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ECOLOGY
State of Washington

Quality Assurance Project Plan

Pine Creek
Toxaphene
Source Assessment

April 2014

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Publication Information

Each study conducted by the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

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EAP: Environmental Assessment Program

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Abstract

Water sampling in the Lower Walla Walla River since 2002 has confirmed a persistent toxaphene source to the river. In particular, sampling of Pine Creek and the Lower Walla Walla has shown that the highest toxaphene concentrations prevail during May and June with another spike in October and November. Both of the high toxaphene periods occur during peak irrigation times. Based on previous work, a possible source for toxaphene in the Pine Creek watershed has been suggested.

Toxaphene is a complex mixture of chlorinated compounds, making it difficult to define typical physical properties and subsequently hard to analyze in environmental samples at low concentrations (ng L^{-1}). Toxaphene is a banned insecticide that was used historically in Washington to reduce pests on livestock and poultry. It was also used as a fish toxicant in lakes to reduce numbers of nuisance fish. Three areas of concern for possible historical use and dump sites have been identified within the Pine Creek watershed.

This Quality Assurance Project Plan details a source assessment for toxaphene in Pine Creek. This project is a tiered investigation, focusing on the irrigation season, with multiple sampling approaches of water, sediments, and soils over the course of one year. After the Washington State Department of Ecology (Ecology) takes some baseline water samples at sites shown to have high toxaphene concentrations in the past, we will conduct an initial synoptic survey in the lower Pine Creek watershed to identify possible toxaphene sources. A targeted investigation of any toxaphene hot spots will follow, with more detailed soil and/or sediment delineation as a final stage in the study.

Background

Pine Creek is a minor tributary to the Walla Walla River in southeast Washington (Figure 1). Previous investigations of the Walla Walla River Basin have highlighted the presence of chlorinated pesticides above Washington State water quality criteria (Johnson et al., 2004). During these investigations, high concentrations of toxaphene were detected in Pine Creek. The concentrations appeared to be significant enough to elevate the concentrations measured in the Lower Walla Walla above water quality criteria. Pine Creek is currently not a 303(d) listed waterbody. However, the investigation of the source of toxaphene within the Pine Creek watershed was a recommendation of the Walla Walla River Total Maximum Daily Load study (TMDL) for chlorinated pesticides.

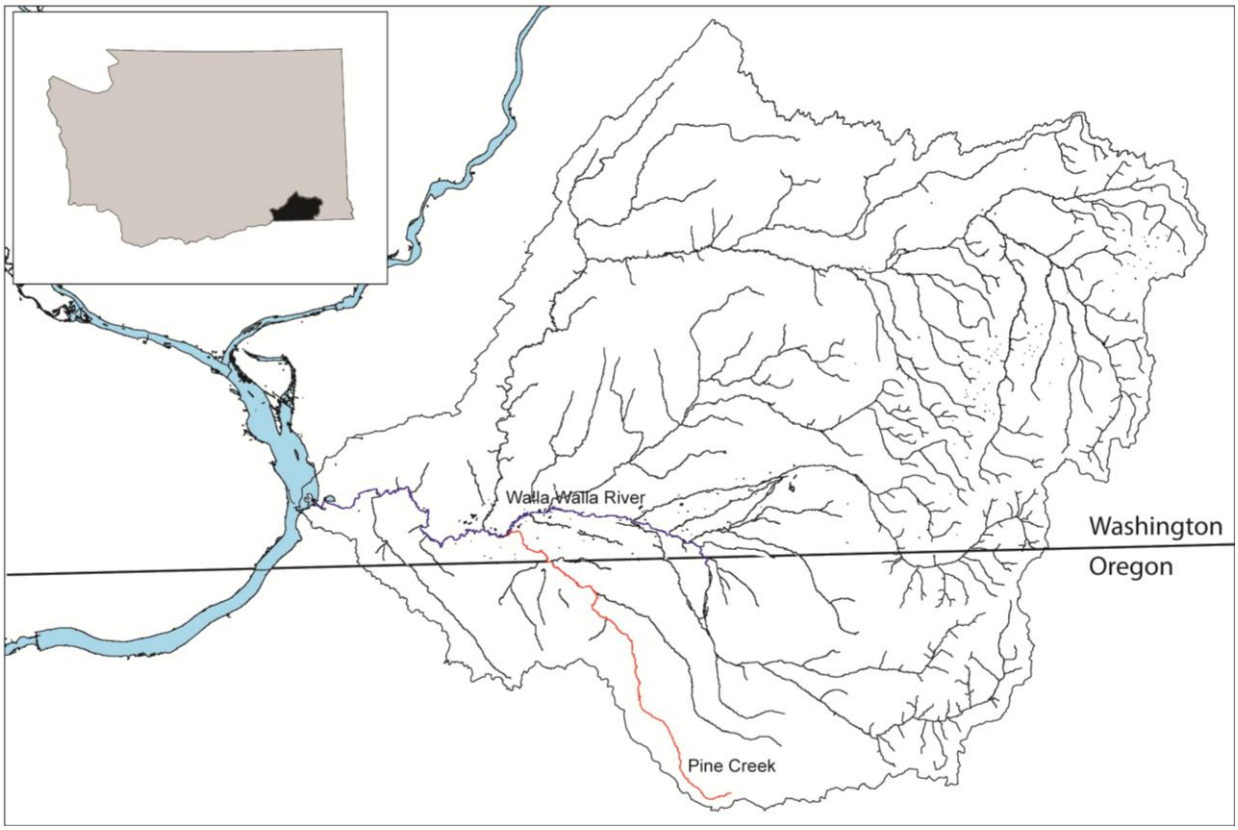

Figure 1. Walla Walla River Basin discharging to the Columbia River.

Pine Creek highlighted in red.

Toxaphene

Sources and characterization

Toxaphene is composed of a complex mixture of chlorinated camphenes and related organics and isomers, making it difficult to define typical physical properties (MacKay et al., 1997). It was developed as an alternative for DDT as an insecticide used primarily on cotton crops in the U.S. southeast (von Rumker et al., 1975; Durkin et al., 1979). Its agricultural use in Washington was largely limited to use on poultry and livestock pest insects, but could have also been used in combination with other insecticides (von Rumker et al., 1975, Johnson et al., 2012). A low-volume usage application of the chemical was on alfalfa, the main crop of the Pine Creek sub-watershed. In addition, it was used in Washington as a fish toxicant to remove unwanted species. A total of 94 lakes were treated in Washington between 1954-1969 (Hisata, 2002; Johnson et al., 2012). Toxaphene was available in various formulations of emulsified concentrate, wettable powder, or dust (von Rumker et al., 1975). All uses were banned in 1990, 8 years after U.S. Environmental Protection Agency (EPA) cancelled its use as a regulated chemical. Toxaphene has a propensity to bind in soils, has low solubility in water, and will evaporate from both soils and water.

Because toxaphene is a mixture of chlorinated organic compounds, measuring concentrations of toxaphene in surface waters has been historically problematic. This has led to an underreported assessment of the current level of toxaphene contamination in Washington waters (Johnson et al., 2012). Recently, work by Johnson et al. (2012) with Ecology's Manchester Environmental Laboratory (MEL) has allowed for higher accuracy in characterizing the chromatographic appearance of toxaphene compounds. This allowed for the investigation of toxaphene in a number of rivers, agricultural drains and irrigation returns, and lakes, the latter being historically treated to eradicate fish (Johnson et al., 2012). The previous work by Johnson et al. (2004; 2012) estimated that 90% of the toxaphene in the mainstem of the Walla Walla is expected to be in dissolved form. This is based on the estimated dissolved concentration from the semi-permeable membrane devices (SPMDs), total organic carbon concentration in the water and the physical properties of the chemical (K_{oc}; the organic carbon-water equilibrium partition coefficient) (Meadows et al., 1998).

The acute toxic effects of toxaphene are well known for aquatic organisms (EPA, 1980). Chronic effects are also known for a number of fishes and invertebrates, but vary among species. Toxaphene bioconcentrates−the concentration of toxaphene in fish tissue will be much greater than the surrounding water (estimated bioconcentration factor is 13,100; EPA, 1980). It is also bioaccumulative: the organism absorbs higher rates of toxaphene through diet and the environment than it can excrete.

Regulatory setting for toxaphene in Washington

The regulatory setting for toxaphene in Washington recognizes the toxicological effects this group of organochlorine compounds has on aquatic life and the criteria are more stringent than human health criteria (Table 1). Protection of human health and aquatic life criteria used by the state of Washington are legislated through the EPA National Toxics Rule (40 CFR 131.36(14)). The criteria for the protection of freshwater aquatic life from chronic effects is the lowest among Washington's 32 regulated chemicals (Table 1; WAC 173-201A). The chronic water quality criteria for chemicals which bioaccumulate are calculated with the goal of protecting wildlife that eat fish / shellfish from adverse effects. 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.

Table 1. Washington State water quality criteria for the protection of human health and aquatic life for toxaphene.

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

Aquatic life (ng L^{-1})†		Human health	
Freshwater chronic	Freshwater acute	Water and fish consumption (ng L^{-1})‡	Edible fish tissue (ug Kg^{-1})
0.20	730	0.73	9.6

† WAC 173-201A
‡ EPA National Toxics Rule
ng L^{-1} = parts per trillion (ppt)

Human health criteria for surface waters are risk-based calculations against 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 1). The risk and subsequent criteria calculations are based on a person of 70kg (154lbs) 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. The actual concentration of toxaphene in edible fish tissue calculated using the risk-based approach is 9.563 ug Kg^{-1} (Table 1).

Toxaphene in the Walla Walla River Basin

The Walla Walla River basin in southeast Washington has been investigated for a number of impairments under the Clean Water Act. Water quality has been impacted by land use categories of agricultural and urban settings and the climatic setting of the region (low precipitation, high summer temperatures). Early investigations of current-use and legacy pesticides within the Walla Walla watershed did not detect toxaphene in the Walla Walla River mainstem or the Pine Creek sub-basin (Davis and Johnson, 1994; Johnson, 1997a; Johnson, 1997b). As discussed previously, this lack of detection was more than likely due to analytical limitations.

The most relevant previous work to the proposed study is the TMDL for chlorinated pesticides and PCBs, which first identified the high concentrations of toxaphene in Pine Creek (Figure 2, sample site PN-02; Johnson et al., 2004). Using passive water samplers (SPMDs) to assess the relative concentrations of chlorinated pesticides throughout the Walla Walla, Johnson et al. (2004) found the highest concentrations of toxaphene in Pine Creek, near the confluence with the Walla Walla (Figure 2; Table 2). The authors suspected that a source of toxaphene within the sub-basin of this tributary could be elevating toxaphene concentrations in the Walla Walla mainstem. A subsequent study confirmed the high toxaphene concentrations in Pine Creek, including a sample from an unnamed tributary that showed the same concentration as Pine Creek (Parsons, 2007; Table 2). The follow-up study by Parsons (2007) also detailed high toxaphene concentrations in Gardena Creek and Gardena Ditch adjacent to the Pine Creek watershed to the west. Gardena Creek and Ditch are not hydrologically connected to Pine Creek but do rely on water siphoned under the Pine Creek watershed from Burlingame Ditch on the eastern side of the

Pine Creek watershed (Figure 2). In addition to previous water samples, two sediment samples collected from sample site PN-01 and PN-02 did not have detectable concentrations of toxaphene.

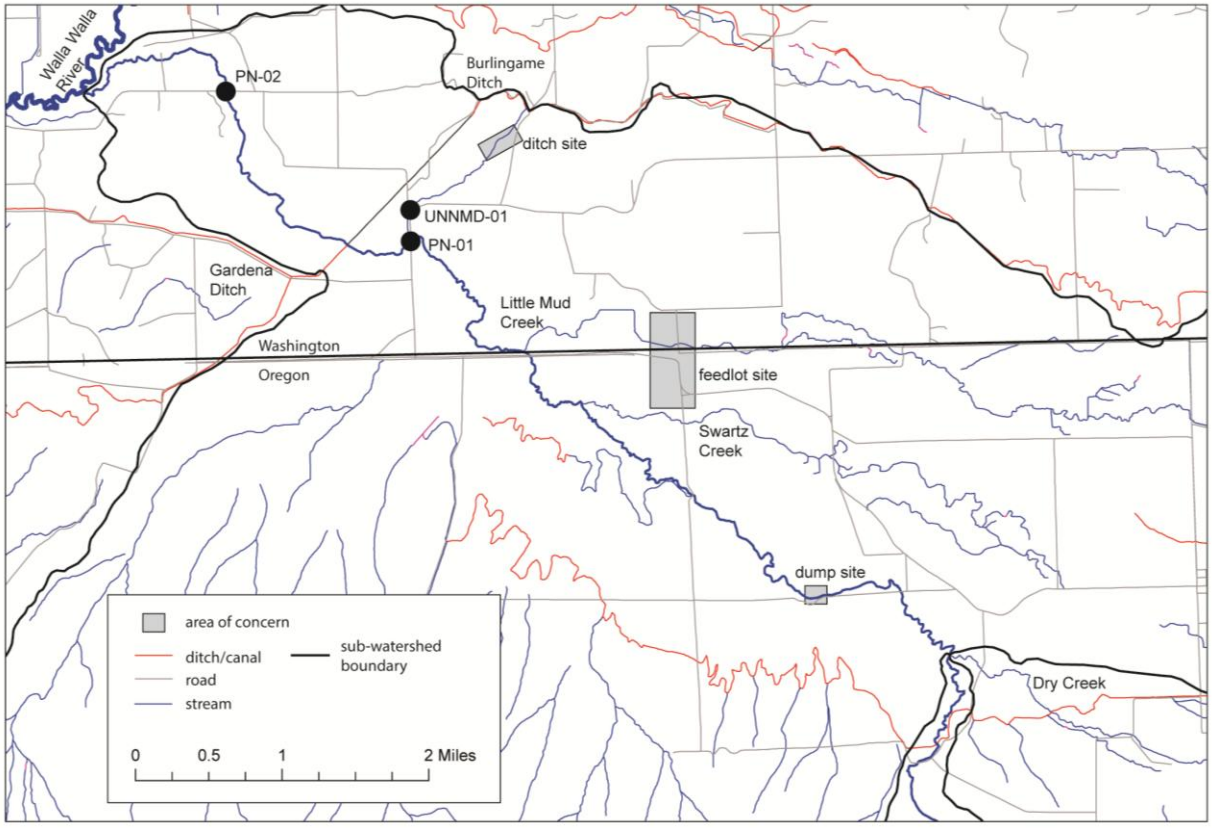

Figure 2. Areas of concern and previous sample sites.

Table 2. Toxaphene concentrations in Pine Creek. Surface water and sediment samples.

Water samples are total concentrations with dissolved concentrations in parentheses. Sample type: (a) grab composite and (b) semi-permeable membrane device.

Date	Pine Creek @ Sand Pit Rd.	Pine Creek @ Barney Road	Unnamed Tributary	Reference
Water samples (ng L^{-1})				
May 1997	<230[a]	ns	ns	Johnson, 1997b
May/June 2002	41 (40)[b]	ns	ns	Johnson et al., 2004
Aug/Sept 2002	1.8 (1.7)[b]	ns	ns	Johnson et al., 2004
Nov/Dec 2002	5.6 (5.4)[b]	ns	ns	Johnson et al., 2004
Feb/Mar 2003	3.5 (3.4)[b]	ns	ns	Johnson et al., 2004
Feb 2007	<1.6[a]	<3.1[a]	ns	Parsons, 2007
May 2007	10[a]	12[a]	10[a]	Parsons, 2007
Apr/May 2011	1.4[b]	ns	ns	Johnson et al., 2012

Sediment samples						
Date	Toxaphene (mg Kg^{-1})	Total organic carbon (mg g^{-1})	Toxaphene (mg Kg^{-1})	Total organic carbon (mg g^{-1})	Reference	
Feb 2007	<0.05	2.9	<0.05	2.3	ns	Parsons, 2007
May 2007	<0.05	3.8	<0.05	0.9	ns	Parsons, 2007

ns = not sampled

In the context of the greater Walla Walla River basin, Pine Creek represents the hotspot for toxaphene contamination. Estimated concentrations during the Johnson et al. (2004) study of the mainstem and tributaries showed that toxaphene concentrations in Yellowhawk, Garrison, and Pine Creeks and the Lower Walla Walla River exceeded human health water quality criteria. Only Pine Creek and the Lower Walla Walla exceed the protection of acute toxicity to aquatic life criteria (chronic toxicological effects criteria for aquatic life is below the analytical reporting limit). In the follow-up Parsons (2007) study, Pine Creek and Gardena Ditch/Creek are the only samples which have concentrations above the method reporting limit (3.1 ng L^{-1}), and therefore above the human health criteria (0.73 ng L^{-1}). Continued monitoring of the Lower Walla Walla River has confirmed the persistence of a toxaphene source (Table 3). Fish tissue from the Upper and Lower Walla Walla River collected in 2002 exceeded the human health criteria for edible fish consumption (9.6 ug Kg^{-1}) for each of the species sampled. The fish tissue residues in the Lower Walla Walla were also higher than the Upper Walla Walla River. Overall, evidence from previous water and fish tissue samples strongly suggest that a possible source within the Pine Creek sub-basin is contributing toxaphene to the Walla Walla River in excess of human and aquatic health criteria and leading to bioaccumulation in resident fishes.

Table 3. Estimated toxaphene concentrations in the Lower Walla Walla River 2002-2011

Date	Season	Toxaphene (ng L^{-1})		Total suspended solids (mg L^{-1})	Reference
		Dissolved	Total		
May/June 2002	spring	8.3	8.5	10	Johnson et al., 2004
Aug/Sept 2002	summer	0.93	1	9	Johnson et al., 2004
Nov/Dec 2002	fall	1.7	1.7	58	Johnson et al., 2004
Feb/Mar 2003	spring	1.9	1.9	161	Johnson et al., 2004
Apr/May 2007	spring	1.1	1.2	27	Sandvik, 2009
Aug/Sep 2007	fall	0.51	0.51	1	Sandvik, 2009
May/June 2008	spring	1.1	1.1	106	Sandvik, 2010
Sep/Oct 2008	fall	0.52	0.52	2	Sandvik, 2010
Apr/May 2009	spring	1	1	96	Sandvik and Seiders, 2011
Apr/May 2010	spring	0.86	0.86	190	Sandvik and Seiders, 2012
Sep/Oct 2010	fall	2.4	2.5	4	Sandvik and Seiders, 2012
May/June 2011	spring	2.1	2.2	62	Sandvik and Seiders, 2012

Additional studies in the Walla Walla basin

Studies on chlorinated pesticides (mainly legacy pesticides) in the Walla Walla basin have highlighted the presence of multiple compounds in excess of the aquatic life criteria throughout the watershed. A strong relationship has been shown between total suspended solids (TSS) and DDT breakdown products, namely 4,4-DDE. It has been proposed that TSS therefore act as a surrogate for monitoring and reduction of DDE loads over time (Johnson et al. 2004; Parsons, 2007). There is insufficient data to conclude whether a relationship exists between toxaphene and TSS in the Pine Creek sub-watershed.

Additional TMDL investigations in the Walla Walla basin have focused on impairments for temperature (Butcher, 2005; Stohr et al., 2007) which are based on the suitability of water temperatures for rearing and spawning of salmonids. The removal of riparian vegetation, trees, and the channelization of streams generally increases the solar heating of the water. Two separate, but complementary, TMDLs have been put together for the Walla Walla basin. The recommendations from these investigations rely heavily on stabilizing and vegetating stream banks and the restoration of channel complexity to more natural conditions.

Study area

Pine Creek flows from the headwaters in the Blue Mountains, Oregon, passing through the small town of Weston, OR, and into Washington (Figure 3). The confluence with the Walla Walla River is just upstream of Touchet, WA, near the U.S. Geological Survey (USGS) gauging station (station #14018500). Pine Creek is approximately 57 kilometers (35 miles) long and the watershed is approximately 440 km^2 (170 sq. miles). The geology of the watershed consists of basalts in the Columbia River Basalt Group in the upper Pine Creek watershed, with a transition to Quaternary deposits of eolian silts and mixed Missoula Flood deposits around Weston, OR. The headwater, upper Pine Creek watershed is predominately in a coniferous zone with mixed willow and alder, paper birch, red osier Dogwood, mixed firs, Ponderosa pine, and Engelmann spruce. There is a biogeoclimatic transition just above Weston, OR, where the vegetation gradually shifts to a deciduous zone of mixed willow and alder, with interspersed black cottonwood. The climate of the region is generally hot and arid in the summer and cold and wetter in the winter. The majority of the precipitation falls as snow in the winter in the Blue Mountains. The amount of precipitation varies from approximately 10 to 30 inches up the watershed from the Walla Walla. Air temperatures have a large range, reaching over 100°F (38°C) in the summer and below 0°F (-18°C) in the winter.

The land use within the watershed is predominately agricultural. The Lower Pine Creek watershed is almost entirely used for agricultural purposes; the main crop is alfalfa seed. The Upper Pine Creek and Dry Creek watersheds are mixed agricultural, residential (the town of Weston, OR), scrubland, and mixed forest. The focus of this study is in the Lower Pine Creek watershed (Figure 3). There are a number of irrigation ditches and canals present within the Lower Pine Creek watershed. A pipeline runs under the watershed from the Burlingame ditch to the Gardena Farms Irrigation District (#13), west of the Pine Creek watershed. Much of the Gardena irrigation is now conveyed by pipe instead of by open canals. The piping of irrigation ditches is not as prevalent in the Lower Pine Creek watershed.

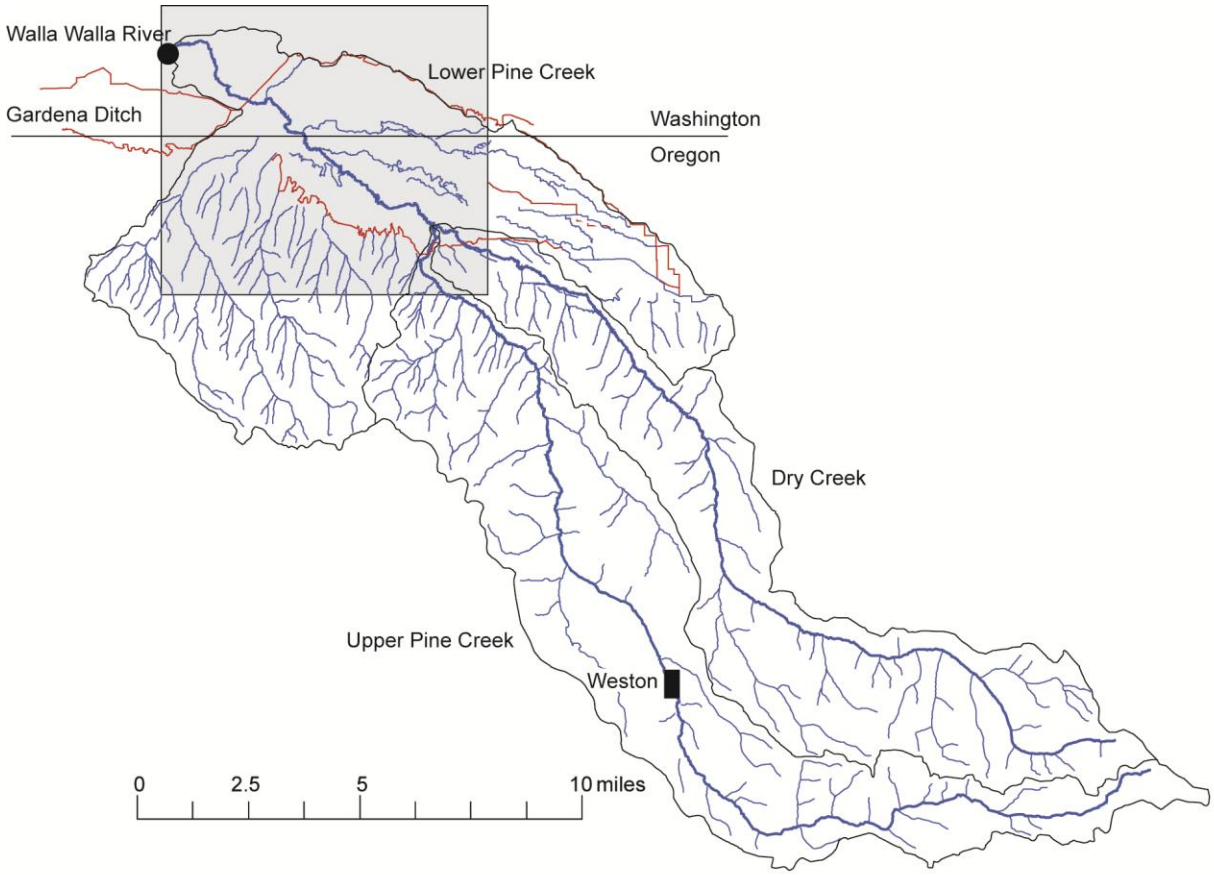

Figure 3. Pine Creek watershed.

Focus of the current investigation outlined in shaded area.
The black dot is the confluence of Pine Creek and the Walla Walla River.

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

This study comprises work in the Walla Walla WRIA (32) and the Walla Walla hydrologic unit 17070102. The sub-basins within the HUC 8 are the Lower Pine Creek (170701020903); Little Dry Creek –Dry Creek (170701020902); and Upper Pine Creek (170701020901).

Project Description

Study objectives

The purpose of this study is to identify the sources of toxaphene within the Pine Creek watershed, a sub-watershed of the Walla Walla River. The existing TMDL for chlorinated pesticides on the Lower Walla Walla (Johnson et al., 2004) recommended the source assessment study. Follow-up studies of chlorinated pesticides in the Pine Creek watershed have also recommended identifying the source of toxaphene (Parsons, 2007; Johnson et al., 2012). This study will use a two-pronged approach: (1) an initial spatial survey of toxaphene in surface waters to narrow source location and sediment samples from suspected disposal sites, and (2) a detailed sampling of water, sediments, and soils to identify the specific source.

Possible toxaphene sources

The likely presence of a toxaphene source in the Pine Creek basin is thought to be associated with livestock operations and the historic use of toxaphene as parasite control. Following the work of Johnson et al. (2004; 2012) presentations were made to stakeholder groups in the Walla Walla basin. Feedback from these discussions suggested that a possible source contributing toxaphene to Pine Creek was a concentrated animal feeding operation (CAFO) (Figure 2 and A-1). In addition to this site, M. Kuttel has identified sites that may have been used for dumping, one of which is an eroded drainage ditch (Figure 2 and A-2). The ditch site is located up a small tributary that was sampled in 2007 and showed elevated toxaphene concentrations (Parsons, 2007). The ditch site was formerly an irrigation ditch that became scoured out over a short period of time in 1926. In total there are three areas of concern as possible toxaphene sources (Appendix A), with the CAFO ranked as the highest priority (Figure 2).

Organization and Schedule

Table 4 lists the people involved in this project. All are employees of the Washington State Department of Ecology. Table 5 presents the proposed schedule for this project.

Table 4. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Mike Kuttel Water Quality Program Eastern Regional Office Phone: 509-329-3414	EAP Client	Clarifies scopes of the project. Provides internal review of the QAPP and approves the final QAPP.
William Hobbs Toxic Studies Unit Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data, analyzes and interprets data, and enters data into EIM. Writes the draft report and final report.
Michael Friese Toxic Studies Unit Phone: 360-407-6737	Field Assistant	Helps collect samples and records field information.
Dale Norton Toxic Studies Unit 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 Eastern Operations Section Phone: 509-454-4244	Section Manager of Project Study Area	Reviews and approves the QAPP, staffing plan, technical study budget, and the technical sections of the report.
Will Kendra Statewide Coordination Section 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.
Jim Bellatty Water Quality Program Eastern Operations Phone: 509-329-3534	Section Manager for the Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Joel Bird Manchester Environmental Laboratory Phone: 360-871-8801	Director	Approves the final QAPP.
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

Table 5. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Field work completed	December 2014	Will Hobbs
Laboratory analyses completed	February 2015	
Environmental Information System (EIM) database		
EIM Study ID	WHOB001	
Product	Due date	Lead staff
EIM data loaded	February 2015	Michael Friese
EIM quality assurance	March 2015	Will Hobbs
EIM complete	April 2015	Michael Friese
Final report		
Author lead / Support staff	William Hobbs / Mike Kuttel and Michael Friese	
Schedule		
Draft due to supervisor	April 2015	
Draft due to client/peer reviewer	May 2015	
Draft due to external reviewer(s)	June 2015	
Final (all reviews done) due to publications coordinator	July 2015	
Final report due on web	August 2015	

Sampling Process Design (Experimental Design)

The inputs of toxaphene to Pine Creek appear to be governed largely by the hydrology of the irrigation season. The sampling program for this study will therefore be timed in order to capture the beginning and end of the irrigation season in the Pine Creek Watershed.

Timing of toxaphene inputs

Observations of the flow data from the Walla Walla River USGS monitoring station near Touchet, WA (USGS station #14018500; downstream of the Pine Creek confluence) have been collected since 1951. The mean monthly hydrograph for the last 30 years shows the discharge for the river increasing in the winter months, reaching the upper range in January to March, and peaking in April to May with the snowmelt from the headwater Blue Mountains (Figure 4). The detailed hydrograph for the most recent water year, 2013, shows a broadly similar pattern punctuated with significant runoff events throughout the winter and early spring. The largest event occurs in late-April. Historic discharge data on Pine Creek near the town of Weston, OR (1965-1985; station 14016200) shows a broadly similar trend to the Walla Walla River, with the exception of an earlier reduction in flow during April/May (Figure 5). Instantaneous flow measurements were collected for Pine Creek in 2002/03 during previous sampling events (Figure 5). The demand for water from the Pine Creek watershed during the spring has lead to a number of irrigation canals within and adjacent to the Pine Creek watershed. The irrigation season begins in March and continues into June. Infiltration and contributions from adjacent canals prolong Pine Creek's flows.

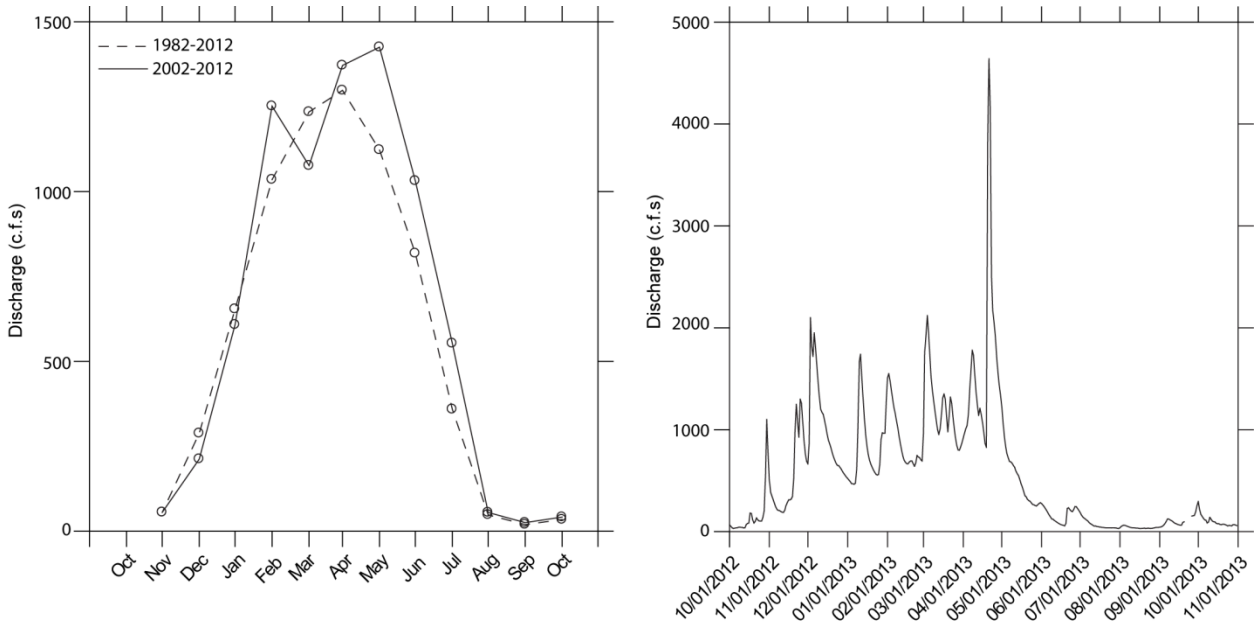

Figure 4.Monthly mean hydrograph for the Walla Walla River near Touchet, WA (USGS#14018500) for the period 1982-2012 (left panel).

Detailed hydrograph of water year 2013 at the same site (right panel).

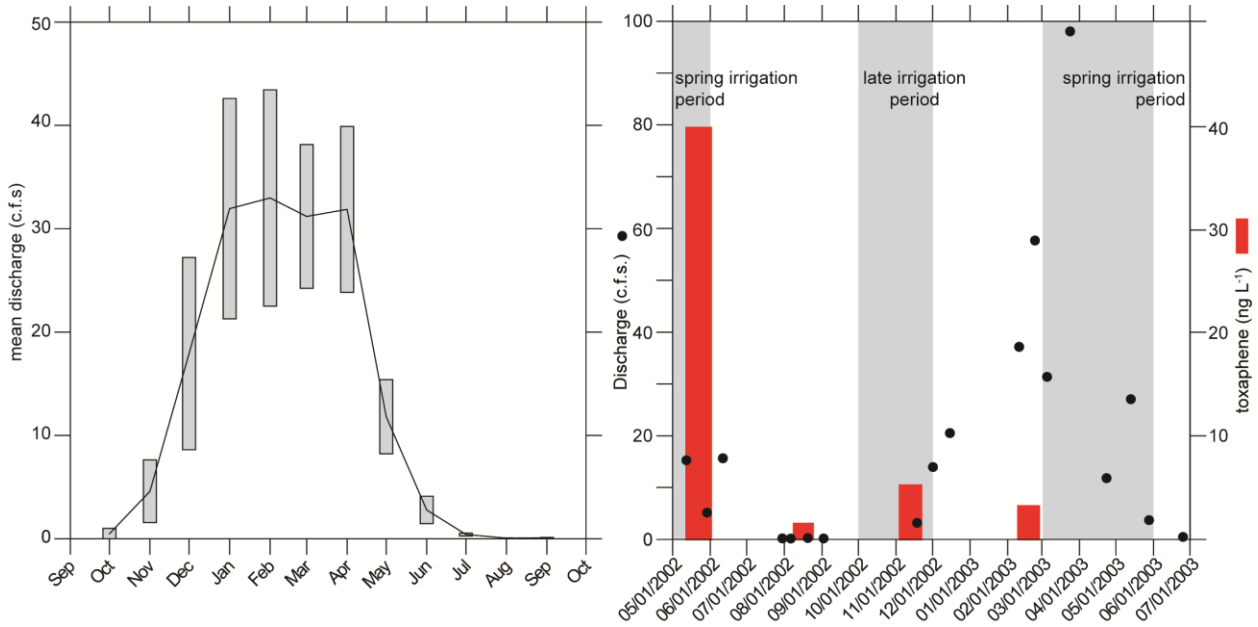

Figure 5. Pine Creek discharge measurements.

Left panel shows historic mean monthly discharge for Pine Creek 1966-1985, with 95% confidence intervals. Right panel shows instantaneous discharge measurements of Pine Creek during 2002/2003 (black dots). Toxaphene concentrations estimated from SPMDs are shown as red bars.

Previous studies have shown that the highest concentrations of toxaphene are measured during the irrigation period (Figure 5; Table 2). Pine Creek flow drops to near zero during the summer, as irrigation stops to allow for the protection of salmonid habitat in the Walla Walla River and tributaries. In the fall, irrigation begins again after harvest to increase soil moisture before winter. Typically, this late season irrigation runs from October into December and yields an increase in Pine Creek flow with an associated elevated toxaphene concentration in water. Samples taken in the summer (August) and winter (February) have yielded low toxaphene concentrations −less than the method reporting limit, in one case (Table 2). Trend monitoring of the Lower Walla Walla River, using passive samplers, has shown very little change in the seasonality of the toxaphene inputs to the Walla Walla over the period 2002/03 and 2007 – 2011 (Figure 6; Table 3). The long term data for the Walla Walla shows how the spring sample is typically more elevated than the fall's, although there is no statistical difference between spring and fall toxaphene concentrations on the Lower Walla Walla when the trend data are pooled (df = 9; p = 0.47).

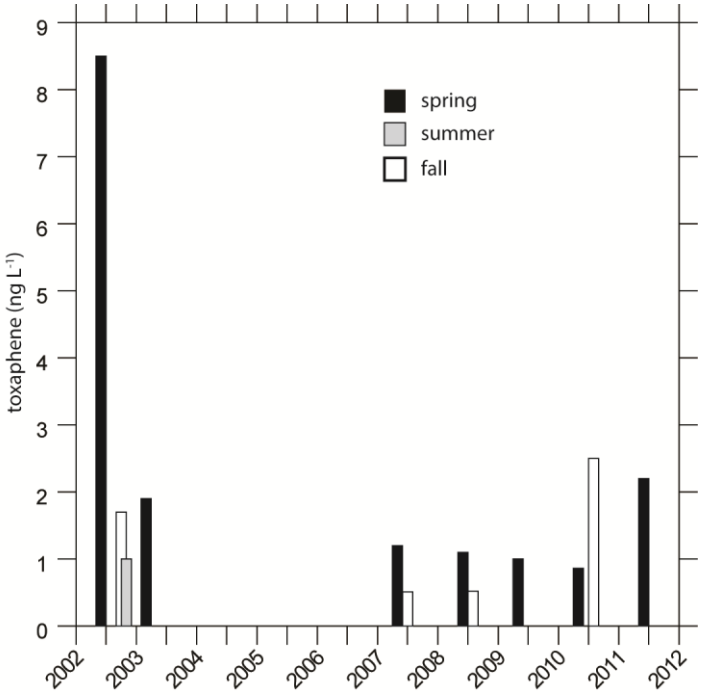

Figure 6. Toxaphene concentrations in the Lower Walla Walla River since 2002; estimated using SPMDs.

Sampling program

The timing of the sampling program will be largely dictated by the irrigation season for the Pine Creek watershed. A baseline-sampling trip will take place in early March 2014 to confirm sample locations for subsequent trips. At this time, we will also collect four samples during a period of higher flow (Figure 5) at locations that have had high toxaphene concentrations in the past and are at the upstream limit of the study area (Table 6). An additional site located at the beginning of the Gardena Ditch will also be sampled for baseline concentrations. The Parsons (2007) study showed the highest toxaphene concentration at the Gardena Creek sample site. This

site is connected to the Gardena Ditch and supplied with water from a pipeline under the Pine Creek watershed that siphons water from Burlingame Ditch (Figure 7). The Gardena sampling will assess whether toxaphene is present within the Gardena irrigation system.

An initial synoptic survey will take place at the end of the spring irrigation season (May / June 2014) to maximize the potential for capturing high toxaphene concentrations in surface water. We will use a number of sampling methods to ensure that we capture enough toxaphene to evaluate the spatial distribution within the watershed. This initial spatial survey of the Pine Creek watershed will focus on an area that encompasses the 3 identified areas of concern as potential sources (Figure 7).

The evaluation of toxaphene concentrations in water will be the primary focus of the initial investigation. Dissolved (and total) toxaphene concentrations in water will be compared with both the state criteria and prior work of Johnson et al. (2012). Following our identification of the potential toxaphene source based on the results from the initial survey, we will conduct a targeted investigation of water, soils and sediments, near the end of the fall irrigation season (Oct / Nov 2014). Sample sites will bracket the potential source and discussion with private landowners may be necessary for site access. Subsequent to the positive identification of a toxaphene source, we will further delineate contaminated soils and/or sediments in the fall of 2014. Sampling events and methods are described in the subsequent section of this plan. A secondary objective of the sampling plan is to assess how the different water sampling methods compare in assessing toxaphene concentrations.

A number of proposed sample locations are located in Oregon. The Oregon Department of Environmental Quality (OR DEQ) and the Walla Walla Basin Watershed Council (WWBWC) are aware of the proposed study and have offered support and interest in field work and results (Don Butcher, personal communication; Brian Wolcott, personal communication).

Table 6. Proposed sample sites for the baseline sampling and initial survey of Pine Creek and tributaries.

Sample site	Surface water			Sediment sample	Latitude	Longitude	Description
	CLAM (SPE)	SPMD	Grab				
Baseline sampling							
PN13-01	X				-118.633	46.028	Pine Creek at Sand Pit Rd.; previously PN-02[a,b]
PN13-02	X				-118.607	46.013	Pine Creek at Burrows Rd.; previously PN-01[a]
GRDN13-01	X				-118.617	46.012	Gardena Ditch at Pine Creek Siphon
PN13-05	X				-118.537	45.96	Pine Creek at Schubert Rd.
Initial survey							
PN13-01[c]	X	X	X		-118.633	46.028	Pine Creek at Sand Pit Rd.; previously PN-02[a,b]
GRDN13-01	X				-118.617	46.012	Gardena Ditch at Pine Creek Siphon
GRDN13-02	X				-118.721	46.017	Gardena Creek at Nelson Rd. / Watson Loop Rd.[a,b]
PN13-02	X	X			-118.607	46.013	Pine Creek at Burrows Rd.; previously PN-01[a]
UNNMD13-01	X			X	-118.592	46.023	Unnamed ditch at Burlingame Canyon
PN13-03	X	X			-118.59	46.001	Pine Creek at Stateline Rd.
LMC13-01	X			X	-118.569	46.002	Little Mud Creek (Demaris Ditch) @ MacDonald Rd.
SWC13-01	X				-118.569	45.994	Swartz Creek at Hudson Bay Rd.
SWC13-02			X		-118.548	45.99	Swartz Creek at Stateline Rd.
PN13-04	X			X	-118.552	45.976	Pine Creek off Troyer Rd.
DRC13-01			X		-118.528	45.969	Dry Creek at Burocker Rd.
PN13-05	X	X			-118.537	45.96	Pine Creek at Schubert Rd.

[a] Parsons, 2007 sample site
[b] Johnson et al., 2004 sample site
[c] CLAM and grab samples will be taken at beginning, midpoint, and end of SPMD deployment

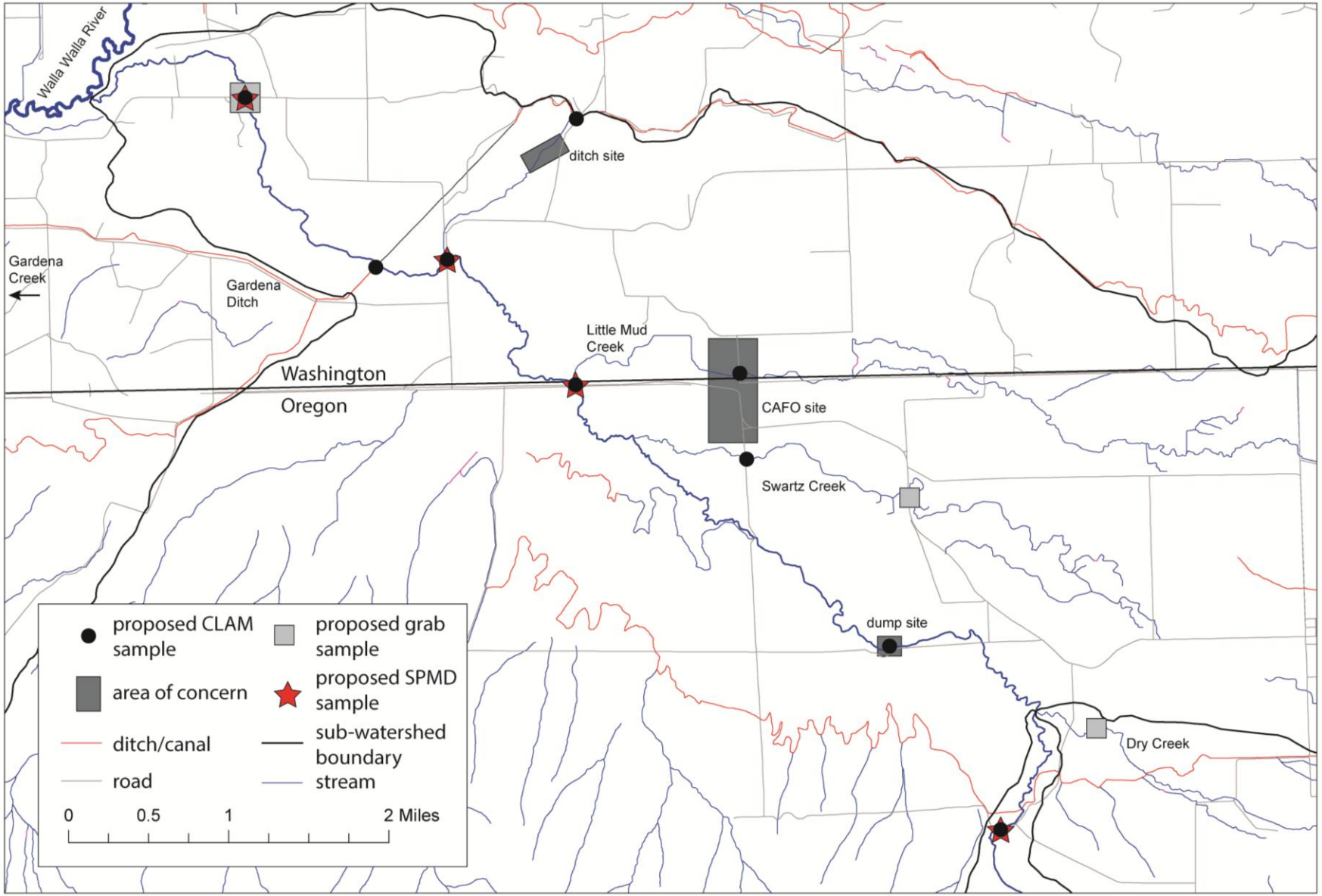

Figure 7. Proposed sample sites.

Sampling Procedures

The media investigated during this source assessment will be surface water and soil/sediment (Table 7). Toxaphene in water has been analyzed in SPMD extracts (Johnson et al., 2004; 2012) and composite grab samples (Parsons, 2007) from the Pine Creek watershed. This study will use a combination of sampling approaches to quantify the spatial distribution of toxaphene in the Pine Creek watershed. The baseline sampling in early March 2014 at the beginning of the irrigation season, and at a period of relatively high flow, will rely on solid phase extraction disks (SPE) deployed in continuous low-level aquatic monitoring (CLAM) samplers. This sampling approach takes an approved laboratory method for concentrating and integrating trace organic contaminants (EPA 3535) and places it in the field. The CLAM device pumps water through the SPE for the period of deployment (typically 24-36 hours), significantly increasing the volume of sample over a simple grab sample. Four sites will be sampled with the CLAM samplers during the baseline event (Table 6).

The initial synoptic survey in May/June 2014 will use a combination of surface water grab samples, SPE disks in CLAM samplers and SPMDs as passive samplers. The redundancy and overlap of sampling methods proposed for the initial survey is due to the necessity to capture the toxaphene pulse at the end of the spring irrigation season. In addition, a secondary objective of this study is to compare the sampling techniques for source assessment. Four SPMDs will be deployed within the Pine Creek channel covering the area of investigation (Figure 7). Previous investigations in Pine Creek and the Lower Walla Walla have had success quantifying toxaphene concentrations using SPMDs (Table 2 and 3 with associated references). Further details of the SPMD sampling are provided in the subsequent subsection.

SPMDs will be deployed for approximately one month and the sample period will overlap with the CLAM samplers at all 4 sites. CLAM samplers will be deployed at the mid-point of the SPMD sampling period at 10 sites throughout the area of investigation (Figure 7). At the sample location PN13-01, a CLAM sample and grab sample will be taken at the time of SPMD deployment, the mid-point, and during retrieval for a more complete comparison of the CLAM and SPMD approaches. Additional water samples will be taken as grab composites from two locations at the edge of the area of investigation (Figure 7). Composite grab samples will be collected following the Ecology Standard Operating Procedure for pesticide grab samples (Anderson, 2006). An integrated or composited sample across the stream is collected by subsampling 3 locations with a 1 L transfer jar. Samples for the parameters of interest are composited in the field at the time of collection.

Based on the results of the initial synoptic survey, a focused sampling investigation will take place during October/November, in the area identified as the likely toxaphene source. Toxaphene concentrations in water will be evaluated using an array of CLAM samplers and composite grab samples. SPMDs will not be deployed during this portion of the investigation, as the expected toxaphene concentrations will be elevated and persistent near the source. Grab samples will also be collected near the expected source. The rationale for the redundancy of sampling with grab samples is to provide an actual and direct measurement of the concentration of toxaphene near the source. In calculating the water concentration from the SPE disk within the CLAM sampler,

an assumption must be made about the total volume of water sampled, making the calculated toxaphene concentration an estimate.

Ancillary parameters will be analyzed in water samples at each sample site, depending on the main sampling approach for toxaphene. For example, those sites where SPMDs will be deployed must be sampled for TSS and total organic carbon (TOC) at the time of deployment, the midpoint of sampling, and at the time of SPMD retrieval. TSS will also be collected at all sites sampled for toxaphene during the baseline and initial synoptic surveys. In addition, pH, conductivity and temperature will be measured during all sampling events in the field with handheld meters.

Sediment samples will be collected in accordance with the Ecology SOP for sampling of freshwater sediments (Blakley, 2008). If the creek and depositional areas are sufficiently deep then a petite ponar sampler will be used, however in shallow waters for sites with small amounts of sediment deposition the direct sampling of the creek bed with stainless steel scoops, followed by homogenization in a stainless steel bowl would be appropriate. Soils will be composited from 5 aliquots of the upper 2 cm of soil at the sample site using stainless steel scoops and a stainless steel bowl. All equipment will be decontaminated prior to the sampling trip, covered in tin foil and transported into the field.

Table 7. Field procedures for water and soil/sediment samples.

Parameter	Matrix	Minimum sample size	Container	Preservation	Holding time
Toxaphene	water	3 L	1 gal glass jar w/ Teflon lid	cool to 4°C	7 days
Toxaphene	SPE disk	1 SPE	CLAM sampler	cool to 4°C	14 days
TSS	water	1 L	1 L poly bottle	cool to 4°C	7 days
TOC	water	20 mL	2 pre-acidified 60 ml bottles	cool to 4°C	28 days
Toxaphene	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

Semi-permeable membrane devices (SPMDs)

We intend to use SPMDs in this project to estimate the dissolved and total toxaphene concentrations in the surface water of Pine Creek. SPMDs are passive sampling devices and have been used by Ecology for a number of years. The use of SPMDs in this project will follow the guidelines outlined in the detailed SOP (Seiders et al., 2012). SPMDs are composed of a thin-walled, layflat polyethylene tube (91.4 cm x 2.5 cm x 70-95 um thickness) filled with 1 ml of triolein, a neutral lipid compound. The goal of any passive sampling device is to emulate natural biological uptake by allowing the media to diffuse through the membrane and concentrate over time. In so doing the SPMD provides a time-integrated sample for the period of deployment

(typically 28 days for SPMDs) which naturally smoothes large fluctuations in concentrations. After deployment, the membrane is removed, extracted and analyzed for the organochlorine compounds of interest.

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 the baseline-sampling event. Each site canister will contain 3 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 toxaphene in the water of Pine Creek, we need to assess the total amount bound to the SPMD residue. For this we use Permeability/Performance Reference Compounds (PRCs), which are spiked prior to 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}). PCB-4, -29, and -50 will serve as PRCs for this project. These congeners are not present in significant amounts in the environment and have shown appropriate rates of loss (20-80%) in past Ecology studies. The spiking level will be 50 ng for PCB-4 and 25 ng for PCB-29 and -50 per sample. MEL will order, prepare, and validate the PCB standard and will provide the PRC spiking solution to EST.

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 stream. The deployment of SPMDs is carried out 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 opposite of deployment, using the same cans for shipping. The cans must be properly sealed and cooled to and kept near freezing until they arrive at EST for the extraction of the membranes.

Continuous low-level aquatic monitoring (CLAM)

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 to 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. TSS has ranged from 6 to 33 mg L^{-1} during previous sampling events in May/June in Pine Creek near Sand Pit Rd. (Johnson et al., 2004; Parsons, 2007). We will try to place the CLAM where TSS may be lower (e.g., in a pool, near vegetation).

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 MEL where they can be cleaned and conditioned with solvents before use in the field. For capturing organochlorine compounds, the HLB media SPE for polar and nonpolar organic compounds will be used.

In Pine Creek, CLAMs will be secured within the water column by tethering or anchoring to rebar or a cement block and deployed for 24 hours. Prior to deployment, the devices are 'calibrated' to assess the flow rate, which is then also assessed upon retrieval. Flow is measured with a syringe on the outlet port of the device and repeated until a consistent result is achieved. The linear flow rate between the two calibration points is used to calculate the estimated sample volume over the period of deployment.

At retrieval, the SPE disks are removed from the devices and cooled on ice. Disks are shipped to MEL for extraction within 14 days. Using the mass of organic compounds analyzed within the SPE and the estimated sample volume, we can calculate an average water concentration over the period of deployment. Calculated concentrations are estimates and therefore data will be qualified as such and not entered into Ecology's EIM system. For a more complete overview of CLAM operating procedures, see Appendix C.

Measurement Procedures

Ecology's MEL will conduct all of the analysis (with exception of grain size on sediments) and reporting. Samples will not be analyzed for a complete suite of chlorinated pesticides (EPA 8081); instead, the analysis will target the group of toxaphene compounds with the help of the refined chromatography from previous investigations (Johnson et al., 2004; 2012). Analysis will be conducted using gas chromatography / electron capture detection (GC/ECD). Grab samples will use large volume injection (LVI), while extracts will be injected at a standard volume. The identification of toxaphene compounds can be interfered with by PCB congeners and chlordane compounds, which can co-elute or be measured at the same time as other compounds. Previous work by MEL and Johnson et al. (2012) has been able to establish a fairly clear toxaphene signal in the Pine Creek samples (M. Mandjikov, personal communication).

MEL will extract the SPE disks from the CLAM samplers and EST laboratory will extract the SPMD, perform the clean-up, and ship the extracts in ampoules to MEL. The PRCs PCB-4, -29, and -50 will be quantified during the GC/ECD run for toxaphene by MEL.

Using the extracts from CLAM-SPEs and SPMDs will allow us to capture enough toxaphene by mass for analysis. Having also sampled a significant volume of water it is expected that MRLs will be below the aquatic life water criteria (0.2 ng L^{-1}). Unfortunately, using a GC/ECD approach on grab samples will yield method reporting limits (MRLs) (~8.3 ng L^{-1}) that exceed the current human health (0.73 ng L^{-1}) and aquatic life (0.2 ng L^{-1}) water criteria. The alternative to achieve MRLs below current water quality criteria for the grab samples is to use high-resolution gas chromatography/mass spectrometry (HR GC/MS). Typically, HR GC/MS samples cost approximately $750 whereas GC/ECD samples cost $160. Given the cost differential, MEL's ability to detect toxaphene patterns using GC/ECD, and the objectives of this study for

identification of high concentrations of toxaphene, the EPA method 8081 (GC/ECD) with LVI on grab samples is appropriate as a screening tool. Excess sample extracts will be saved by MEL for a period of 60 days after MEL reports the data.

Ancillary water samples will be analyzed for TSS and TOC. pH and conductivity will be measured in the field at the time of sampling. TSS will only be analyzed during the baseline and initial synoptic survey to gain further understanding of the relationship between TSS and toxaphene. Samples for TOC in water will be collected only at those sites with SPMDs, in order to allow for necessary calculations of total toxaphene burdens within the membranes (Huckins et al., 2006). Soil and/or sediment samples will be analyzed for TOC and sediment samples will be analyzed for grain size by an outside laboratory; MEL will oversee reporting and quality control. Given the propensity of organochlorine compounds to bind with carbon, an understanding of the carbon content and size fractions of the sediment is useful in interpreting toxaphene concentrations during the initial survey. The follow-up detailed sampling event will not analyze sediments for TOC or grain size, because (1) the concentrations are expected to be high and (2) contaminated sediments that require disposal or treatment are typically evaluated using concentrations expressed as dry weight (Michelson, 1992). Specific analytical methods for all analyses are detailed in Table 8.

Table 8. Laboratory procedures.

Analysis	Sample matrix	Approx. number of samples*	Expected range of results	Reporting limit	Sample prep method	Analytical method
Toxaphene (grab)	surface water	10	< 3 - 12 ng L^{-1}	3.34 ng L^{-1}	EPA 3510M	LVI/EPA 8081
Toxaphene (SPE)	SPE disk	24	unknown	5-10 ng	EPA 3535	EPA 3620, 3665, 8081
Toxaphene (SPMD)	SPMD	4 (each 3 membranes)	500 - 14000 ng	5-10 ng	dialysis/GPC‡	EPA 3620, 3665, 8081
TSS	surface water	27	5 - 200 mg L^{-1}	1 mg L^{-1}	N/A	EPA 160.2
TOC	surface water	4	2 - 20 mg L^{-1}	1 mg L^{-1}	N/A	SM 5310B
Toxaphene	soil/ sediment	26	0.5 - 10 ug Kg^{-1}	0.5 - 100 ug Kg^{-1}	EPA 8081	SW 846; EPA 8081
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
‡ EST SOPs E14, E15, E19, E33, E44, E48
¥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

Quality Control Procedures

All samples will be analyzed by MEL, with the exception of grain size on sediments. The method quality objectives (MQOs) set by MEL to meet the QC objectives of reliable, useable data are shown in Table 9. MEL will oversee the submission and quality control procedures for the grain size analysis by an outside lab. MQOs and data quality will be reviewed after each sampling event and adjustments to the sampling or analysis approach will be made accordingly.

Table 9. Measurement quality objectives for the Pine Creek toxaphene source assessment.

Analysis	Check stds/lab control samples (% recov)	Duplicate samples (RPD)	Surrogates (% recov)	Matrix spikes (% recov)	Lowest concentration of interest
Water samples					
Toxaphene (grab)	50-150%	NA*	50-150%	NA	< 3 ng L^{-1}
TSS	80-120%	± 20%	NA	NA	1 mg L^{-1}
SPMD and SPE Extracts					
Toxaphene (SPE)	50-150%	NA*	50-150%	50-150%	10 ng
Toxaphene (SPMD)	50-150%	NA*	50-150%	50-150%	10 ng
Soil/Sediment samples					
Toxaphene	50-150%	NA*	50-150%	NA	1.25 ug Kg^{-1}, dw
grain size	NA	± 20%	NA	NA	NA
TOC	75-125%	± 20%	NA	NA	0.1 ug Kg^{-1}

NA = not analyzed
* field replicates analyzed

Field

Field replicates will be collected during each sampling event at a frequency of no less than 10% of the total sample number per sampling event (Table 10). A replicate is an individual sample collected using the same field methods and as close to the same time location as possible. A transfer blank for the grab samples will be carried in the field to assess possible contamination arising from field methods, sample techniques, and sample containers. Ultra-clean water will be obtained from MEL, carried into the field, and transferred to another sample container at designated field location.

Field trip blanks will also be conducted for the SPMDs and CLAM samplers. The field blank SPMD is taken into the field and opened for the same duration of time 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. There are no specific protocols for field blanks of the CLAM samplers. We will transport the field blank SPE into the

field, open the luer locks which exposes the SPE media for the duration of CLAM deployment and retrieval, and submit it to MEL as a field blank.

Table 10. Field quality control samples.

Parameter	Matrix	Replicates	Blanks
Site reconnaissance			
Toxaphene (SPE)	water	1	1
TSS	water	1	N/A
Initial survey			
Toxaphene (SPE)	water	2	1
Toxaphene (SPMD)	water	1	1
Toxaphene (grab)	water	1	1
TSS	water	2	N/A
TOC	water	1	N/A
Toxaphene	soil/sediment	1	N/A
TOC	soil/sediment	1	N/A
grain size	soil/sediment	1	N/A
Focused sampling			
Toxaphene (SPE)	water	2	1
Toxaphene (SPMD)	water	1	1
Toxaphene	soil/sediment	2	N/A
Contaminated site samples			
Toxaphene	soil/sediment	2	N/A

The estimated equipment costs incurred for the SPMDs and CLAM samplers are detailed in Table 11.

Table 11. Estimated costs for SPMD and CLAM samplers.

Equipment	Sites	QA/QC	Cost	Total
SPMD (3 membrane)	4	2	$ 600.00	$ 3,600.00
CLAM rental	24	4	$ 180.00	$ 5,040.00
SPE disks	24	11	$ 79.00	$ 2,765.00
Equipment costs				$ 11,405.00
Total SPMD costs				$ 5,200.00

Laboratory

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 (Table 12). 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.

Table 12. Laboratory quality control samples.

Parameter	Matrix	Method blanks	Check stds/LCS	Duplicates	Surrogate spikes	MS & MSD	OPR stds / Labeled compounds
Toxaphene	water	1/batch	2/batch	1/batch	all samples	1/batch	N/A
Toxaphene	SPE	1/batch	2/batch	N/A	all samples	1/batch	each batch
Toxaphene	SPMD	1/batch	2/batch	N/A	all samples	1/batch	N/A
TSS	water	1/batch	2/batch	1/batch	N/A	N/A	N/A
TOC	water	1/batch	2/batch	1/batch	N/A	N/A	N/A
Toxaphene	soil/sediment	1/batch	2/batch	1/batch	all samples	1/batch	N/A
TOC	soil/sediment	1/batch	2/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

The tracking and calculation of check standards, spikes, and blanks for the SPMDs follow the SPMD SOP (Seiders et al., 2012) and SPMD data management SOP (Seiders and Sandvik, 2012). The relevant *draft* worksheets for the Spike solutions, Master sample and analysis plan, and Sample-Spike-Split-Analysis table are included in Appendix B. SPMDs require a detailed method blank procedure that is carried out by both EST and MEL. The following method blanks will be prepared by EST:

1. A spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples.
2. A day-zero SPMD blank to serve as a reference point for PRC loss.
3. A dialysis blank-SPMDs from the same lot as the project batch, to represent background during dialysis and cleanup.
4. A day-zero blank SPMD (fresh day blank), prepared just prior to dialysis, to serve as a control.

MEL will analyze blank 2 and 3, with the remainder stored frozen at MEL. Should there be an issue with blank contamination, these additional blanks will be analyzed.

EST will add surrogate compounds, Tetrachloro-m-xylene and 4,4-dibromooctafluorobi-phenyl, to each SPMD membrane prior to dialysis. The surrogates will be supplied by MEL and spiked at 80 ng each. A matrix spike on one membrane will be carried out by EST and held at MEL. MEL will provide all necessary solutions to EST for spikes and PRCs and generate a certificate for both the spike solution standard and the PRCs.

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. Experience with previous analysis of surface water grab samples using LVI and EPA method 8081 has yielded a method reporting limit of ~ 8.3 ng L^{-1}. As discussed previously, this is above the human health and chronic effects aquatic life water criteria, but it is below previously documented concentrations of toxaphene in Pine Creek.

A turn-around time of approximately 45-60 days is requested for the analysis and preliminary review of the data by MEL. All laboratory analysis will be completed by January 2015. The estimated analytical budget for this project will total $15,752 (Table 13), which includes all in-house laboratory costs and review of QA/QC.

Table 13. Laboratory cost estimate for Pine Creek toxaphene source assessment.

Analysis	Matrix	Number of sites	Number of QA samples	Cost per sample	MEL subtotal
Baseline sampling					
Toxaphene	SPE disk	4	2	$160	$960
TSS	water	4	1	$12	$60
Initial survey					
Toxaphene	water	5	2	$160	$1,120
TSS	water	23	4	$12	$324
TOC	water	12	3	$36	$540
Toxaphene	SPMD extract	4	6	$160	$1,600
Toxaphene	SPE disk	12	3	$160	$2,400
Toxaphene	soil/sediment	6	2	$150	$1,200
TOC	soil/sediment	6	2	$46	$368
Grain Size	soil/sediment	6	1	$100	$700
Focused sampling					
Toxaphene	water	5	2	$160	$1,120
Toxaphene	SPE disk	8	2	$160	$1,600
Toxaphene	soil/sediment	10	2	$150	$1,800
Contaminated site samples					
Toxaphene	soil	10	2	$150	$1,800
				Lab total:	$15,592

Data Management Procedures

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. 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 *Data Verification and Validation*).

All laboratory data will be accessed and downloaded from MEL's Laboratory Information Management System (LIMS) into Excel spreadsheets. After project personnel verify and validate data, they will enter data into Ecology's Environmental Information Management System (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.

The appendices within the SOP for SPMDs (Seiders et al., 2012) detail the available templates for data reduction and planning. Toxaphene residual concentrations from the SPMDs will be used to calculate an estimated dissolved toxaphene concentration in water. The model developed by David Alvarez, USGS to calculate estimated water concentrations from the total toxaphene burdens in the SPMDs and the PRC sampling rates is on the Ecology shared server (Y:\Shared\SPMDs\). Before any calculations take place, we will confirm that the current version is the most up to date. Given the nature of the source assessment project, we will not correct for the field blank. Total toxaphene concentrations will be calculated following Meadows et al. (1998), using TOC data.

Data Verification and Validation

MEL will oversee the review of all laboratory data packages and descriptions. MEL will verify compliance with the methods and protocols outlined in this project plan. Checks will be carried out on the quality control measures (spikes and surrogate recovery), calibrations and consistency and completeness of the data. MEL will provide assurances that the data is correct and without errors and omissions. Typical parameters verified by MEL are: acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will generate a data verification report that meets requirements of a case summary addressing the MQOs and previously mentioned data checks.

Following MEL's review and recommendations on data completeness, the project lead will review the lab data packages. The data will be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered. MQOs will be assessed between the field and laboratory duplicates. The evaluation of method detection limits and reporting limits will be reviewed by both MEL and the project lead. Reporting limits for the parameters of interest will be evaluated and non-detectable results and values exceeding the lowest concentration of interest will be identified.

Data Quality (Usability) Assessment

The project lead assesses the data quality to determine whether reliable decisions can be made to meet the goals of the study. If the MQOs have not been met, the project lead, in consultation with MEL, will decide whether the data can be used. In the case where sample variability at a site does not meet the MQO but all samples are well above the criteria, the data would still be useful. However, a bias within the samples at low concentrations may affect our ability to assess concentrations relative to the human health criteria. The professional judgment of scientists at MEL and Ecology will be relied on to determine data usability.

Audits and Reports

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.

MEL will review the data package prior to reporting to the project lead. Discussion among project scientists and evaluation of sampling and analytical results is expected following each sampling event. The project plan can then be adjusted, if needed. Draft report writing will take place during the winter of 2014/15, with the final report expected by June/July 2015. The data on Ecology's EIM system will be published by April 2015.

The goal of this study is to identify and begin to delineate the source of toxaphene to Pine Creek, in the Walla Walla River basin. The deliverables from this work will detail: (1) a synoptic survey of toxaphene concentrations in water and sediment throughout the Lower Pine Creek watershed during the spring irrigation period, (2) follow-up sampling in the late irrigation period in the fall, and (3) recommendations on how to address any identified toxaphene source.

References

Anderson, P., 2006. Standard Operating Procedures for Sampling of Pesticides in Surface Waters Washington State Department of Ecology, Olympia, WA. SOP Number EAP003. www.ecy.wa.gov/programs/eap/quality.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

Blakley, N., 2008. Standard Operating Procedure for Obtaining Freshwater Sediment Samples. Washington State Department of Ecology, Olympia, WA. SOP Number EAP040. www.ecy.wa.gov/programs/eap/quality.html

Butcher, D., 2005. Walla Walla subbasin stream temperature total maximum daily load and water quality management plan. State of Oregon, Department of Environmental Quality. Portland, OR. http://www.deq.state.or.us/WQ/TMDLs/docs/umatillabasin/wallawalla/tmdlwqmp.pdf

Butcher, D., 2014. Personal Communication. Basin Coordinator, Oregon Department of Environmental Quality.

Coes, A.L., N.V. Paretti, W.T. Foreman, J.L. Iverson, and D.A. Alvarez, 2014. Sampling trace organic compounds: 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. Quality Assurance Project Plan: Burnt Bridge Creek PCB and Dieldrin Screening Study. Washington State Department of Ecology, Olympia, WA. Publication No. 14-03-101. https://fortress.wa.gov/ecy/publications/summarypages/1403101.html

Davis, D. and A. Johnson, 1994. Washington State Pesticide Monitoring Program: Reconnaissance Sampling of Fish Tissue and Sediments (1992). Washington State Department of Ecology, Olympia, WA. Publication No. 94-194. https://fortress.wa.gov/ecy/publications/summarypages/94194.html

Durkin, P.R., P.H. Howard, J. Saxena, S.S. Lande, J. Santodonato, J.R. Strange, and D.H. Christopher, 1979. Reviews of the environmental effects of pollutants, X: Toxaphene. Oak Ridge National Laboratory ORNL/EIS-130 and US Environmental Protection Agency EPA-600/1-79-044. 497p.

EPA, 1980. Ambient water quality criteria for toxaphene. Office of Water Regulations and Standards, Criteria and Standards Division, US Environmental Protection Agency, Washington, D.C. EPA 440/5-80-076.

EPA, 1994. Water Quality Standards Handbook, second edition. Updated in 2012. EPA-823-B-12-002. Office of Water, US Environmental Protection Agency, Washington, D.C. Available at: http://water.epa.gov/scitech/swguidance/standards/handbook/index.cfm

Hisata, J., 2002. Lake and stream rehabilitation: rotenone use and health risks. Final supplemental environmental impact statement. Washington Department of Fish and Wildlife, Fish Program. http://wdfw.wa.gov/licensing/sepa/2002/2002fnl.pdf

Huckins, J.N., J.D. Petty, and K. Booij, 2006. Monitors of organic chemicals in the environment: Semipermeable membrane devices. Springer, New York, USA. 223p.

Johnson, A., 1997a. Pesticides detected in the Walla Walla drainage, April and June 1996. Memorandum to C. Nuechterlein, D. Knight, and J. Jacobson. Washington State Department of Ecology, Olympia, WA. Publication No. 97-e03. https://fortress.wa.gov/ecy/publications/summarypages/97e03.html

Johnson, A., 1997b. Results from additional pesticide sampling in the Walla Walla drainage, April and May 1997. Memorandum to C. Nuechterlein, D. Knight, and J. Jacobson. Washington State Department of Ecology, Olympia, WA. Publication No. 97-e06. https://fortress.wa.gov/ecy/publications/summarypages/97e06.html

Johnson, A., B. Era-Miller, R. Coots, and S. Golding, 2004. A total maximum daily load evaluation for chlorinated pesticides and PCBs in the Walla Walla River. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-032. https://fortress.wa.gov/ecy/publications/summarypages/0403032.html

Johnson, A., K. Carmack, and B. Era-Miller, 2012. Toxaphene: Improved recognition in Washington streams, rivers and lakes. Washington State Department of Ecology, Olympia, WA. Publication No. 12-03-004. https://fortress.wa.gov/ecy/publications/summarypages/1203004.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.

Mandjikov, M., 2014. Personal Communication. Chemist, Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Meadows, J.C., K.R. Echols, J.N. Huckins, F.A. Borsuk, R.F. Carline, and D.E. Tillitt, 1998. Estimation of uptake rates for PCB congeners accumulated by semipermeable membrane devices and brown trout (Salmo trutta). Env. Sci. & Technol. 37: 667-671.

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

Michelson, T., 1992. Organic Carbon Normalization of Sediment Data. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-032. https://fortress.wa.gov/ecy/publications/summarypages/0509050.html

Parsons, 2007. Walla Walla River chlorinated pesticides source characterization. Prepared for U.S. Environmental Protection Agency Region 10 and Washington State Department of Ecology. 152p.

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

Sandvik, P., 2010. Washington State Toxics Monitoring Program: Trend Monitoring for Chlorinated Pesticides, PCBs, PAHs, and PBDEs in Washington Rivers and Lakes, 2008. Washington State Department of Ecology, Olympia, WA. Publication No. 10-03-027. https://fortress.wa.gov/ecy/publications/summarypages/1003027.html

Sandvik, P. and K. Seiders, 2011. Washington State Toxics Monitoring Program: Monitoring with SPMDs for PBTs in Washington Waters in 2009. Washington State Department of Ecology, Olympia, WA. Publication No. 11-03-029. https://fortress.wa.gov/ecy/publications/summarypages/1103029.html

Sandvik, P. and K. Seiders, 2012. Washington State Toxics Monitoring Program: Evaluation of SPMDs for Trend Monitoring of PBTs in Washington Waters, 2010-2011. Washington State Department of Ecology, Olympia, WA. Publication No. 12-03-036. https://fortress.wa.gov/ecy/publications/summarypages/1203036.html

Seiders, K., P. Sandvik, and A. Johnson, 2012. Standard Operating Procedures for Conducting Studies using Semi-Permeable Membrane Devices (SPMDs). Washington State Department of Ecology, Olympia, WA. SOP Number EAP001. www.ecy.wa.gov/programs/eap/quality.html

Seiders, K. and P. Sandvik, 2012. Standard Operating Procedure for Semi-Permeable Membrane Devices (SPMDs) Data Management and Data Reduction. Washington State Department of Ecology, Olympia, WA. SOP Number EAP079. www.ecy.wa.gov/programs/eap/quality.html

Stohr, A., M. LeMoine, and G. Pelletier, 2007. Walla Walla River tributaries temperature total maximum daily load study. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-014. https://fortress.wa.gov/ecy/publications/summarypages/0703014.html

von Rumker, R., E.W. Lawless, A.F. Meiners, K.A. Lawrence, G.L. Kelso, and F. Horay, 1975. Production, distribution, use, and environmental impact potential of selected pesticides. Office of Pesticide Programs, U.S. Environmental Protection Agency. EPA 540/1-74-001. 453 p.

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

Weakland, J., 2014. Personal Communication. Organics Supervisor, Manchester Environmental Laboratory, Washington Department of Ecology.

Wolcott, B., 2014. Personal Communication. Executive Director, Walla Walla Basin Watershed Council.

Appendices

Appendix A. Detailed Maps of Areas of Concern

Figure A-1. Detail of the CAFO site on the Washington – Oregon border. Proposed sample site LMC13-02 on Little Mud Creek off MacDonald Rd.

Figure A-2. Detail of the enlarged gulley upstream of sample site UNNMD13-01.

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Figure A-3. Detail of possible dump site adjacent Pine Creek off Troyer Rd. Proposed sample site PN13-05 shown.

Appendix B. SPMD SOP Plan Worksheets (DRAFT)

The table numbering follows the appendix numbering of the SOP (Seiders et al., 2012).

Appendix C-2. Spiking Solutions Worksheet

A	B	C	D	E	F	G	H	I	J	K
Spiking Solution	Preparer	# of Spikes[a]	Calc. of Total Volume to Prepare Needed	Estimated Total Volume to Prepare	Compounds	Concentration per Analyte (ng/uL)	Spiking Amount (uL)[a]	# of Membranes Spiked per Sample	Calc. for Total Spiking Level per Sample (ng)	Total Spiking Level per Sample (ng)
PRCs	MEL/EST	28	2.8	6 mL	PCB--004	0.2	100	3	60	50
					PCB-029, PCB-050	0.1		3	30	25
Surrogate: chlorinated pesticide	MEL	10	0.5	2 mL	tetrachlor-m-xylene (TCMX), 4,4-dibromo-octafluorobiphenyl (DBOB)	8.0	50	1	400	400
Matrix Spike: chlorinated pesticides	MEL	1	0.1	1 mL	various compounds	0.8	100	1	80	80

a. See EST order for sample information including which samples to spike.

EST = Environmental Sampling Laboratories.

MEL = Manchester Environmental Laboratories.

Appendix J. Master Sample and Analysis Plan.

Project: Pine Creek Toxaphene Source Assessment — **Deployment Dates: May/June 2014**

Use of fields: R = Required field, O = Optional field

O	O	R	R	R	R	R	R	R	R	R	R	R	R	R
				cost/unit -->	$ 57	$ 1	$ 1	$ 1	$ 265	$ 160	$ 12	$ 34		

Site and Sample Information						Spiking by EST			Extraction	Lab Analyses on Extracts	Ancillary Analyses		Notes
Field Replicate	Field Trip Blanks	Sites	Lab ID # = work order + last 2 digits	Field ID	EST: # of membranes mfg	PRCs: PCB-004, 029, 050 (spike each membrane)	Membrane Spike: various CP (spike 1 membrane)	Surrogates: CP (spike 1 membrane per sample)	EST: SPMD Dialysis + GPC	# Toxaphene Analysis (MEL)	# TSS (MEL)	# TOC (MEL)	Comment
		Pine Creek @ Sand Pit Rd.		PN13-01	3	3	0	1	1	1	1	1	MEL to analyze for PRCs
		Pine Creek @ Burrows Rd.		PN13-02	3	3	0	1	1	1	1	1	MEL to analyze for PRCs
		Pine Creek @ Stateline Rd.		PN13-03	3	3	0	1	1	1	1	1	MEL to analyze for PRCs
		Pine Creek @ Schubert Rd.		PN13-06	3	3	0	1	1	1	1	1	MEL to analyze for PRCs
x		Field Replicate: Pine Creek at Sand Pit Rd.		REPLPN13-02	3	3	0	1	1	1	1	1	MEL to analyze for PRCs
	x	Field Trip Blank: Pine Creek at Sand Pit Rd.		TBLKSPOK	3	3	0	1	1	1	0	0	MEL to analyze for PRCs
		Day 0-Dialysis Blank		DAY0DIAL	3**	3**	0	1	1**	1	0	0	
		Day 0-Method Blank		DAY0-MB	3	3**	0	1	1	1	0	0	
		Fresh Day 0 Blank		FRDAY0	3	3**	0	1	1		0	0	Hold frozen at MEL.
		Spiked Solvent		SPKSOLVNT	0	1**	0	1	1**		0	0	Solvent spiked with PRCs and Surrogates. Hold frozen at MEL.
		Membrane Spike for CP		MSCLPBDPH	1**	0	1**	0	1**	1	0	0	1 separate membrane for MEL only.
		PRC Solution		PRCSOLN	3	0	0	0	0		0	0	Hold frozen at MEL.
		Surrogate Solution		SURROSOLN	0	0	0	0	0		0	0	Hold frozen at MEL.
		Sum (does not include items with asterix)			**27**	**18**	**0**	**10**	**8**	**9**	**5**	**5**	
		Total Costs			**$ 1,539**	**$ 18**	**$ -**	**$ 10**	**$ 2,120**	**$ 1,440**	**$ 60**	**$ 171**	

*No charge unless analyzed. Sample held frozen at MEL.

** Usually no charge from EST because they consider it part of their QC.

MEL = Manchester Environmental Laboratory

Appendix K. Samples, Spikes, Splits, and Analyses Plan.

Spike volumes are based on target mass for most samples as determined by lab that provides spiking solution and analyzes extract.

Sample Info				Spiking Instructions: uL to spike in number of membranes (e.g. 50 in 1/3 = spike 50 uL into one of three membranes)			Sample Extractions, Splits, and Analyses (shows # analyses for target analytes and lab)			
		Source of Spiking Solution ->		MEL	MEL	MEL				
			ID of Spike Solution->							
Field ID ("Field Station Identification" on LAR)	**MEL Sample Number on LAR: 1106028-**	**Sample Description**	**# of membranes in sample**	**PRCs: PCB-004, 029, 050**	**Surrogates: CP**	**CP MS**	**Dialysis + GPC (EST) ?**	**Extract Split 50:50 by EST ?**	**CP (MEL)**	**Comment**
PN13-01		"Field Sample"	3	100 in 3/3	50 in 1/3	-	yes	no	1	MEL to quantify PRCs
PN13-02		"Field Sample"	3	100 in 3/3	50 in 1/3	-	yes	no	1	MEL to quantify PRCs
PN13-03		"Field Sample"	3	100 in 3/3	50 in 1/3	-	yes	no	1	MEL to quantify PRCs
PN13-06		"Field Sample"	3	100 in 3/3	50 in 1/3	-	yes	no	1	MEL to quantify PRCs
REPLPN13-02		"Field Replicate"	3	100 in 3/3	50 in 1/3		yes	no	1	MEL to quantify PRCs
TBLKSPOK		"Field Blank"	3	100 in 3/3	50 in 1/3	-	yes	no	1	MEL to quantify PRCs
DAYZD-1		QC sample: "Day-0 Dialysis Blank"	3	100 in 3/3	50 in 1/3	-	yes	no	1	
DAY0-MB		QC sample: a "Day-0 Dialysis Blank" used as the method blank for PCB congener method	3	100 in 3/3	50 in 1/3	-	yes	no	1	
MSCP		QC sample: "Membrane Spike for CPs "	1	-	25 in 1/1	50 in 1/1	yes	no	1	
FRDAY0		QC sample: "Fresh Day-0 Blank". Extracts from individual membranes are composited before splitting.	3	100 in 3/3	50 in 1/3	-	yes	no	0	Hold at MEL
SPKSOLVNT		QC sample: "Spiked Solvent" - spiked solvent run through dialysis and GPC	0	250 into dialysis /GPC solvent	50 into dialysis/GPC solvent	-	yes	no	0	Hold at MEL
PRCSOLN		QC sample: "PRC Solution" - PRC solution.	0	-	-	-	no	no	0	

Abbreviations:

CP: chlorinated pesticides.
FB: sample type is a Field Blank
FS: sample type is Field Sample
MB: method blank
MEL: Manchester Environmental Laboratory
MS: membrane spike.
PRCs: Performance Reference Compounds, PCB-004, -029, -050.
Surrogate: PBDEs and CPs (in 1 solution) from MEL.

Appendix C. Continuous Low-Level Aquatic Monitoring (CLAM) sampling

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); 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/). MEL has used this guidance in conditioning SPE disks. 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 stream bed 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.

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 MEL, accompanied by a standard chain of custody form. SPE disks are considered “other” by MEL and not water samples. While there is not an established SOP for the CLAM deployed SPEs, MEL does have an SOP for large volume extraction in the lab using similar or the same media. Established preparatory procedures are in place from previous projects using CLAM samplers (J. Weakland, personal communication).

To analyze the total contaminant concentration bound to the SPE media, MEL 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.

Appendix D. Glossary, Acronyms, and Abbreviations

Glossary

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.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

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.

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

Reach: A specific portion or segment of a stream.

Salmonid: Fish that belong to the family *Salmonidae*. Basically, any species of salmon, trout, or char. www.fws.gov/le/ImpExp/FactSheetSalmonids.htm

Streamflow: Discharge of water in a surface stream (river or creek).

Surface waters of the state: Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands and all other surface waters and water courses within the jurisdiction of Washington State.

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

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody 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 requires Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standard and are not expected to improve within the next two years.

90th percentile: A statistical number obtained from a distribution of a data set, above which 10% of the data exists and below which 90% of the data exists.

Acronyms and Abbreviations

e.g.	For example
Ecology	Washington State Department of Ecology
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
PCB	polychlorinated biphenyls
QA	Quality assurance
RPD	Relative percent difference
SOP	Standard operating procedures
TMDL	(See Glossary above)
TOC	Total organic carbon
TSS	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
dw	dry weight
g	gram, a unit of mass
km	kilometer, a unit of length equal to 1,000 meters
mg	milligram
ug Kg	micrograms per kilogram (parts per billion)