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Pine Creek (Walla Walla Basin) Toxaphene Source Assessment

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Pine Creek
Toxaphene
Source Assessment

by

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

- Walla Walla WRIA 32 and the Walla Walla hydrologic unit 17070102.

- Sub-basins within the HUC 8: Lower Pine Creek (170701020903);
  Little Dry Creek –Dry Creek (170701020902); and Upper Pine Creek (170701020901).

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Abstract

Toxaphene is a chlorinated pesticide that was used historically in the Walla Walla basin on alfalfa crops. Previous sampling in the watershed strongly suggests that a possible source within the Pine Creek sub-basin is contributing toxaphene to the Walla Walla River. The purpose of this study was to identify the sources of toxaphene within the Pine Creek watershed.

The present 2014 study focused on lower Pine Creek which is dominated by agricultural land use. Samples were collected prior to spring irrigation, during the spring/summer irrigation season, and during the fall/winter irrigation season. Soils from alfalfa fields contained toxaphene, confirming persistence for the last ~ 40 years. An overflow ditch from an irrigation canal that drains into Pine Creek is a source of toxaphene during spring freshet/irrigation and fall/winter irrigation. Sediment and upland soil samples confirm the presence of toxaphene in areas that are easily eroded by wind and runoff into the overflow ditch. There is a lower toxaphene concentration in the upper portion of Pine Creek, above the overflow ditch, which appears to be associated with groundwater inputs or contaminated bank sediments.

The historic use of toxaphene on alfalfa seed crops has led to contamination of the Pine Creek watershed. Previously suspected concentrated animal feeding operation (CAFO) sites are not a source of ongoing toxaphene contamination. The analytical chromatography of toxaphene in different media from different sites suggests that the same degraded toxaphene is being transported throughout the watershed. The long-term inputs of toxaphene from Pine Creek to the Lower Walla Walla River appear to have changed very little over the last 10 years.

We recommend (1) update the assessment of fish tissue concentrations in the Walla Walla River, (2) conduct monthly or every-other-week trend sampling of toxaphene at the downstream Pine Creek site, and (3) assess and reduce sediment inputs from the Burlingame overflow ditch.

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Introduction

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 (not meeting) 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 River above water quality criteria and therefore lead to concentrations in fish tissue above human health criteria. In addition, follow-up studies of chlorinated pesticides in the Pine Creek watershed have recommended identifying the source of toxaphene (Parsons, 2007; Johnson et al., 2012).

Pine Creek is currently not a 303(d) listed waterbody for toxaphene. 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 (Johnson et al., 2004).
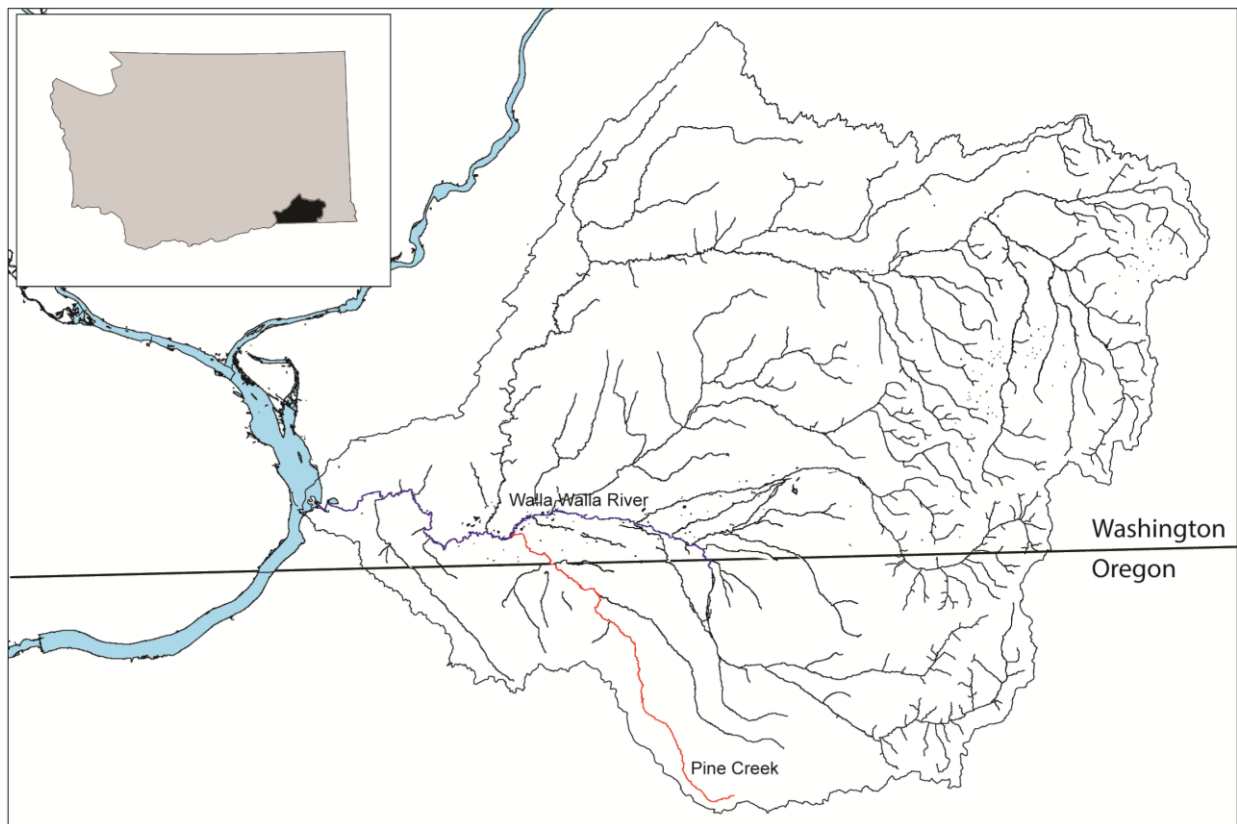

Figure 1: Walla Walla River basin discharging to the Columbia River.

Pine Creek highlighted in red.

The purpose of this study was to identify the sources of toxaphene within the Pine Creek watershed. This study used a two-pronged approach: (1) an initial spatial survey of toxaphene in surface waters to narrow source location, and (2) a detailed sampling of water, sediments, and soils to further identify a suspected source.

Background

Toxaphene Sources and Effects

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). All uses were banned in 1990, 8 years after the 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 (MacKay et al., 1997).

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

Toxaphene in the Walla Walla River Basin

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). This lack of detection was more than likely due to analytical limitations. Using passive, semi-permeable membrane devices (SPMDs) to assess the relative concentrations of chlorinated pesticides in water throughout the Walla Walla basin. Johnson et al. (2004) found the highest concentrations of toxaphene in Pine Creek, near the confluence with the Walla Walla River (Table 1). It was estimated that 90% of the toxaphene in the mainstem of the Walla Walla was in dissolved form. The authors suspected that a source of toxaphene within the Pine Creek sub-basin could be elevating toxaphene concentrations in the Walla Walla mainstem.

A subsequent study confirmed the high toxaphene concentrations in water samples from Pine Creek, including a sample from an unnamed tributary that showed the same concentration as Pine Creek (Parsons, 2007; Table 1). The follow-up study by Parsons (2007) also detailed high

toxaphene concentrations in water samples from the Gardena Farms Irrigation District adjacent to the Pine Creek watershed to the west. The Gardena system is hydrologically connected to Pine Creek during the irrigation season by an overflow ditch which begins at the point water is siphoned under the Pine Creek watershed from Burlingame Canal on the eastern side of the watershed (Figure 2). This overflow ditch runs through a deeply incised gulley, locally referred to as the Little Grand Canyon. In addition to previous water samples, two sediment samples (PN-01 and PN-02) did not have detectable concentrations of toxaphene (Table 1).

Table 1. 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 Road (PN-02)		Pine Creek @ Barney Road (PN-01)		Unnamed Tributary (UNNMD-01)	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
Date	Toxaphene (mg Kg^{-1})	Total organic carbon (mg g^{-1})	Toxaphene (mg Kg^{-1})	Total organic carbon (mg g^{-1})	Reference	
Sediment samples						
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
< - not detected below value shown

In the context of the greater Walla Walla River basin, Pine Creek represents the suspected source for toxaphene contamination. Toxaphene concentrations in Pine Creek and the Lower Walla Walla River were above both human health water quality criteria and protection of acute toxicity to aquatic life criteria. In the follow-up Parsons (2007) study, whole-water samples from Pine Creek and Gardena Ditch/Creek had 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 (Sandvik, 2009; 2010; Sandvik and Seiders, 2011; 2012).

Fish tissue collected from the Upper and Lower Walla Walla River in 2002 exceeded the human health criteria for edible fish consumption (9.6 ug Kg^{-1}) for each of the species sampled.   Fish tissue residues in the Lower Walla Walla were also higher than in the Upper Walla Walla River

(Johnson et al., 2004). 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.
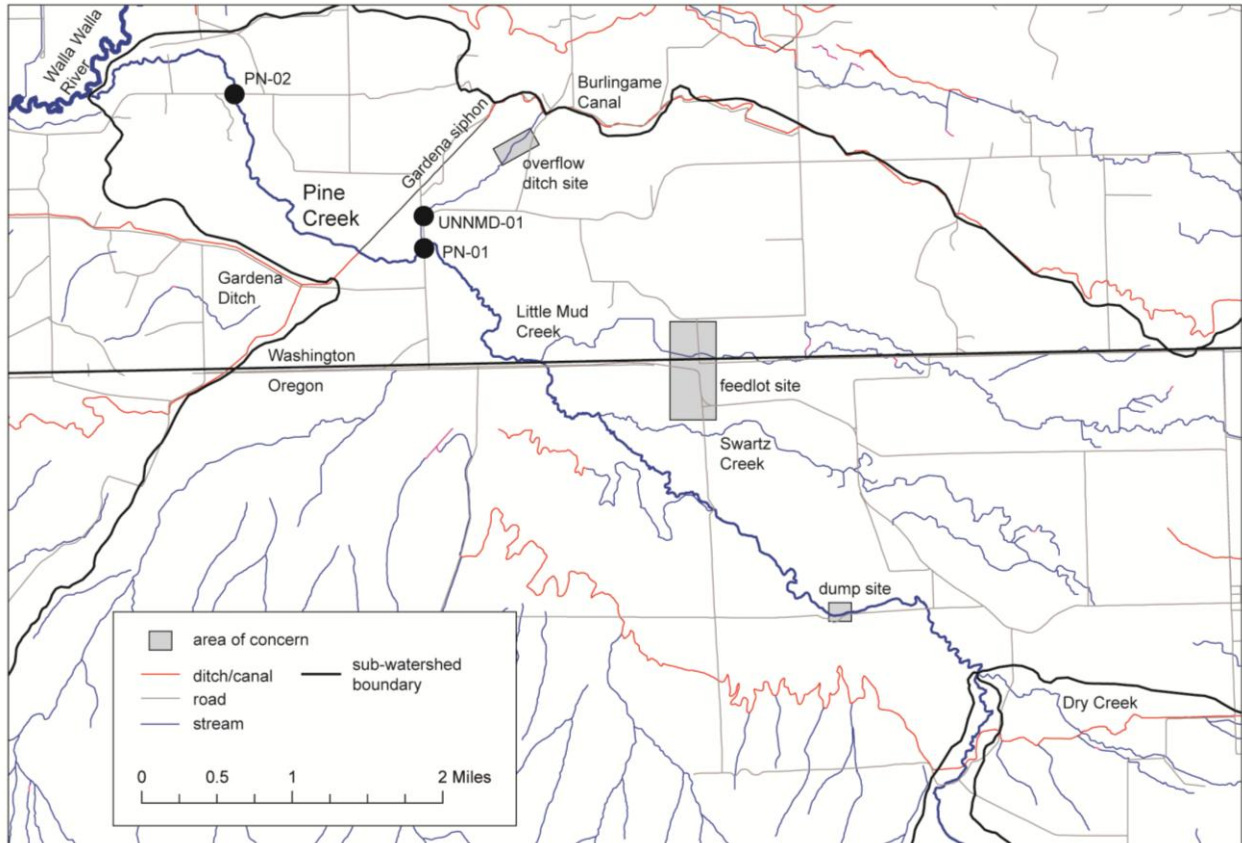
Figure 2: Areas of concern and previous sample sites.

There are three main areas of concern which were assessed during this project (Figure 2): (1) old dump sites along the overflow ditch site, (2) an old dump site on the Oregon side of the watershed, and (3) a concentrated animal feeding operation (CAFO) which straddles the OR/WA border. An additional CAFO near the Burlingame canal was identified during the study.

Methods

Study Area

Pine Creek flows from the headwaters in the Blue Mountains, Oregon, through the 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 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.
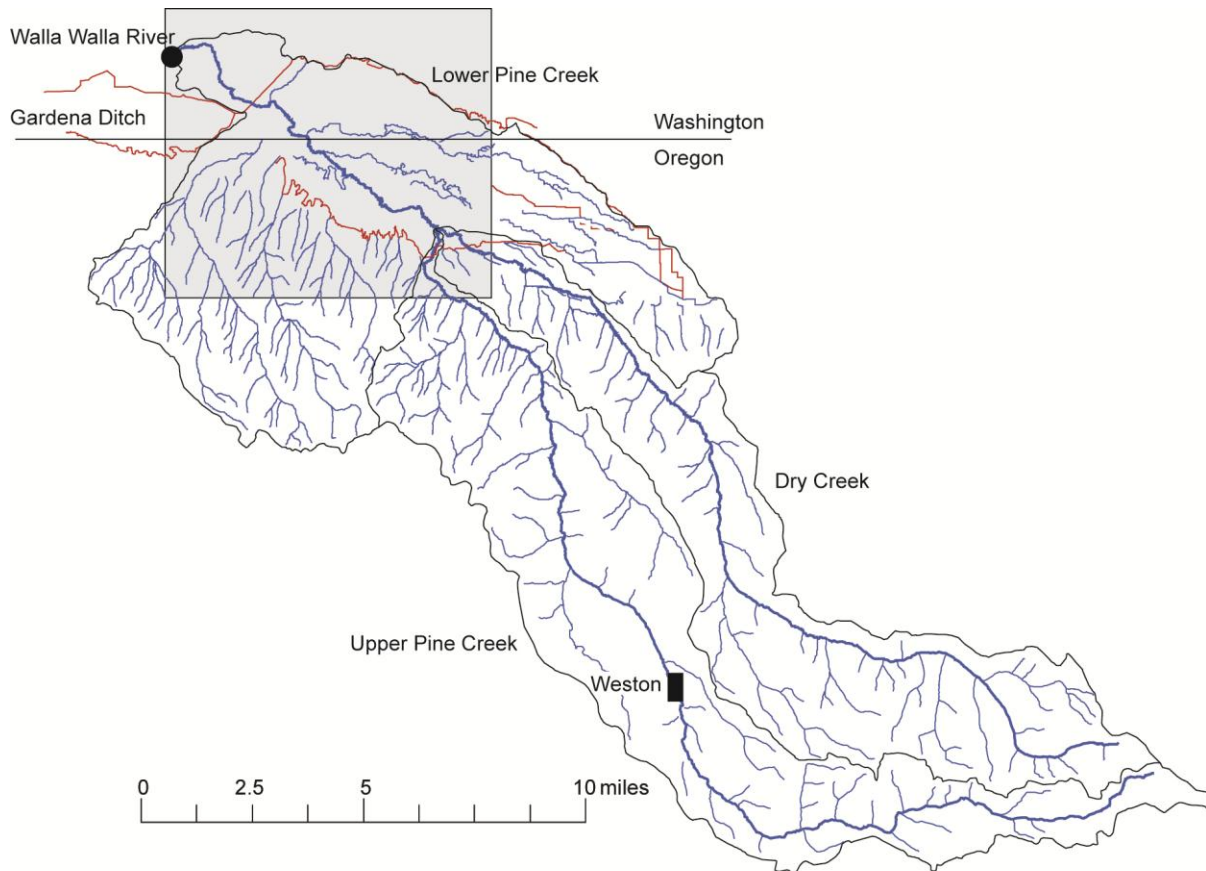
Figure 3: Pine Creek watershed.

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

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 River. Air temperatures have a large range, reaching over 100°F (38°C) in the summer and below 0°F (-18°C) in the winter.

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). A number of irrigation ditches and canals are within the lower Pine Creek watershed. A siphon/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.

There are currently no permanent discharge gages on Pine Creek. Historic discharge data near the town of Weston, OR (1965-1985; USGS station #14016200) show peak flow beginning in January and continuing through April/May (Figure 4), which is a broadly similar trend to the Walla Walla River. Early peak discharge is mainly snowmelt from the headwater Blue Mountains, while later (April/May) the discharge is affected by irrigation. The spring irrigation season begins in March and continues into June. Instantaneous flow measurements were collected for Pine Creek in 2002/03 during previous sampling events (Figure 4).

The highest concentrations of toxaphene are often measured during the irrigation period (Figure 4). 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 downstream of the overflow ditch from the Burlingame Canal. Overall, the hydrology of lower Pine Creek is complex and highly regulated by irrigation withdrawals and inputs.
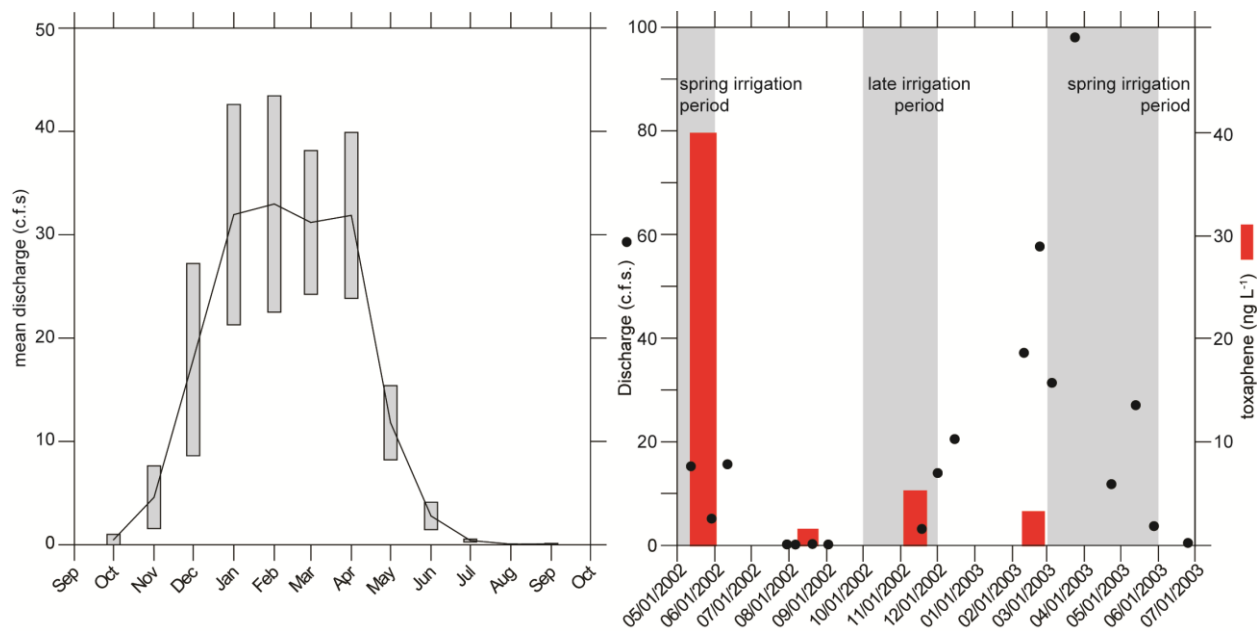
Figure 4: Pine Creek discharge measurements.

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

Regulatory Setting for Toxaphene in Washington

The State of Washington recognizes the toxicological effects toxaphene has on aquatic life, and the aquatic life criteria are more stringent than human health criteria (Table 2). Protection of human health and aquatic life criteria used by Washington are legislated through the Environmental Protection Agency (EPA) National Toxics Rule (40 CFR 131.36(14); EPA, 1992). The criterion for the protection of freshwater aquatic life from chronic effects is the lowest among Washington's 32 regulated chemicals (WAC 173-201A). The chronic water quality criteria for chemicals that 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.

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 2). The risk and subsequent criteria calculations are based on a person of 70 kg (154 lbs) consuming 6.5 grams 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.

There are no criteria for toxaphene under the Sediment Management Standards (WAC 173-204) for the protection of freshwater benthic communities.

Table 2. Washington State water quality criteria for the protection of aquatic life and human health for toxaphene.

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

Aquatic life (ng L^{-1})[†]		Human health (ng L^{-1})[‡]
Freshwater chronic	Freshwater acute	Water and fish consumption
0.20	730	0.73

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

Sampling Program

Sampling of various environmental media during this study was completed in multiple stages:

- a baseline sample (March 2014)
- an initial synoptic survey (May-June 2014)
- a detailed survey (November-December 2014)

Water samples were collected using either grabs, continuous low-level aquatic monitoring (CLAM) devices, or semi-permeable membrane devices (SPMDs). Sample sites are detailed in Figure 5 and Table A-1. At a number of sites, multiple water sampling techniques were used to roughly compare the results obtained by each. Furthermore, the use of SPMDs that are deployed for a month ensured that any pulses of toxaphene would not be missed by the shorter grab or CLAM sampling.
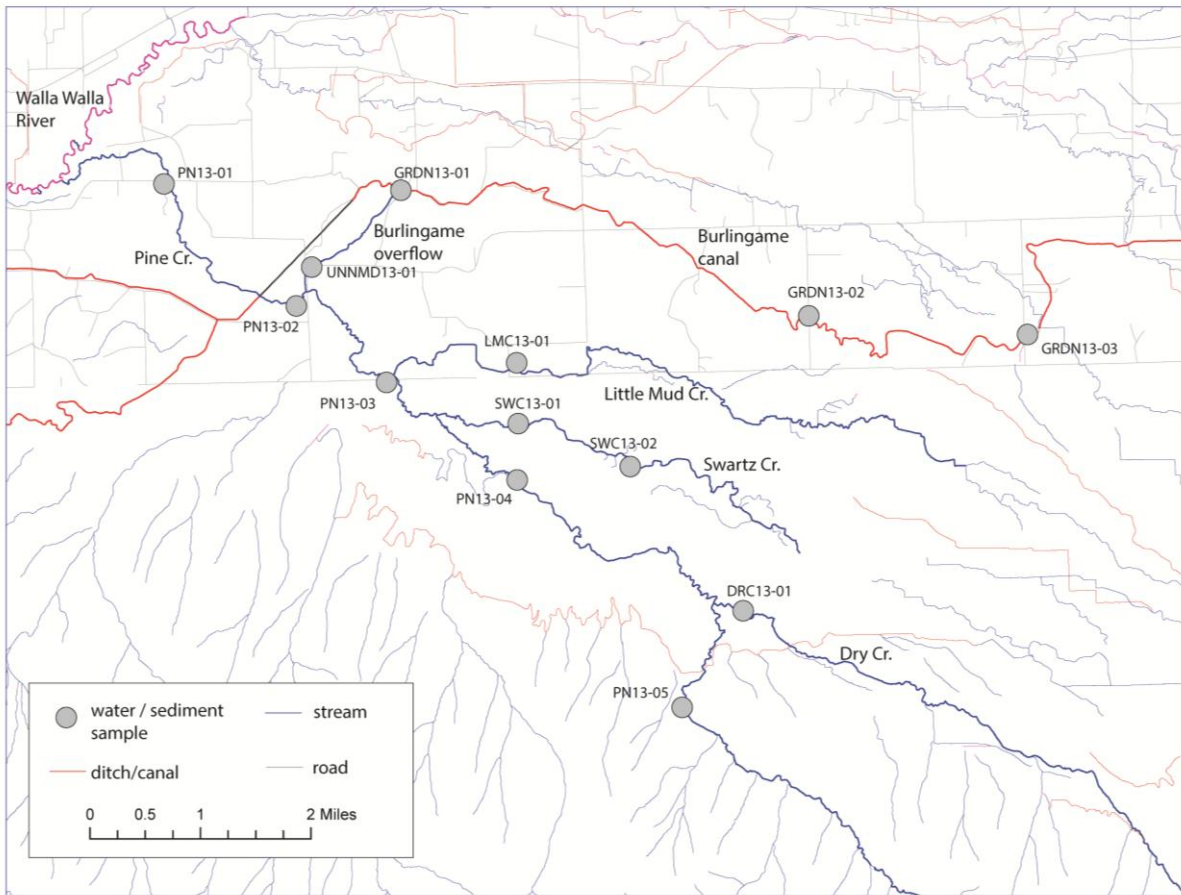
Figure 5: Sample sites for water and sediment.

CLAM Samplers

CLAM samplers are vessels for solid-phase extraction (SPE) disks, which are more commonly used in a laboratory setting to concentrate organic contaminants from large volumes of sample (EPA 3535). CLAMs contain a small, sealed pump behind the SPE that draws water through the device at an average rate of 30-60 ml per minute and is deployed for 24 to 36 hours. The SPE disks are shipped and secured in a high-density polypropylene cartridge. SPE disks were supplied by CI Agent Storm-Water Solutions, the supplier of the CLAM device.

CLAMs were deployed within the water column by tethering or anchoring to rebar or a cement block (Figure 6). Prior to deployment, the devices are calibrated to assess the flow rate. The flow rate is then also assessed upon retrieval. Flow is measured with a graduated cylinder 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 were removed from the devices and cooled on ice. Disks were shipped to the analytical laboratory for extraction within 14 days. Using the mass (in grams) of

organic compounds analyzed within the SPE and the estimated sample volume, we can calculate an average water concentration over the period of deployment.

Figure 6: Deployment of CLAM in Burlingame Canal, June 2014.

SPMDs

SPMDs are passive sampling devices and have been used by Ecology for a number of years (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 (typically a 28-day deployment). After deployment, the membrane is removed, extracted, and analyzed for the organochlorine compounds of interest.

SPMDs were deployed in secure areas (i.e., to minimize vandalism and avoid strong currents), using stainless steel canisters and spindle devices provided by Environmental Sampling Technologies (EST). Each site canister contained 3 membranes that were preloaded onto spindles by EST and shipped in solvent-rinsed metal cans under argon gas. A StowAway® TidbiT™ temperature logger was attached to the canister to continuously monitor the water temperature during deployment. A second datalogger was attached nearby to monitor air temperature. The data collected from the temperature loggers are used to confirm that the SPMD remained submerged during the sampling period.

SPMDs were exposed for no more than 45 seconds at each site during deployment and retrieval. Nitrile gloves were used at all times. The same cans were used during retrieval. They were properly sealed, cooled, and kept near freezing until arrival at EST for the extraction of the membranes (dialysis).

Often performance reference compounds (PRCs) are spiked into the membranes in order to assess biofouling and the non-equilibrium uptake of the compounds of interest (Huckins et al., 2006). The use of PRCs is essentially an *in situ,* site-specific calibration technique based on the observation that the rate of residue loss is proportional to the rate of residue uptake. Unfortunately, laboratory error during the manufacturing of the SPMDs led to PRCs not being added to the Pine Creek samplers.

Dissolved toxaphene concentrations were calculated from the toxaphene mass extracted and measured from the SPMDs using the most recent USGS model (Alvarez, 2010; pers. comm..). The model is based on the octanol-water partition coefficient (MacKay et al., 1997), the physical properties of the SPMD, water temperature, and the length of deployment. The model used in this project is specific to estimations when SPMDs do not contain PRCs (version 4.1; Huckins et al. 2006). Total toxaphene concentrations were estimated based on the formula (Meadows et al., 1998):

(1) $$Ctot = Cw \left(1 + [TOC]\left(\frac{Koc}{Mw}\right)\right)$$

Where C_{tot} is the total toxaphene concentration (pg L^{-1}), C_w is the dissolved concentration estimated in water (pg L^{-1}), TOC is the total organic carbon concentration (mg L^{-1}), K_{oc} is the organic carbon-water partition coefficient (median value from Mackay et al., 1997), and Mw is the mass of water (10^6 mg L^{-1}).

Sediments

Sediment samples were collected by compositing 5 aliquots of bottom sediment from Pine Creek in a stainless steel bowl or by capturing suspended and re-suspended sediments in the creek using a Hamlin sampler. The latter technique was originally designed for storm drain sediments (Lubliner, 2012) but has been used successfully in creeks prior to this study (Marshall et al.,

2014). The sampler was mounted on a concrete block and positioned off the creek bottom. It was used only at one sample location (PN13-01) and deployed for a 2-week period (Figure 7).

Figure 7: Sediments collected using the Hamlin sampler.

Ancillary Parameters

Ancillary parameters (total organic carbon and total suspended solids) were collected at the time of SPMD deployment, midpoint, and retrieval, and were coincident with toxaphene grab and CLAM samples. Ancillary parameters were collected as grab samples. Temperature, pH, and conductivity were measured *in situ* at the time of any water sampling using a Hach pH meter and DiST Hanna EC/TDS conductivity meter.

Analytical Program

Accredited Methods

Ecology's Manchester Environmental Laboratory (MEL) conducted most of the analysis and reporting. Analytical Resources Inc. conducted the analysis of grain size on the sediment and soil samples. Samples were not analyzed for a complete suite of chlorinated pesticides (EPA 8081); instead, the analysis targeted the group of toxaphene compounds with the help of the refined chromatography from previous investigations (Johnson et al., 2004; 2012). Analysis was conducted using gas chromatography / electron capture detection (GC/ECD). Grab samples were analyzed using large volume injection (LVI), while extracts from CLAMs and SPMDs were injected at a standard volume. MEL extracted the SPE disks from the CLAM samplers. EST extracted the SPMDs, performed the clean-up, and shipped the extracts in ampoules to MEL. The accredited methods used and the reporting limits obtained in this study are detailed in Table 3.

Table 3. Laboratory methods and reporting limits.

Analysis	Sample matrix	Number of samples*	Reporting limit	Sample prep method	Analytical method
Toxaphene (grab)	surface water	9	$7.9 - 8.3$ ng L^{-1}	Modified EPA 3510C	EPA 3620, 3665; LVI/EPA 8081C
Toxaphene (SPE)	SPE disk	20	25 ng	CIAgent method	EPA 3620, 3665, 8081
Toxaphene (SPMD)	SPMD	4 (each 3 membranes)	25 - 120 ng	dialysis/GPC[ǂ]	EPA 3620, 3665, 8081
TSS	surface water	32	$1 - 2$ mg L^{-1}	N/A	EPA 160.2
TOC	surface water	19	1 mg L^{-1}	N/A	SM 5310B
Toxaphene	soil/sediment	20	2.5 - 300 ug Kg^{-1}	EPA 8081	SW 846; EPA 8081
TOC	soil/sediment	18	0.10%	N/A	PSEP, 1986[¥]
Grain size	soil/sediment	13	0.10%	N/A	PSEP, 1986[¥]

* excluding field replicates and field blanks.
[ǂ] EST Standard Operating Procedures (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.

Quality Control Procedures

The method quality objectives (MQOs) set by MEL to meet the quality control (QC) objectives for reliable, useable data are shown in Table 4. Field replicates were collected during each sampling event at a frequency of no less than 10% of the total sample number per sampling event. Field trip blanks were used for the SPMDs and CLAM samplers. The field blank SPMD was taken into the field and opened for the same duration of time the sample SPMD was exposed to the air during deployment. The blank was sealed, transported cold back to Ecology, and stored frozen. The blank was then taken back into the field and exposed to air for the same duration as the sample SPMD during retrieval. One field blank was used. The field blank SPE was taken into the field, and the Luer locks were opened, exposing the SPE media for the duration of CLAM deployment and retrieval.

All laboratory quality assurance / quality control (QA/QC) measures are documented in MEL's Laboratory Quality Assurance Manual (MEL, 2012). Laboratory QC measures include the analysis of check standards, duplicates, spikes, and blanks. These are documented in the QA project plan (QAPP) for this study (Hobbs, 2014). Tracking and calculating check standards, spikes, and blanks for the SPMDs followed the SPMD SOP (Seiders et al., 2012) and SPMD data management SOP (Seiders and Sandvik, 2012). SPMDs require a detailed method blank procedure that is carried out by both EST and MEL. The following method blanks were prepared by EST:

- *A spiking (method) blank*: SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples.

- *A dialysis (day-zero) blank*: SPMD from the same lot as the project batch, to represent background during dialysis and cleanup.

- *A membrane (matrix) blank*: a single membrane from the same lot as the project batch, not spiked.

Table 4. Laboratory measurement quality objectives (MQOs) for the Pine Creek toxaphene source assessment.

Analysis	Check stds/lab control samples (% recovery)	Duplicate samples (RPD)	Surrogates (% recovery)	Matrix spikes (% recovery)
Water Samples				
Toxaphene (grab)	50-150%	NA*	30-150%	NA
Total suspended solids (TSS)	80-120%	± 20%	NA	NA
SPE and SPMD extracts				
Toxaphene (SPE)	50-150%	NA*	70-150%	50-150%
Toxaphene (SPMD)	50-150%	NA*	30-150%	50-150%
Soil/Sediment Samples				
Toxaphene	50-150%	NA*	30-130%	NA
grain size	NA	± 20%	NA	NA
Total organic carbon (TOC)	75-125%	± 20%	NA	NA

NA: not analyzed.   * field replicates analyzed

With the exception of the laboratory error of excluding the PRC compounds from the SPMDs, all MQOs were met for this project. All method and field blanks for the project were below method detection limits, confirming no manufacturing or ambient contamination. The relevant surrogate recoveries for the toxaphene analysis are included with the results in the subsequent report section.

The field replicates were generally acceptable; however, 1 individual sample event for toxaphene (using CLAMs), TSS, and TOC was above 30% relative percent difference (RPD) (Table 5 and 6). The TSS and TOC concentrations were fairly low and the RPD is more sensitive to differences near the detection limit. It is likely that the sampling variability does not impact our interpretation of these ancillary parameters. The toxaphene replicates using the CLAM were also low, and while this does increase the sensitivity of the RPD calculation, there was also a lower recovery of surrogates in one of the samples (1406045-17; Table 6). We therefore choose to use the result from the replicate sample 1046045-18 as the environmental data point. Overall, the recovery of surrogates from the CLAMs was excellent, suggesting that any residues accumulated during deployment would be successfully eluted from the sample media (SPE disk).

Table 5. Field replicates and surrogate recovery for water grab samples.

Sample >30% Relative percent difference in bold font.

Sample Site	Sample Date	Lab ID	Matrix	TSS (mg/L)	%RPD	TOC (mg/L)	%RPD	Toxaphene (ng/L)	%RPD	Decachloro-biphenyl (DCB)	Tetrachloro-m-xylene
PN13-01	6/2/2014	1406045-01	water	6		1.6		3.1		78	44
PN13-01	6/2/2014	1406045-02	water	7	15%	1.6	0%	3.1	0%	78	46
PN13-01	6/16/2014	1406050-01	water	13		1.9		3		80	53
PN13-01	6/16/2014	1406050-04	water	9	**36%**	1.8	5%	3	0%	74	59
PN13-01	11/5/2014	1411027-11	water	2		7					
PN13-01	11/5/2014	1411027-12	water	2	0%	3	**80%**				

Table 6. Field replicates and surrogate recovery for CLAM and SPMD samples.

Sample >30% Relative percent difference in bold font.

Sample Site	Sample Date	Lab ID	Matrix	Toxaphene (ng)	Toxaphene (ng/L)	%RPD	Decachloro-biphenyl (DCB)	Tetrachloro-m-xylene
PN13-01	5/20/2014	1405047-07	SPE	25 U	0.9		87	72
PN13-01	5/20/2014	1405047-08	SPE	28.9	0.9	4%	91	83
PN13-01	6/3/2014	1406045-17	SPE	32.8	0.6		76	65
PN13-01	6/3/2014	1406045-18	SPE	51	1.2	**59%**	87	80
PN13-01	6/17/2014	1406050-03	SPE	83	2.0		87	72
PN13-01	6/17/2014	1406050-05	SPE	85.8	2.0	1%	87	73
PN13-01	11/5/2014	1411027-11	SPE	109	2.3		93	91
PN13-01	11/5/2014	1411027-12	SPE	112	2.6	13%	109	102
PN13-01	6/16/2014	1406064-01	SPMD		1.1		79*	58
PN13-01	6/16/2014	1406064-02	SPMD		1.4	27%	85*	57

* 2,2',4,4',5,5'-hexabromobiphenyl (HBBP) is the surrogate.

Results

Baseline Sampling

The goal of the baseline sampling event was to assess toxaphene concentrations at previously sampled sites during a time when irrigation was not a dominant hydrologic input. Sampling took place on March 6, 2014. Pine Creek was very turbid at the time of sampling because the Gardena Irrigation District opened up the overflow ditch from the Burlingame Canal into Pine Creek, representing the beginning of the spring irrigation season (Figure C-1). This limited our use of the CLAM devices due to clogging with suspended materials. Estimated total suspended solids (TSS) concentrations ranged from 632 to 3380 mg L^{-1} (Table B-1 and B-2). Only one CLAM sample, near the Burlingame canal siphon, was successfully measured for toxaphene (8.3 ng L^{-1}). Two grab samples were analyzed from Pine Creek and had concentrations of 8.1 and 7.9 ng L^{-1}, which were at the analytical reporting limit. Given the high TSS load, an opportunistic sample of suspended material was collected in a cleaned glass jar and analyzed for toxaphene (2.2 µg Kg^{-1}; Table B-3).

Synoptic Sampling

The synoptic survey relied on passive (SPMDs) and active (CLAMs and grab) water sampling techniques and sediment samples to assess the spatial distribution of toxaphene during the irrigation season. The SPMDs were deployed for approximately 1 month (May 20 – June 16, 2014). One of the SPMDs (PN13-01) became exposed to the air during 2 short (< 6 hours) irrigation withdrawals (Appendix D). Given that the duration of exposure was short and the field blank at the same location showed no evidence of ambient contamination, we feel the data derived from this sample are acceptable. All other samples remained submerged for the duration of the deployment. Sample PN13-05 was situated in a pool at an irrigation diversion, and flow decreased to near zero midway through the deployment, which represents different deployment conditions compared to the other SPMDs.
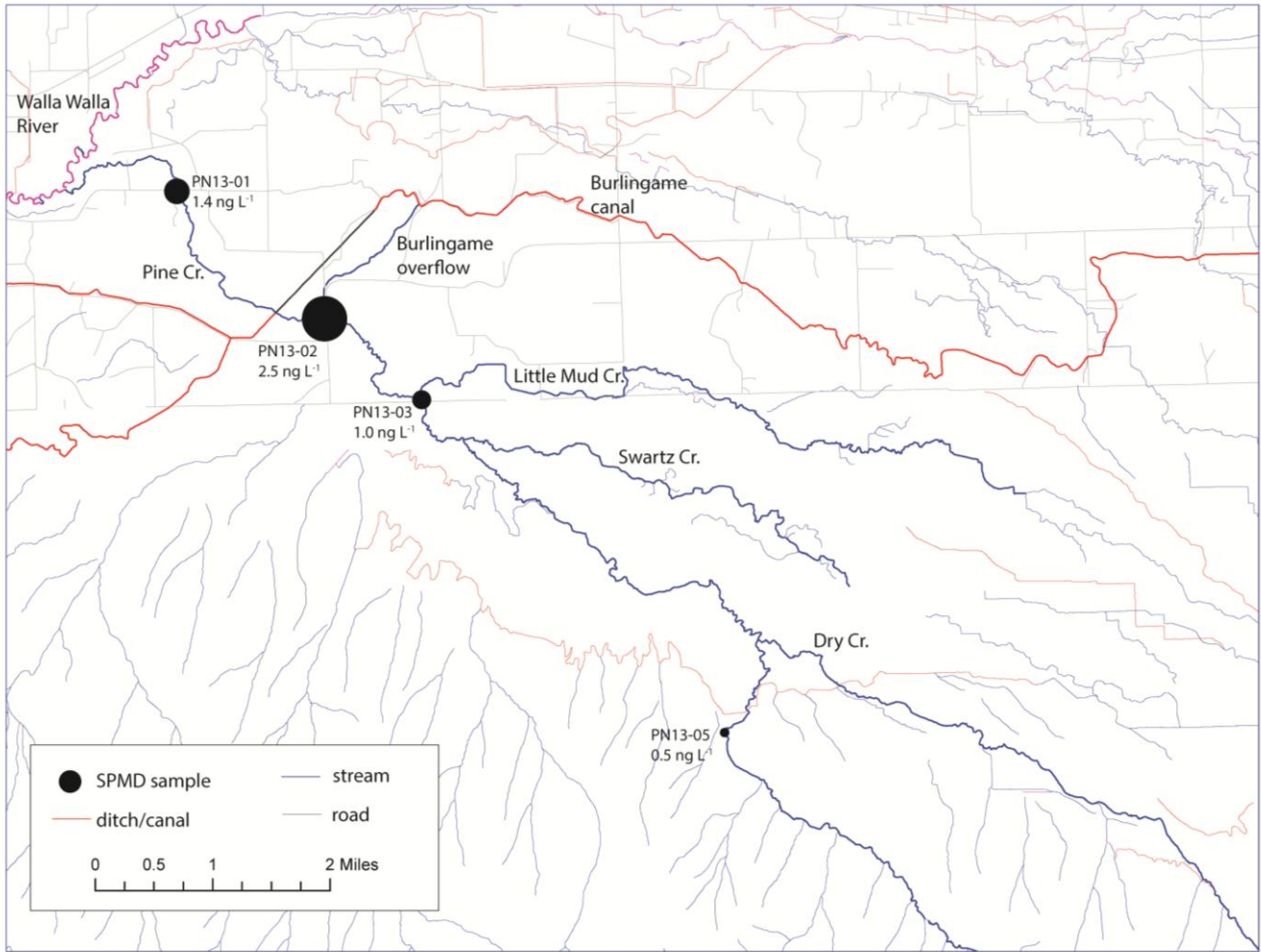
Figure 8: Estimated total toxaphene concentrations from SPMDs.

Sample points are proportional to toxaphene concentrations.

The SPMDs showed a fairly clear hotspot of toxaphene in the vicinity (just downstream) of the overflow ditch /tributary from the Burlingame Canal (PN13-02; Figure 8). Toxaphene was measurable throughout the length of Pine Creek that was sampled. Total organic carbon (TOC) concentrations were sampled at deployment, midpoint, and retrieval of the SPMDs, and all were fairly low. This suggests that most of the measured toxaphene was in dissolved form (Table 7).

Table 7. Estimated water concentrations for SPMDs.

sample site	TOC $(mg\ L^{-1})$	TSS $(mg\ L^{-1})$	SPMD dissolved toxaphene $(ng\ L^{-1})$	SPMD total toxaphene $(ng\ L^{-1})$	% dissolved
PN13-01	1.9	9.0	1.4	1.4	96%
PN13-02	2.1	14.7	2.4	2.5	96%
PN13-03	2.1	9.0	1.0	1.0	96%
PN13-05	3.3	7.0	0.4	0.5	94%

* mean of deployment, midpoint, and retrieval sampling events

The synoptic survey using CLAM samplers took place at the midpoint of the SPMD deployment. At sample site PN13-01, CLAMs were also used at the deployment and retrieval times of the SPMDs. This overlap was an effort to compare the estimated toxaphene concentrations from both techniques. The CLAM samples had toxaphene concentrations of 0.9 ng L^{-1}, 1.2 ng L^{-1}, and 2.0 ng L^{-1} at SPMD deployment, midpoint, and retrieval, respectively, at site PN13-01 (Table B-2). The SPMD samples averaged a total toxaphene concentration of 1.4 ng L^{-1}. In addition, grab samples for toxaphene were taken at PN13-01 during the deployment, midpoint, and retrieval of the SPMDs. Concentrations in each of the grab samples were not detected above the reported sample quantitation limit of ~ 3.0 ng L^{-1} and therefore not comparable to the CLAM and SPMD results.

The CLAMs were deployed for an average of 16 hours, and TSS concentrations ranged from 2 to 24 mg L^{-1} (Table B-2). Pump rates for the CLAMs decreased dramatically after the first few hours, due to clogging of the SPE disks from the TSS concentrations. Because of the non-linear decrease in pump rate, it's likely that the linear interpolation technique typically used to calculate the total volume (Hobbs, 2014), overestimates the actual volume pumped. This means that the estimated toxaphene concentrations would be underestimated. The underestimation is systematic and would likely not interfere with interpretations of spatial trends on a relative basis.

Spatially the toxaphene results for the CLAM samples showed a slightly different distribution than the SPMD results. All detectable concentrations were in Pine Creek; however, the highest concentration was observed at PN13-01, the furthest site downstream (Figure 9). Toxaphene concentrations did have a fairly narrow range (0.9 – 1.2 ng L^{-1}), which makes it difficult to say any site is a true hotspot. Toxaphene was not detectable in any of the sediment samples collected in tributaries or PN13-01 from the synoptic sampling event (Table B-3).
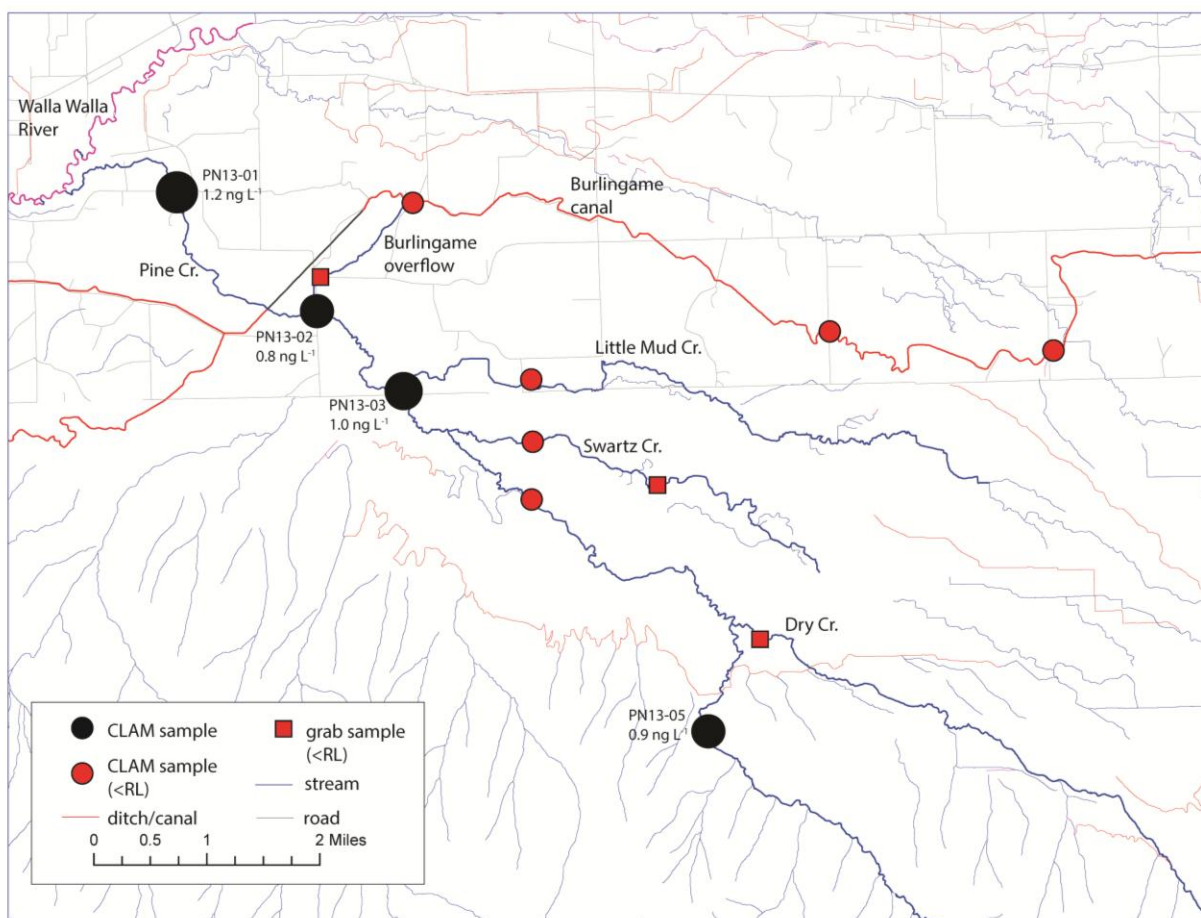
Figure 9: Estimated toxaphene concentrations from CLAMs and measured concentrations from grab samples.

Sample points are proportional to toxaphene concentrations. RL: Reporting Limit.

Detailed Sampling

The goal of the detailed sampling event was to sample water at some of the previous sampling sites during the fall irrigation season and sample soils and sediments in areas suspected of being hotspots. Sampling took place on November 5-6, 2014, with follow-up soil sampling on December 8, 2014. CLAMs were deployed for an average of 17 hours, and TSS ranged from $1 – 28$ mg L^{-1}, similar to the previous synoptic survey (Table B-2). The concentrations of toxaphene in CLAM samples from the lower reach (downstream of the Burlingame overflow) of Pine Creek were higher than the synoptic survey.

The hydrology of the creek at the time of sampling was groundwater/baseflow upstream of sample site PN13-02, where the Burlingame overflow enters. Downstream of this sample point, the flow was dominated by the overflow from the Burlingame Canal. The toxaphene concentration entering the overflow ditch from the canal was 3.3 ng L^{-1} (Figure 10). The overflow ditch travels through the deeply-incised "Little Grand Canyon" (site UNNMD13-01), where an additional 1.3 ng L^{-1} is contributed (total of 4.6 ng L^{-1}). The concentration measured at

PN13-02 was the same as in the ditch. Downstream (PN13-01) the concentration attenuates to 2.4 ng L^{-1}. The upstream sample sites likely represent contributions from groundwater (PN13-03 – 0.5 ng L^{-1} and PN13-04 – 1.1 ng L^{-1}). Site PN13-05 was dry at the time of the detailed survey.
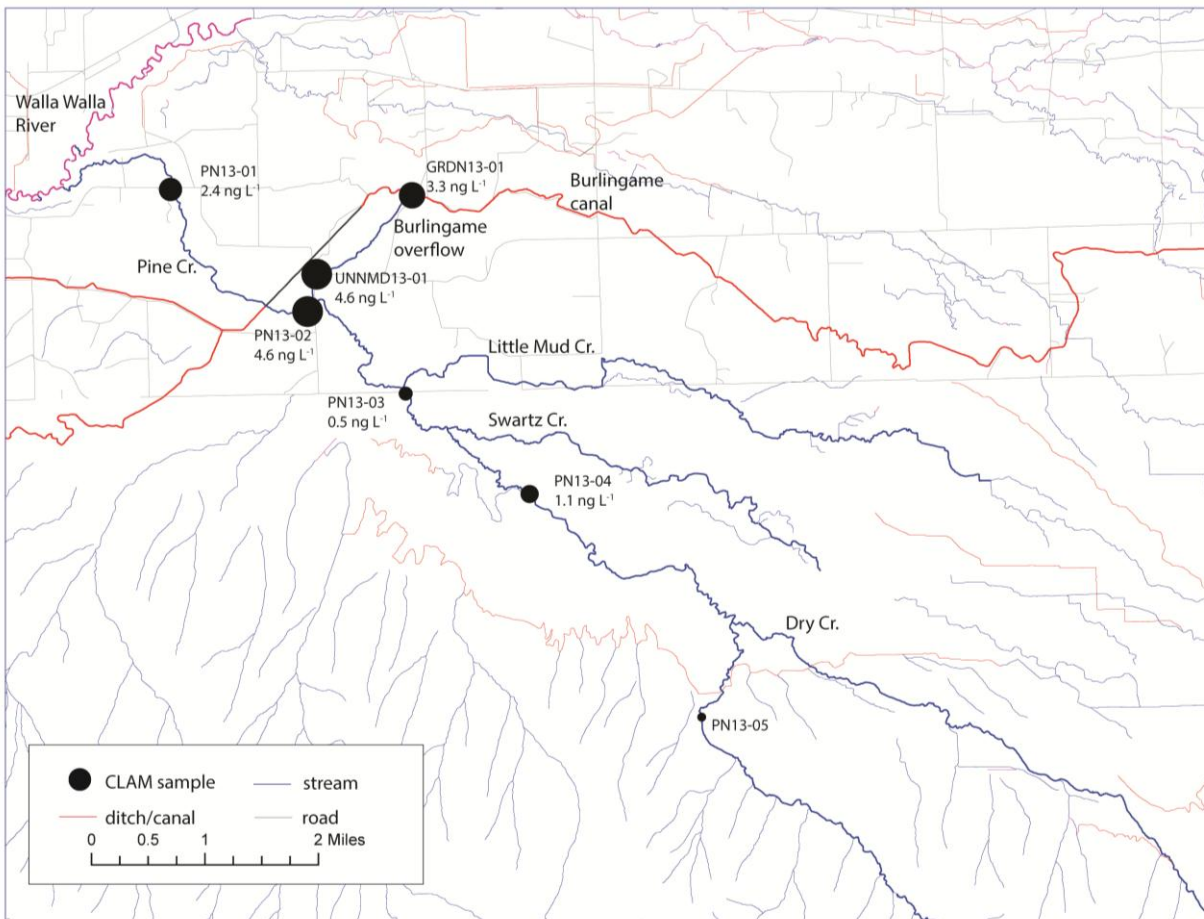
Figure 10: Estimated toxaphene concentrations from CLAMs during the detailed survey.

Sample points are proportional to toxaphene concentrations

To confirm that toxaphene continues to persist in the soils of the Pine Creek watershed, three alfalfa fields were sampled. Soils were composited from the upper 40 cm (12 inches) at two locations per field (Table 8). Two fields were adjacent to Pine Creek, and the third was in the Gardena Irrigation District. The two in the Pine Creek watershed were suspected of having toxaphene used on them in the past (late 1960s – early 1970s), while the Gardena field was known to have received treatments of toxaphene (pers. comm. Mark Wagoner and Edward Chvatal). While all soils had detectable amounts of toxaphene, soils from the field known to have received toxaphene treatments approximately 40 years ago (Gardena) contained the highest concentrations (Table 8; 1200 and 1500 μg Kg^{-1} dry weight).

Table 8. Toxaphene concentrations in soils and sediments during the detailed survey.

Sample Site	Sample Date	Lab ID	Matrix	TOC (mg g^{-1})	Toxaphene (µg Kg^{-1} DW)	Toxaphene (ng g-1 OC)	% Surrogate Recovery	
							Decachlor-obiphenyl (DCB)	Tetrachloro-m-xylene
PN13-01	11/5/2014	1411027-21	sediment	0.86	5.8	6.7	97	89
PC soil-1	11/5/2014	1411027-22	soil	1.8	19	10.6	108	92
PC soil-2	11/5/2014	1411027-23	soil	1.75	13	7.4	108	90
PC soil-3	11/5/2014	1411027-24	soil	0.74	9.8	13.2	111	87
PC soil-4	11/5/2014	1411027-25	soil	0.36	3	8.3	111	86
PC soil-5	11/5/2014	1411027-26	soil	1.39	1200	863.3	114	80
PC soil-6	11/5/2014	1411027-27	soil	1.43	1500	1049.0	125	85
LGC-1	12/8/2014	1412043-01	sediment	0.3	63	210.0	104	72
LGC-2	12/8/2014	1412043-02	soil	0.75	570	760.0	100	75
LGC-3-UP	12/8/2014	1412043-03	soil	0.6	410	683.3	136	97
LGC-3	12/8/2014	1412043-04	sediment	0.16	18	112.5	102	100
LGC-4	12/8/2014	1412043-05	sediment	0.21	14	66.7	94	67
LGC-4-UP	12/8/2014	1412043-06	soil	1.97	180	91.4	120	68
LGC-5	12/8/2014	1412043-07	sediment	0.43	57	132.6	103	91
White Bag	12/8/2014	1412043-08	soil	ns	330	na	91	74

ns: not sampled
na: not applicable
DW: dry weight basis
OC: normalized to organic carbon

Following the CLAM and SPMD results showing higher concentrations of toxaphene in the area of the Burlingame overflow ditch (Figure 11), soil and sediment samples were collected from upland and creek bank sites suspected of being former dump sites (pers. comm. Edward Chvatal). Detectable concentrations of toxaphene were found in all samples, including a buried bag suspected of being a sand bag or deicer gravel (Figure 11). Generally, the upland soils had concentrations an order of magnitude higher than concentrations in the creek bank sediments.

Figure 11: Burlingame overflow ditch in the vicinity of sample site LGC-1 (left). Buried bag of sand and gravel in the vicinity of LGC-2 (*White Bag* sample) (right).

Discussion

Comparison of Sampling Techniques

At a number of sample locations in Pine Creek, SPMDs and CLAMs were deployed simultaneously. The CLAM concentrations represent 1 day (June 3) at the midpoint of the 27-day SPMD deployment (May – June, 2014). The results are not strongly comparable (Figure 12), suggesting that the toxaphene concentrations in Pine Creek were not constant over the month of sampling. The site which is the most dissimilar (PN13-02) is heavily influenced by the Burlingame overflow ditch. The upstream site PN13-03 that appears to be influenced strongly by groundwater did not vary much over the 27-day sampling period.
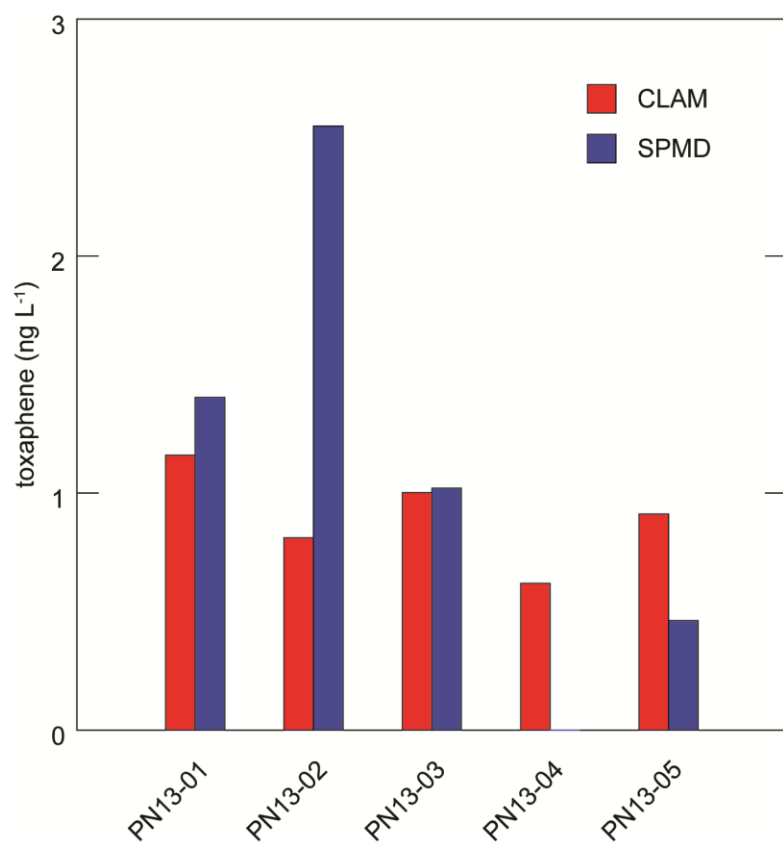
Figure 12: Comparison or CLAM and SPMD toxaphene concentrations.

At sample site PN13-01, water concentrations were estimated and measured using SPMDs, CLAMs, and grab samples over a more comparable sampling frequency (Figure 13). The grab samples were not detectable at concentrations low enough to directly compare. The CLAM and SPMD samples had good agreement in estimated total toxaphene concentrations in water over the 27-day sampling period. An average of the three CLAM samples yields an estimated concentration of 1.35 ng L^{-1}, which is very similar to the estimated 1.40 ng L^{-1} from the SPMD. This comparison highlights how the CLAM can attain the average concentration over a month from three 1- day sample events.
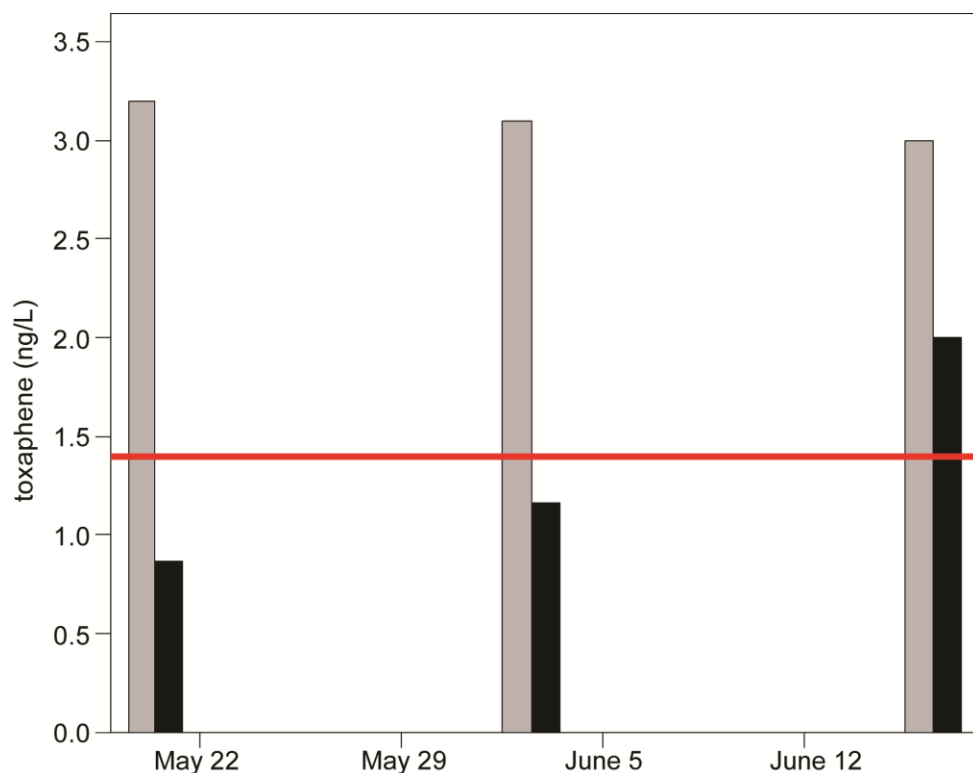
Figure 13: Comparison of CLAM, SPMD, and grab sample results at site PN13-01.

SPMD concentration is the solid red line, CLAMs are the solid black bars, and grab samples are the grey bars (detection limits).

Total Suspended Solids (TSS) as a Toxaphene Surrogate

Concurrent with each toxaphene sample, TSS was sampled in order to test whether it could be used as a suitable surrogate. The transport of suspended sediment-bound toxaphene has been measured in larger rivers of Midwest states (Raff and Hites, 2004), but measurement in Washington has focused on the dissolved phase and fish tissue (Johnson et al., 2012). Whole-water samples, which incorporate the sediment-bound phase are only possible to quantify in systems with very high concentrations (e.g., Johnson et al., 2010).

We tested our complete CLAM data set of TSS and toxaphene results using linear regression, with data log-transformed for normality. After dropping the baseline sample from GRDN13-01 as an outlier for toxaphene (Table B-2), there is no linear relationship between TSS and toxaphene data ($r^2 = 0.06$, p=0.33). It is possible that the grab samples for TSS do not sufficiently represent the 1-day CLAM samples for toxaphene and are therefore not directly comparable. TSS is being used as a suitable surrogate in the Walla Walla River for DDT contamination (Johnson et al., 2004). The chemical properties of DDT and toxaphene would suggest that a similar relationship between toxaphene and TSS should be present.

Using the detailed sample event only, where the influence of the Burlingame overflow ditch is evident, there is a significant linear relationship between TSS and toxaphene (r^2=0.45; p=0.01). However, less than half the variation in toxaphene is explained by TSS. This suggests that

dissolved fractions are important or that TOC or turbidity may be a more suitable surrogate. Future sampling in Pine Creek using the CLAM sampler should characterize the TSS concentrations at deployment and retrieval, as well as investigate other possible surrogates. In any follow-up actions in Pine Creek, it would be informative to explore the phase partitioning of toxaphene at certain times of the year; this would provide an understanding of what phase (dissolved and sediment-bound) dominates the transport of toxaphene.

Spatial Distribution of Toxaphene

Toxaphene was found throughout the lower Pine Creek watershed in dissolved form in water, in creek sediments, and in alfalfa field soils. The highest concentrations were found in the area of the Burlingame canal overflow ditch (locally known as the "Little Grand Canyon") and downstream. The sites upstream of where the overflow ditch enters Pine Creek (PN13-02) appear to have a fairly consistent concentration that ranges from 0.5 - ~1.0 ng L^{-1}. There does not appear to be a hotspot in this upper section of Pine Creek. Furthermore, the small tributaries that contribute to this section of Pine Creek (Dry Creek, Swartz Creek, and Little Mud Creek) do not appear to contribute any detectable concentrations of toxaphene. The upstream toxaphene concentration likely represents a contribution from groundwater or residues in creek bank sediments. This estimated upstream concentration is above (does not meet) the State of Washington aquatic life criteria of 0.2 ng L^{-1}.

Both the CLAM and SPMD sampling suggest that there are higher concentrations in Pine Creek downstream of the Burlingame overflow ditch. Concentrations measured in the Burlingame Canal also show that toxaphene is being contributed from this system that is outside the Pine Creek watershed. During the March and November sampling events, toxaphene concentrations found in Pine Creek and the Burlingame Canal were both high. Conversely, during the June sampling event when the Burlingame Canal concentrations were low (less than the analytical reporting limit), the Pine Creek concentrations were low and similar to the upstream concentrations.

Sediment samples of the creek bed and banks in the downstream locations show little evidence for a hotspot in the channel of Pine Creek. Concentrations of repeat sampling at PN13-01 (the furthest downstream site) ranged from 2.2 (less than the analytical reporting limit) to 5.8 µg Kg^{-1} dry weight. The toxaphene found in the upland soils and near the Burlingame overflow ditch provides evidence for: (1) the persistence of toxaphene in the soils of the Pine Creek watershed for approximately 40 years, and (2) nearby agricultural soils could contribute toxaphene to the creek during wind and runoff erosion.

It is worth noting that previous sampling in 2007 of the Gardena ditch showed concentrations (90 and 140 µg Kg^{-1} dry weight) in sediments comparable to those found in the Burlingame overflow ditch (Parsons, 2007). The Gardena ditch is outside the Pine Creek watershed to the west, and most of the Gardena Irrigation system has been piped since the 2007 sampling. There is no longer a discharge from what was Gardena Creek to the Walla Walla River (pers. comm. Stuart Durfee).

Toxaphene Source

Toxaphene is a group of chlorinated compounds that, when measured using gas chromatography, the numerous peaks of the compounds combine to give the total toxaphene concentration. Hence there is a chromatogram that describes the toxaphene at each sample site and will reflect the degradation and transformation over time from the original technical mixture of toxaphene.

We examined the chromatograms from multiple samples across different matrices and found a strong similarity in the appearance of the toxaphene measured (Appendix E). This suggests that the toxaphene found in the water of Pine Creek has undergone similar degradation to that which is measured in the soils and sediments of the watershed. This evidence strongly supports the idea that toxaphene is carried into Pine Creek bound to watershed inputs (soils and silts from the landscape). It is also possible that contamination of the Pine Creek channel and banks occurred during the era of toxaphene use in the watershed, and sediments are slowly transported and deposited sporadically based on the hydrology of the creek. The impact of degraded toxaphene on aquatic life is not significantly different than technical grade (fresh) toxaphene; both causing cell mutations (Young et al., 2009).

The soils analyzed from alfalfa fields where toxaphene was previously applied confirm the persistence approximately 40 years after application. Toxaphene was introduced as a replacement for DDT and was often used in concert with it on alfalfa crops (pers. comm. Mark Wagoner). Further anecdotal observations suggest that empty barrels floating in Pine Creek were not an uncommon sight during the spring freshets. It was previously speculated that CAFO operations may have been the source of toxaphene in the watershed; however, we found this not to be the case. The maximum toxaphene concentrations that we found in soils from our study are comparable to those documented in a survey of cotton fields in the U.S. Southwest (Bidleman and Leone, 2004). The Bidleman and Leone (2004) study also found that there was a net volatilization of toxaphene at these soil concentrations, which locally disperses the toxaphene.

Based on the three sampling events we conducted, the peak toxaphene concentrations appear to occur during the spring freshet/beginning of the spring irrigation and the fall/winter irrigation periods. This finding is somewhat counter to previous work and deserves further sampling at higher frequency to determine a more precise temporal trend of toxaphene inputs over a water year.

Long-term Trend of Toxaphene Inputs

Toxaphene concentrations in Pine Creek measured in this study are comparable to those found previously in Pine Creek and in Walla Walla River (Figure 14). Noteworthy in Figure 14 is that the initial concentrations in Pine Creek were estimated to be around 40 ng L^{-1} in June 2002. These concentrations have not been measured since this time. In fact, all estimated and measured concentrations are an order of magnitude lower. The long-term trend of toxaphene in the Lower Walla Walla River and Pine Creek appears to have changed very little in the last 10 years.
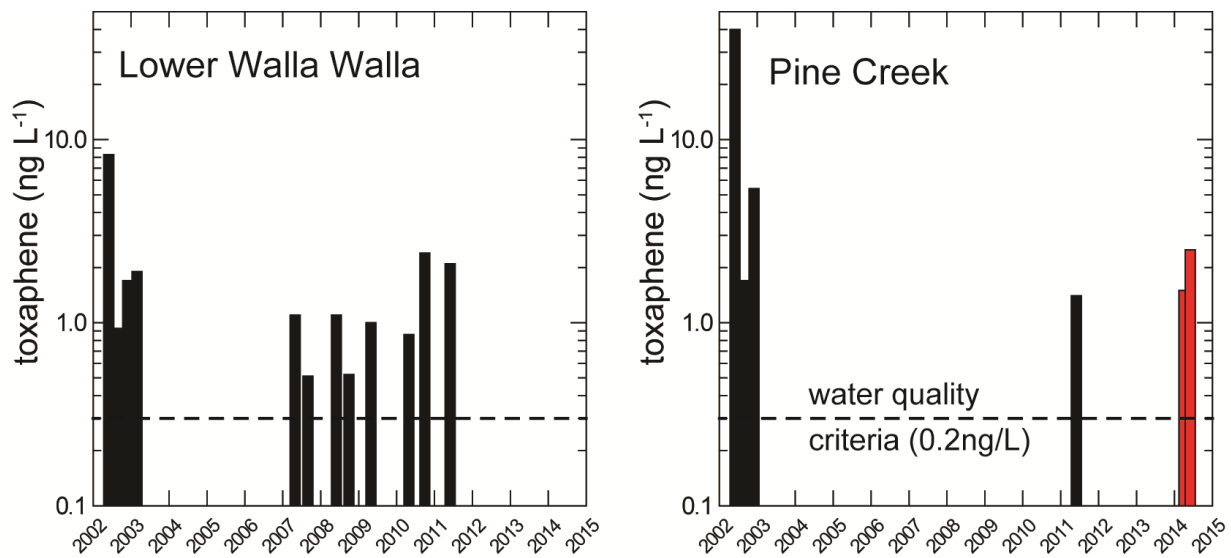
Figure 14: Long-term trend of estimated toxaphene concentrations from SPMDs in the Lower Walla Walla River (left) and Pine Creek (right).

Samples from this study are in red.

Historical data are from Johnson et al. (2004), Parsons (2007), Sandvik (2009), Sandvik (2010), Sandvik and Seiders (2011), Sandvik and Seiders (2012) and Johnson et al. (2012).

Conclusions

This 2014 study aimed to identify the source of toxaphene in the Pine Creek Watershed, which is likely responsible for the elevated concentrations in the Lower Walla Walla River. This study supports the following findings:

- The widespread use of toxaphene in the late 1960s to early 1970s on alfalfa seed crops has led to the contamination of the Pine Creek Watershed. Previously suspected CAFO sites are not a source of ongoing toxaphene contamination.

- Toxaphene persists in the soils of alfalfa fields in all the soils tested.

- The analytical chromatography of toxaphene in different media at different sites was very similar. This suggests that the same degraded toxaphene is being transported throughout the Pine Creek watershed.

- Estimated concentrations of toxaphene in water using an active sampler (CLAM) and passive sampler (SPMD) were very similar.

- The overflow ditch from the Burlingame Canal that drains into Pine Creek is a source of toxaphene during the spring freshet/irrigation season and the fall/winter irrigation season.

- Sediment and upland soil samples from the deeply-incised Burlingame overflow ditch confirm the presence of toxaphene in areas that are easily eroded by wind and runoff into the overflow ditch.

- There is a background toxaphene concentration in Pine Creek ($0.5 - 1.0$ ng L^{-1}), upstream of the Burlingame overflow ditch, that appears to be associated with groundwater inputs or contaminated bank sediments.

- The long-term inputs of toxaphene from Pine Creek to the Lower Walla Walla River appear to have changed very little over the last 10 years; however, the concentrations are consistently an order of magnitude below the 40 ng L^{-1} once measured in 2002.

Recommendations

The findings from this study support the following recommendations:

- The last fish tissue sample collection in the Lower Walla Walla River was conducted in the summer of 2002. Since this time, irrigation water from the Gardena Irrigation District has been largely piped and no longer discharges to the Walla Walla River. Water concentrations of toxaphene are currently below those measured in 2002. The Freshwater Fish Contaminant Monitoring Program (FFCMP[1]) is scheduled to sample the Walla Walla River in 2016. Collect a sufficient number of fish of same species previously sampled, to make the comparison to the 2002 fish tissue results for toxaphene statistically possible.

- Monitor the downstream sample site PN13-01 or PN13-02 at a high frequency (monthly or every other week) to detail the temporal trend of toxaphene inputs over a water year. Grab samples will require high-resolution mass spectrometry techniques. Or use a lower resolution method with the CLAM or SPMD sampler. Consider dovetailing the sampling with the effectiveness monitoring scheduled for early 2016 as part of the Walla Walla Total Maximum Daily Load study for chlorinated pesticides.

- If results from the above recommendations continue to show toxaphene concentrations in the Lower Walla Walla River above state water quality and human health criteria, consider ways to reduce sediment inputs to the Burlingame overflow ditch. Begin with a detailed water sampling program at a time of year when concentrations are high, to identify susceptible sections of the ditch. Measure streamflow at the time of sampling to quantify toxaphene load.

- Determine the phase partitioning of toxaphene at the downstream sample sites in Pine Creek. Define the fraction of toxaphene being contributed bound to sediment and in dissolved phase.

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[1] http://www.ecy.wa.gov/programs/eap/toxics/wstmp.html

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Appendices

Appendix A. Sample Sites

Table A-1. Study sample site coordinates.

Site ID	Name	Latitude	Longitude
PN13-01	Pine Cr. at Sandpit Rd	-118.633	46.028
PN13-02	Pine Cr. at Burrows Rd	-118.607	46.013
PN13-03	Pine Cr. at Stateline Rd	-118.59	46.001
PN13-04	Pine Cr. at Hudson Bay Rd	-118.568	45.987
PN13-05	Pine Cr. at Schubert Rd	-118.538	45.959
UNNMD13-01	Little Grand Canyon overflow	-118.607	46.015
DRC13-01	Dry Cr. off Buroker Rd.	-118.528	45.969
GRDN13-01	Burlingame canal nr. Siphon	-118.59	46.025
GRDN13-02	Burlingame canal off Rainville Rd.	-118.513	46.008
GRDN13-03	Burlingame canal off Locher Rd.	-118.473	46.004
LMC13-01	Little Mud Cr. off MacDonald Rd.	-118.569	46.002
SWC13-01	Schwartz Cr. off Hudson Bay Rd.	-118.569	45.994
SWC13-02	Schwartz Cr. off Umapine Rd.	-118.548	45.990
PC soil-1	Alfalfa field	-118.632	46.028
PC soil-2	Alfalfa field	-118.632	46.029
PC soil-3	Alfalfa field	-118.598	46.000
PC soil-4	Alfalfa field	-118.598	46.001
PC soil-5	Alfalfa field	-118.679	46.020
PC soil-6	Alfalfa field	-118.679	46.020
LGC-1	Little Grand Canyon sediments	-118.596	46.020
LGC-2	Little Grand Canyon upland soils	-118.596	46.020
LGC-3-UP	Little Grand Canyon upland soils	-118.597	46.019
LGC-3	Little Grand Canyon sediments	-118.597	46.019
LGC-4	Little Grand Canyon sediments	-118.598	46.019
LGC-4-UP	Little Grand Canyon upland soils	-118.598	46.019
LGC-5	Little Grand Canyon sediments	-118.599	46.018
White bag	Little Grand Canyon upland buried gravel	-118.596	46.020

Appendix B. Analytical Results

Table B-1. Analytical results of water grab samples.

Sample Site	Sample Date	Lab ID	pH	Temperature	Conductivity	TSS (mg/L)		TOC (mg/L)	Toxaphene (ng/L)		% Surrogate Recovery	
											Decachlor-obiphenyl (DCB)	Tetrachloro-m-xylene
Baseline Sampling												
PN13-01	3/6/2014	1403038-01	7.8	10	113	3380	J	ns	8.1	U	74	71
PN13-03	3/6/2014	1403038-05	7.8	9.5	80	1930	J	ns	7.9	U	71	67
Synoptic Sampling												
PN13-01	5/20/2014	1405047-05	8.25	17.4	91	8		2.1	3.2	U	78	56
UNNMD13-01	5/20/2014	1405047-04	7.88	17.7	95	56		ns	3.3	U	80	54
DRC13-01	6/3/2014	1406045-09	7.15	15.9	168	5		ns	3.1	U	83	53
PN13-01	6/2/2014	1406045-01	7.63	22	81	6.5		1.6	3.1	U	78	45
SWC13-02	6/3/2014	1406045-10	7.65	20.6	148	47		ns	3.1	U	78	51
PN13-01	6/16/2014	1406050-01	7.69	16.6	102	13		1.9	3	U	77	56
UNNMD13-01	6/17/2014	1406050-10	7.13	13.9	60	92	J	ns	3.1	J	77	51

J: the analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
U: the analyte was not detected at or above the reported sample quantitation limit
ns: not sampled

Table B-2. Analytical results of CLAM – solid phase extraction disks.

Site ID	Sample Date	Lab ID	TOC	TSS	Toxaphene (ng)		Volume Sampled (L)	Toxaphene (ng L-1)		% Surrogate Recovery	
										Decachlor-obiphenyl (DCB)	Tetrachloro-m-xylene
Baseline Sampling											
GRDN13-01	3/6/2014	1403038-04	ns	632	46.6		5.6	8.3		92	81
Synoptic Sampling											
PN13-01	5/20/2014	1405047-08	2.1	8	28.9		33.1	0.9		91	83
PN13-01	6/3/2014	1406045-18	1.6	6.5	51		44.0	1.2		87	80
PN13-02	6/3/2014	1406045-19	2	9	27.4		33.8	0.8		69	56
PN13-03	6/3/2014	1406045-21	2	9	45.2		45.1	1.0		82	72
PN13-04	6/3/2014	1406045-22	ns	2	25	U	40.4	0.6	U	81	73
PN13-05	6/3/2014	1406045-23	3.6	6	38.8		42.6	0.9		81	76
SWC13-01	6/3/2014	1406045-24	ns	24	25	U	32.2	0.8	U	92	62
LMC13-01	6/3/2014	1406045-25	ns	23	25	U	36.3	0.7	U	78	73
GRDN13-01	6/4/2014	1406045-26	ns	6	25	U	48.4	0.5	U	83	68
GRDN13-02	6/4/2014	1406045-27	ns	18	25	U	36.0	0.7	U	80	68
GRDN13-03	6/4/2014	1406045-28	ns	17	25	U	41.9	0.6	U	80	64
PN13-01*	6/17/2014	1406050-03/05	1.9	13	84.4		42.1	2.0		87	73
Detailed Sampling											
PN13-01*	11/5/2014	1411027-11	2	5	110.5		45.4	2.4		101	97
PN13-02	11/5/2014	1411027-15	1.4	28	219		47.3	4.6		100	94
PN13-03	11/5/2014	1411027-16	3.6	3	27.9		50.8	0.5		89	84
PN13-04	11/5/2014	1411027-17	2.8	1	53.7		50.3	1.1		97	91
UNNMD13-01	11/5/2014	1411027-13	1.5	7	210		45.3	4.6		108	88
GRDN13-01	11/5/2014	1411027-14	1	14	142		43.3	3.3		84	81

* mean of the replicates taken
U: the analyte was not detected at or above the reported sample quantitation limit.
ns: not sampled

Table B-3. Analytical results of sediment and soil samples.

Sample Site	Sample Date	Lab ID	Matrix	TOC (mg g⁻¹)	Toxaphene (ug Kg⁻¹ DW)		Toxaphene (ng g-1 OC)	% Surrogate Recovery	
								Decachlor-obiphenyl (DCB)	Tetrachloro-m-xylene
Baseline Sampling									
PN13-01	3/6/2014	1403038-02	sediment	ns	2.2		na	78	77
Synoptic Sampling									
LMC13-01	6/3/2014	1406045-16	sediment	4.06	4.4	U	1.1	74	57
PN13-01*	6/3/2014	1406045-15	sediment	0.86	2.5	U	2.9	75	61
UNNMD13-01	6/3/2014	1406045-14	sediment	0.27	1.9	U	7.0	71	59
PN13-01*	6/16/2014	1406050-02	sediment	0.64	5.6	U	8.8	79	71
Detailed Sampling									
PN13-01	11/5/2014	1411027-21	sediment	0.86	5.8		6.7	97	89
PC soil-1	11/5/2014	1411027-22	soil	1.8	19		10.6	108	92
PC soil-2	11/5/2014	1411027-23	soil	1.75	13		7.4	108	90
PC soil-3	11/5/2014	1411027-24	soil	0.74	9.8		13.2	111	87
PC soil-4	11/5/2014	1411027-25	soil	0.36	3		8.3	111	86
PC soil-5	11/5/2014	1411027-26	soil	1.39	1200		863.3	114	80
PC soil-6	11/5/2014	1411027-27	soil	1.43	1500		1049.0	125	85
LGC-1	12/8/2014	1412043-01	sediment	0.3	63		210.0	104	72
LGC-2	12/8/2014	1412043-02	soil	0.75	570		760.0	100	75
LGC-3-UP	12/8/2014	1412043-03	soil	0.6	410		683.3	136	97
LGC-3	12/8/2014	1412043-04	sediment	0.16	18		112.5	102	100
LGC-4	12/8/2014	1412043-05	sediment	0.21	14		66.7	94	67
LGC-4-UP	12/8/2014	1412043-06	soil	1.97	180		91.4	120	68
LGC-5	12/8/2014	1412043-07	sediment	0.43	57		132.6	103	91
White Bag	12/8/2014	1412043-08	soil	ns	330		na	91	74

* samples at PN13-01 are Hamlin suspended sediment samples; others are creek bed composites
ns: not sampled   na: not applicable
OC: organic carbon normalized   DW: dry weight
U: the analyte was not detected at or above the reported sample quantitation limit.

Table B-4. Grain size results for the soil and sediment samples.

Sample Site	Sample Date	Lab ID	TOC (mg g^{-1})	%gravel (> 2,000 μm)	%sand (2,000 - 63 μm)	%silt (63 - 4 μm)	%clay (<4 μm)
LMC13-01	6/3/2014	1406045-16	4.06	1	20.6	64.4	14
PN13-01*	6/3/2014	1406045-15	0.86	0	21.2	72.8	5.9
UNNMD13-01	6/3/2014	1406045-14	0.27	0	56.9	40.7	2.4
PN13-01*	6/16/2014	1406050-02	0.64	2.5	44.6	48.5	4.4
PN13-01	11/5/2014	1411027-21	0.86	1.2	40.1	54.6	4.1
Chvatal-1	11/5/2014	1411027-22	1.8	0.2	5.9	81.6	12.3
Burlin-1	11/5/2014	1411027-24	0.74	0	12.2	74.5	13.3
Wagon-1	11/5/2014	1411027-26	1.39	0.2	18.5	66.7	14.6
LGC-1	12/8/2014	1412043-01	0.3	5	30.5	52.5	12
LGC-2	12/8/2014	1412043-02	0.75	0.1	22.9	70.1	6.9
LGC-4*	12/8/2014	1412043-05	0.21	0	34.1	62.5	3.3

* mean of the replicates taken

# Appendix C. Burlingame Overflow Ditch

Figure C-1: Burlingame overflow ditch before and after opening. (Upper) looking upstream and (Lower) looking downstream. March 6 and 7, 2014.
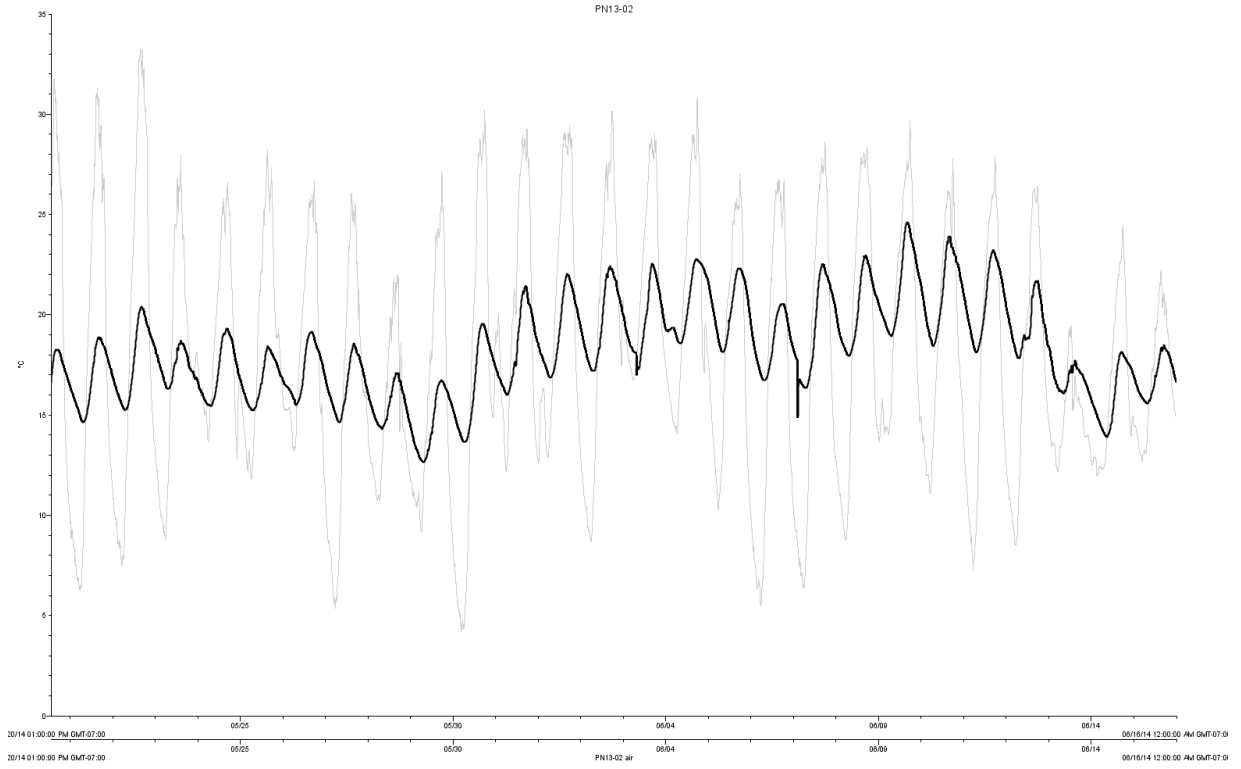
Appendix D. TidbiT Temperature Logger Data

Graphs represent the air temperature logger (grey line) and the water temperature logger (black line) for the SPMDs. Two periods of air exposure are highlighted for sample site PN13-01.
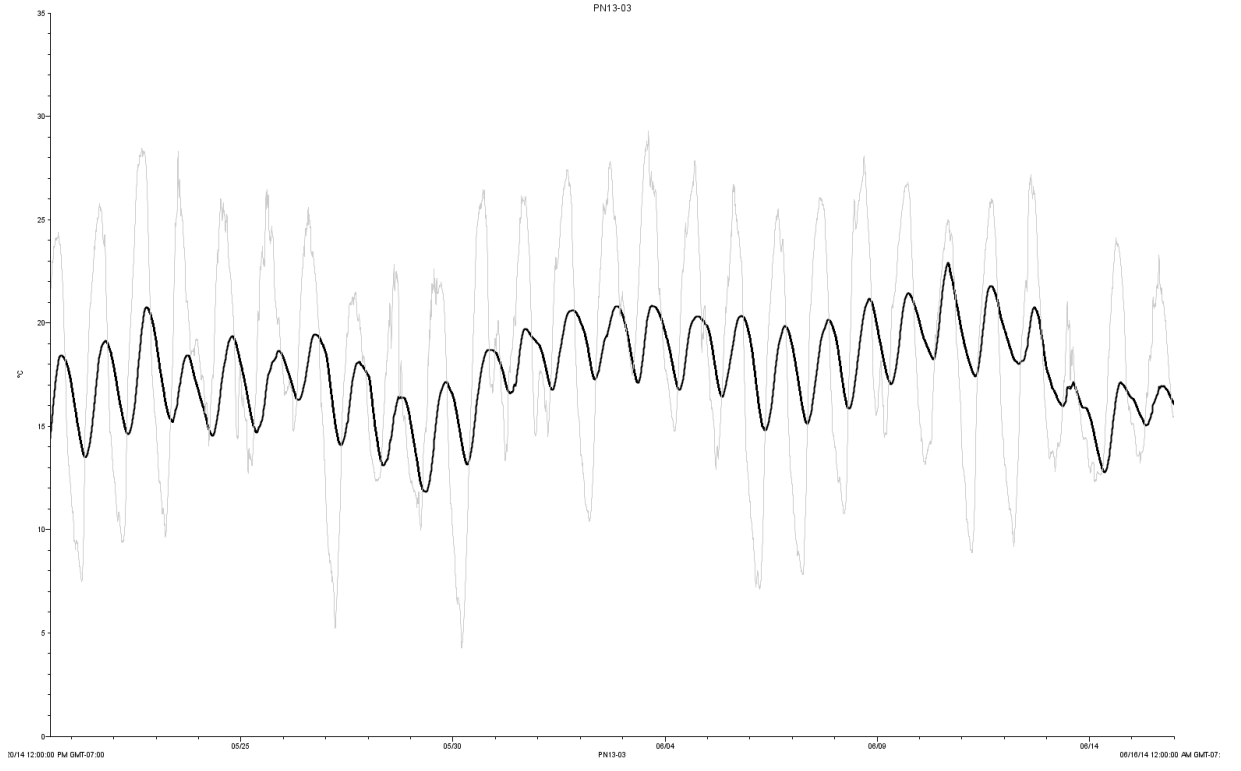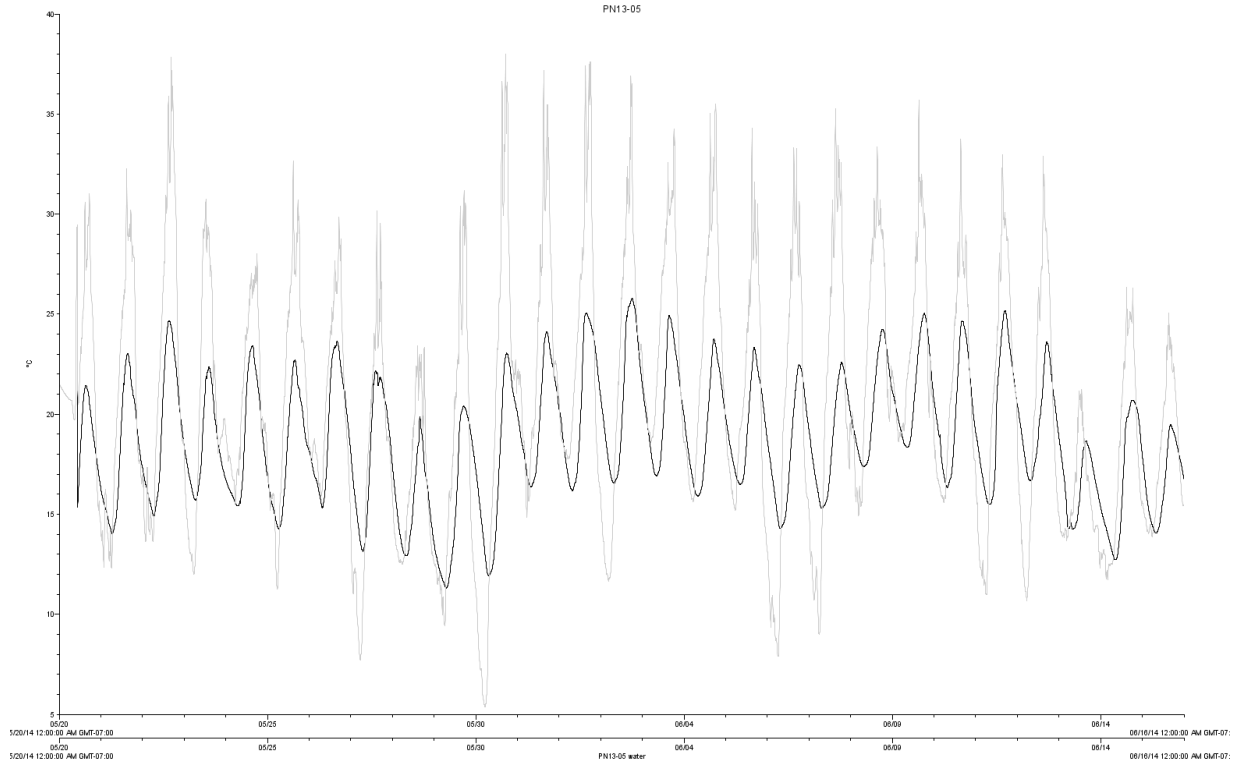
PN13-01
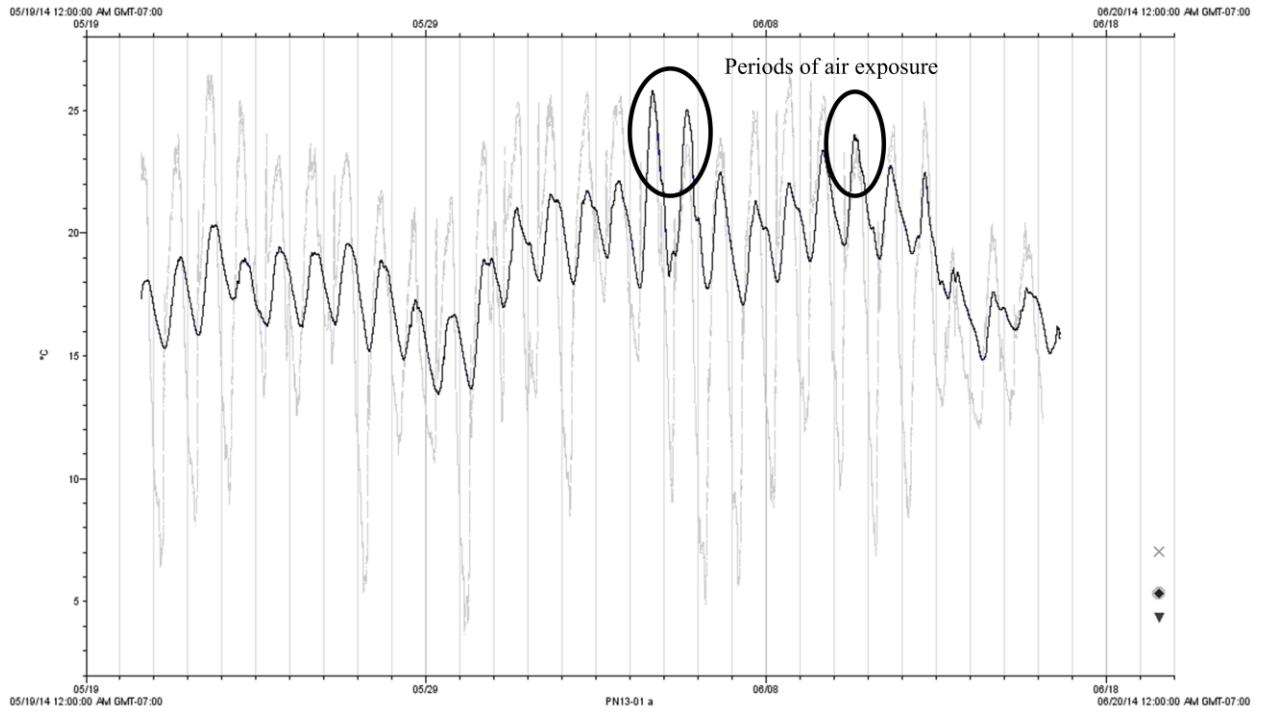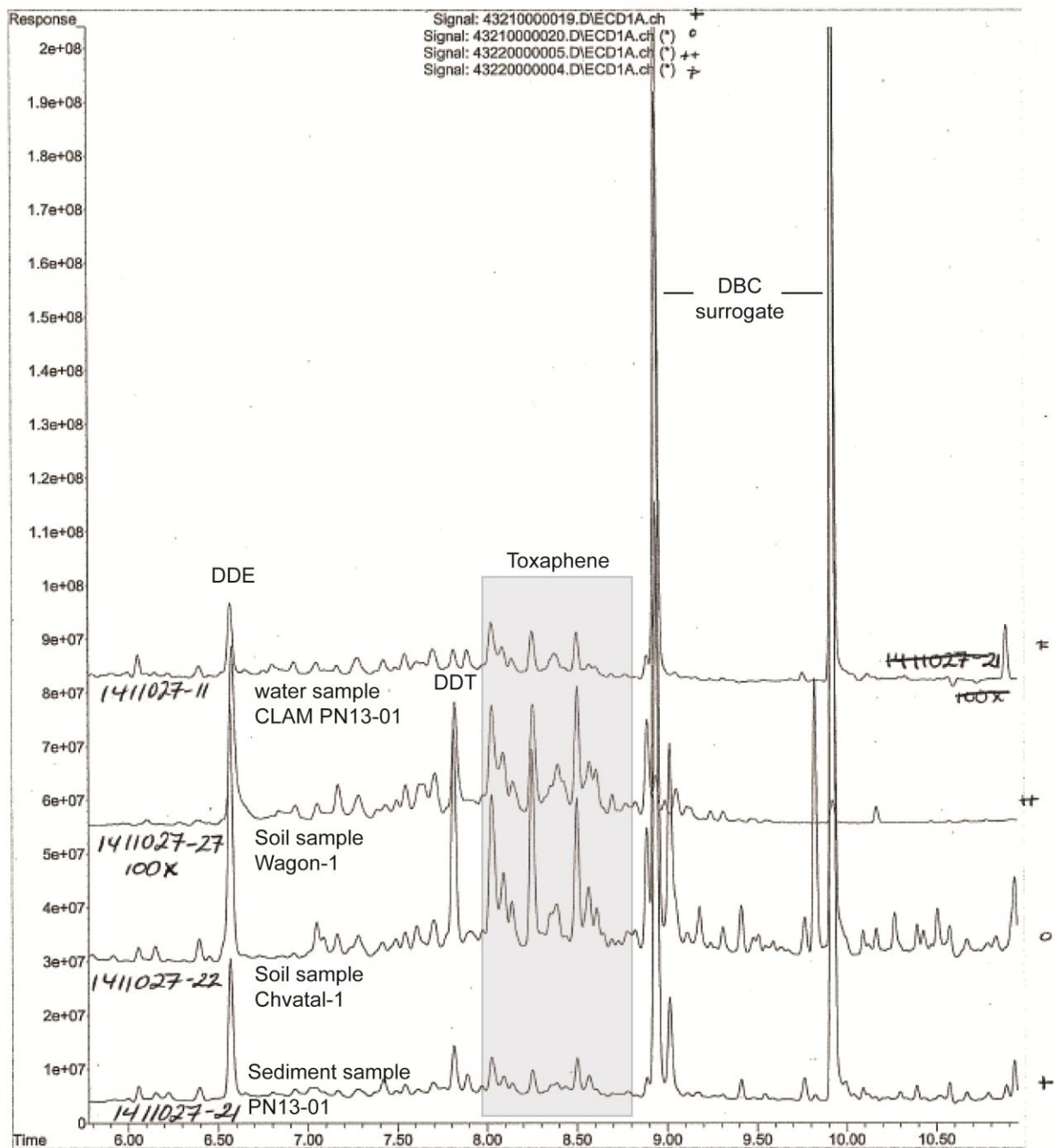
**PN13-02**

PN13-03

PN13-05

Appendix E. Sample Chromatograms


```
File       :U:\14 321\SINBAD 17NOV_14  - 219\43210000019.D
Operator   : SYSTEM
Acquired   : 17 Nov 2014  19:18 pm using AcqMethod PESTPCB_2013.M
Instrument :   GCI
Sample Name: 1411027-21
Misc Info  :
Vial Number: 15
```

File   :U:\14 321\SINBAD 17NOV_14 - 219\43210000010.D
Operator   : SYSTEM
Acquired   : 17 Nov 2014 16:07 pm using AcqMethod PESTPCB_2013.M
Instrument :   GCI
Sample Name: (4G20608) 500 pg/uL Tox
Misc Info : mix [L8,SA]
Vial Number: 6

Comparison of 21,22 & Accustandard Standard
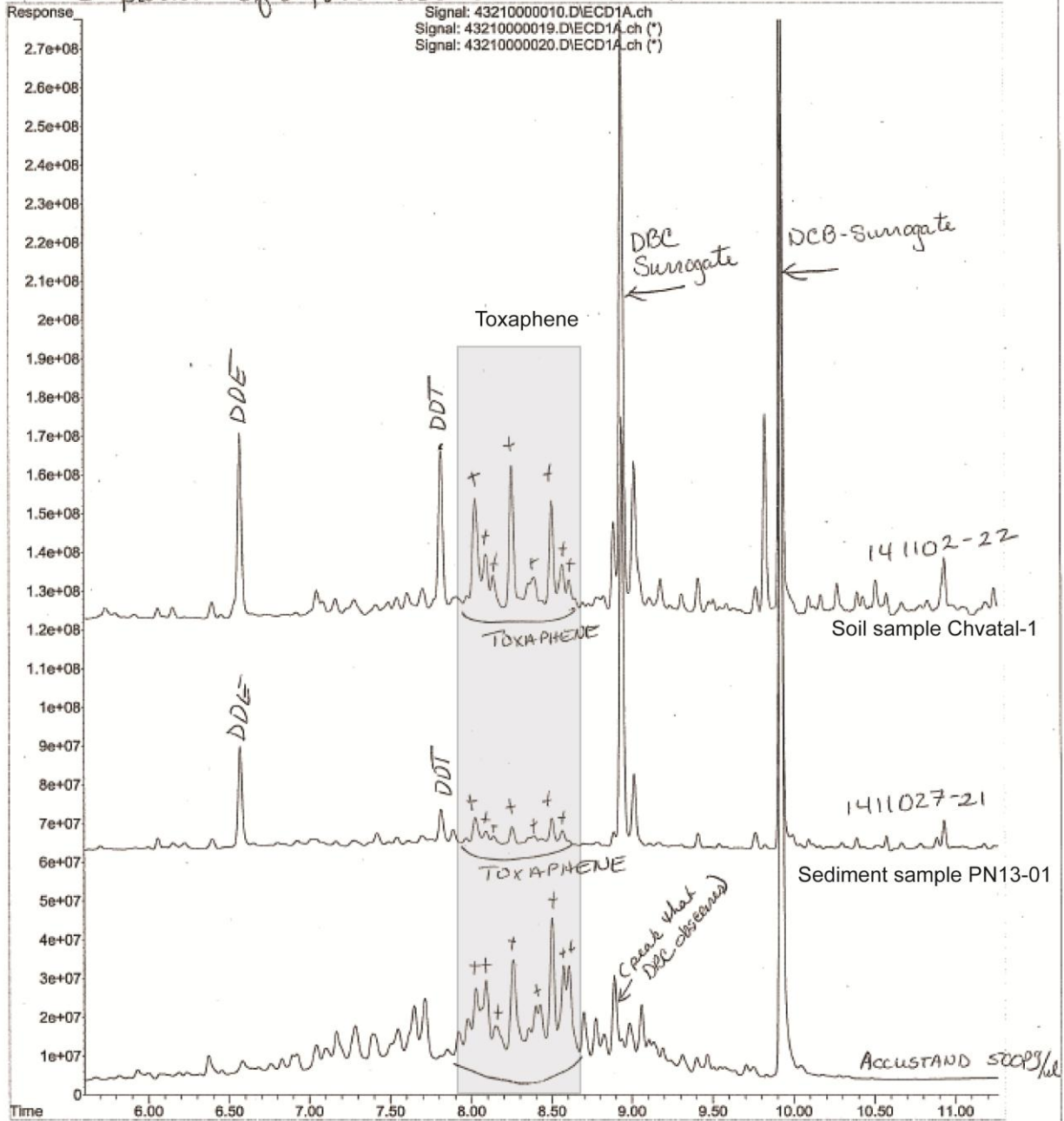
Appendix F. Glossary, Acronyms, and Abbreviations

Bioaccumulate: Process by which a chemical substance is absorbed in an organism by all routes of exposure as occurs in the natural environment (i.e., dietary and ambient environmental sources). The net result of chemical uptake into the organism at the respiratory surface and from diet and chemical elimination from the organism including respiratory exchange, fecal egestion, metabolic biotransformation or the parent compound and growth dilution.

Bioconcentrate: Process by which a chemical is absorbed by an organism from the ambient environment only through its respiratory and dermal surfaces (i.e., chemical exposure from diet is not included).

Camphene: A terpene compound that is bicyclic (two-rings) and very soluble in common solvents. It is insoluble in water but volatizes readily.

Chromatogram: A time-based graphic record of a chromatographic separation; expressed as a concentration of eluted materials.

Continuous low-level aqueous monitoring (CLAM): Active in situ aqueous sampling device consisting of a pump and media disk which binds the compounds of interest.

Isomer: One of two or more compounds, radicals, or ions that contain the same number of atoms of the same elements but differ in the structural arrangement and chemical properties.

Lipid: One of various naturally occurring substances that contains fat.

Organochlorine: Compounds that contain carbon, chlorine, and hydrogen. The chlorine-carbon bonds are very strong so they do not break down easily. They are highly insoluble in water, but bind readily to fats.

Parameter: Water quality constituent being measured (analyte). 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.

Performance reference compounds (PRCs): Analytically non-interfering compounds with moderate to relatively high fugacities or tendency to migrate between media, which are added to a passive sampler (e.g. the lipid of SPMDs) prior to deployment. The rate of in situ PRC loss during an exposure can be used to estimate in situ sampling rates of analytes of interest.

Semi-permeable membrane device (SPMD): Aqueous passive sampler consisting of a thin-walled, layflat polyethylene tube filled with 1 ml of triolein, a neutral lipid compound. Used for in situ sampling of bioavailable dissolved aqueous-phase hydrophobic organic compounds.

Total Maximum Daily Load (TMDL): Water cleanup plan. 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.

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

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

Acronyms and Abbreviations

CAFO	Concentrated animal feeding operation
CLAM	Continuous low-level aquatic monitoring
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
EST	Environmental Sampling Technologies
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objectives
PRC	Performance reference compounds
RPD	Relative percent difference
SOP	Standard operating procedures
SPE	Solid-phase extraction
SPMD	Semi-permeable membrane devices
TMDL	(See Glossary above)
TOC	Total organic carbon concentration
TSS	Total suspended solids
USGS	U.S. Geological Survey
WAC	Washington Administrative Code

Units of Measurement

°C	degrees centigrade
dw	dry weight
kg	kilograms, a unit of mass equal to 1,000 grams
km	kilometer, a unit of length equal to 1,000 meters
mg	milligram
mg L^{-1}	milligrams per liter (parts per million)
ng L^{-1}	nanograms per liter (parts per trillion)
ug Kg^{-1}	micrograms per kilogram (parts per billion)
ug L^{-1}	micrograms per liter (parts per billion)