilot study for PCB source assessment within the Wenatchee River Basin, which included 8 sediment samples from tributaries and the Lower Wenatchee River (Fig. 6). No detectable concentrations were found in these samples; however, recommendations from this sampling included further detailed sediment sampling based on a proposed follow-up survey for areas of fine sediment accumulation. Also in 2010 and in 2011, sediment and soil samples were taken from the former powerhouse site in Tumwater Canyon (Ridolfi, 2011a; 2011b). Sediment samples from the adjacent Wenatchee River showed no detectable concentrations of PCBs. Soils samples collected at the surface and down to a foot depth showed detectable concentrations of PCB Aroclor 1254 at all 5 locations sampled. All samples were below the soil cleanup levels for total PCB concentrations under the Washington State Model Toxics Cleanup Act (WAC 173-340). It is unclear whether PCB residues in the soils of this site are influencing dissolved or total PCB concentrations of the Wenatchee River.

Sediments from Lake Wenatchee were assessed for compatibility for use as representatives of statewide freshwater sediment background (Sloan and Blakely, 2009). Three surface sediment grab samples from Lake Wenatchee were taken in 2008 and showed concentrations less than method detection limits (EPA 8082) for Aroclor mixtures. It should be noted that the sediment samples were ~ 80% sand and not located in true depositional areas of the lake.

PCBs in mink and otter

Elliot et al. (1999) found detectable PCB concentrations in mink and otter trapped near Wenatchee. However, levels were not very elevated compared with sampling from other regions, including the Lower Columbia. PCB congener analysis showed the prevalence of mono-ortho PCBs in the penta-chlorobiphenyl range, similar to that found in fish of the Lower Wenatchee.

PCB Aroclor and homologue patterns

The patterns of PCB congeners and their similarity to Aroclor mixtures have been summarized and used in environmental science as a means to fingerprint and source PCB contamination (Johnson et al., 2000). However, in investigations over large spatial scales and across a number of trophic levels in the aquatic food web, this approach is not particularly useful, although it may be possible to disentangle some of the physical and biological effects (Sather et al., 2001). Degradation and preferential uptake by an organism confound any signature of the original source. The usefulness of congener and Aroclor patterns in the Wenatchee River is relevant to the spatial assessment of PCB composition within a particular media.

Details of Aroclor mixtures in the PCB burdens of the fish tissue are available for 45 samples over the entire period of investigation on the Wenatchee. There is an overwhelming dominance of PCB congeners similar to the mixture in Aroclor 1254 in the fish species sampled throughout the Wenatchee over multiple species. The presence of Aroclor 1260 is also significant as a secondary component. No information is available for the Aroclor mixtures of dissolved PCB concentrations in water.

The congener patterns in the few analyzed fish are dominated primarily by pentachlorobiphenyls, with tetra- and hexachlorobiphenyls (Fig. 5). Congener patterns in the water sample analyzed by the USGS (MacCarthy and Gale, 1999) and Ecology (Sandvik, 2009) were dominated by tri- and tetrachlorobiphenyls (ortho-substituted PCBs). In the USGS sample, congener 37 and 77 were considerably elevated relative to other sites; this was not the case in the Ecology samples. PCB-37 and -77 were not noticeably higher in fish tissue samples collected in 2003 and 2004. Further definition of the congener patterns in water and periphyton over the Wenatchee River Basin will enable us to assess whether a PCB source is present, resulting in a change to the congener pattern along the sampling transect.

DDT in the Wenatchee River Basin

DDT in fish

The concentrations of DDT and metabolite compounds (DDE and DDD), hereafter collectively referred to as total-DDT (t-DDT), in Mountain Whitefish tissue appear to have decreased since 1984 (one sample of 1221 µg Kg^{-1}). However, there is no difference between the 2003/04 samples and the 2010 samples. The 2003/04 and 2010 samples are more comprehensive and include tissue samples from the Leavenworth area down to the Columbia River. The t-DDT results from 2003/04 and 2010 suggest that fish from the Lower Wenatchee and the Columbia Rivers confluence are exposed to greater amounts of the pesticide (Fig. 8). This supports the suspicion that the Mission Creek sub-basin is a major source of DDT to the Wenatchee River; however, this has not been comprehensively shown.

DDT in the Mission Creek sub-basin

In 2004, Serdar and Era-Miller conducted a Total Maximum Daily Load study of the Mission Creek sub-basin for DDT contamination and transport. This study included Yaksum and Brender Creeks. This study found that the soils of the lower Mission Creek basin contained considerable amounts of DDT and ultimately were the upland source for Mission Creek. The movement of contaminated soil into the creeks is through surface runoff and wind. The concentrations of DDT

in bed sediments of Yaksum Creek were found to contain and be most representative of the DDT concentrations in orchard soils.

Whole water concentrations of 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT were found to be in excess of one or both of the aquatic life criteria and the human health criteria in all 3 creeks (Yaksum, Brender, and Mission). Yaksum Creek had concentrations 2 orders of magnitude above the human health standard and contributes 80-90% of the DDT load in Mission Creek. Serdar and Era-Miller (2004) also sampled the groundwater and found no significant contributions to the Mission Creek basin. Despite a fairly strong relationship between total suspended solids (TSS) and DDT in Yaksum Creek and a moderately strong relationship in Brender Creek, Mission Creek DDT concentrations do not correlate with TSS concentration. Indeed, it was estimated that ~25% of the t-DDT was dissolved in Mission Creek. This finding suggests that DDT enters bound to upland soils and remains associated with suspended material in Yaksum and Brender Creeks, but a significant portion is then dissolved in the lower Mission Creek reaches before entering the Wenatchee River. A later study using SPMDs in the Lower Wenatchee River showed detectable dissolved concentrations of DDT (and metabolites); however, none of these estimated concentrations exceeded water quality criteria (Sandvik, 2009).

DDT in wastewater

The recent study by Morace (2012), did not detect DDT in suspended solids filtered from stormwater collected in a City of Wenatchee catch basin. The Morace study did not analyze for DDT in effluent from WWTPs. However, both the City of Wenatchee WWTP and stormwater discharge to the Columbia River. In a study of the Yakima River Basin, Johnson et al. (2010b) did not detect DDT in WWTP effluent but did detect it in discharges to surface waters from fruit packing facilities.

Current monitoring of DDT

The ongoing *Pesticides in Salmon-Bearing Streams* project has a detailed data set of surface water composite grab samples from 2007 to 2013 from Mission, Peshastin, and Brender Creeks, and the Wenatchee River (Sargeant et al., 2013). Brender Creek continues to show elevated t-DDT concentrations compared with the Washington State Freshwater Aquatic Life chronic effects criteria. The Mission and Peshastin sites show less than the analytical quantitation limits or are no longer being analyzed for t-DDT. In some cases, however, the detection limits are above Washington State Freshwater Aquatic Life acute effects criteria and Human Health criteria. There is a weak DDT- TSS relationship for Brender and Mission Creeks. The current TSS concentrations in Brender Creek are well above what the Total Maximum Daily Load (TMDL) (Serdar and Era-Miller, 2004) recommended as surrogate targets to reduce the DDT load (~1 mg L^{-1}). The Washington State Department of Agriculture is scheduled to continue the monitoring of Brender and Mission Creeks. The department dropped the Wenatchee River sample site from the program due to high flow and a history of no detections. Ecology will not conduct further sampling of the Mission Creek sub-basin during this proposed project because of the continued monitoring by Washington State Department of Agriculture.

3.1.5 Regulatory context

The Wenatchee River has been listed on the 303(d) list under the Clean Water Act for PCBs and DDT since early the 2000s (Table 8). These listings are driven by PCB and DDT burdens in fish tissue and DDT in whole water samples (Table 9). A TMDL study for DDT has been completed for the Mission Creek sub-basin (Serdar and Era-Miller, 2004), but the additional listings are based on repeated monitoring activities by Ecology (Seiders et al., 2012). The criteria for the protection of aquatic life in the State of Washington is regulated under Chapter 173-201A of the Washington Administrative Code (WAC 173-201A). As defined by the EPA (1994), the exposure periods assigned to the acute criteria are expressed as: (1) an instantaneous concentration not to be exceeded at any time or (2) a 1-hour average concentration not to be exceeded more than once every three years on the average. The exposure periods for the chronic criteria are either: (1) a 24-hour average not to be exceeded at any time or (2) a 4-day average concentration not to be exceeded more than once every three years on the average.

Human health criteria for surface waters are risk-based calculations of the exposure of humans to carcinogens and non-carcinogenic illness from the consumption of fish and water. Criteria are available for fish consumption alone and fish and water consumption (Table 9). The risk and subsequent criteria calculations are based on a person of 70 kg (154 lbs) consuming 6.5 g of fish per day and drinking 2 liters of water per day (if freshwater) over the course of 70 years. In Washington, this full exposure is then used to calculate a cancer risk where no more than 1 in 1,000,000 people (cancer risk level of 10^{-6}) would be likely to develop cancer as a result of consuming water and fish at criteria levels.

The freshwater sediment standards for cleanup and screening are based on the protection of the benthic community and are established under the Sediment Management Standards WAC 173-204 (Table 9). Cleanup standards are expressed as dry weight and not normalized to organic carbon content (Michelson, 1992).

4.0 Project Description

4.1 Project goals

The goal of this study is to identify and prioritize sources of PCBs and DDT in the Wenatchee River Basin (WRIA 45).

4.2 Project objectives

The specific objectives of the study are:
(1) to conduct an initial synoptic survey to assess the spatial distribution of PCBs, DDT, DDD, and DDE in the mainstem of the Wenatchee River.
(2) to identify and characterize sources of these compounds to the Wenatchee River, based on the results of the synoptic survey.

Phase 1 of the project (the initial synoptic survey) will focus on dissolved PCBs and DDT in water and PCB burdens in attached algae (periphyton) in the Wenatchee River and select tributaries at low flow. Water samples will be collected using SPMDs, and periphyton will be collected at the same sample site. Phase 1 will allow us to assess the spatial distribution of PCBs and DDT within the Wenatchee River Basin.

Phase 2 of the project (the detailed sampling) will take place over two sample events and include sample media such as water, soil/sediment, periphyton, and macroinvertebrates. The detailed sampling will be described in an addendum to this Quality Assurance Project Plan, so that the location and sample media reflect the findings of the synoptic survey. Phase 2 will allow us to assess how PCBs are moving and where they are accumulating within the food web.

This project will encompass and rely on participation from Ecology's Central Regional Office (CRO), the Yakama Nation, Chelan County, and local stakeholders (e.g., sport fishers and rafting companies). The sampling program for this project will take place during the summer of 2014 (Phase 1) and spring and summer of 2015 (Phase 2). This Quality Assurance Project Plan (QAPP) was prepared following the guidance in Lombard and Kirchmer (2004).

4.3 Information needed and sources

We will seek historical information on the location, uses, and practices that pertain to potential PCB and DDT sources from local stakeholders in the Wenatchee River Basin. We will conduct a literature review. In collaboration with Chelan County and the Water Quality Subcommittee for the Wenatchee Watershed Planning Unit, we will work with local landowners to gain knowledge of historical practices that may relate to PCB and DDT use and disposal.

4.4 Target population

Mountain whitefish (MWF; *Prosopium williamsoni*) have routinely been the resident fish species with the highest documented PCB and DDT concentrations in the Wenatchee River (Seiders et al., 2012). Further sampling of MWF is planned for 2018 under the Washington State Toxics Monitoring Program (K. Seiders, personal communication). Phase 1 of the proposed project will focus on evaluating PCB concentrations in water and algae, and DDT will be assessed in water.

4.5 Study boundaries

The boundary of this study is the Wenatchee River Basin in the Water Resource Inventory Area (WRIA) 45. The Hydrologic Unit Code (HUC) number is 17020011.

4.6 Tasks required

The project is anticipated to run through until the summer of 2016. The overall study approach is to:

- Conduct a review of existing data.
- Review information on potential sources of PCBs and DDT.
- Prepare and approve a Quality Assurance Project Plan (QAPP).
- Conduct an initial visual survey to assess potential sources and identify sample sites (e.g., transformers and agricultural returns).
- Conduct an initial synoptic survey of Wenatchee River and select tributaries.
- Analyze data, develop sampling plan for detailed sampling and write QAPP Addendum.
- Conduct detailed source sampling based on the results of the synoptic survey.
- Complete final data analysis, report writing, and public presentation.

4.7 Practical constraints

The main constraint affecting the success of the proposed sampling program is our ability to recover adequate and accurate amounts of PCBs from the proposed sample media. Low-level PCB contamination of aquatic ecosystems has proven difficult to monitor and characterize (Serdar et al., 2011; Sandvik and Seiders, 2012). To address this, we propose a variety of abiotic and biotic media for sampling and analysis.

Previous studies using SPMDs in the Wenatchee River suggest that higher concentrations of PCBs are recoverable during low-flow periods (MacCarthy and Gale, 1999; Sandvik, 2009). We have scheduled our initial survey of the river basin using SPMDs to target similar low-flow conditions. Follow-up sampling will also target high-flow periods.

There are no foreseeable issues with site access or landowners.

4.8 Systematic planning process

This Quality Assurance Project Plan is the systematic planning process.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

Organization of project staff and responsibilities are presented in Table 11.

5.2 Special training and certifications

All personnel participating in the project field work have the necessary Ecology safety training and experience in using the equipment required for the collection of the proposed sample media. Staff will be familiar with applicable Ecology Standard Operating Procedures (SOPs) that are detailed in *Section 6.2.2.1 Comparability*.

5.3 Organization chart

The key personnel from Ecology involved in this project are listed in Table 11. The project also requires additional collaboration from the Yakama Nation, Chelan County, Wenatchee Watershed Planning Unit, Washington Department of Fish and Wildlife, and U.S. Fish and Wildlife.

5.4 Project schedule

The overall project timeline is detailed in Table 12.

5.5 Limitations on schedule

The schedule of the sampling program relies on being able to successfully retrieve and reliably measure the SPMD membranes and periphyton. We will ensure that site access is not an impediment and site security is sufficient to prevent vandalism over the 30-day deployment. A midpoint sampling and check of the SPMDs will also be carried out. There is also sufficient time in the project to adapt to any unforeseen issues with the SPMD survey.

5.6 Budget and funding

Phase 1 laboratory analysis will be completed by January 2015. The estimated analytical budget for Phase 1 of this project will total $35,220 (Table 13), which includes estimated laboratory costs and review of QA/QC. Costs for Phase 2 of the project will be detailed in an Addendum to this QAPP.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

There are no specific decision quality objectives for this project. Phase 2 of the project in 2015 will be based on the relative concentrations of the contaminants of concern throughout the sampled portion of the basin.

6.2 Measurement Quality Objectives

A complete summary of measurement quality objectives (MQOs) for this project is detailed in Table 10.

6.2.1 Targets for Precision, Bias, and Sensitivity

6.2.1.1 Precision

Field replicate samples will be collected at a frequency of 1 in 10. The defined relative percent difference for water and passive samplers is ± 20% and generally ± 40% for solids which tend to be more heterogeneous in nature. Replicates are collected either simultaneously or as close together as possible. Field splits will be possible for the periphyton and invertebrate tissues, where samples are split following homogenization in the lab.

Field trip blanks will be conducted for the SPMDs. The field blank SPMD is taken into the field and opened for the same duration of time that the sample SPMD is exposed to the air during deployment. The blank is sealed, transported cold back to Ecology, and stored frozen. The blank is then taken back into the field and exposed to air for the same duration as the sample SPMD during retrieval. One field blank will be used.

6.2.1.2 Bias

The bias of the lab instruments will be assessed by MEL and the contract lab. The data package from the contract lab will provide MEL with all the raw data which will include, but is not limited to, a text narrative; and analytical result reports; analytical sequence (run) logs, chromatograms, and spectra for all standards, environmental samples, and batch QC samples; and preparation benchsheets. In addition, all of the necessary quality assurance and control documentation will be provided, including results from matrix spikes, replicates, and blanks. The expected bias for the high-resolution analysis of PCBs and DDT is 50-150% recovery of matrix spikes (Table 10)

6.2.1.3 Sensitivity

The expected lowest concentration of interest for each parameter is detailed in Table 10. These values are based on the method detection limits for each parameter.

6.2.2 Targets for Comparability, Representativeness, and Completeness

6.2.2.1 Comparability

To ensure comparability among projects, the following standard operating procedures will be followed:

1. Standard Operating Procedures for Conducting Studies using Semi-Permeable Membrane Devices (SPMDs) (Seiders et al., 2012b).
2. Standard Operating Procedure for Semi-Permeable Membrane Devices (SPMDs) Data Management and Data Reduction (Seiders and Sandvik, 2012).
3. Standard Operating Procedures for the Collection of Periphyton Samples for TMDL studies (Mathieu et al., 2013).
4. Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014).

The objective of this sampling plan is to provide a spatial survey of contaminants using SPMDs and not a temporal comparison.

6.2.2.2 Representativeness

Previous sampling of the Wenatchee River suggests that periods of low-flow are the opportune time to capture high concentrations of PCBs in the water (MacCarthy and Gale, 1999; Sandvik, 2009). The initial survey using SPMDs is therefore planned to coincide with the documented low-flow period in late summer (Fig. 3). The late-summer /early-fall sampling is also the opportune period to sample periphyton growth in the Wenatchee River (Carroll et al., 2006), as the high flow period scours most of the periphyton growth. Sampling periphyton near the end of the growing season will also integrate more time to bind PCBs. It should be acknowledged that low-flow is perhaps not the opportune period to capture peak DDT concentrations, as DDT is often associated with particulates during higher flow (Serdar and Era-Miller, 2004). However, a significant portion of dissolved DDT is contributed to the Wenatchee River from Mission Creek, and, given the opportunity to analyze such a large array of passive samplers for both contaminants, a compromise in sample timing seems justified.

In order to assess the representativeness of the SPMDs *in-situ* exchange of PCBs and DDT into the membranes, performance reference compounds (PRCs) are used. These are explained in more detail in subsequent sections. The PRCs are labeled compounds that are incorporated into the membrane and allow for the calculation of the sampling rate of the target contaminants by measuring the rate of loss of the PRCs.

6.2.2.3 Completeness

To ensure completeness of sampling the river using SPMDs, we propose to deploy duplicate canisters of membranes near each other, so if one is physically lost we have a redundant sample to analyze. These redundant membranes will not be analyzed. In addition, a minimum of 2 reliable detections of low-level PCBs in each section of the Wenatchee River Basin (Fig. 9) will give a minimum completeness coverage of the basin.

7.0 Sampling Process Design (Experimental Design)

7.1 Study Design

This study has been initiated because resident fish species in the Wenatchee River, particularly mountain whitefish (MWF; *Prosopium williamsoni*), have routinely had the highest documented PCB concentrations in Washington (Seiders et al., 2012). MWF tissue is also contaminated with DDT and metabolites. Wenatchee MWF are accumulating PCBs and DDT from their diet and possibly absorbing dissolved PCBs from the water column. The Phase 1 sampling program was designed to assess water and algae concentrations. The Phase 2 sampling program will consider multiple media.

Water samples will allow us to evaluate the spatial distribution and relative concentrations of dissolved PCBs and DDT within the Wenatchee River Basin. Biotic sampling will allow us to assess how PCBs are moving and accumulating within the food web of the Wenatchee River, ultimately leading to excessive concentrations in fish tissue.

7.1.1 Field measurements

The Phase 1 initial survey of the Wenatchee River Basin will focus on a spatial assessment of PCB congeners and DDT and metabolite concentrations in water and PCB burdens in periphyton (attached algae). The basin will be divided into three sections (Fig. 9) and areas of potential sources will be targeted. In order to assess PCB and DDT concentrations in water, passive samplers (semi-permeable membrane devices) will be deployed during low-flow conditions (Fig.3; August/September). These samplers will take a time-integrated sample for approximately 30 days. There will be an SPMD replicate at each sample site to protect against loss from natural conditions or vandalism. The residues which accumulate in the SPMDs will allow us to assess the relative PCB and DDT burdens across the basin and estimate the concentrations in the water. At each SPMD location, a sample of periphyton will be collected and analyzed for PCB concentrations. The objectives of analyzing periphyton samples are to (1) quantify the PCB concentrations in the lower trophic levels of the food web, (2) establish whether periphyton accumulate PCBs at concentrations proportional to the water concentrations, and (3) to show that this media can be used in the second phase of the project.

Following the results of the Phase 1 synoptic survey, we will adapt the Phase 2 detailed sampling plan to focus on the area of potential contaminant sources. During this phase of the project, sampling will address concentrations at high and low flow. Possible sample media during Phase 2 include:

- Water (sampled using continuous low-level aquatic monitoring (CLAM) pumps with solid phase extraction disks)
- Conventional parameters in water collected using grab samples
- Wastewater treatment plant effluent

- Municipal stormwater discharge and catch basin sediments
- Suspended sediments (collected using in-stream sediment traps or continuous flow centrifugation)
- Periphyton
- Macroinvertebrates

7.1.2 Sampling location and frequency

Nine SPMD sampling locations will be established and PCB congeners and t-DDT will be analyzed at each (Table 14 and Fig. 9). The locations of the SPMDs are based on the identified potential sources of the contaminants (Tables 2 and 3; *Section 3.1.3*). In July, before the sampling program begins, we will conduct a reconnaissance of the proposed sites with the assistance of Chelan County and local land owners. At this time we will discuss the position of the SPMDs, access to the sample sites, and the security of the devices over the 30-day sampling period. In mid-August, also before the sampling program begins, we will walk or paddle the Lower Wenatchee River section to confirm whether any electrical equipment (i.e., transformers) is present within the channel near the town of Cashmere. At the time of SPMD deployment, the midpoint and retrieval, samples will be collected for ancillary parameters in support of SPMDs and periphyton. Further detail is provided in the *Sampling Procedures* section.
The detailed sampling will be designed and guided by the spatial survey of contaminants from the synoptic survey. Sampling will likely take place in the spring (May) and late summer (September) of 2015.

7.1.3 Parameters to be determined

The contaminants of concern are PCBs and t-DDT. PCBs are the main focus of the study; the assessment of DDT has been included to take advantage of the sampling effort being undertaken. High resolution gas chromatography/mass spectrometry (HR GC/MS) will be carried out in the initial phase of the project to characterize PCB congener patterns in water throughout the watershed and to gain suitably low detection limits. Samples for conventional parameters and ancillary parameters necessary for the passive samplers are detailed in Table 15.

7.2 Maps or diagram

The proposed locations of the SPMD passive samplers are detailed in Figure 9 and Table 14. These preliminary sites will be verified prior to sampling by Ecology, the Yakama Nation, and Chelan County. The rationale for the site locations is detailed in Tables 2 and 3.

7.3 Assumptions underlying design

During the initial basin-wide survey SPMDs and periphyton samples will be analyzed for PCB congeners. SPMDs are an accepted and proven tool for sampling low-level PCBs in water and have been used successfully in the Wenatchee River (Sandvik, 2009). Periphyton sampling for the accumulation of organochlorine compounds has proven successful in a number of studies (Hill and Napolitano, 1996; Berglund, 2003), but it is not a widely used sample media. The

initial sampling has been designed to explicitly test whether there is a strong relationship between PCB burdens in the water and periphyton biomass in the Wenatchee River.

SPMDs will be located near the thalweg of the river, where the river is assumed to be well-mixed. There will not be any assessment of possible variation in contaminant sources in right versus left bank positions. The Wenatchee River is high energy and the assumption about mixing seems fair.

7.4 Relation to objectives and site characteristics

At the completion of the synoptic survey, we will have an understanding of the spatial distribution of PCBs and t-DDT in the mainstem of the Wenatchee River Basin. We should also be able to address the hypothesis that Mission Creek represents the main source of DDT to the Wenatchee River. Recommendations for follow-up actions to the t-DDT sampling will be made at the end of the synoptic survey. The detailed sampling plan will be designed following the initial survey. Sampling approaches and methodologies will be described in a QAPP Addendum submitted and approved prior to the anticipated field work in May 2015. By defining the detailed sampling plan based on the synoptic survey, we will increase our ability to focus additional source assessment on the appropriate location and sample media.

7.5 Characteristics of existing data

There is a great deal of historic data for PCBs and DDT in fish tissues from the Wenatchee River. This data set has been accumulated over the last ~ 15 years and describes a persistent contaminant source within the Wenatchee Basin. The proposed study will investigate reaches of the Wenatchee River in order to identify possible localized contaminant sources.

Data are lacking for the Wenatchee MWF life history traits. There has been no study of the diet and migratory range of these fish populations. Comprehensively addressing this data gap could be considered as a follow-up action to this source assessment. No additional sampling of WMF is planned under this project, because the most recent 2010 samples should be sufficient to characterize current PCB burdens in MWF (Seiders et al., 2012). Future sampling of MWF in the Wenatchee River is tentatively scheduled for 2018 under Ecology's Freshwater Fish Contaminant Monitoring Program (K. Seiders, personal communication).

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

8.1.1 Water sampling

Water samples will be collected using passive samplers (SPMDs) for PCBs and DDT and grab samples for conventional and ancillary parameters.

Ecology has frequently used SPMDs when investigating toxics in surface waters throughout Washington (Sandvik and Seiders, 2012). While SPMDs have not been recommended for use in trend monitoring of low-level PCBs, they are an effective tool in source assessment studies. The goals of deploying SPMDs during a spatial survey can be two-fold: (1) to assess the relative PCB residues from site to site over the area of interest, and (2) to calculate estimated water concentrations from the SPMD residues. Issues with SPMD quality control would affect our ability to attain data for the second goal. However, for the purpose of this source assessment we can achieve our study objectives if we are only able to assess the relative PCB residues from site to site. A well-established SOP for the use of SPMDs will be followed (Seiders and Sandvik, 2012). Data for estimated water concentrations calculated from the SPMDs cannot be entered into Ecology's EIM system, but they are uploaded to an SPMD data repository where they are available upon request.

SPMDs will be deployed in secure areas (i.e., minimizing vandalism and located out of strong currents), using stainless steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). Secure sample locations will be verified during an initial site reconnaissance. In order to provide completeness and redundancy to the sampling, two canisters will be independently deployed at each site in case one is physically lost. If both canisters are retrieved, only one will be analyzed. Each site canister will contain 5 membranes that are preloaded onto spindles by EST and shipped in solvent-rinsed metal cans under argon gas. The SPMDs will be secured within the creek and a StowAway® TidbiTs^{TM} temperature logger will be attached to continuously monitor the water temperature during deployment. A second datalogger will be attached nearby to monitor air temperature. The data collected from the temperature loggers will be used to confirm that the SPMD remained submerged during the sampling period.

To determine the average concentration of PCBs and t-DDT in the water of the Wenatchee River, we need to assess the total amount bound to the SPMD residue. For this we use Permeability/Performance Reference Compounds (PRCs) that are spiked before deployment. The use of PRCs is essentially an *in situ* calibration technique based on the observation that the rate of residue loss is proportional to the rate of residue uptake. These rates are governed by the physical properties of the compounds of interest, namely the octanol-water partition coefficient (K_{ow}). We will use isotopically labeled (^{13}C) PCB congeners PCB-31, -95, and -153 as PRCs, in addition to PCB-14, -29 and -50, which are not labeled but commonly used. The labeled congeners are not present in significant amounts in the environment and have shown appropriate rates of loss (20-80%). The spiking level will be 2 ng of each PRC congener per membrane. The PRCs are added to the triolein oil before the manufacture of the SPMD membranes. The contract

lab will order, prepare, and validate the PCB standard and will provide the PRC spiking solution to EST. The amount of PRC necessary for each sample site will be discussed in a project kick-off meeting with Ecology, EST, and contract lab staff.

At each sample site, once we have established the anchoring system, we will pry open the cans containing SPMDs, slide them into the canisters, and tether them in the river. SPMDs are deployed as quickly as possible, to limit air contamination. We will handle SPMD spindles with nitrile gloves, taking care not to touch the membranes. The period of deployment will be 28 days, as per the recommendations of USGS and EST. The retrieval procedure is the reverse order of deployment steps, using the same cans for shipping. The cans must be properly sealed and cooled to−and kept near−freezing until they arrive at the contract lab for the extraction of the membranes.

8.1.2 Periphyton

Periphyton is algae attached to the river bottom, rocks, or debris in the river. Previous investigations on the Wenatchee River have collected periphyton for biomass analysis (Carroll et al., 2006). The investigators determined that most of the periphyton were diatoms, microscopic single-celled algae. Periphyton will be sampled at low-flow conditions at the end of the summer, allowing time for colonization and adsorption of PCB compounds. Standard protocols exist for sampling attached algae (Stevenson and Bahls, 1999; Mathieu et al., 2013). Periphyton will be scraped from rocks and collected in a stainless bowl for weighing in the field in order to confirm that sufficient biomass has been retrieved. Samples will be transferred from the bowl to a cleaned glass jar. The area of each rock that is scraped for periphyton will be measured by cutting a piece of tinfoil tracing the sample location and measuring it at Ecology. Before submitting to the lab, Ecology will homogenize samples in the EAP sample prep room.

8.2 Containers, preservation methods, holding times

Details of sample containers, preservation and holding times are found in Table 15.

8.3 Invasive species evaluation

There is a low probability of aquatic invasive species within the Wenatchee River Basin (Parsons et al., 2012). We will take standard precautions, not wearing felt-soled boots and decontaminating any equipment between uses if necessary.

8.4 Equipment decontamination

Periphyton samples will be collected in a stainless steel bowl before transfer to a cleaned glass jar. A sufficient number of stainless steel bowls will be washed, hexane-acetone rinsed, and then covered in tinfoil before use in the field (Friese et al., 2014). No solvents will be brought into the field.

SPMD canisters and shade devices will be acetone-hexane rinsed before deployment and will be pressure-washed and rinsed after retrieval from the field.

8.5 Sample ID

Site identification will follow the previous TMDL by Carroll et al. (2006); the WRIA number-Waterbody abbreviation-river mile (45WR25.5) is the Wenatchee River Basin WRIA 45 – the Wenatchee River mainstem – 25.5 river mile.

8.6 Chain-of-custody, if required

We will follow standard chain-of-custody protocols as outlined in the *Manchester Environmental Lab Users Manual, 9th edition* and will follow those protocols used by the contract laboratory.

8.7 Field log requirements

The field log for SPMD projects is defined by the SOP (Appendix A; Seiders and Sandvik, 2012). The log will be printed on waterproof paper.

8.8 Other activities

Periphyton samples will homogenized in the EAP sample prep room. Homogenization techniques will vary, depending on the nature of the sample (i.e., filamentous algae or fine flocculent algae). A stainless steel scalpel may be used to cut and mix the sample for larger filamentous algae or for soft flocculent algae. Centrifugation and mixing in stainless steel buckets may be required to remove excess water from the sample.

9.0 Measurement Methods

9.1 Field procedures table/field analysis table

No field analyses are planned, with the exception of monitoring field pH, specific conductance (µS cm^{-1}) and temperature (°C) at each site where a sample is collected. River discharge data will be accessed from gauging stations (USGS and Ecology) on the Wenatchee River.

9.2 Lab procedures table

Laboratory procedures are detailed in Table 16. The contract lab will be responsible for the analysis of PCB congeners in SPMDs and periphyton, which will provide consistency in the lab environment, methods, and QC. DDT and metabolites will be analyzed from the same SPMD

extract, using high-resolution mass spectrometry. MEL will conduct analysis of lipids and ancillary parameters.

9.3 Sample preparation method(s)

Established sample preparation methods are detailed in Table 16.

9.4 Special method requirements

The use of SPMDs requires additional and detailed QC, which is described in the subsequent sections. The chain-of custody for SPMDs has been detailed in the SOP (Seiders and Sandvik) and has been followed in developing and initiating the proposed project. We are requesting the services of a contract lab that can receive the SPMDs directly from the field and must complete the following steps during processing:

- removal of exterior surficial periphyton and debris,
- organic solvent dialysis,
- size-exclusion chromatography (SEC), such as Gel Permeation Chromatography, when required, and per laboratory-defined procedures and
- chemical class-specific fractionation using Florisil, silica gel, and alumina sorption chromatography, per laboratory-defined procedures.

By requesting a contract lab that can complete the dialysis and analysis of the extract, Ecology reduces a potential source of contamination during handling. This has been made possible by the expiration of patents on the dialysis process have expired, and should be an update to the SPMD SOP.

9.5 Lab(s) accredited for method(s)

All lab methods proposed here are accredited by Ecology's Laboratory Accreditation Program. A contract lab will be awarded a portion of the analysis, based on their documented experience with the necessary methods, their ability to achieve the QC standards, and cost-efficiency. A 2nd tier solicitation of services has been issued under the original Solicitation for State Master Contract #02413.

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

The necessary QC procedures for field and laboratory methods are detailed in Table 17. Furthermore, the QC measures specific to the SPMDs are detailed in Table 18 and include the performance reference standards (PRCs).

All laboratory quality assurance/quality control (QA/QC) measures are documented in MEL's Laboratory Quality Assurance Manual (MEL, 2012). Laboratory quality control measures include the analysis of check standards, duplicates, spikes, and blanks. Check standards or laboratory control samples are perhaps the most important for the evaluation of analytical precision and bias. Duplicates and spikes help to evaluate any effects of sample matrix on the data quality, while blanks aid in determining interferences and precision for low concentrations near analytical detection limits.

The tracking and calculation of check standards, spikes, and blanks for the SPMDs follow the SPMD SOP (Seiders et al., 2012b) and SPMD data management SOP (Seiders and Sandvik, 2012). In 2012, Ecology completed an assessment of the utility of SPMDs for use in measuring long-term contaminant trends in fresh waters. At low t-PCB concentrations, similar to that found in the Wenatchee River, results can be confounded by laboratory contamination of the SPMD. Sandvik (2009) showed t-PCB residues in SPMDs from the Wenatchee River of 170 ng and 140 ng, compared with 100 ng from the laboratory blank. Laboratory contamination in the blank accounted for 60-90% of the residue, while air exposure during deployment and retrieval accounted for 10-30% and 0-15%, respectively (Sandvik and Seiders, 2012). This interference presents considerable variability when measuring low PCB concentrations. Since the 2007 sampling (Sandvik, 2009) additional quality control measures have been taken to constrain laboratory contamination if present. The contract lab will retain and analyze if necessary:

- An aliquot of PRC solution
- An aliquot of original surrogate solution
- An aliquot of triolein oil, spiked with PRC

SPMDs require a detailed method blank procedure that is carried out by both EST and the contract lab. The goal of the blanks is to verify or quantify contamination during transport, deployment, and retrieval. It is not to enable a blank subtraction, where the concentrations of the blank are subtracted from the concentrations at the study site. The following method blanks will be prepared by EST and held frozen at -20°C at the contract lab:

1. A membrane spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at the contract lab and later dialyzed with project samples.
2. A day-zero SPMD fabrication blank to serve as a reference point for PRC loss.

The contract lab will be responsible for the dialysis of the SPMDs, cleanup of the extracts as per EPA 1668C and 1699, and analysis of the SPMD extracts for both PCB congeners and DDT (and

metabolites). Before dialysis, SPMDs will be spiked with labeled PCB congeners and p,p'-DDT compounds. Dialysis will be conducted twice on each membrane and the 5 membranes from each sample canister (site) will be combined into one sample. A solvent or reagent blank will also be extracted, cleaned, and analyzed using comparable volumes to the SPMDs.

Establishment of the method detection limits (MDLs) will be overseen by MEL. MDLs will be based on laboratory QA considerations (information from blank or control samples and surrogate recoveries) and the number of samples. Anticipated MDLs and reporting limits are detailed in Table 16.

10.2 Corrective action processes

Any instances where the QC measures are not met will be discussed among Ecology, MEL, and the contract lab (if applicable). A range of responses to results fall outside the MQOs and project QC; these are discussed in more detail *Section 14.0* on data usability.

In general, samples which are to be run by a contract lab and MEL will have a portion of the extract held, in case it is necessary to re-run a sample. In addition, total PCB congeners in the method blank must not exceed the sum of the minimum levels of all congeners. If this limit is exceeded, the project lead will be contacted to discuss actions to take. Any blanks with individual results greater than half the quantitation limit should be investigated using the SPMD materials being held by the contract lab (described in the previous section).

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

Field data collected during the project will be copied and filed as a hard copy, and notes will be typed into project Excel spreadsheets as metadata. The appendices within the SOP for SPMDs (Seiders et al., 2012b) detail the available templates for data reduction and planning. PCB and DDT residual concentrations from the SPMDs will be used to calculate an estimated dissolved concentration in water. The model developed by David Alvarez, USGS to calculate estimated water concentrations from the total burdens in the SPMDs and the PRC sampling rates is on the Ecology shared server (Y:\Shared\SPMDs\). Ecology has the most recent version of this calculator. Given the nature of the source assessment project, we will not correct for the field blank. Total concentrations will be calculated following Meadows et al. (1998), using TOC data. We will therefore have the relative contaminant residuals from the SPMDs throughout the basin (similar to MacCarthy and Gale, 1999) and the estimated water concentrations (dissolved and total).

11.2 Laboratory data package requirements

The laboratory data package will be generated or overseen by MEL. MEL will provide a project data package that will include: a narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. Quality control results will be evaluated by MEL (discussed below in *Section 13.0 Data Verification*).

11.3 Electronic transfer requirements

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. The contract lab will provide an electronic data deliverable (EDD) that meets the format defined by MEL.

11.4 Acceptance criteria for existing data

The following data qualifiers will be used:

- "J" – The analyte was positively identified. The associated numerical result is an estimate.
- "UJ" – The analyte was not detected at or above the estimated reporting limit.
- "NJ" – The analysis indicates the presence of an analyte that has been "tentatively identified" and the associated numerical value represents its approximate concentration.

The qualifiers will be used in accordance with the method reporting limits such that:

- For non-detect values, the estimated detection limit (EDL) is recorded in the "Result Reported Value" column and a "UJ" the "Result Data Qualifier" column.
- No results are reported below the EDL.
- Only results for those congeners that have a value at least FIVE times the signal-to-noise ratio, and that meet ion abundance ratios required by the method are reported.
- Detected values that are below the quantitation limits (QL) are reported and qualified as estimates ("J").
- Results that do not meet ion abundance ratio criteria are reported with "NJ". If an Estimated Maximum Possible Concentration (EMPC) value is calculated and reported, the calculation is explained in the narrative, and an example calculation used for this value is provided.
- Results that contain interference from Polychlorinated Diphenyl Ethers (PCDPE) are qualified with "NJ".

11.5 EIM/STORET data upload procedures

After project personnel verify and validate data, they will enter data into Ecology's Environmental Information Management System (EIM). Data generated by SPMDs are considered an estimate and therefore not approved for entry into EIM. In accordance with the SOP for SPMD data management and data reduction (Seiders and Sandvik, 2012), an index of records and necessary data from the SPMDs will be saved to the Ecology data repository for SPMDs.

12.0 Audits and Reports

12.1 Number, frequency, type, and schedule of audits

Auditing of the data collected as part of this project will consist of review of data quality and usability by MEL, and review of the data entered into EIM (as per *Section 5.4*). Data review will occur following the initial survey (winter 2014/15) and following the detailed sampling (fall 2015). Discussion among project scientists and evaluation of sampling and analytical results are expected after each sampling event. The project plan can then be adjusted, if needed.

The Ecology Environmental Laboratory Accreditation Program evaluates a laboratory's quality system, staff, facilities and equipment, test methods, records, and reports. It also establishes that the laboratory is capable of providing accurate, defensible data. All assessments are available from Ecology upon request, including MEL's internal performance and audits.

12.2 Responsible personnel

The quality assurance officer for MEL, Karin Feddersen, will carry out the review of all MEL and contract lab data packages.

12.3 Frequency and distribution of report

Given the local (Wenatchee Valley) attention this project will generate, we anticipate issuing a fact sheet or press release of the project plan in the winter of 2014/15. As the project evolves and data are generated, interim fact sheets in the spring of 2015 and winter of 2015 will be distributed to the Wenatchee Watershed Planning Unit, the Yakama Nation, and Chelan County and made available to the general public.

12.4 Responsibility for reports

Draft report writing will take place during the winter of 2015/16, with the final report expected by June or July 2016. The project lead will be the lead author.

13.0 Data Verification

13.1 Field data verification, requirements, and responsibilities

The field assistant will review field notes once they are entered into Excel spreadsheets. Keith Seiders, author of the SOP for SPMDs, will review the calculations necessary for the SPMDs will be carried out by.

13.2 Lab data verification

As previously described, MEL will oversee the review and validation of all laboratory data packages. All data generated by the contract lab must be included in the final data package, including but not limited to: a text narrative; analytical result reports; analytical sequence (run) logs, chromatograms, spectra for all standards, environmental samples, batch QC samples, and preparation benchsheets. All of the necessary QA/QC documentation must be provided, including results from matrix spikes, replicates, and blanks.

13.3 Validation requirements, if necessary

It is expected that external data validation will not be necessary for this project. However, David Alvarez, USGS and author of the SPMD calculator, would be available for assistance should it be necessary.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining whether project objectives have been met

The primary objective of this project is to conduct a broad spatial survey of the Wenatchee River for PCB and t-DDT contamination. The study is purposefully designed to allow the review and planning of the detailed sampling following the results of the initial survey. If we find that some of the MQOs were not met in initial survey, we will have the opportunity to address these gaps in the follow-up sampling.

14.2 Data analysis and presentation methods

No specific numerical analyses are necessary for this project. Simple summary statistics will be used for conventional parameters sampled over the period of SPMD deployment. Regression

analysis will be used in determining whether TSS, turbidity, PCB burdens in periphyton correlate with PCBs and/or DDT in the SPMDs.

14.3 Treatment of non-detects

The handling of non-detects will be relevant to the summing of PCBs and t-DDT. Non-detect values (U, UJ) are assigned a value of zero for the summing process when the group of analytes being summed has both detected and non-detected results. Alternatively, for results with large numbers of non-detects, the Kaplan-Meier method can be used to compute the mean concentration that is then multiplied by the number of analytes (Helsel, 2012). This latter method was recently verified in an Ecology study on PCBs and found to give total PCB sums that were not significantly different from substitution methods (Coots, 2014).

If qualified data comprise more than 10% of the total summed concentration, then the total concentration should be qualified. If qualified data make up less than 10% of the total summed concentration, the total should not be qualified. Data sums will be qualified with: "J" if that is the only qualifier used; with "NJ" if that is the only qualifier used; and "J" if there is a mix of "J" and "NJ" qualifiers. When all values for individual analytes in the group are reported as non-detects, and the reporting limits are different, the highest value present is assigned as the "total" value. The sum "total" will be qualified with: "U" if all values are qualified as U, "UJ" if all the values are qualified as UJ, and "U" if there is a mix of both U and UJ.

14.4 Sampling design evaluation

The study design for Phase 1 of this project is a simple spatial survey. Sample distribution is targeted to suspected contaminant sources and a *background* sample site is included. The rationale for site coordinates is detailed in Table 2. The timeline of the project incorporates sufficient opportunity to adapt and evaluate the sampling approach following initial sample collection.

14.5 Documentation of assessment

The final report will present the findings, interpretations, and recommendations from this study. The goal of the project is to provide evidence of the distribution of 303(d)-listed contaminants; this evidence can then be used in the development of a source control plan.

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16.0 Figures

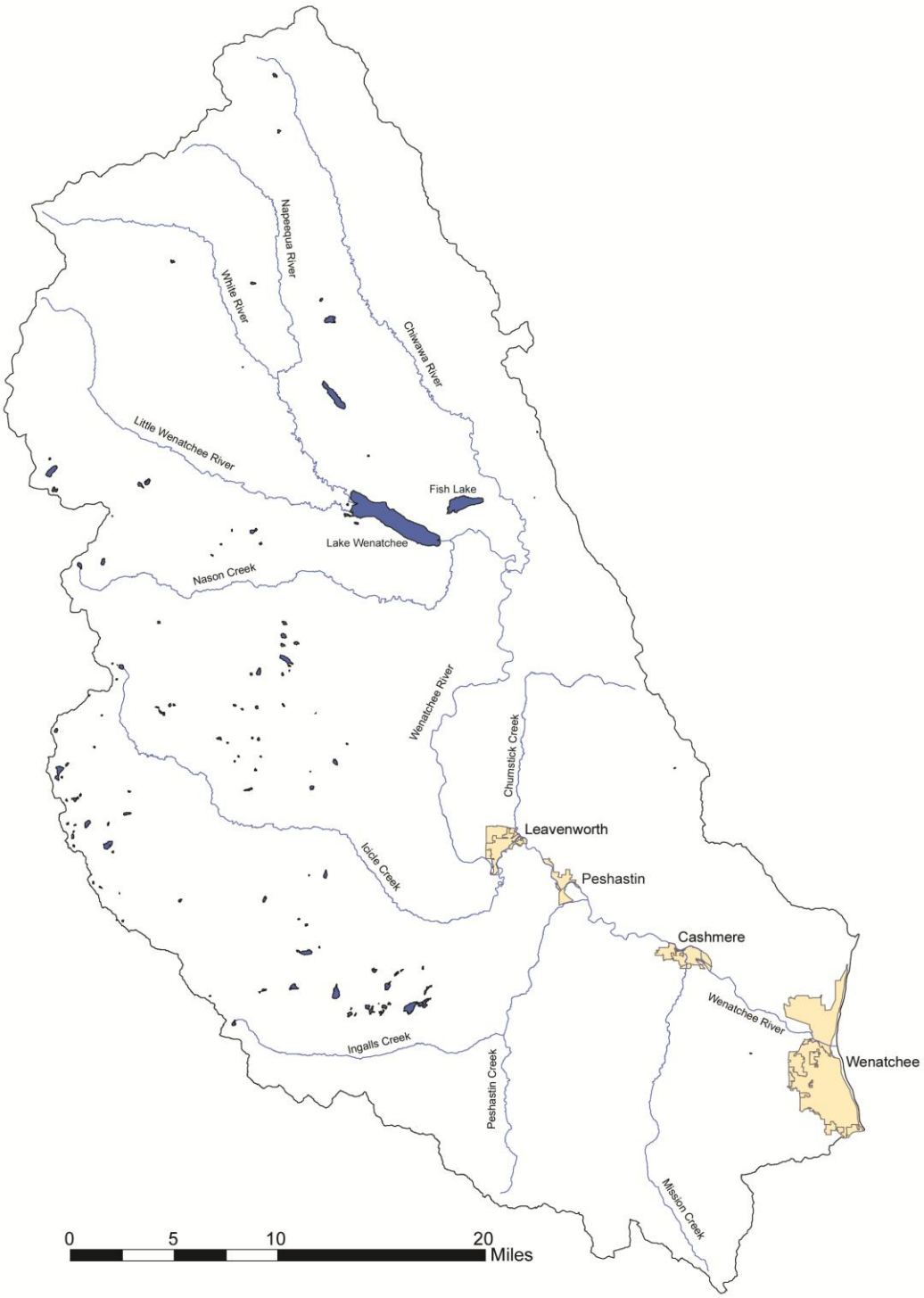

Figure 1. Wenatchee River Basin detailing major tributaries and urban centers.

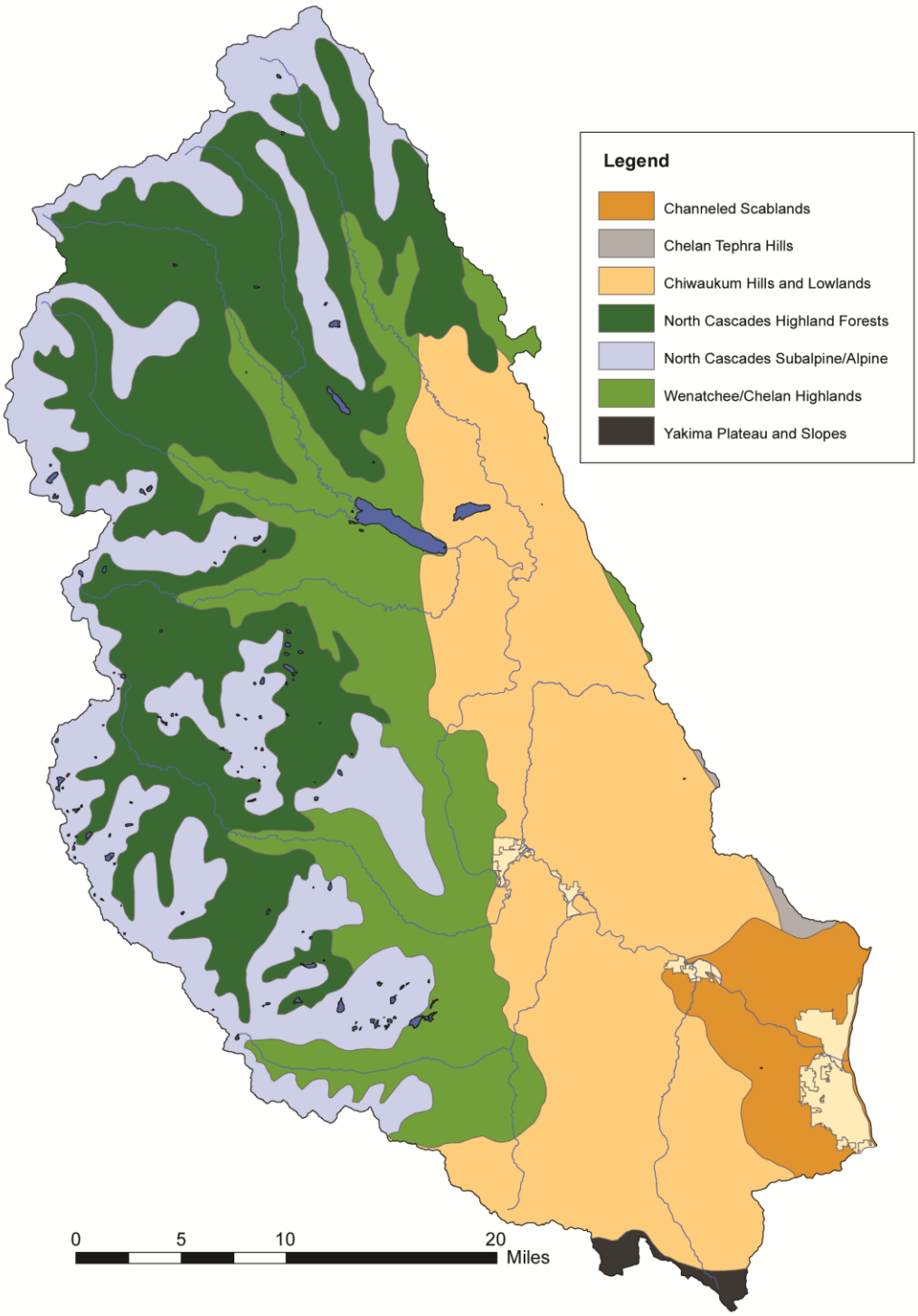

Figure 2. Biogeoclimatic zones of the Wenatchee River Basin.

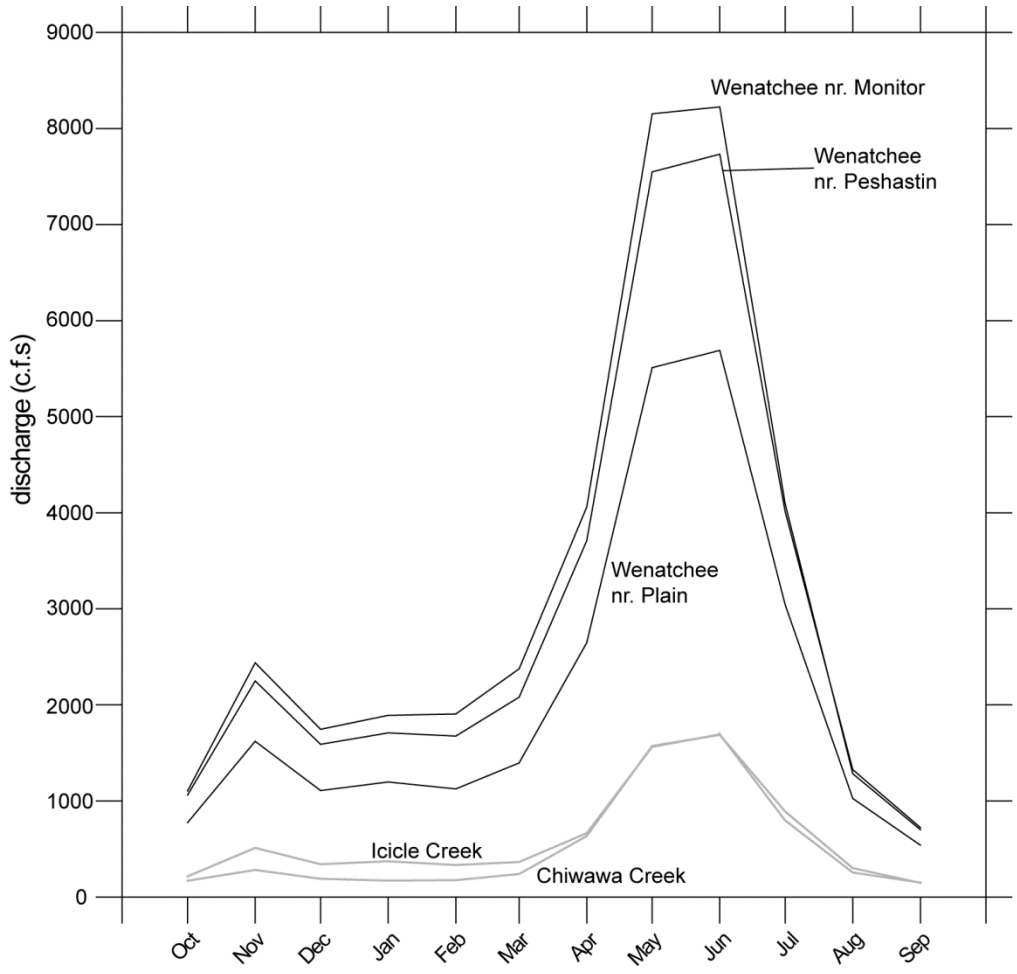

Figure 3. Mean monthly discharge for the Wenatchee River and tributaries, Icicle and Chiwawa Creeks.

Data Source: US Geological Survey.

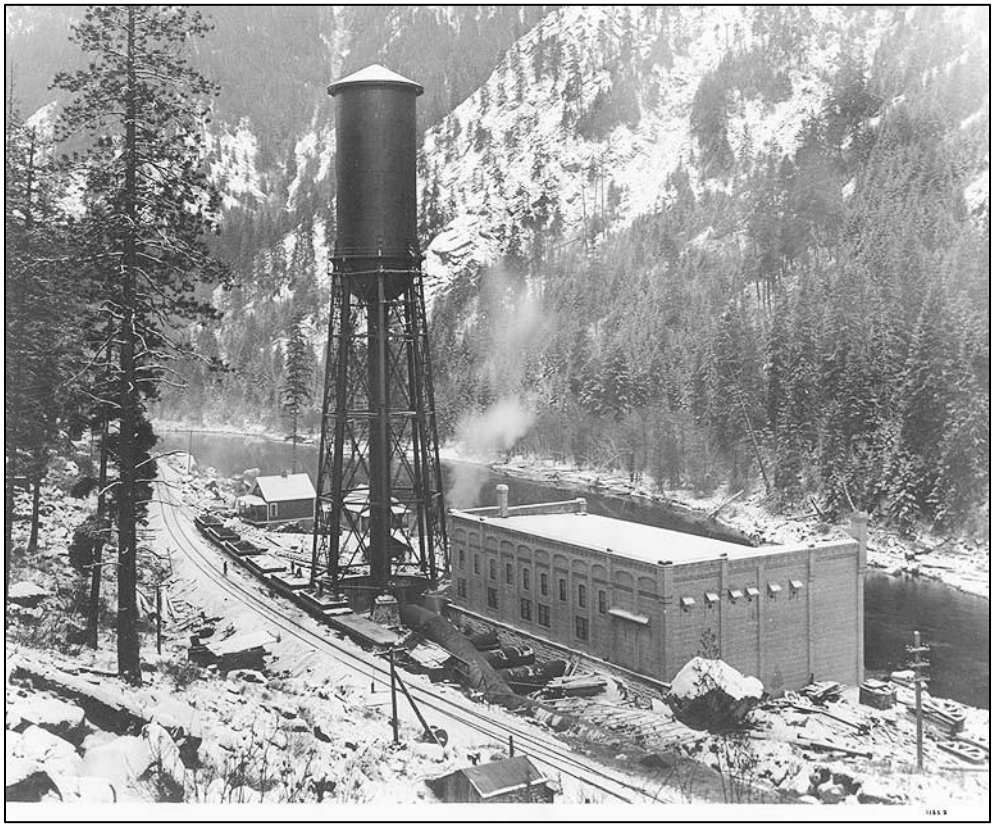

Figure 4. Great Northern Railway powerhouse in Tumwater Canyon 1908.

Reprinted with permission Digital Collections, University of Washington (CUR544). Photo credit: Asahel Curtis.

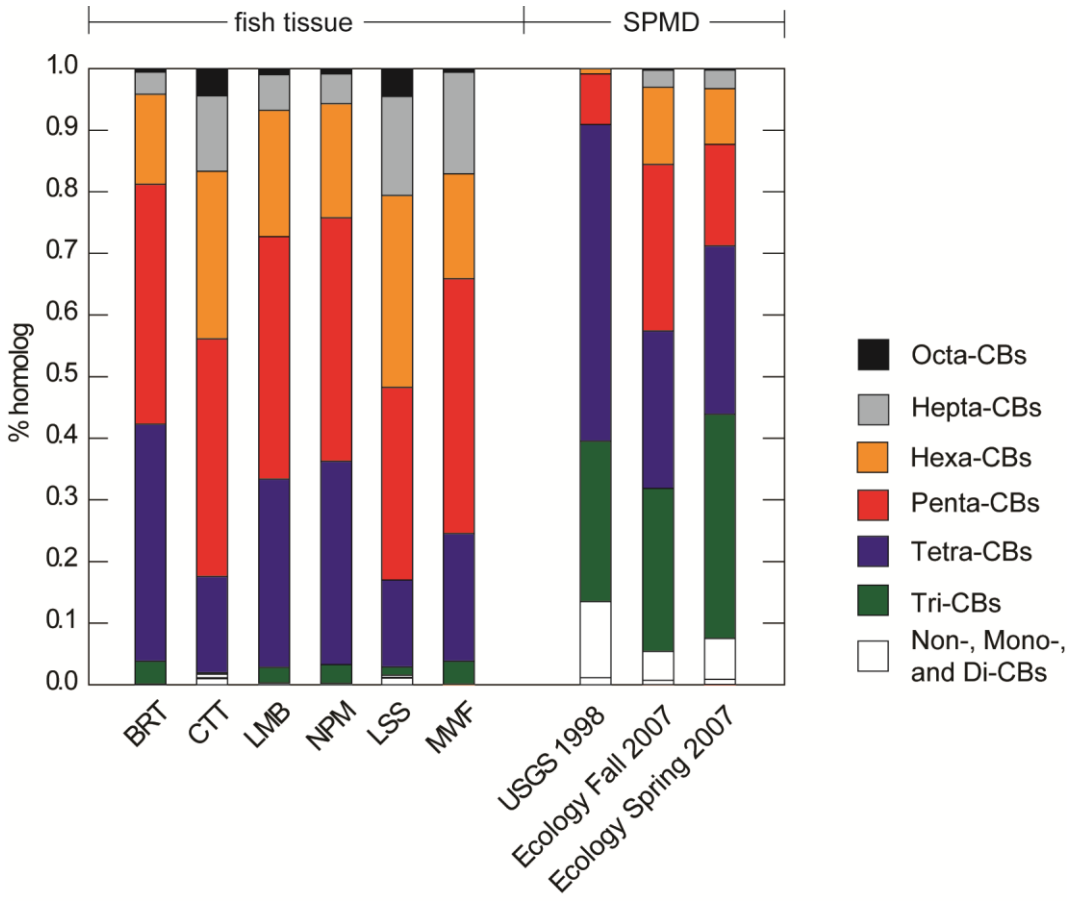

Figure 5. PCB homologue composition (% abundance) in fish tissue and water samples from the Wenatchee River.

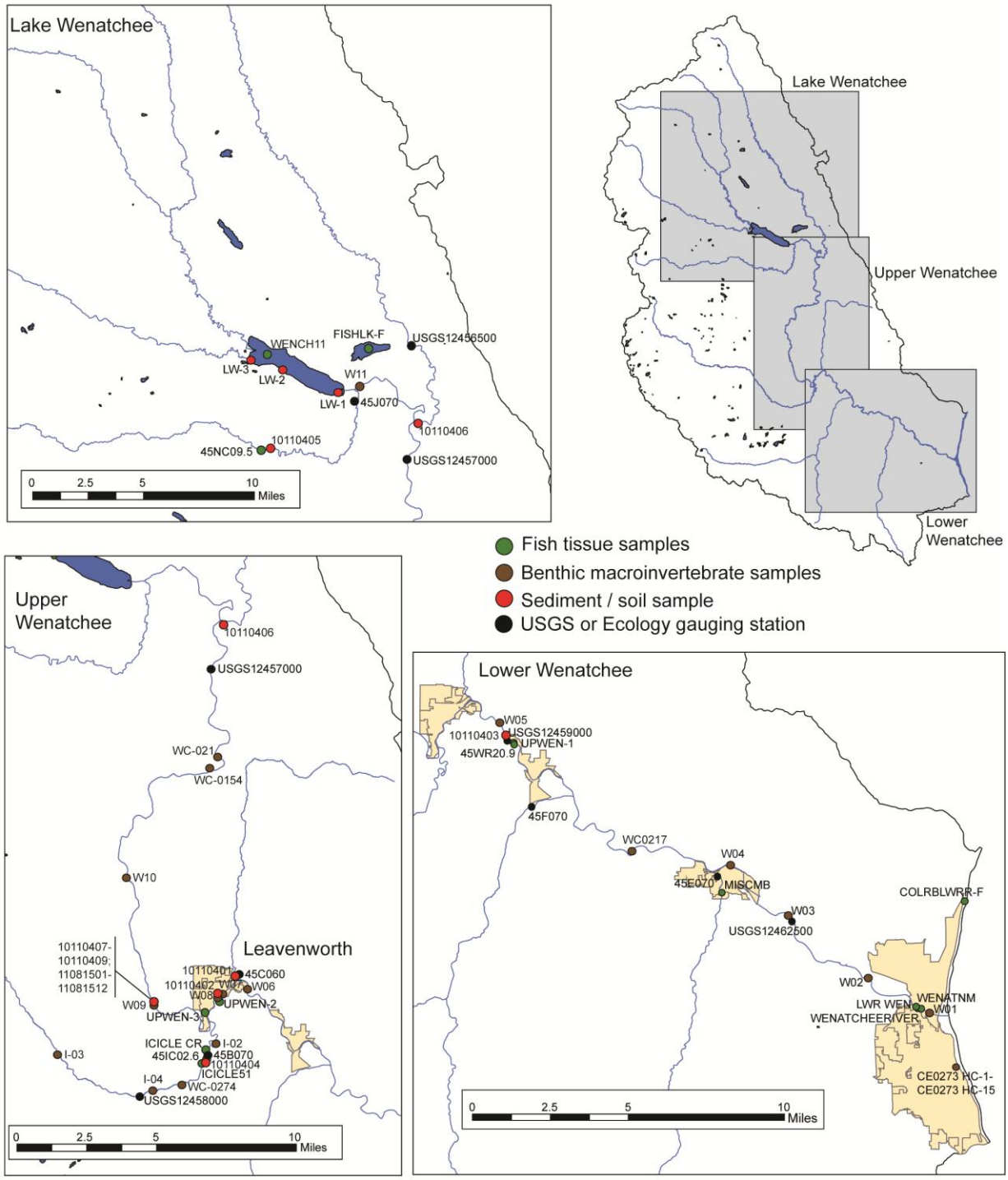

Figure 6. Former sampling sites within the Wenatchee Basin.

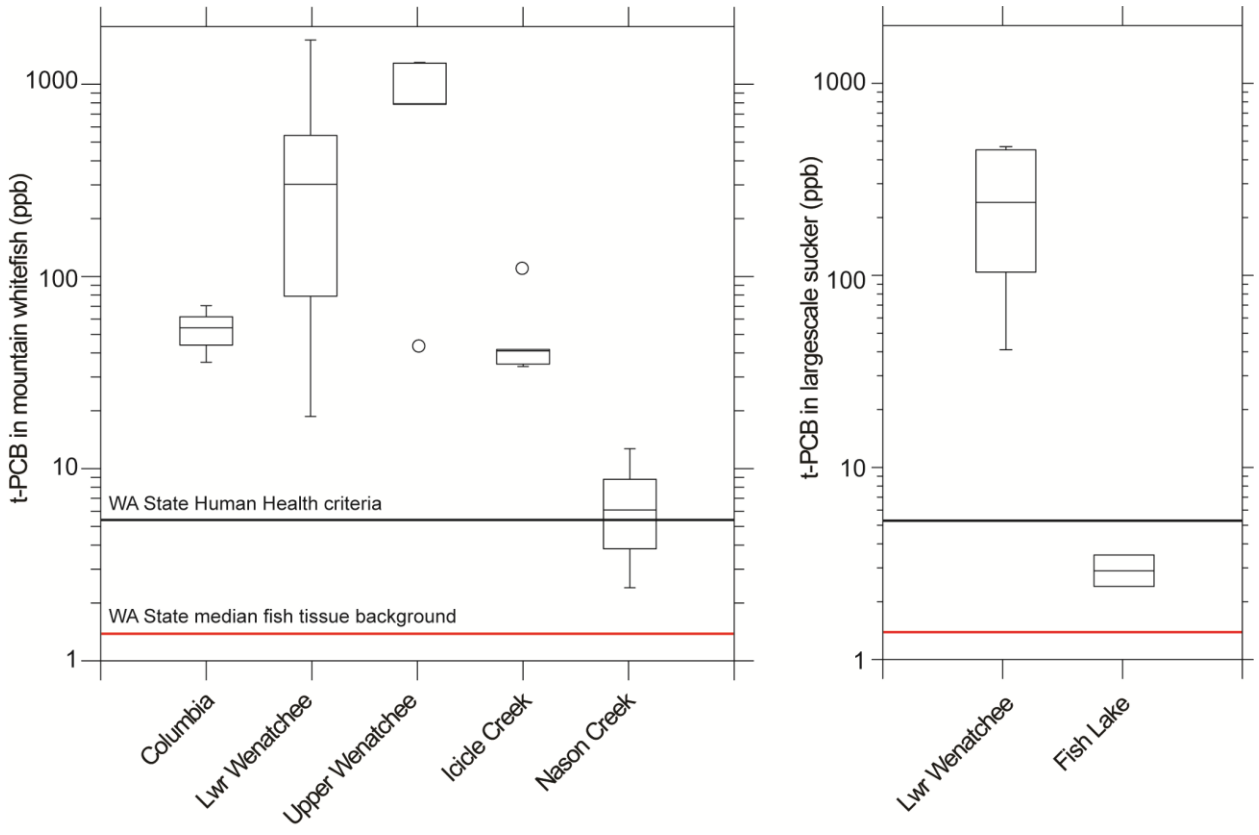

Figure 7. Box plot on log scale of total PCB concentrations in mountain whitefish and largescale suckers across the Wenatchee River Basin.

Boxes are median values and 25th and 75th percentiles.

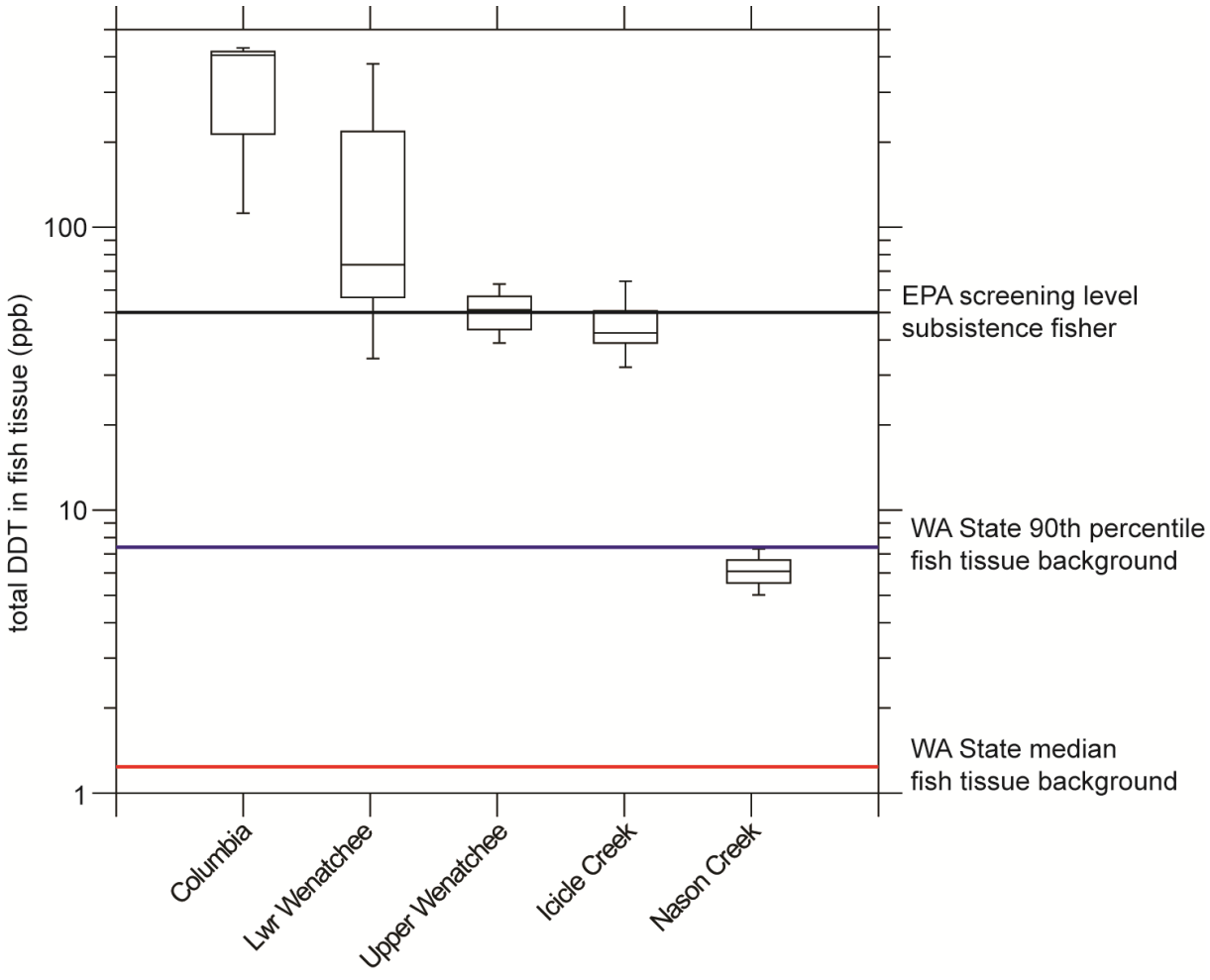

Figure 8. Box plot on log scale of total DDT concentrations in mountain whitefish within the Wenatchee River Basin and Columbia River.

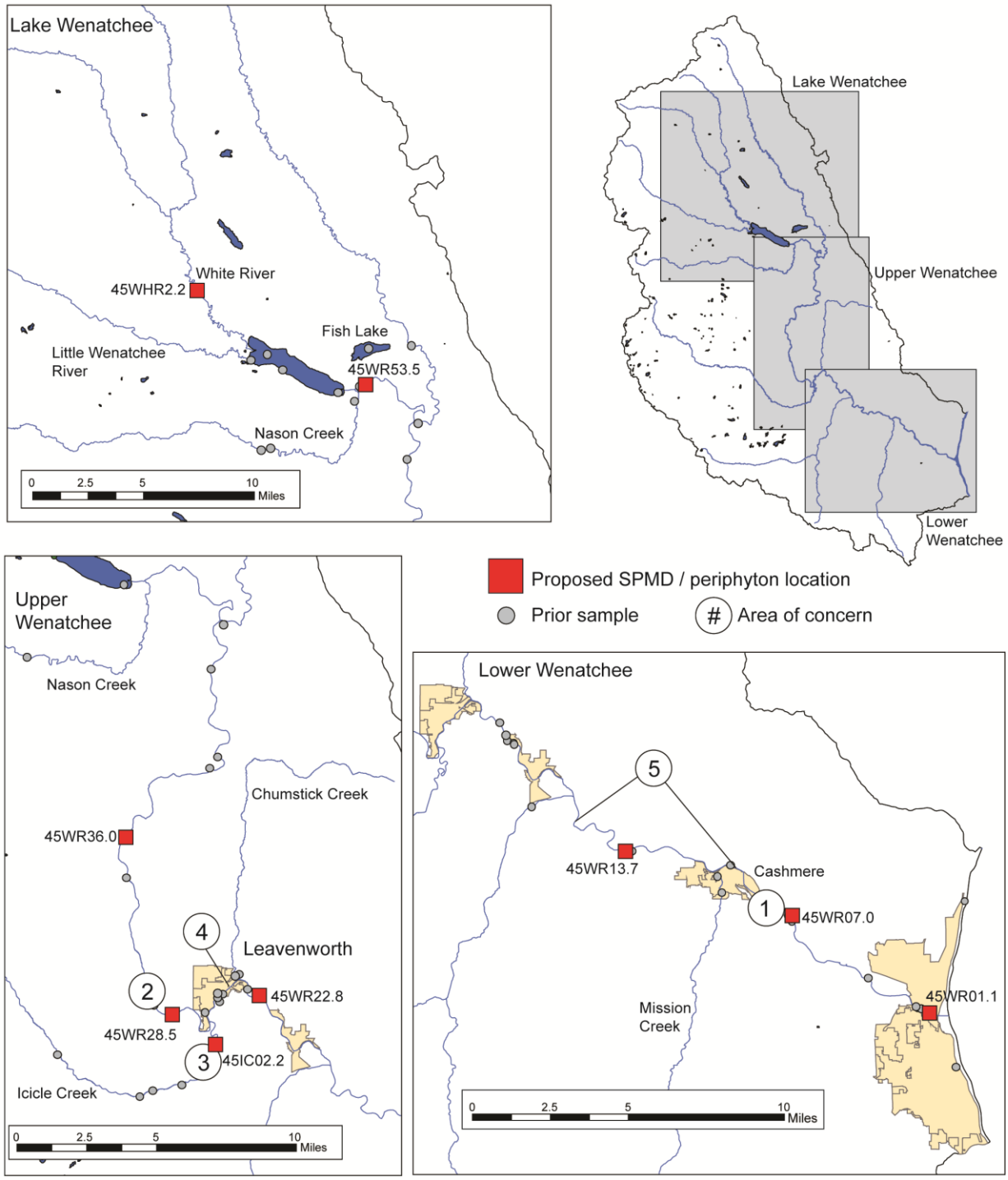

Figure 9. Proposed SPMD and periphyton sampling sites within the Wenatchee River Basin.

17.0 Tables

Table 1. Summary of Aroclor mixture physical properties, isomer composition and former uses.

Physical properties		Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268
molecular weight		257.9	200.7	232.2	266.5	294	328	357.7	389	453
water solubility (mg/L)[a]		0.84	3.5-15	1.45	0.5	0.32	0.14	0.08	0.052	0.3
octanol-water partition (K_{ow})[a]		4.4-5.8	4.1-4.7	4.1-5.2	4.5-5.8	5.8-6.3	6.1-6.8	6.3-7.5	no data	no data
sorption partition (K_{oc}) sediments[a]		4.25	3.76	2.89	3.8	5.44	5.61	6.83	no data	no data
Bioconcentration factor (BCF)[a]		3.11-4.5	3.34	2.54	3.2-4.51	4.5-5	4.8-5.51	5-6.2	no data	no data
PCB % isomer composition[b]										
mono-CBs		1	60	28	1	<1	<1	<1	<1	no data
di-CBs		18	33	27	15	2	<1	<1	<1	no data
tri-CBs		55	4	26	45	21	<1	<1	1	no data
tetra-CBs		22	1	11	20	33	5	<1	<1	no data
penta-CBs		5	1	9	19	43	71	9	3	no data
hexa-CBs		nd	nd	<1	<1	2	22	43	26	no data
hepta-CBs		nd	nd	<1	nd	<1	1	39	48	no data
octa-CBs		nd	nd	nd	nd	nd	nd	8	20	no data
nona-CBs		nd	nd	nd	nd	nd	<1	1	2	no data
deca-CBs		nd	nd	nd	nd	nd	nd	nd	nd	no data
Former Uses[b]	% of domestic PCB sales[c]									
capacitors	50	x	x				x			
transformers (incl. heat transfer)	29				x		x	x		
hydraulic fluids	6			x	x	x	x	x		
vacuum pumps	2					x	x			

Physical properties		Aroclor 1016	Aroclor 1221	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260	Aroclor 1262	Aroclor 1268
gas-transmission turbines			x		x					
rubbers			x	x	x	x	x			
synthetic resins						x	x	x	x	x
carbonless paper	4				x					
adhesives	9		x	x	x	x	x			
wax extenders					x		x			x
dedusting agents							x	x		
inks							x			
cutting oils							x			
pesticide extenders							x			
sealants and caulking compounds							x			

a. MacKay et al., 1992
b. HHSPHS, 2000
c. Erikson and Kaley II, 2011
nd = less than detection limit

Table 2. PCB sources, location, Phase 1 sampling approach, and rank of concern.

Figure Location	Source	Notes / Rationale	Sampling approach	Rank
1	Transformer in river bed	During a survey of the riverbed for steelhead spawning by Washington Department of Fish and Wildlife in April 2009, a suspected transformer was noted in the mid-channel downstream of Cashmere. Further investigation of the suspected transformer location is necessary at low flow. Walking or paddling the Lower Wenatchee at low flow would address whether the reported transformer is present.	Water and periphyton in the vicinity of the transformer location	High
2	GNR Powerhouse	The initial section of the Great Northern Railway (GNR) within the Wenatchee River Basin ran from Wenatchee, up Tumwater Canyon, over the Cascade Mountains. A dam and powerhouse were constructed, with 3 large turbines and 3, 2000 kW generators. The powerhouse and dam remained in operation until 1956. Further clarification on the location and magnitude of GNR operations in Leavenworth could yield an additional potential PCB source.	Water and periphyton in the vicinity of the site	High
3	Leavenworth Fish Hatchery (LFH)	The LFH has conducted previous investigations into PCBs in paint on the rearing tanks (raceways), in the fish food, Chinook salmon fry and pre-smolts, and the sediments within Icicle Creek and an on-site retention pond. PCBs were detected on-site, but not in the Icicle Creek sediments. Further investigation of the receiving environment seems warranted.	Water and periphyton in the vicinity of the site	High
4	POTWs on the Wenatchee River	POTWs and stormwater effluent have been observed to be a dominant source of PCBs in the Spokane River. There is not a large industrial presence in the towns along the Wenatchee River. Sources of PCBs in an urban environment are old transformers and capacitors, inks (e.g., paper recycling facilities), and sealants and caulking in buildings and piping.	Initial river survey of water. Possible follow-up of water at the point of discharge to the Wenatchee River	Medium
4	Stormwater discharging to the Wenatchee River			Medium
5	Contaminated Sites	Washington State Department of Ecology maintains the Integrated Site Information System (ISIS) which the Toxics Cleanup Program uses to prioritize and track the remediation of contaminated sites. Searching this database for sites along the Wenatchee River returned a number of locations with possible or confirmed PCB contamination. Currently all but 2 sites do not require further action. The remaining 2 sites are old, small landfills which do not appear to pose a significant risk.	Initial river survey of water	Low

Figure Location	Source	Notes / Rationale	Sampling approach	Rank
N/A	Irrigation returns	PCBs are not a suspected contaminant in the application of pesticides or insecticides on agricultural land. However, the irrigation returns which drain these lands and discharge to the Wenatchee River can act as conduits for various pollutants that may be associated with historical practices, dumpsites, or atmospheric deposition. No major agricultural drains discharge to the Wenatchee River, but some minor irrigation returns may.	Initial river survey of water	Low
N/A	Atmospheric deposition	Cold trapping or cold condensation of PCBs suggests that greater amounts of PCBs are deposited at higher elevations compared with the Lower Wenatchee Valley. The PCBs deposited from atmospheric deposition are likely to also have a different congener pattern. It is more likely that the deposition of atmospheric PCBs emanating from the Puget Sound region takes place on the western side of the Cascades.	Initial river survey of water to test whether PCB congeners are indicative of atmospheric deposition	Low
N/A	Returning salmon	Returning hatchery Chinook salmon (*Oncorhynchus tshawytscha*) are the most abundant anadromous fish in the Wenatchee River. A PCB burden in each returning salmon could be transferred to the Wenatchee River food web when the salmon dies and decays. This does not appear to be a significant PCB source.	Initial river survey of water to assess whether spawning areas suggest this is significant	Low

Table 3. DDT sources, location, Phase 1 sampling approach, and rank of concern.

Figure Location	Source	Notes / Rationale	Sampling approach	Rank
Lower Panel	Mission Creek sub-basin	The Mission Creek sub-basin has a 303(d) listing for 4,4'-DDD, 4,4'DDE, and 4,4'DDT. This sub-basin is suspected of being the major source of DDT to the Lower Wenatchee River.	Place SPMD above and below the confluence of Mission Creek and the Wenatchee River.	High
N/A	Irrigation returns	The main pathway for DDT to enter waterways from agricultural soils is through storm and irrigation runoff. Many minor irrigation returns were identified during a previous nutrient TMDL on the Lower Wenatchee River (Carroll et al., 2006).	Assess major inputs through initial synoptic survey.	High
N/A	Stormwater discharges	Stormwater discharges from fruit packaging plants and orchard facilities to irrigation returns or ditches can contain residue pesticides. These discharge points will need identifying in the Lower Wenatchee River.	Assess major inputs through initial synoptic survey.	Medium
N/A	Wastewater treatment facilities	Wastewater treatment plants can receive discharge waters from agricultural facilities. Possible WWTP discharges exist in Leavenworth, Peshastin, Dryden, Cashmere, and Wenatchee.	Assess major inputs through initial synoptic survey.	Medium
5	Contaminated Sites	There are two known historic landfill sites adjacent to the Wenatchee River (Cashmere and Dryden). Ecology does not consider these a concern. Further unidentified dump sites may be present along the Lower Wenatchee.	Assess major inputs through initial synoptic survey.	Medium

Table 4. Registered PCB contaminated sites in the vicinity of the Wenatchee River. Includes suspected, confirmed, and remediated sites.

Site	City	Latitude	Longitude	Activity	Cleanup site ID	FS ID	Notes - Ecology status
*Chelan County PUD Worthen St Substation	Wenatchee	47.43124	-120.31369	Remediated; below cleanup level	3182	21729	No further action required
*Lincoln Park Landfill	Wenatchee	47.40442	-120.30299	Federal site inspection completed in 1987	4755	339	No further action required
*Dovex Fruit Olds Station 1 and 2	Wenatchee	47.46798	-120.3229	Independent report on halogenated organics	998	5785963	No further action required
*Home Depot Wenatchee	Wenatchee	47.45301	-120.33642	Independent report on soils in burn pit	267	3768681	No further action required
Cashmere Landfill	Cashmere	47.52417	-120.46783	Contaminants listed as halogenated and conventional organics, and pesticides	4710	335	Unknown; Cleanup started; currently has a park on it
Filion Landfill	Cashmere	47.52662	-120.46264	Inert demo site; suspected conventional organics in soils	11540	8454524	Unknown; Construction complete; low risk
Dryden Landfill	Dryden	47.54596	-120.57167	Decommissioned 1987; EPA recommends no further action; no PCBs found in groundwater	4084	336	Cleanup complete

Note: the term *halogenated organics* was a broad term used before PCBs were defined in the ISIS database.
* The facility is located in the City of Wenatchee, which could discharge storm and wastewater to the Columbia River.

Table 5. Publicly Owned Treatment Works facilities or industrial discharges to POTWs in the Wenatchee River Basin.

Facility	Permit #	Permit type	Location	City	Discharge
Peshastin POTW	WA0052175	Municipal NPDES IP	10395 Mill Rd	Peshastin	Wenatchee River
Lake Wenatchee POTW	WA0052094	Municipal NPDES IP	21251 State Hwy 209	Leavenworth	Wenatchee River
Leavenworth POTW	WA0020974	Municipal NPDES IP	1402 Commercial St	Leavenworth	Wenatchee River
Wenatchee POTW	WA0023949	Municipal NPDES IP	201 N Worthen St	Wenatchee	Columbia River
Cashmere POTW	WA0023183	Municipal NPDES IP	Riverfront Dr	Cashmere	Wenatchee River
Stevens Pass Sewer District	WA0029521	Municipal NPDES IP	Yodelin Place 2 Mi E Stevens Pass	Leavenworth	Nason Creek
Wenatchee City	WAR046011	Municipal SW Phase II Eastern WA GP	129 S Chelan St	Wenatchee	Columbia River
Chelan County Public Works Wenatchee	WAR046002	Municipal SW Phase II Eastern WA GP	350 Orondo Ave	Wenatchee	Columbia River
Dryden POTW	ST0005562	Municipal to ground SWDP IP	Drainfield 600 ft N of Dryden	Dryden	To Ground
Chateau Faire Le Pont Winery	ST0009264	Industrial (IU) to POTW/PRIVATE SWDP IP	1 Vinyard Way	Wenatchee	Wenatchee POTW
Pacific Aerospace & Electronics	ST0009231	Industrial (IU) to POTW/PRIVATE SWDP IP	434 Olds Station Rd	Wenatchee	Wenatchee POTW
Crunch Pak LLC	ST0009237	Industrial (IU) to POTW/PRIVATE SWDP IP	300 Sunset Hwy	Cashmere	Cashmere POTW
Tree Top Inc Cashmere	ST0009187	Industrial (IU) to POTW/PRIVATE SWDP IP	200 Titchenal Way	Cashmere	Cashmere POTW
Leavenworth Water Treatment Plant	WAG645001	Water Treatment Plant GP	Icicle Rd	Leavenworth	Icicle Creek

Table 6. Total PCB and DDT concentrations in fish tissue for the Wenatchee River Basin.

Sample site	Species	Sample year	Total PCB aroclors (ug/kg)	Total DDT	Lipid (%)	Mean total length (mm)	Mean weight (g)	Mean age (years)	Reference
Mountain Whitefish (*Prosopium williamsoni*)									
Columbia R, blw Rocky Reach Dam	MWF	2004	36	112	3	279	187	2	Seiders et al., 2007
Columbia R, blw Wanapum Dam	MWF	2004	54	406	7	355	472	3	Seiders et al., 2007
Columbia R, blw Wells Dam	MWF	2004	71	430	4	353	454	4	Seiders et al., 2007
Wenatchee river (45A070)	MWF	1984	46	1221	7	unk	unk	unk	Hopkins, 1985
Wenatchee R nr Hwy 2/97 Br	MWF	2003	302	273	4	297	226	3	Era-Miller, 2004
Wenatchee R nr Hwy 2/97 Br	MWF	2003	267	74	3	254	139	2	Era-Miller, 2004
Wenatchee R, nr Wenatchee	MWF	2004	542	378	4	297	226	3	Seiders et al., 2007
Wenatchee R nr Monitor Br	MWF	2010	1700	174	4	386	575	8	Seiders et al., 2012
Wenatchee R nr Monitor Br	MWF	2010	690	59	4	341	336	3	Seiders et al., 2012
Wenatchee R nr Peshastin	MWF	2003	331	54	4	312	271	4	Era-Miller, 2004
Wenatchee R nr Peshastin	MWF	2010	79	74	3	309	282	4	Seiders et al., 2012
Wenatchee R nr Peshastin	MWF	2010	19	34	2	260	155	2	Seiders et al., 2012
Wenatchee R nr Leavenworth - Bbird Is	MWF	2003	43	39	4	375	473	7	Era-Miller, 2004
Wenatchee R nr Leavenworth - Golf#11	MWF	2003	787	63	4	391	645	9	Era-Miller, 2004
Wenatchee R nr Leavenworth - Golf#11	MWF	2003	792	51	4	391	645	9	Era-Miller, 2004
Wenatchee R, nr Leavenworth	MWF	2004	1300	43	3	271	182	2	Era-Miller, 2004
Wenatchee R nr Leavenworth -Bbird Is	MWF	2004	1289	57	3	271	182	2	Seiders et al., 2007
Icicle Cr	MWF	2003	35	32	4	373	505	6	Era-Miller, 2004
Icicle Cr	MWF	2003	34	39	4	373	505	6	Era-Miller, 2004
Icicle Cr	MWF	2010	42	51	4	410	612	9	Seiders et al., 2012
Icicle Cr	MWF	2010	109	64	4	369	429	5	Seiders et al., 2012
Icicle Cr	MWF	2010	41	42	3	333	321	3	Seiders et al., 2012
Nason Cr	MWF	2010	6	5	3	387	621	10	Seiders et al., 2012
Nason Cr	MWF	2010	13	7	4	334	407	6	Seiders et al., 2012
Nason Cr	MWF	2010	2	6	4	277	187	3	Seiders et al., 2012

Sample site	Species	Sample year	Total PCB aroclors (ug/kg)	Total DDT	Lipid (%)	Mean total length (mm)	Mean weight (g)	Mean age (years)	Reference
Suckers									
Wenatchee River (45A070)	BLS	1984	41		0	unk	unk	unk	Hopkins, 1985
Wenatchee R, nr mouth	LSS	1993	450		unk	unk	unk	unk	Davis et al., 1993
Wenatchee R, nr mouth	LSS	1993	468		unk	unk	unk	unk	Davis et al., 1993
Wenatchee R, nr mouth	LSS	1993	104		unk	unk	unk	unk	Davis et al., 1993
Wenatchee R, nr mouth	LSS	2003	142	61	1	unk	unk	15	Era-Miller, 2004
Wenatchee R, nr mouth	LSS	2003	405	163	2	unk	unk	15	Era-Miller, 2004
Fish Lake	LSS	2008	4		3	409	804	8	Johnson et al., 2010
Fish Lake	LSS	2008	2		2	370	571	6	Johnson et al., 2010
Other salmonids and Northern Pikeminnow									
Mission Cr. nr Mouth	RBT	1993	<MRL		unk	unk	unk	unk	Davis et al., 1993
Icicle Creek51	CHI	1997	17		unk	unk	unk	unk	EPA, 2002
Icicle Creek51	CHI	1997	19		unk	unk	unk	unk	EPA, 2002
Icicle Creek51	CHI	1997	19		unk	unk	unk	unk	EPA, 2002
Icicle Creek51	CHI	1997	13		unk	unk	unk	unk	EPA, 2002
Icicle Creek51	CHI	1997	16		unk	unk	unk	unk	EPA, 2002
Icicle Creek51	CHI	1997	17		unk	unk	unk	unk	EPA, 2002
Fish Lake	LMB	2008	25		2	425	1371	7	Johnson et al., 2010
Fish Lake	NPM	2008	38		3	404	620	7	Johnson et al., 2010
Fish Lake	RBT	2008	5		0	313	241	1	Johnson et al., 2010
Fish Lake	BNT	2008	88		7	487	1430	4	Johnson et al., 2010
Lake Wenatchee	CTT	2010	2	3	1	271	190	2	Seiders et al., 2012
Lake Wenatchee	NPM	2010	8	9	3	394	607	12	Seiders et al., 2012

MWF = mountain whitefish; BLS = bridgelip sucker; LSS = largescale sucker; RBT = rainbow trout; CHI = Chinook salmon; LMB = largemouth bass; NPM = northern pikeminnow; BNT = brown trout; CTT = cutthroat trout

Table 7. Results from 2005 sediment and juvenile salmon samples at Leavenworth National Fish Hatchery.

Mean concentrations in µg Kg^{-1} (ppb).

	Chinook Fry		Pre-smolt	Sediment Samples		
	fiberglass raceways	painted raceways		upstream of LFH	downstream of LFH	settling pond
Total PCB	17.6	20	31.7	5.16	5.38	69.3
Aroclor 1242	<1.05	<1.22	2.04	<0.42	<0.38	5.3
Aroclor 1248	<1.05	2.13	4.67	<0.42	<0.38	<1.1
Aroclor 1254	<1.05	2.72	8.62	<0.42	<0.38	<1.1
Aroclor 1260	<1.05	3.91	1.94	<0.42	<0.38	25.9
Aroclor 1268	<1.05	<1.22	<0.51	<0.42	<0.38	<1.1

Table 8. Current 303(d) listings for PCB and DDT impacted reaches in the Wenatchee river

Icicle Creek	Yaksum - Brender - Mission Creek	Wenatchee River	Columbia River
PCB[a]	4,4'-DDD[b]	4,4'-DDE[a]	4,4'-DDE[a]
	4,4'-DDE[a,b]	PCB[a]	PCB[a]
	4,4'-DDT[a,b]		

Note: Yaksum-Brender-Mission Creeks are listed as 4A

[a] fish tissue

[b] water

Table 9. Washington State water and sediment criteria for the protection of human health and aquatic life for DDT and PCBs.

Calculated risk-based fish tissue criteria based on water quality criteria.

Parameter	Aquatic life (ng L^{-1})†		Human health		Parameter	Freshwater sediment (µg Kg-1 dry weight) ‖	
	Freshwater chronic	Freshwater acute	Water and fish consumption (ng L^{-1})‡	Edible fish tissue (µg Kg^{-1})		Sediment cleanup objective	Sediment screening level
t-PCBs	14	2000	0.17	5.3	t-PCBs	110	2500
4, 4' DDE	1	1100	0.59	32	t-DDE	310	860
4,4' DDD	1	1100	0.83	45	t-DDD	21	33
4,4' DDT	1	1100	0.59	32			
t-DDT	1	1100			t-DDT	100	8100

† WAC 173-201A
‡ EPA National Toxics Rule
‖ WAC 173-204

Table 10. Measurement Quality Objectives**.**

Laboratory Analyses of Water Samples*

Parameter	Verification Standards (LCS,CRM,CCV)	Duplicate Samples	Matrix Spikes	Matrix Spike-Duplicates	Surrogate Standards	Lowest Concentrations of Interest
	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Relative Percent Difference (RPD)	% Recovery Limits	Units of Concentration
Water samples						
TSS	80-120%	± 20%	NA	± 20%	NA	1 mg L^{-1}
Turbidity	80-120%	± 20%	NA	± 20%	NA	0.5 NTU
Conductivity	80-120%	± 20%	NA	± 20%	NA	1 µmhos cm^{-1}
Total Organic Carbon	80-120%	± 20%	75-125%	± 20%	NA	1 mg L^{-1}
SPMD						
PCB congeners	50-150%	± 20%	50-150%	± 20%	50-150%	50 pg per sample
t-DDT	50-150%	± 20%	50-150%	± 20%	50-150%	2 ng per sample
Tissue (periphyton)						
PCB congeners	50-150%	± 40%	NA	± 20%	50-150%	4 pg g^{-1}
lipids	75-125%	± 20%	NA	± 20%	NA	0.10%
ash-free dry weight	NA	± 20%	NA	± 20%	NA	1.00%

Table 11. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Lynda Jamison, WQP Central Regional Office Phone: 509 575-2434	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Chris Coffin, WQP Central Regional Office Phone: 509-575-2821	Unit Supervisor	Provides internal review of the QAPP and approves the final QAPP.
Charlie McKinney, WQP Phone: 509-457-7107	Client's Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
William Hobbs, EAP Toxic Studies Unit SCS Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the lab. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Michael Friese, EAP Toxic Studies Unit SCS Phone: 360-407-6765	Field Assistant	Helps collect samples and records field information.
Dale Norton, EAP Toxic Studies Unit SCS Phone: 360-407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Tom Mackie, EAP Central Regional Office Phone: 509-454-4244	Section Manager for the Study Area	Provides internal review of the QAPP and approves the final QAPP.
Will Kendra, EAP SCS Phone: 360-407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird, EAP MEL Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
Georgina Brooks, AXYS Analytical Services Ltd.	Project Manager	Coordinates with MEL QA Coordinator
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
WQP: Water Quality Program
SCS: Statewide Coordination Section

Table 12. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Phase 1 Field work completed	October 2014	William Hobbs
Phase 1 Laboratory analyses completed	January 2015	
Phase 2 Field work completed	October 2015	William Hobbs
Phase 2 Laboratory analyses completed	January 2016	
Environmental Information System (EIM) database		
EIM Study ID	WHOB002	
Product	Due date	Lead staff
EIM data loaded	February 2016	Melissa McCall
EIM data entry review	March 2016	William Hobbs
EIM complete	June 2016	Melissa McCall
Reporting		
Author lead / Support staff	William Hobbs / Michael Friese and Lynda Jamison	
Schedule		
Draft QAPP Addendum for Phase 2	February 2015	
QAPP Addendum approved	March 2015	
Draft final report to supervisor	March 2016	
Draft final report to client/peer reviewer	April 2016	
Draft final report to external reviewer(s)	May 2016	
Final (all reviews done) due to publications coordinator	June 2016	
Final report due on web	July 2016	

Table 13. Laboratory cost estimate for Wenatchee PCB and DDT source assessment.

Analysis	Matrix	Number of sites	Number of QA samples	Cost per sample	Contract Lab subtotal	MEL subtotal
Initial survey						
TSS	water	27	3	$12		$360
TOC	water	27	3	$36		$1,080
DOC	water	27	3	$40		$1,200
PCB congeners	SPMD extract	9	5	$775	$10,850	
DDT	SPMD extract	9	5	$500	$7,000	
PCB congeners	periphyton	9	1	$775	$7,750	
lipids	periphyton	9	1	$33		$330
ash-free dry weight	periphyton	9	1	$25		$250
				Lab subtotal	$25,600	$3,220
SPMD: semi-permeable membrane device				MEL contracting		$6,400
					Phase 1 Lab total	$35,220

Table 14. Proposed sample sites for the synoptic survey.

Sample site	River mile	Latitude	Longitude	Description	Rationale
45WHR8.8	6.4	47.874	-120.871	White River at the ECY gauging station 45K090	background from a major headwater tributary (atmospheric deposition)
45WR53.5	53.5	47.8098	-120.7154	Wenatchee River below Lake Wenatchee Bridge; nr ECY gauging station 45A240	downstream of Nason Creek confluence and Wenatchee Lake
45WR36.0	36	47.680664	-120.72891	Wenatchee River nr ECY gauging station 45G060	upstream of former GNR Power plant
45IC02.2	2.2	47.564	-120.668	Icicle Creek nr USGS gauging station 12458000	upstream of Leavenworth Fish Hatchery
45WR25.5	25.5	47.587	-120.708	Wenatchee River downstream of former GNR Power plant	downstream of GNR Power plant
45WR22.8	22.8	47.594343	-120.63813	Wenatchee River near irrigation pipeline crossing	downstream of Leavenworth POTWs and stormwater; upstream of Dryden landfill
45WR13.7	13.7	47.5326	-120.53273	Wenatchee River nr Dryden	downstream of Dryden Landfill; upstream of Cashmere (reported sighting of transformer)
45WR07.0	7	47.49953	-120.42411	Wenatchee River nr USGS gauging station 12462500	downstream of Cashmere Landfill and reported sighting of transformer
45WR0.1.1	1.1	47.458651	-120.33616	Wenatchee River near Hwy 2 and confluence with Columbia River	near confluence with the Columbia River

Table 15. Sample containers, preservation, and holding times.

Parameter	Matrix	Minimum Quantity Required	Container	Preservative	Holding Time
Initial Survey					
PCB congeners and t-DDT	SPMD	N/A	sealed transport can	under Ar gas	1 month
PCB congeners and t-DDT	SPMD extract	N/A	sealed ampoule following dialysis	N/A	1 month
PCB congeners	periphyton	10 g w/w	8 oz. glass jar w/ teflon lid	cool to 4°C	14 days
% lipids	periphyton	2 g w/w	2 oz. clear glass jar w/ closed teflon lid	cool to 4°C	14 days
ash-free dry weight	periphyton	2 g w/w	2 oz. clear glass jar w/ closed teflon lid	cool to 4°C	14 days
TSS	water	1 L	1 L poly bottle	cool to 4°C	7 days
TOC	water	20 mL	1 pre-acidified 125 ml bottle	cool to 4°C	28 days
Turbidity	water	100 ml	500 ml ploy bottle	cool to 4°C	48 hours

Table 16. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results	Reporting Limit	Sample Prep Method	Analytical (Instrumental) Method
PCBs Congeners	periphyton	11	unknown	4 pg g-1 w/w per congener	EPA 1668C	EPA 1668C
lipids	periphyton	11	0.5 - 2.0 %	0.10%	N/A	MEL SOP 730009[†]
ash-free dry mass	periphyton	11	60-90%	1.0 %	N/A	PSEP, 1986[¥]
PCBs Congeners	SPMD extract	14	100 - 200 ng (t-PCBs)	0.5 pg per congener	dialysis; EPA 1668C	EPA 1668C
t-DDT	SPMD extract	14	100 - 200 ng (t-DDT)	0.2 ng	dialysis; EPA 1699	EPA 1699
TSS	surface water	40	5 - 200 mg L^{-1}	1 mg L^{-1}	N/A	EPA 160.2
Turbidity	surface water	25	2 - 100 NTU	0.5 NTU	N/A	EPA 180.1
TOC	surface water	30	2 - 20 mg L^{-1}	1 mg L^{-1}	N/A	SM 5310B

Table 17. QC samples, types, and frequency.

Parameter	Matrix	Field		Laboratory		
		Blanks	Replicates	Check Standards	Method Blanks	Matrix Spikes
Initial survey						
PCB Congeners and DDT	SPMD extract	1	1	1/batch	1/batch	All samples
PCB Congeners	periphyton	N/A	1	1/batch	1/batch*	All samples
TSS	water	N/A	1	1/batch	1/batch	N/A
TOC	water	N/A	1	1/batch	1/batch	N/A
turbidity	water	N/A	1	1/batch	1/batch	N/A

* includes a fabrication "Day-0" blank and a membrane blank

Table 18. Detailed summary of the number of SPMD samples and necessary quality control.

Sample Type	Sample Quantity	# of membranes per sample	# total Membranes	Number of membranes to be spiked with PRC solution	Spiking (total # of spike aliquots per item)		# of SPMD Dialyses (extractions)	# of SPMD Analyses
					Extraction Internal Standards (EIS): (spike 1 membrane per sample)	OPR: native congeners (spike 1 membrane)		
Field Sample	10	5	50	50	10	-	5*10 = **50**	10
Dummy Sample	8	5	40	40	8	-	40	-
Field Blank	1	5	5	5	1	-	5	1
SPMD "Day-0" Method Blank	1	5	5	5	1	-	5	1
OPR for PCB congeners and DDT	1	1	1	1	1	1	1	1
Total (Field Samples, Field Blanks + lab QC)	21	1 to 5 per sample	101	101	21	1	101	13
Store one aliquot of PRC solution	1	0	0	1	-	-	-	(1; only if needed)
Store one aliquot of EIS solution	1	0	0	-	1	-	-	(1; only if needed)

PCB: polychlorinated biphenyls.

EIS: PCB and DDT extraction internal standards from EPA Methods 1668C and 1699.

OPR: ongoing performance and recovery/initial precision and recovery native spike of PCBs from EPA Method 1668C, and of DDT by EPA Method 1699; prepared by Successful Bidder.

PRC: Performance Reference Compounds spiking solution prepared by Successful Bidder (SB) and sent to EST prior to deployment.

"Day-0": Fabrication Blank; sometimes called the Day-0 dialysis blank

18.0 Appendices

Appendix A. SPMD Field log

Field Log for SPMD Project:

Site Name: **Date:**

Crew:

Circle type of field action: Deployment Midcheck Retrieval

Perform tasks and record data in boxes below as designated for Deployment, Midcheck, or Retrieval

	v	v	v			
SPMD Field Sample						
Record Field ID, MEL Sample #, Number of SPMD membranes	D					
Depth of water where SPMD deployed	D	M	R			
Depth to shallowest part of SPMD canister	D	M	R			
Canister Tidbit: record long serial #; whether Present or Absent	D		R			
Time of day at deployment, midcheck, or retrieval	D	M	R			
Total time membranes exposed to air (Min:Sec or Sec)	D		R			
Air Tidbit: record long serial #, and whether Present or Absent	D	M	R			
Level of biofouling recorded on other side of this log? (Yes or No)		M	R			
Gently swish canister to remove biofouling (Yes or No)		M	R			
Check Ecology ID tag and whether Present or Absent	D	M	R			

SPMD Field Replicate Sample

Record Field ID, MEL Sample #, Number of SPMD membranes	D					
Depth of water where SPMD deployed	D	M	R			
Depth to shallowest part of SPMD canister	D	M	R			
Canister Tidbit: record long serial #; whether Present or Absent	D		R			
Time of day at deployment, midcheck, or retrieval	D	M	R			
Total time membranes exposed to air (Min:Sec or Sec)	D		R			
Air Tidbit: record long serial #, and whether Present or Absent	D	M	R			
Level of biofouling recorded on other side of this log? (Yes or No)		M	R			
Gently swish canister to remove biofouling (Yes or No)		M	R			
Check Ecology ID tag and whether Present or Absent	D	M	R			

SPMD Field Blank

Record Field ID, MEL Sample #, Number of SPMD membranes	D		R			
Time of day of exposure	D		R			
Total time membranes exposed to air	D		R			

Water Samples

Record Field ID and MEL Sample #	D	M	R		
Time of water samples (TSS, TOC)	D	M	R		
Time of field measurements (temperature, conductivity)	D	M	R		

Water temperature value and UOM	D	M	R	
Conductivity value and UOM	D	M	R	

More Observations to Record on Other Side

Field Log continued:

Site Name: **Date:**

Observations to Record for All Field Visits: circle or underline the best descriptors in each category, fill in blanks where located.

Weather:

Clouds: % cover _____; Thickness: thick, moderate, thin; Height: high, middle, low

Precipitation: dry, mist, drizzle, rain, downpour

Wind: calm (0-5 mph), light (5-10 mph), moderate (10-15 mph), windy (15-20 mph), high (>20 mph)

Air temperature _____.

Water Velocity at SPMDs:

Still: < 0.1 fps. Slow: 0.1 - 0.5 fps. Moderate: 0.5 - 2.0 fps. Fast: >2.0 fps.

Biofouling on SPMD Canister: % of holes blocked on canister.

Field Sample: Low: 0% - 20%. Medium: 20% - 60%. High: 60% - 100%.

Field Replicate: Low: 0% - 20%. Medium: 20% - 60%. High: 60% - 100%.

Turbidity - Water Clarity at SPMDs:

Clear: little to no cloudiness, visibility > 3'

Cloudy: low turbidity, visibility 1' - 3'

Muddy: moderate turbidity, visibility 1" - 1'

Opaque: highly turbid, visibility < 1"

Turbulence of Surface of Water:

Calm: little or no waves (<3"), water movement smooth and fairly steady

Choppy: some waves (3"-9"), mostly not splashing, generally won't loosen small rocks

Moderate: many waves (9" - 18"), rolling or splashing water, capable of loosening small rocks and carrying small debris

Rough: turbulent, splashing, large waves (>18"), capable of loosening large rocks and carrying large debris

Water level:

Low: defined by little/no land vegetation because normally underwater, dried aquatic plants or algae on exposed surfaces

Medium: land vegetation above water level, some shoreline, aquatic vegetation submerged as should be

High: inundation of a normally dry area (flooding), some land vegetation underwater, waterbody may be changing course

Other:

Latitude:_____ Longitude: _____

Source and datum for coordinates above: _____

Photo of Air Tidbit? Circle: Yes or No.

Other photos? (e.g., unusual water level, observations, etc.) comment:

Other notes or observations: (e.g., unusual deployment location, method):

Appendix B. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Effluent: An outflowing of water from a natural body of water or from a man-made structure. For example, the treated outflow from a wastewater treatment plant.

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.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites that clear more than 5 acres of land.

Salmonid: Fish that belong to the family *Salmonidae*. Any species of salmon, trout, or char.

Sediment: Soil and organic matter that is covered with water (for example, river or lake bottom).

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Synoptic survey: Data collected simultaneously or over a short period of time.

Total Maximum Daily Load (TMDL): A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of

safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): Portion of solids retained by a filter.

Turbidity: A measure of water clarity. High levels of turbidity can have a negative impact on aquatic life.

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, requiring 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

DDT	dichloro-diphenyl-trichloroethane
DOC	dissolved organic carbon
Ecology	Washington State Department of Ecology
e.g.	For example
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)PBDE polybrominated diphenyl ethers
PBT	persistent, bioaccumulative, and toxic substance
PCB	polychlorinated biphenyls
QA	Quality assurance
RM	River mile
RPD	Relative percent difference
SOP	Standard operating procedures
TMDL	(See Glossary above)
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	United States Geological Survey
WAC	Washington Administrative Code

WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resource Inventory Area
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
K_{oc}	octanol-water partition coefficient
K_{WA}	water-air partition coefficient
ng/L	nanograms per liter (parts per trillion)
NTU	nephelometric turbidity units
pg/g	picograms per gram (parts per trillion)
pg/L	picograms per liter (parts per quadrillion)
ug/Kg	micrograms per kilogram (parts per billion)
ug/L	micrograms per liter (parts per billion)
µm	micrometer
umhos/cm	micromhos per centimeter
uS/cm	microsiemens per centimeter, a unit of conductivity
ww	wet weight

Quality Assurance Glossary

Accreditation: A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

Accuracy: The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms precision and bias be used to convey the information associated with the term accuracy. (USGS, 1998)

Analyte: An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella. (Kammin, 2010)

Bias: The difference between the population mean and the true value. Bias usually describes a systematic difference reproducible over time, and is characteristic of both the measurement system, and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI). (Kammin, 2010; Ecology, 2004)

Blank: A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process. (USGS, 1998)

Calibration: The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured. (Ecology, 2004)

Check standard: A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards, but should be referred to by their actual designator, e.g., CRM, LCS. (Kammin, 2010; Ecology, 2004)

Comparability: The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator. (USEPA, 1997)

Completeness: The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator. (USEPA, 1997)

Continuing Calibration Verification Standard (CCV): A QC sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run. (Kammin, 2010)

Control chart: A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system. (Kammin, 2010; Ecology 2004)

Control limits: Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean. (Kammin, 2010)

Data Integrity: A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading. (Kammin, 2010)

Data Quality Indicators (DQI): Data Quality Indicators (DQIs) are commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity. (USEPA, 2006)

Data Quality Objectives (DQO): Data Quality Objectives are qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. (USEPA, 2006)

Data set: A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010)

Data validation: An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment, and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier, data is usable for intended purposes.
- J (or a J variant), data is estimated, may be usable, may be biased high or low.
- REJ, data is rejected, cannot be used for intended purposes (Kammin, 2010; Ecology, 2004).

Data verification: Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set. (Ecology, 2004)

Detection limit (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero. (Ecology, 2004)

Duplicate samples: Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis. (USEPA, 1997)

Field blank: A blank used to obtain information on contamination introduced during sample collection, storage, and transport. (Ecology, 2004)

Initial Calibration Verification Standard (ICV): A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples. (Kammin, 2010)

Laboratory Control Sample (LCS): A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

Matrix spike: A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects. (Ecology, 2004)

Measurement Quality Objectives (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness. (USEPA, 2006)

Measurement result: A value obtained by performing the procedure described in a method. (Ecology, 2004)

Method: A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed. (USEPA, 1997)

Method blank: A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples. (Ecology, 2004; Kammin, 2010)

Method Detection Limit (MDL): This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of

an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero. (Federal Register, October 26, 1984)

Percent Relative Standard Deviation (%RSD): A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010)

Parameter: A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all "parameters." (Kammin, 2010; Ecology, 2004)

Population: The hypothetical set of all possible observations of the type being investigated. (Ecology, 2004)

Precision: The extent of random variability among replicate measurements of the same property; a data quality indicator. (USGS, 1998)

Quality Assurance (QA): A set of activities designed to establish and document the reliability and usability of measurement data. (Kammin, 2010)

Quality Assurance Project Plan (QAPP): A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives. (Kammin, 2010; Ecology, 2004)

Quality Control (QC): The routine application of measurement and statistical procedures to assess the accuracy of measurement data. (Ecology, 2004)

Relative Percent Difference (RPD): RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

Replicate samples: Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled. (USGS, 1998)

Representativeness: The degree to which a sample reflects the population from which it is taken; a data quality indicator. (USGS, 1998)

Sample (field): A portion of a population (environmental entity) that is measured and assumed to represent the entire population. (USGS, 1998)

Sample (statistical): A finite part or subset of a statistical population. (USEPA, 1997)

Sensitivity: In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit. (Ecology, 2004)

Spiked blank: A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method. (USEPA, 1997)

Spiked sample: A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency. (USEPA, 1997)

Split Sample: The term split sample denotes when a discrete sample is further subdivided into portions, usually duplicates. (Kammin, 2010)

Standard Operating Procedure (SOP): A document which describes in detail a reproducible and repeatable organized activity. (Kammin, 2010)

Surrogate: For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis. (Kammin, 2010)

Systematic planning: A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning. (USEPA, 2006)

References for QA Glossary

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