DEPARTMENT OF
ECOLOGY
State of Washington

Addendum to
Quality Assurance Project Plan

Wenatchee River
PCB and DDT
Source Assessment

April 2015

Publication No. 15-03-107

Publication Information

Addendum

This addendum is on the Department of Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/1503107.html

This addendum is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID WHOB002.

Activity Tracker code

Ecology's Activity Tracker code for this addendum is 14-040.

Original Publication

Quality Assurance Project Plan: Wenatchee River PCB and DDT Source Assessment

Publication No. 14-03-117
https://fortress.wa.gov/ecy/publications/SummaryPages/1403117.html

Authors and Contact Information

William Hobbs
Environmental Assessment Program
Washington State Department of Ecology
Olympia, Washington 98504-7710

For more information contact: Communications Consultant, phone 360-407-6834.

Addendum to Quality Assurance Project Plan

Wenatchee River PCB and DDT Source Assessment

April 2015

Approved by:

Signature:	Date: April 2015
Lynda Jamison, Client, Water Quality Program, Central Regional Office	
Signature:	Date: April 2015
Chris Coffin, Client's Unit Supervisor, Water Quality Program, Central Regional Office	
Signature:	Date: April 2015
Charlie McKinney, Client's Section Manager, Water Quality Program, Central Regional Office	
Signature:	Date: April 2015
William Hobbs, Author / Project Manager, EAP	
Signature:	Date: April 2015
Dale Norton, Author's Unit Supervisor, EAP	
Signature:	Date: April 2015
Tom Mackie, Section Manager for the Study Area, EAP	
Signature:	Date: April 2015
Will Kendra, Author's Section Manager, EAP	
Signature:	Date: April 2015
Joel Bird, Director, Manchester Environmental Laboratory	
Signature:	Date: April 2015
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

1.0 Table of Contents

List of Figures and Tables

Page

Figures

Tables

2.0 Abstract

No changes.

3.0 Background

The Quality Assurance Project Plan (QAPP) for the Wenatchee River PCB and DDT Source Assessment was written to allow the project to be carried out in two phases (Hobbs, 2014). Phase 1 of the project (the initial synoptic survey) focused 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 were collected using SPMDs, and periphyton were collected at the same sample site. Phase 1 allowed us to assess the spatial distribution of PCBs and total DDT (t-DDT; DDT, DDD, and DDE) within the Wenatchee River Basin. Results of the Phase 1 sampling are detailed in *Section 7.5*. The second phase of the project is described within this addendum.

4.0 Project Description

4.2 Project objectives

The specific objectives of Phase 2 (the detailed sampling) of this study are to identify and characterize sources of PCBs and t-DDT to the Wenatchee River, based on the results of the synoptic survey in Phase 1 of the project.

Detailed sampling will take place over two sample events (high and low flow) and include samples of water, sediment, periphyton, and macroinvertebrates. Water samples will be collected using a submersible pump (continuous low-level aquatic monitoring device; CLAM). The switch from SPMDs to the CLAM is driven by the CLAM's lower cost and knowledge of PCB and t-DDT concentrations from the initial survey. In Phase 2 we will assess how contaminants are moving and where they are accumulating within the food web.

4.7 Practical constraints

The main constraint affecting the success of the Phase 2 sampling program is our ability to sample adequate sediment mass and reliably measure the total volume of water sampled by the CLAM. The Wenatchee River has very suspended sediment concentrations and little sediment accumulation for most of the mainstem. Many of our samples will be taken in tributaries that accumulate sediments to a larger degree. Sediment sampling will help the spatial assessment of PCBs and t-DDT and will reveal whether sediments influence the movement of PCBs and t-DDT into the food web. We will employ additional sediment samplers (e.g., the Johnson trap) as a measure of redundancy.

The measurement of water pumped through and sampled by the CLAM will be quantified at each site, with the use of a new optical sensor from the manufacturer. This device has proven accurate (within 1%) in the lab and in preliminary field trials. It deserves mention as a practical constraint because it has not been tested in a true field deployment.

5.0 Organization and Schedule

5.4 Project schedule

The overall project timeline is detailed in Table 1.

5.6 Budget and funding

Phase 2 laboratory analysis will be completed by January 2016. The estimated analytical budget for Phase 2 of this project will total $87,226 (Table 2), which includes estimated laboratory costs and review of QA/QC.

6.0 Quality Objectives

6.1 Decision Quality Objectives (DQOs)

There are no specific decision quality objectives for this project.

6.2 Measurement Quality Objectives

A complete summary of measurement quality objectives (MQOs) for this project is detailed in Table 3. 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 bias. Duplicates and matrix spikes help to evaluate any effects of sample matrix on the data quality. Blanks aid in determining interferences and bias for low concentrations near analytical detection limits.

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 CLAM samplers is ± 20% and generally ± 40% for solids that 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.

6.2.1.2 Bias

The bias of the lab instruments will be assessed by MEL and the contract lab through lab blanks and recovery of LCS and matrix spikes. The expected bias for the high-resolution analysis of PCBs and t-DDT is 50-150% recovery of matrix spikes (Table 3).

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

Laboratory CLAM blanks on sample media and materials will also be carried out. Raw solid-phase extraction (SPE) media and three assembled SPE disks will be analyzed to quantify the background manufacturing contamination.

6.2.1.3 Sensitivity

The expected lowest concentration of interest for each parameter is detailed in Table 3. 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 (SOPs) will be followed:

- Standard Operating Procedures for the Collection of Periphyton Samples for TMDL studies (Mathieu et al., 2013).
- Standard Operating Procedures and Minimum Requirements for the Collection of Freshwater Benthic Macroinvertebrate data in Wadeable Streams and Rivers (Adams, 2010).
- Standard Operating Procedure for Obtaining Freshwater Sediment Samples (Blakley, 2008).
- Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment (Friese, 2014).

There is no approved SOP for the CLAM device. A detailed overview of the sampler is found in Appendix A.

6.2.2.2 Representativeness

Sampling will take place during a high-flow period (May) and a low-flow period (September). We anticipate that the river at higher flow will have a higher sediment load, calculated as total suspended sediment (TSS). We will assess the PCB load under these conditions. Based on previous work in the Wenatchee River and Mission Creek, May is a period when high TSS can

be expected (Serdar and Era-Miller, 2004; Carroll and O'Neal, 2005). This approach will not quantify the partitioning of PCBs in the river, but it will show us spatially where there is potential for accumulation of PCB-laden sediments. In addition, the contribution of t-DDT from tributaries and irrigation returns to the Wenatchee River is likely to be greater during high flow/high TSS conditions.

We will also repeat the timing of the low-flow sampling to be comparable to Phase 1 sampling and to represent baseflow conditions. Periphyton sampling proved an effective media to assess the spatial distribution of contaminants in the Wenatchee River. Phase 2 (detailed sampling) will include further periphyton samples for spatial assessment; they integrate PCBs over a longer period of time than the CLAM does. In addition, we will use periphyton and invertebrates to establish the pathway of PCBs and t-DDT to mountain whitefish.

In order to assess the retention of contaminants in the CLAM –SPE disks, the contract lab will spike labeled congeners and compounds into the disks prior to deployment in the field. This effort is akin to using the performance reference compounds (PRCs) in the SPMDs during the first phase of the project.

6.2.2.3 Completeness

Similar to Phase 1, a minimum of 2 reliable detections of low-level PCBs in the lower reach of the Wenatchee River (Fig. 9) will give a minimum completeness coverage of the basin. We will not be duplicating the field deployment of CLAMs, as we did in Phase 1 sampling. This is because the budget is limited and because the deployment time of only 36 hours decreases the likelihood of vandalism.

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 among 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 t-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 t-DDT within the Wenatchee River Basin. Through biotic and sediment sampling, we can assess how contaminants move and accumulate within the food web of the Wenatchee River and lead to excessive concentrations in fish tissue.

7.1.1 Field measurements

Field observations of river flow, turbidity, and site conditions will be recorded at the time of sampling. Field measurements of pH, conductivity, and temperature will also be taken in concert with sampling at each site.

7.1.2 Sampling location and frequency

The Phase 2 detailed sampling plan will focus on (1) the Lower Wenatchee River, from Dryden downstream and Icicle Creek for PCB sources, and (2) the Lower Wenatchee River, tributaries, and irrigation returns from Leavenworth downstream for t-DDT contributions. Sampling will address concentrations at high and low flow.

Nine CLAM sampling locations will be established to further identify the source of PCBs. Eleven CLAM locations will be used to assess t-DDT levels (Figure 1 and 2; Table 4). The locations of the CLAMs are based on the Phase 1 initial survey that used SPMDs. Sampling will take place in spring (May) and late summer (September) of 2015. CLAM devices will be secured to cement blocks, tethered to the bank with rebar and cable, and immersed at the study site for approximately 36 hours. Ancillary parameters will be measured in grab samples collected at the time of CLAM deployment. All proposed sites have been previously verified through the Phase 1 sampling and the previous TMDL (Carroll and O'Neal, 2005). During the low-flow sampling, sites will be sampled for periphyton, invertebrates, and sediments (Table 4)

Further field activities will include:

- Collecting mountain whitefish to analyze gut contents during the May sampling event. This is to confirm diet prior to the invertebrate sampling and provide data for any bioaccumulation models in the future.
- Surveying the river at low-flow to follow up on the discovery and removal of a transformer from the Wenatchee River near the City of Cashmere.

7.1.3 Parameters to be determined

Media and parameters included in the sampling program are:

- Water (sampled using continuous low-level aquatic monitoring (CLAM) pumps with solid phase extraction disks) – PCBs and DDT.
- Water (collected as grab samples) – total suspended solids (TSS), total organic carbon (TOC), dissolved organic carbon (DOC).
- Suspended sediments (collected using in-stream sediment traps) – PCBs, DDT, grain size, and TOC.
- Periphyton – PCBs, DDT (select samples), lipid content, carbon and nitrogen composition and stable isotope ratios, and ash-free dry weight.
- Macroinvertebrates – PCBs, DDT (select samples), lipid content, carbon and nitrogen composition and stable isotope ratios, and ash-free dry weight.

High resolution gas chromatography/mass spectrometry (HR GC/MS) will be carried out to characterize PCB congener patterns (all 209 congeners will be reported) in media, except the CLAM-SPE disks, for the area of concern and to gain suitably low detection limits. Total-DDT will also be analyzed using HR GC/MS, except for the CLAM-SPE disks. For the CLAM-SPE disks, low resolution (LR) GC/MS will be used to analyze for all 209 PCB congeners and t-DDT. The concentrations measured in Phase 1 of the project are high enough that LR GC/MS will suffice and will save money for the project.

Stable isotope ratios and elemental abundance of carbon (C) and (N) will be added to the suite of analysis on the biotic media. The use of nitrogen stable isotopes ($\delta^{15}N$) in particular has been helpful in previous studies to infer trophic position within the food web at a specific site (McIntyre and Beauchamp, 2007). Trophic position is an important factor in the accumulation of organochlorine and other bioaccumulative compounds. By analyzing the $\delta^{15}N$ and PCB and t-DDT concentrations of biotic tissues in this study, we can show how the contaminants accumulate within the food web of the Wenatchee River.

7.2 Maps or diagram

The findings from Phase 1 of the investigation are shown in Figures 3 through 6. In general, there is a clear pattern for both PCBs and DDT, which will help focus our efforts in Phase 2.

The proposed locations of the CLAM samplers are detailed in Figures 1 and 2, and Table 4. The rationale for the site locations is detailed in Table 4.

7.3 Assumptions underlying design

During the initial basin-wide survey, concentrations of dissolved PCBs and DDT were assessed using SPMDs and periphyton samples. The timing of this event was at low-flow (base flow) when groundwater was likely a significant hydrologic input. We are therefore assuming that the spatial distribution of PCBs and DDT during higher flow would have a similar distribution across the basin. Based on previous sampling using SPMDs, higher concentrations of PCBs prevail during low-flow periods (MacCarthy and Gale, 1999; Sandvik, 2009).

7.4 Relation to objectives and site characteristics

No changes.

7.5 Characteristics of existing data

The Phase 1 initial survey using SPMDs and periphyton showed some distinct spatial trends (Figure 3 and 4). The following observations can be made about PCBs in the Wenatchee River:

- PCB concentrations increase by an order of magnitude at Old Monitor Bridge, downstream of Cashmere (Table 5).

- Minor contamination (based on the periphyton sample) is present in Icicle Creek.
- Concentrations of PCBs bound to attached algae (periphyton) show a very similar trend to SPMDs (Figure 5). Periphyton represents the base of the food web in the Wenatchee River.
- Total suspended sediments and dissolved organic carbon were less than method detection limits during sampling, suggesting that most (~ 95%) of the measured PCBs were in dissolved form.
- PCB congener patterns at the highest measured sites (Table 5; Old Monitor and Confluence) suggest different sources.

The following observations can be made about t-DDT in the Wenatchee River:

- Total-DDT contamination is present from downstream of Leavenworth to the confluence with the Columbia River (Figure 6; Table 5).
- Possible inputs to the mainstem Wenatchee include: Chumstick Creek, Peshastin Creek, Mission Creek (Serdar and Era-Miller, 2004), and irrigation returns.
- Total suspended sediments and dissolved organic carbon were less than method detection limits during sampling, suggesting that most (~ 95%) of the measured t-DDT was in dissolved form.
- Significantly higher (by an order of magnitude) concentrations were measured at the confluence with the Columbia River, where waters are mixed.

8.0 Sampling Procedures

8.1 Field measurement and field sampling SOPs

8.1.1 Water sampling

CLAM samplers are vessels for solid-phase extraction (SPE) disks, which are mainly used in a laboratory setting to concentrate organic contaminants from large volumes of sample (EPA 3535). Similar to SPMDs, they provide a time-integrated sample; however, they are not passive devices. CLAMs contain a small, sealed pump behind the SPE that draws water through the device at a rate of 5-70 ml per minute. The typical period of deployment is 24-36 hours. Biofouling of the device is the primary concern during deployment and therefore sampling during a period of high TSS may reduce the efficacy of the sampler.

There is no established SOP for CLAMs; however, they are being used in a number of studies at Ecology (Coots, 2014; Hobbs, 2014). A more extensive description of the device and limitations can be found in Appendix A. The C-18 SPE media for hydrophobic compounds will be used in this sampling program. The SPE disks are shipped and secured in a high-density polypropylene cartridge. SPE disks will be supplied by CI Agent Storm-Water Solutions, the supplier of the CLAM device. Disks will be shipped directly to the contract laboratory where they can be cleaned and conditioned with solvents prior to use in the field. The SPE media will be spiked

with the same labeled PRC compounds as the SPMDs (PCB-31L, PCB-95L, and PCB 153L), however these compounds are present only to observe retention of PCBs in the field. For capturing organochlorine compounds, the C-18 media SPE will be used.
CLAMs will be secured within the water column by tethering or anchoring to rebar or a cement block and deployed for ~ 36 hours. At retrieval, the SPE disks are removed from the devices and cooled on ice. Disks are shipped for extraction within 14 days. Using the mass of organic compounds analyzed within the SPE and the measured sample volume, an average water concentration over the period of deployment can be calculated.

8.1.2 Biotic media

8.1.2.1 Periphyton

Described in the original QAPP (Hobbs, 2014).

8.1.2.2 Macroinvertebrates

Benthic macroinvertebrates have been collected at some sites in the Wenatchee River Basin in previous studies (Adams, 2012). However, the goal of the previous assessments was taxonomic, leading to the calculation of biotic indices of environmental quality based on community structure. Indices were used to describe impacted areas of the river relative to nutrient, temperature, and dissolved oxygen stresses. In this study we are primarily interested in the PCB burdens of caddisfly larvae (*Trichoptera* spp.) and mayfly larvae (*Ephemeroptera* spp.). These two organisms are most abundant (Adams, 2012; Table 6), have similar diets and feeding habits (collector-filterers and collector-gatherers), and are likely the main food source for mountain whitefish (Northcote and Ennis, 1994). Samples will be collected using the standard kick-net approach (Adams, 2010) and picking specimens from overturned rocks in the riverbed. Taxonomic sampling usually targets complete community representation, but sampling for contaminant burdens requires only attaining enough sample mass from a consistent functional group. Staff will wear nitrile gloves while sampling and will pick specimens from either the net or the underside of rocks, using stainless steel tweezers. Specimens will be immediately placed in a cleaned glass jar and stored on ice.

8.1.2.3 Mountain Whitefish (MWF) Stomach Contents

We will verify the diet of resident MWF before we sample invertebrates and will use this information in future bioaccumulation modeling. We will catch a small number of MWF in the spring of 2015 and analyze their gut contents. Fish will be caught, using hook and line, in locations near Leavenworth and Wenatchee, near the confluence. These two locations have historically shown the highest PCB concentrations in MWF (Seiders et al., 2012). Protocols of the Freshwater Fish Contaminant Monitoring Program will be followed, including gathering weight and length data in the field (Seiders et al., 2012). Approximately 10 fish at each location will be gathered for analysis. Fish will be stored on ice and transported back to Ecology for processing. Fish guts will be extracted and analyzed at the Ecology Benthic Lab. Age structures will be removed and each fish will be sexed. Tissue samples will be composited to give two,

five-fish composites. A small aliquot will be analyzed for C and N stable isotopes and the remainder archived for future analysis.

8.1.3 Suspended Particulate Material/River Bed Sediments

Suspended sediment samples will be passively collected using sediment traps over a 2- to 4-week period. We will deploy samplers that have been designed for stormwater studies but function well in rivers (Lubliner, 2012). The Hamlin sampler is designed to segregate sediments into broad grain size subsamples, isolating the finer material. This finer material is of interest when organochlorine compounds are analyzed, because it contains a greater portion of particulate organic carbon to bind PCBs and DDT. The Johnson trap is an additional style of sediment trap that will also be deployed for redundancy. It collects suspended sediment in a polycarbonate tube fixed vertically to a cement block. We anticipate that with both deployments the suspended material will be a combination of fine bedload, bank erosion, and tributary inputs. We will retrieve and homogenize sediments in a stainless steel bowl, prior to subsampling in cleaned glass jars.

8.2 Containers, preservation methods, holding times

Details of sample containers, preservation, and holding times are found in Table 7.

8.8 Other activities

Invertebrate samples will be crushed and homogenized in stainless steel bowls using scalpels and spoons, to minimize the loss of tissue. We will not process the samples as we would fish tissue (Sandvik, 2014), because this would result in a loss of mass. The entire collected tissue mass will be extracted.

9.0 Measurement Methods

9.2 Lab procedures table.

Laboratory procedures are detailed in Table 8. The same contract lab used in the Phase 1 initial sampling will be responsible for the analysis of PCB congeners and t-DDT in SPE media (contained in CLAM samplers), periphyton, invertebrates, and sediments. This will provide consistency in the lab environment, methods, and QC. Analysis of ancillary parameters will be carried out by MEL.

9.3 Sample preparation method(s)

Established sample preparation methods are detailed in Table 8.

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 9 and 10.

A detailed QC program for CLAMs, the SPE disks, and the raw media has not been formerly defined in an SOP. The following steps will be taken prior to and concomitant with the field work to assess potential contamination from manufacturing:

- C-18 media will be used in SPE disks.
- All SPE media will be acquired from the same manufactured batch, with the assistance of CIAgent Solutions (CLAM supplier).
- All SPE disks will be cleaned as per specified recommendations of the manufacturer and spiked with ^{13}C labeled congeners (PCB-31, PCB-95, and PCB-153) and DDT compounds for use as field standards to verify retention.
- Laboratory blanks will include one raw media and three cleaned disk blanks. The lab blanks will also be spiked and act as an on-going performance and recovery (OPR).

Following field deployment additional laboratory QC will be completed:

- Spike the disks with EPA 1668C and 1699 surrogate solution and extract (or elute) the disks.
- Assess the retention of labeled congeners.
- Analyze field replicate.

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 reporting limits are detailed in Table 8.

11.0 Data Management Procedures

11.1 Data recording/reporting requirements

PCB and t-DDT residual concentrations from the CLAM-SPE disks will be used to calculate an estimated dissolved concentration in water. A detailed methodology of calculating the estimated water concentration is found in Appendix A.

11.2 Laboratory data package requirements

The data package from the contract lab will provide MEL with all the raw data that will include, but not be limited to, a text narrative; 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.

11.5 EIM/STORET data upload procedures

Data generated by CLAM-SPE disks are considered an estimate and therefore not approved for entry into EIM. Similar to the SPMDs used in Phase 1, an index of records and necessary data will be saved to the Ecology data repository for SPMDs and CLAM.

12.0 Audits and Reports

No changes.

13.0 Data Verification

No changes.

14.0 Data Quality (Usability) Assessment

14.4 Sampling design evaluation

The study design for Phase 2 of this project is targeted to suspected contaminant sources based on the Phase 1 results. Reliable and clear data were obtained from the initial SPMD survey. All proposed sample sites and media are justified to achieve the goals of this study.

15.0 References

Adams, K., 2010. Standard Operating Procedures and Minimum Requirements for the Collection of Freshwater Benthic Macroinvertebrate data in Wadeable Streams and Rivers. Washington State Department of Ecology, Olympia, WA. SOP Number EAP073. www.ecy.wa.gov/programs/eap/quality.html

Adams, K., 2012. Status of the Benthic Macroinvertebrate Community in the Wenatchee River 2010. Washington State Dept. of Ecology. Olympia, WA. Publication No. 12-03-016. https://fortress.wa.gov/ecy/publications/summarypages/1203016.html

Anderson, P and D. Sargeant, 2009. Quality Assurance Project Plan: Skagit-Samish Watershed Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-120. https://fortress.wa.gov/ecy/publications/summarypages/0903120.html

Carroll, J. and S. O'Neal, 2005. Wenatchee River Basin Fecal Coliform Bacteria Total Maximum Daily Load Study. Washington State Dept. of Ecology. Olympia, WA. Publication No. 05-03-012. https://fortress.wa.gov/ecy/publications/summarypages/0503012.html

Carroll, J., S. O'Neal, and S. Golding, 2006. Wenatchee River Basin Dissolved Oxygen, pH, and Phosphorus Total Maximum Daily Load Study. Washington State Dept. of Ecology. Olympia,

WA. Publication No. 06-03-018.
https://fortress.wa.gov/ecy/publications/summarypages/0603018.html

Coots, R., 2014. PCB Method Comparison of High and Low Resolution Sediment Analysis. Washington State Dept. of Ecology. Olympia, WA. Publication No.14-03-009.
https://fortress.wa.gov/ecy/publications/summarypages/1403009.html

Friese, M., 2014. Standard Operating Procedures for Decontaminating Field Equipment for Sampling Toxics in the Environment. Washington State Department of Ecology, Olympia, WA. SOP Number EAP090. www.ecy.wa.gov/programs/eap/quality.html

Hobbs, W., 2014. Quality Assurance Project Plan: Wenatchee River PCB and DDT Source Assessment. Washington State Dept. of Ecology. Olympia, WA. Publication No. 14-03-117.
https://fortress.wa.gov/ecy/publications/summarypages/1403117.html

Lombard, S. and C. Kirchmer, 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-030.
https://fortress.wa.gov/ecy/publications/SummaryPages/0403030.html

Lubliner, B., 2012. Evaluation of Stormwater Suspended Particulate Matter Samplers. Washington State Dept. of Ecology. Olympia, WA. Publication No. 12-03-053.
https://fortress.wa.gov/ecy/publications/summarypages/1203053.html

MacKay, D., W.Y. Shui, and K.C. Ma, 1997. Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Vol. 5: Pesticide chemicals. CRC Press, Boca Raton, FL.

MacCarthy, K.A. and R.W. Gale, 1999. Investigation of the Distribution of Organochlorine and Polycyclic Aromatic Hydrocarbon Compounds in the Lower Columbia River Using Semipermeable Membrane Devices. U.S. Geological Survey, Portland, Oregon. Water Resources Investigations Report 99-4051.

Mathieu, N., S. Collyard, and T. Mohamedali, 2013. Standard Operating Procedures for the Collection of Periphyton Samples for TMDL studies. Washington State Department of Ecology, Olympia, WA. SOP Number EAP085. www.ecy.wa.gov/programs/eap/quality.html

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

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

McIntyre, J. and D. Beauchamp, 2007. Age and trophic position dominate bioaccumulation of mercury and organochlorines in the food web of Lake Washington. Science of The Total Environment, 372(2-3), 571-584.

Northcote, T.G. and G.L. Ennis, 1994. Mountain Whitefish Biology and Habitat Use in Relation to Compensation and Improvement Possibilities. Review in Fisheries Science. 2: 347-371.

Sandvik, P., 2009. Washington State Toxics Monitoring Program: Trends Monitoring for Chlorinated Pesticides, PCBs, and PBDEs in Washington Rivers and Lakes, 2007. Washington State Dept. of Ecology. Olympia, WA. Publication No. 09-03-013. https://fortress.wa.gov/ecy/publications/summarypages/0903013.html

Sandvik, P., 2014. Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples. Washington State Department of Ecology, Olympia, WA. SOP Number EAP007. www.ecy.wa.gov/programs/eap/quality.html

Sargeant, D., E. Newell, P. Anderson, and A. Cook, 2013. Surface Water Monitoring Program for Pesticide in Salmon-Bearing Streams, 2009-2011 Triennial Report. A Cooperative Study by the Washington State Departments of Ecology and Agriculture. Washington State Dept. of Ecology. Olympia, WA. Publication No. 13-03-002. https://fortress.wa.gov/ecy/publications/summarypages/1303002.html

Seiders, K., C. Deligeannis, and M. Friese, 2012. Washington State Toxics Monitoring Program: Freshwater Fish Tissue Component, 2010. Washington State Dept. of Ecology. Olympia, WA. Publication No. 12-03-023. https://fortress.wa.gov/ecy/publications/summarypages/1203023.html

Serdar, D. and B. Era-Miller, 2004. DDT Contamination and Transport in the Lower Mission Creek Basin, Chelan County. Washington State Dept. of Ecology. Olympia, WA. Publication No. 04-03-043. https://fortress.wa.gov/ecy/publications/summarypages/0403043.html

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/laws-rules/ecywac.html

WAC 173-204. Sediment Management Standards in the State of Washington. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/laws-rules/ecywac.html

16.0 Figures

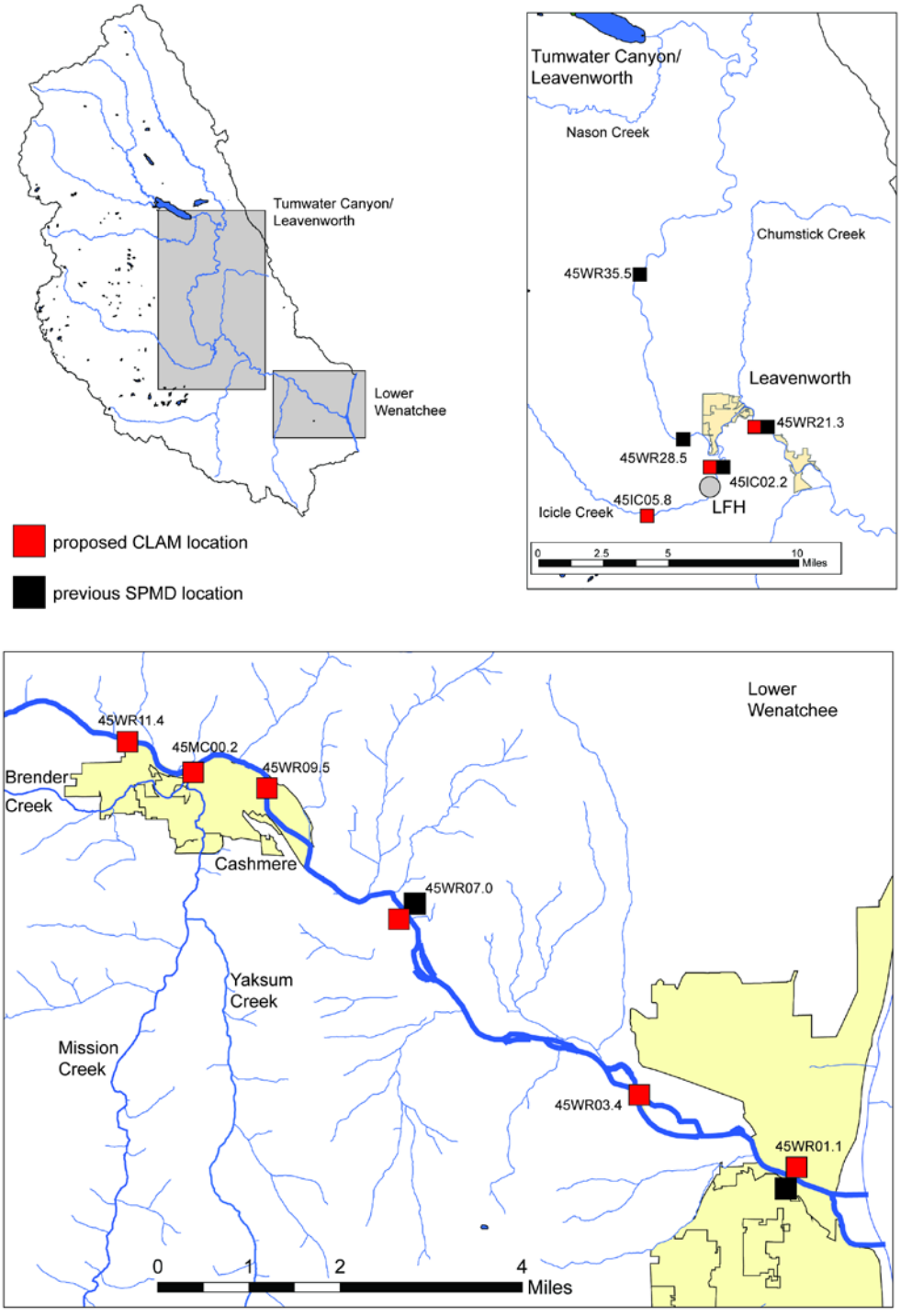

Figure 1: Proposed sample sites for Phase 2 PCB investigation.

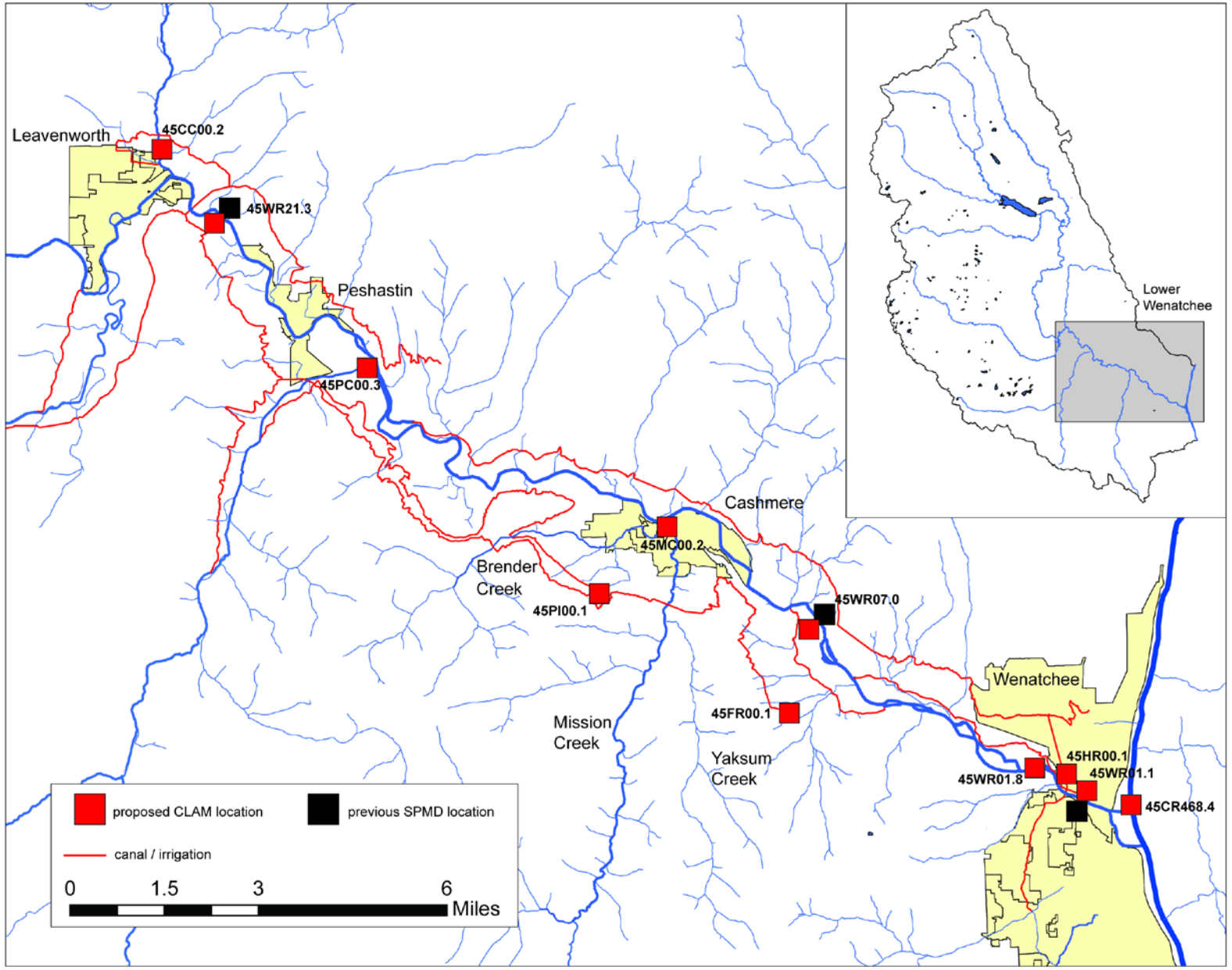

Figure 2: Proposed sample sites for Phase 2 DDT investigation. Irrigation canals are in red.

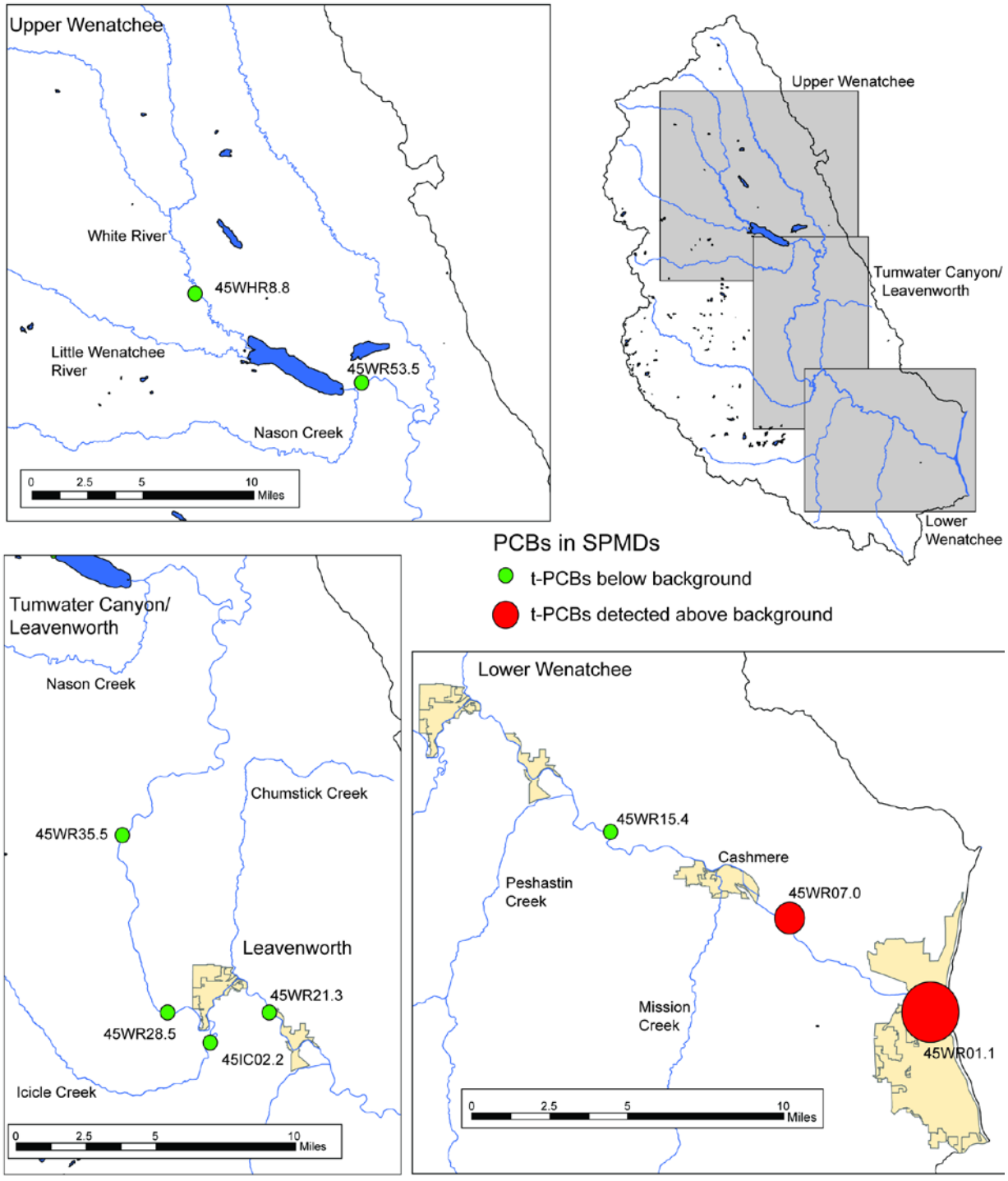

Figure 3: Results from Phase 1 survey showing relative concentrations of PCBs in water (estimated from SPMDs).

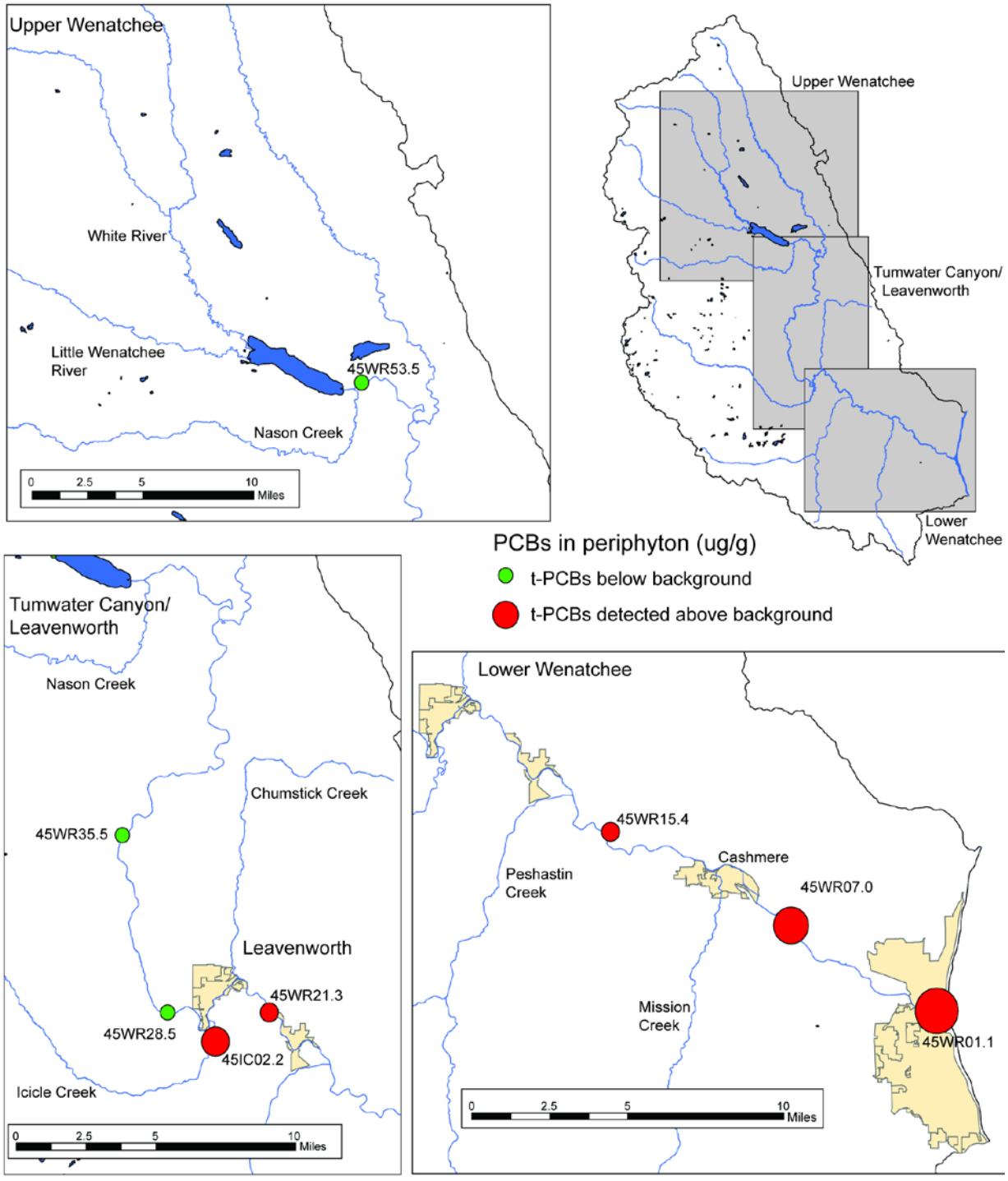

Figure 4: Results from Phase 1 survey showing relative concentrations of PCBs in periphyton.

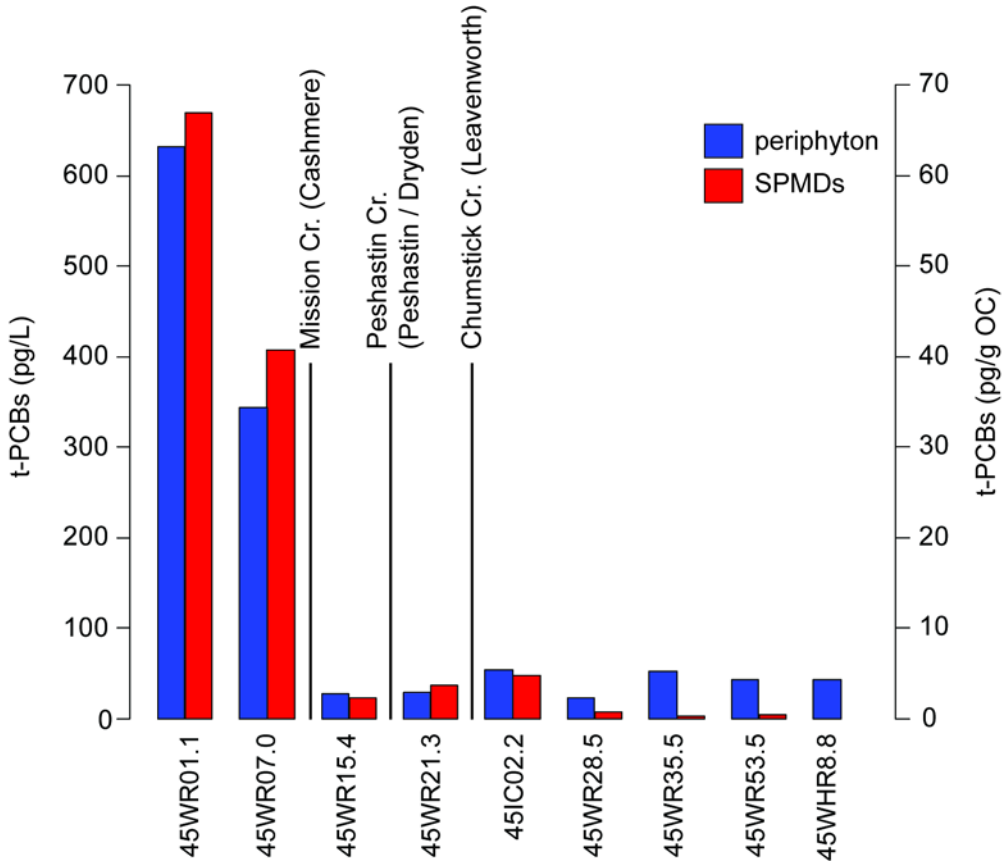

Figure 5: Barplot of PCB results for water concentrations (SPMDs, red bars, primary y-axis) and periphyton concentrations (blue bars, secondary y-axis).

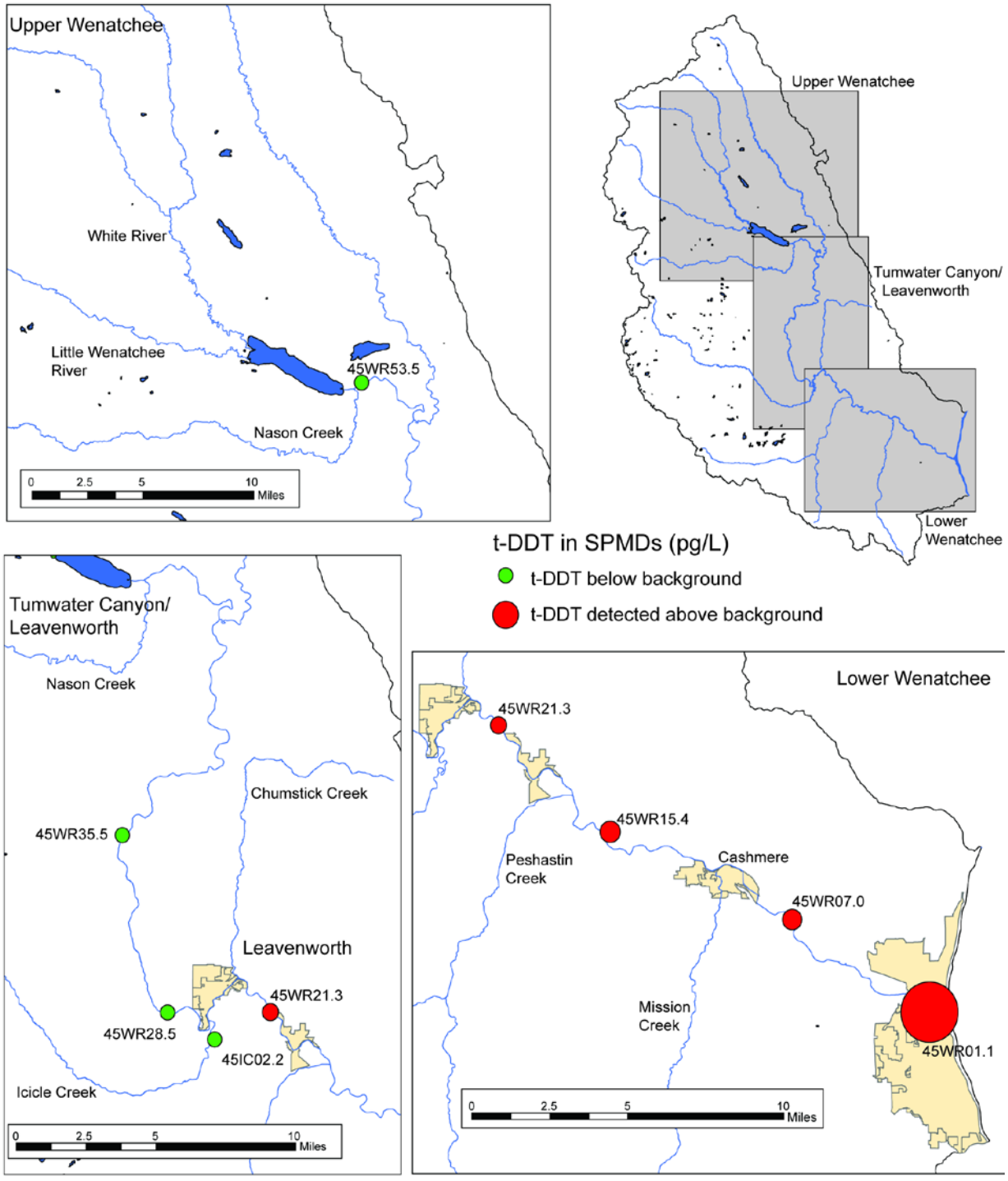

Figure 6: Results from Phase 1 survey showing relative concentrations of DDT in water (estimated from SPMDs).

17.0 Tables

Table 1: 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	April 2016	Melissa McCall
EIM data entry review	May 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 2: Laboratory cost estimate for Phase 2 Wenatchee PCB and DDT source assessment.

Analysis	Matrix	Number of samples	Number of QA samples	Cost per sample	Contract lab subtotal	MEL subtotal
High Flow Sampling (FY15)						
TSS	water	9	1	$12		$120
TOC	water	9	1	$36		$360
DOC	water	9	1	$40		$400
PCB congeners (low-res)	SPE	9	6	$400	$6,000	
DDT	SPE	11	6	$500	$8,500	
PCB congeners	sediment/SPM	7	1	$775	$6,200	
DDT	sediment	11	2	$500	$6,500	
TOC	sediment/SPM	7	1	$46		$368
grain size	sediment/SPM	7	1	$60		$480
Low Flow Sampling (FY16)						
TSS	water	9	1	$12		$120
TOC	water	9	1	$36		$360
DOC	water	9	1	$40		$400
PCB congeners (low-res)	SPE	9	2	$400	$4,400	
DDT	SPE	11	2	$500	$6,500	
PCB congeners	macroinvertebrates	7	1	$775	$6,200	
lipids	macroinvertebrates	7	1	$33	$264	
C : N	macroinvertebrates	14	6	$10		$200
PCB congeners	periphyton	7	2	$775	$6,975	
DDT	periphyton	3	1	$500	$2,000	
lipids	periphyton	7	2	$33	$297	
ash-free dry weight	periphyton	7	1	$25		$200
C : N	periphyton	14	6	$10		$200
PCB congeners	sediment/SPM	7	1	$775	$6,200	
DDT	sediment	11	2	$500	$6,500	
TOC	sediment/SPM	7	1	$46		$368
grain size	sediment/SPM	7	1	$60		$480
				Subtotal	$27,200	$1,728
SPM = suspended particulate matter				MEL contracting		$6,800
SPE = solid phase extraction				**FY15 total**		**$35,728**
				Subtotal	$39,336	$2,328
				MEL contracting		$9,834
				FY16 total		**$51,498**
				Lab Total		**$87,226**

Table 3: Measurement Quality Objectives**.**

Analysis	Check stds./lab control samples (% recov.)	Duplicate samples (RPD)	Surrogates (% recov)	Matrix spikes (% recov)	Lowest concentration of interest
Water samples					
TSS	80-120%	± 20%	NA	NA	1 mg L^{-1}
Conductivity	80-120%	± 20%	NA	NA	1 µm hos cm^{-1}
Total Organic Carbon	80-120%	± 20%	NA	75-125%	1 mg L^{-1}
Dissolved Organic Carbon	80-120%	± 20%	NA	NA	1 mg L^{-1}
SPE Extracts					
PCB congeners	50-150%	± 20%	50-150%	50-150%	50 pg
t-DDT	50-150%	± 20%	50-150%	50-150%	2 ng
Tissue (periphyton and invertebrates)					
PCB congeners	50-150%	± 40%	50-150%	NA	4 pg g^{-1}
lipids	75-125%	± 20%	NA	NA	0.10%
ash-free dry weight	NA	± 20%	NA	NA	1.00%
C:N	NA	± 20%	NA	NA	0.10%
Soil/Sediment samples					
PCB congeners	50-150%	± 40%	50-150%	NA	4 pg g^{-1}
grain size	NA	± 20%	NA	NA	NA
TOC	75-125%	± 20%	NA	NA	0.1 µg Kg^{-1}

NA = not analyzed

Table 4: Proposed sample sites.

Sample site	River mile	Latitude	Longitude	Description	Rationale	Water	Sediment Traps	Invertebrates*	Periphyton*
Sample sites for PCBs									
45IC05.8	5.8	47.54121	-120.72003	Icicle Creek @ USGS gauge 12458000	upstream of Hatchery	x			
45IC02.2	2.2	47.56352	-120.66799	Icicle Creek @ ECY gauge 45B070	downstream of Hatchery	x	x		
45WR21.3	21.3	47.58218	-120.61456	Osprey pull-out site nr USGS 12459000	mainstem background	x	x	x	x
45WR11.4	11.4	47.52754	-120.48926	Goodwin Rd., Bridge	upstream of Cashmere	x	x	x	x
45MC00.2	0.2	47.52249	-120.47503	Mission Creek @ ECY gauge 45E070	tributary	x	x	x	x
45WR09.5	9.5	47.52049	-120.45763	Cotlets Way Bridge, Cashmere	downstream of transformer site; upstream of Cashmere treatment plant	x		x	x
45WR07.7	7.7	47.50089	-120.42565	Old Monitor Bridge @ USGS gauge 12462500	downstream of Cashmere treatment plant	x	x	x	x
45WR03.4	3.4	47.47229	-120.37115	Sleepy Hollow Rd. Bridge	downstream of Monitor	x	x	x	x
45WR01.1	1.1	47.4588	-120.33682	Hwy 285 Bridge, Wenatchee	confluence site with Columbia	x	x	x	x
Sample sites for DDT									
45CC00.2	0.2	47.60514	-120.64879	Chumstick Cr. nr mouth, upstream of irrigation return	tributary downstream of Leavenworth, upstream of Peshastin	x	x		
45FR00.1	0.1	47.4841465	-120.41859	Icicle Irrigation return @ Fairview Canyon Rd.	irrigation return nr Monitor	x	x		

Sample site	River mile	Latitude	Longitude	Description	Rationale	Water	Sediment Traps	Invertebrates*	Periphyton*
45HR00.1	0.1	47.4657473	-120.35039	Highline Canal return @ mouth	irrigation return nr Wenatchee (north side of river)	x	x		
45MC00.2	0.2	47.52249	-120.47503	Mission Creek @ ECY gauge 45E070	tributary downstream of Peshastin; known DDT source	x	x		
45PC00.3	0.3	47.5573	-120.5804	Peshastin Cr. nr mouth	tributary downstream of Leavenworth, upstream of Dryden	x	x		
45PI00.1	0.1	47.5168459	-120.4726	Peshastin Canal Irrigation return	Peshastin irrigation return prior to Mission Creek discharge	x	x		
45WR21.3	21.3	47.58218	-120.61456	Osprey pull-out site nr USGS 12459000	quantify load in mainstem	x	x	x	x
45WR07.7	7.7	47.50089	-120.42565	Old Monitor Bridge @ USGS gauge 12462500	quantify load in mainstem	x	x	x	x
45WR01.8	1.8	47.46476	-120.35335	Wenatchee mainstem upstream of mouth	prior to Highline irrigation return and mixing with Columbia	x	x		
45WR01.1	1.1	47.4588	-120.33682	Hwy 285 Bridge, Wenatchee	confluence site with Columbia	x	x	x	x
45CR468.4	468.4	47.4590429	-120.3238	Confluence State Park	Columbia River prior to mixing with Wenatchee	x	x		

* Only sampled during low flow conditions

Table 5: Summary results from Phase 1 of the Wenatchee River PCB and DDT Source Assessment.

Site	Site Name	River Mile	Discharge (cfs)	SPMD t-PCBs (pg/L)	Qualifier*	PCB load‡ (mg/day)	SPMD t-DDT (pg/L)	Qualifier*	DDT load (mg/day)	Periphyton t-PCBs (pg/g)	Periphyton t-PCBs (pg/g OC)
45WR01.1	Confluence	1.1	-	632.2		-	1791.8		-	473.0	67.0
45WR07.0	Old Monitor	7	21732.8	343.3		644.5	345.2		648.2	581.0	40.8
45WR15.4	Dryden	15.4	-	27.8	U	-	346.5			50.5	2.2
45WR21.3	Osprey	21.3	22994.2	28.8	U	76.6	107.0		212.5	92.3	3.6
45IC02.2	Icicle	26	4190.1	53.1	U	14.0	23.6		8.5	181.0	4.8
45WR28.5	Powerhouse	28.5	-	22.9	U	-	29.2			18.3	0.7
45WR35.5	Tumwater	35.5	17068.2	52.0	U	56.9	26.6		39.2	24.2	0.3
45WR53.5	Lk Wenatchee	53.5	12799.5	42.7	U	42.6	33.2		36.8	11.7	0.4
45WHR8.8	White R	60	9347.4	42.7	U	31.1	22.7		18.3	ns	ns

ns - not sampled

U - The analyte was not detected above the reported sample quantitation limit.

* qualifiers based on method quantitation limits calculated from SPMD blanks (t-PCBs = 60 pg/L; t-DDT = 6.5 pg/L)

‡ loads for censored concentrations are based on the environmental background concentration (mean of sites upstream of Dryden)

Table 6: Summary of the dominant macroinvertebrates found in the Wenatchee River (summarized from Adams, 2012).

Sample ID	Location	Number of individuals	% in sample	Specimen	Taxonomic level	Functional feeding group	Common name
WENTMDL-W05	Bridge b/w Leavenworth and Dryden	324	0.648	Brachycentrus occidentalis	SPECIES	collector-filterer	mother's day caddisfly
WENTMDL-W05	Bridge b/w Leavenworth and Dryden	76	0.152	Glossosoma	GENUS	collector-filterer	saddle case caddisfly
WENTMDL-W06	1st Rapid Below Leavenworth	150	0.3	Orthocladius	GENUS	collector-gatherer	non-biting midge larvae
WENTMDL-W07	Leavenworth Beach	95	0.19	Brachycentrus occidentalis	SPECIES	collector-filterer	mother's day caddisfly
WENTMDL-W07	Leavenworth Beach	54	0.108	Naidinae	SUBFMLY	collector-gatherer	oligochaete worm
WENTMDL-W07	Leavenworth Beach	134	0.268	Orthocladius	GENUS	collector-gatherer	non-biting midge larvae
WENTMDL-I04	Icicle Ref 1	59	0.118	Dolophilodes	GENUS	collector-filterer	tiny black gold speckled caddisfly
WENTMDL-I04	Icicle Ref 1	58	0.116	Tvetenia bavarica Group	SPECIES	collector-gatherer	non-biting midge larvae
WENTMDL-W01	Confluence Park	116	0.232	Cheumatopsyche	GENUS	collector-filterer	caddisfly
WENTMDL-W01	Confluence Park	52	0.104	Ephemerella inermis	SPECIES	collector-gatherer	mayfly
WENTMDL-W04	Dryden River Park	192	0.384	Brachycentrus occidentalis	SPECIES	collector-filterer	mother's day caddisfly
WENTMDL-W04	Dryden River Park	70	0.14	Lepidostoma	GENUS	shredder	caddisfly
WENTMDL-I02	Icicle @ Town	78	0.156	Glossosoma	GENUS	collector-filterer	saddle case caddisfly
WENTMDL-I02	Icicle @ Town	56	0.112	Optioservus	GENUS	omnivorous	riffle beetle
WENTMDL-W02	Sleepy Hollow Bridge	59	0.118	Brachycentrus occidentalis	SPECIES	collector-filterer	mother's day caddisfly
WENTMDL-W02	Sleepy Hollow Bridge	130	0.26	Cheumatopsyche	GENUS	collector-filterer	caddisfly
WENTMDL-W02	Sleepy Hollow Bridge	83	0.166	Ephemerella	GENUS	collector-gatherer	mayfly
WENTMDL-W02	Sleepy Hollow Bridge	59	0.118	Microtendipes	GENUS	collector-gatherer	non-biting midge larvae
WENTMDL-W03	Old Monitor Bridge	126	0.252	Brachycentrus occidentalis	SPECIES	collector-filterer	mother's day caddisfly
WENTMDL-W03	Old Monitor Bridge	128	0.256	Microtendipes	GENUS	collector-gatherer	non-biting midge larvae

Sample ID	Location	Number of individuals	% in sample	Specimen	Taxonomic level	Functional feeding group	Common name
WENTMDL-W08	Leavenworth Put-in	216	0.432	Ephemerella inermis	SPECIES	collector-gatherer	mayfly
WENTMDL-W09	Lower Canyon Bridge Pulloff	67	0.134	Ephemerella inermis	SPECIES	collector-gatherer	mayfly
WENTMDL-W09	Lower Canyon Bridge Pulloff	134	0.268	Lepidostoma	GENUS	shredder	caddisfly
WENTMDL-W10	Ref. Tumwater Canyon 1st Pullout	79	0.158	Cladotanytarsus	GENUS	collector-gatherer	non-biting midge larvae
WENTMDL-W10	Ref. Tumwater Canyon 1st Pullout	255	0.51	Lepidostoma	GENUS	shredder	caddisfly
WENTMDL-W11	Ref. Lake Wenatchee Bridge	109	0.218	Ephemerella inermis	SPECIES	collector-gatherer	mayfly
WENTMDL-W11	Ref. Lake Wenatchee Bridge	161	0.322	Lepidostoma	GENUS	shredder	caddisfly

Table 7: Sample containers, holding times, and preservation.

Parameter	Matrix	Minimum sample size	Container	Preservation	Holding time
PCB congeners and t-DDT	SPE disk	N/A	HDPE filter case; CLAM sampler	cool to 4°C	14 days
PCB congeners and t-DDT	periphyton and invertebrates	10 g w/w	8 oz. glass jar w/ teflon lid	cool to 4°C	14 days
C:N and stable isotopes	periphyton and invertebrates	10 mg d/w	freeze-dried material in specimen cup	cool to 4°C	6 months
ash-free dry weight	periphyton and invertebrates	2g w/w	8 oz. glass jar w/ teflon lid	cool to 4°C	14 days
PCB congeners and t-DDT	soil/sediment	250 g	8 oz. glass jar w/ teflon lid	cool to 4°C	14 days
TOC	soil/sediment	25 g	2 oz. clear glass jar w/ teflon lid	cool to 4°C	14 days
Grain size	soil/sediment	100 g	8 oz. plastic jar	cool to 4°C	6 months

Table 8: Measurement methods (laboratory)

Analysis	Sample matrix	Approx. number of samples*	Expected range of results	Reporting limit	Sample prep method	Analytical method
PCBs Congeners	SPE extract	9	100 - 200 ng (t-PCBs)	0.5 ng per congener	elution; EPA 1668C	MLA-007
t-DDT	SPE extract	11	100 - 200 ng (t-DDT)	0.2 ng	elution; EPA 1699	MLA-007
TSS	surface water	11	5 - 200 mg L^{-1}	1 mg L^{-1}	N/A	EPA 160.2
TOC	surface water	11	2 - 20 mg L^{-1}	1 mg L^{-1}	N/A	SM 5310B
DOC	surface water	11	<RL - 2 mg L-1	1 mg L^{-1}	N/A	SM 5310B
PCB Congeners	periphyton and invertebrates	9	unknown	4 pg g-1 w/w per congener	EPA 1668C	EPA 1668C
t-DDT	periphyton and invertebrates	4	unknown		EPA 1699	EPA 1699
lipids	periphyton and invertebrates	9	0.5 - 2.0 %	0.10%	N/A	MEL SOP 730009[†]
ash-free dry mass	periphyton and invertebrates	9	0.5 - 3.0 %	1.00%	N/A	SM10300C
C:N	periphyton and invertebrates	9	0.1 - 2.0 (%N); 1.0 - 15 (%C)	0.10%	N/A	[ǂ] stable isotopes of N and C
PCB Congeners	soil/sediment		unknown	0.5 - 100 µg Kg^{-1}	EPA 1668C	EPA 1668C
t-DDT	soil/sediment		unknown	0.2 µg Kg^{-1}	EPA 1699	EPA 1699
TOC	soil/sediment	6	0.1 - 6%	0.10%	N/A	PSEP, 1986[¥]
grain size	soil/sediment	6	unknown	0.10%	N/A	PSEP, 1986[¥]

* Excluding field replicates and field blanks.

[¥]Puget Sound Estuary Program, Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound, Conventional Sediment Variables, Total Organic Carbon (TOC), March 1986.

[†]Manual of Analytical Methods for the Analyses of Pesticides in Humans and Environmental Samples. EPA-600 8-80-038.

[ǂ] Costech Elemental Analyzer, Conflo III, MAT253.

Table 9: Field quality control samples.

Parameter	Matrix	Replicates	Blanks
PCB Congeners and DDT	SPE extract	2	4
TSS, TOC, DOC	water	2	N/A
PCB Congeners and DDT	Periphyton and invertebrates	1	N/A
C:N and stable isotopes	Periphyton and invertebrates	1	N/A
PCB Congeners and DDT	soil/sediment	1	N/A
Grain size	soil/sediment	1	N/A

Table 10: Laboratory quality control samples, type, and frequency.

Parameter	matrix	Method blanks	Check stnds/LCS	Duplicates	Surrogate spikes	MS & MSD	OPR stnds / Labelled cmpds.
PCBs and DDT	SPE	4/batch*	1/batch	N/A	all samples	1/batch	all samples
PCBs and DDT	periphyton and invertebrates	N/A	1/batch	N/A	all samples	1/batch	N/A
C:N and stable isotopes	periphyton, invertebrates, and fish tissue	N/A	1/batch	triplicate analysis of each sample	N/A	N/A	all samples
TSS	water	1/batch	1/batch	1/batch	N/A	N/A	N/A
TOC	water	1/batch	1/batch	1/batch	N/A	N/A	N/A
PCBs and DDT	soil/sediment	1/batch	1/batch	1/batch	all samples	1/batch	N/A
TOC	soil/sediment	1/batch	1/batch	1/batch	N/A	N/A	N/A
Grain size	soil/sediment	N/A	N/A	1/batch	N/A	N/A	N/A

* includes a raw SPE media (1) and cleaned disk blank (3)

18.0 Appendix A. Continuous low-level aquatic monitoring

The continuous low-level aquatic monitoring (CLAM™) sampling device is a submersible, low-flow sampler that continuously and actively draws water through filtration and solid-phase extraction (SPE) media. The main supplier of the devices and the SPE disks used in this study is CIAgent (http://www.ciagent-stormwater.com). The pumps were commercially introduced in 2007, but the technology for SPE disks has been in laboratory use for the last 15 years under established EPA protocols (EPA3535A). Recent work by Coes et al. (2014) has documented the efficacy of CLAM™ devices when compared to both grab samples and passive samplers. Ecology has also begun using CLAM™ samplers on a more regular basis (Anderson and Sargeant, 2009; Coots, 2014; Hobbs, 2014); however, there is no established SOP and therefore the technique is still in trial.

Solid-Phase Extraction (SPE) Disks

The CLAM device is simply a vessel for the SPE disk, which binds organic contaminants as water is pumped through. The pore size of the disks is 1.5 micrometers. The SPE media is specific to the contaminant of interest. C-18 extraction media is composed of a bonded silica filter with an octadecyl functional group that binds semi-volatile and non-volatile organic compounds (e.g., organochlorine pesticides, PCBs, and PAHs). The hydrophilic/lipophilic balanced (HLB) media uses a modified styrene polymer to effectively bind polar and non-polar compounds. The HLB disk has been used to sample many different pesticides, pharmaceuticals, and emerging contaminants.

The manufacturer of the CLAM device has conducted a retention and depletion bench study of the pump and the SPE disks for non-polar compounds. They found that there was excellent retention of spiked PAH and pesticide compounds in the disks following 100L of flushing with de-ionized water (DI) (Aqualytical, 2014; available at http://www.ciagent-stormwater.com/documents/watermonitoring/RetentionandDepletionofIntegratedAnalytesintheCLAM.pdf). The manufacturers of the SPE media and the lab suppliers have also conducted many retention studies for a variety of compounds.

The disks themselves are not directly handled by the lab or the field personnel. Disks are ordered and come contained in a sealed HDPE filter case with lure-locks at either end. Before deployment, the disks require conditioning with solvent, which rids the disk of any possible residual contamination. A complete step-by-step procedure is outlined in the manufacturer's laboratory application notes available online (http://www.ciagent-stormwater.com/new-water-monitoring/). Briefly, the disks are cleaned with 50ml of dichloromethane (DCM), conditioned with 50ml of methanol, and rinsed with 50ml of reagent quality DI water. Residual DI water is left in the disk to maintain the pore space in the glass pre-filter that has been established by the conditioning rinse. The disks are capped and placed back in the foil pouch for shipment to the field. Conditioned disks can be kept refrigerated for up to 30 days; unconditioned disks are stable for up to a year.

Deployment

The CLAM devices can be secured to suit the sample site. During deployment, the device must be carefully situated so that it does not obstruct the intake port. Typically in small streams the CLAM is

positioned with the intake facing downstream and the device is suspended at 2/3 the channel depth. In a shallow stream (such as Pine Creek) U-shaped rebar can be hammered into the streambed and the device suspended horizontally. In a deeper stream or lake, a concrete block with a float attached by cable and positioned just below the water surface can be used as line to attach the CLAM to (Anderson and Sargeant, 2009).

Before deployment, the flow rate of the device must be measured. Protocols describing a step-by-step method can be found at the manufacturer's website (http://www.ciagent-stormwater.com/new-water-monitoring/). The device is assembled and the battery pack is hooked up; this starts the internal pump. The device and extraction media are not compromised if the pump runs out of the water during set-up. A stainless steel bucket is filled with water from the site and the CLAM is placed in the bucket. Air is purged from the filter and then flow rate can be measured. A syringe is attached to the discharge port of the CLAM, with tubing, and the collected water volume is measured in the syringe and timed with a stopwatch. This procedure is repeated until the flow rate is consistent. The device can now be deployed and time of deployment recorded.

Recent additions to the CLAM system include an independent flow totalizer. An optical flow meter is attached in-line with the discharge tube of the device to accurately (within 1%) record the total volume pumped in milliliters.

Retrieval

The typical time of deployment for the CLAM is 12 to 36 hours. The device's battery pack limits the maximum time of deployment, and the water turbidity limits the minimum time of deployment. Suspended solids can slow flow rate by clogging the filter, ultimately stopping flow; this could result in a lost sample. Therefore, in turbid waters field personnel need to either return to the pump periodically to verify the pump is still running or deploy the pump for less time. There are no experimentally derived guidelines for time of deployment in turbid waters, since times vary dramatically with particle size and streamflow.

Before removing the device, personnel should take notes on its condition and exact time of retrieval. The flow rate of the CLAM is then measured as per the deployment. Currently, the user must then assume that the flow rate between the time of deployment and retrieval is linear. This flow rate is then used to calculate the total volume of water extracted over the period of deployment.

The following example illustrates this process. The CLAM is deployed at 1500 on March 3 and retrieved at 1200 March 4. The flow rate at deployment was 50 ml min^{-1} and at retrieval had decreased to 20 ml min^{-1}. The mean flow is therefore 35 ml min^{-1} and the total time of deployment is 21 hours. The total volume of water extracted is 44.1 L.

The CLAM is pulled from the water and disassembled at the site. The SPE disk is removed and placed back in the foil shipping pouch. The disks are placed in a cooler on ice until shipped directly to the lab. Refrigerated SPE disks have a holding time of 14 days.

Analysis

SPE disks are shipped directly to the lab, accompanied by a standard chain of custody form. SPE disks are generally considered "other" as a matrix description and not water samples. While there is not an established SOP for the CLAM deployed SPEs, the contract lab should have an SOP for large volume extraction in the lab using similar or the same media. Established preparatory procedures should be in place from previous projects using CLAM samplers.

To analyze the total contaminant concentration bound to the SPE media, the lab must completely elute the deployed disks into separatory funnels. The disks are first rinsed with acetone to remove any water from the disk and then rinsed with dichloromethane to elute the disk. Before the DCM is added, the disk is spiked with a surrogate for laboratory QC of the separatory funnel extraction. The sample is concentrated using micro-Kuderna-Danish distillation under an N_2 atmosphere. The final extract volume is 1.0 mL. The extract is then run according to the methods pertaining to the contaminant of concern (e.g., GC/ECD in the case of toxaphene).

Data Calculations and Reporting

The final quantified concentration is derived from the mass of the compound per milliliter of extract. The concentration of the compound in the sampled water is then calculated, using the total volume of water pumped through the CLAM.

The following example illustrates this process. If the concentration of toxaphene in the extract is 5.05 ng ml^{-1}, and the final volume of extract was 2.0 ml, there is 10.1 ng of toxaphene in the sample. If 44.1 L of water were sampled, as described earlier, the concentration is therefore 0.23 ng L^{-1}. Given that we are assuming the flow rate of the device is linear from deployment to retrieval, we can only consider the total water volume sampled to be an estimate. Therefore, the derived water concentration is an estimate and should be qualified as such.

References

Anderson, P and D. Sargeant, 2009. Quality Assurance Project Plan: Skagit-Samish Watershed Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-120. https://fortress.wa.gov/ecy/publications/summarypages/0903120.html

Coes, A.L., N.V. Paretti, W.T. Foreman, J.L. Iverson, and D.A. Alvarez, 2014. Sampling trace organic compounds in water: A comparison of a continuous active sampler to continuous passive and discrete sampling methods. Science of the Total Environment, 473-474: 731-741.

Coots, R., 2014. PCB Method Comparison of High and Low Resolution Sediment Analysis. Washington State Dept. of Ecology. Olympia, WA. Publication No.14-03-009. https://fortress.wa.gov/ecy/publications/summarypages/1403009.html