



DEPARTMENT OF
ECOLOGY
State of Washington

Quality Assurance Project Plan

Analyzing Toxaphene at Water Quality Criteria Levels in Treated Lakes and Agricultural Streams

September 2010

Publication No. 10-03-115

Publication Information

This plan is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/1003115.html.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search User Study ID, AJOH0062.

Ecology's Activity Tracker Code for this study is 11-067.

Waterbody Number: Lakes and streams statewide.

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Quality Assurance Project Plan

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September 2010

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Abstract

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance (QA) Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve them. After completion of the study, a final report describing the results will be posted to the Internet.

This QA Project Plan describes a study that will analyze toxaphene, a legacy pesticide, at water quality criteria levels in two areas where it was used: (1) lakes where it was used to eradicate undesirable fish species and (2) streams potentially impacted by its use to control insect pests on livestock. Ecology will use a passive sampling technique to concentrate and measure toxaphene residues from the water column. Ecology will sample nine lakes and fifteen streams during the fall and spring of 2010-2011.

Background

Toxaphene, once touted as a replacement for DDT, was the last of the chlorinated pesticides to be banned in the United States (1990). It is a complex mixture of over 600 chlorinated camphenes (Figure 1) and is difficult to analyze. Although routinely included as a target compound when EPA- priority pollutants are analyzed in environmental samples, reporting limits are often high and detection infrequent.

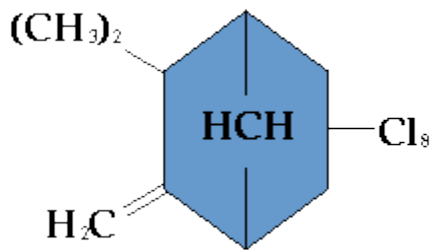


Figure 1. General Structure of Toxaphene (chlorine content 67-69% by weight).

For example, there are currently 3,355 records for toxaphene in fish, water, and sediment in the Washington State Department of Ecology (Ecology) Environmental Information Management (EIM) system. Overall detection frequency is only 3.3% percent of samples (6.3% for fish, 1.3% for water, and 0.8% for sediment). A pattern of low detection frequency is also seen nationally for toxaphene (Raff and Hites, 2004).

Ecology has conducted several recent studies where low-level methods were used to analyze toxaphene in surface water or fish tissue. A number of the lakes, rivers, and streams investigated were found to exceed water quality criteria. The results raised questions about the source of contamination. Two historical uses of toxaphene in Washington are the focus of the present study: lake restoration programs to enhance sport fisheries and control of insect pests on livestock.

Project Description

This Quality Assurance (QA) Project Plan describes a study that will use low-level methods to analyze toxaphene at water quality criteria levels (< 1 part per trillion) in treated lakes and agricultural streams where this pesticide is known or likely to have been used. The study will employ a passive sampling technique using a semipermeable membrane device (SPMD) to concentrate toxaphene residues from the water column. The SPMD extracts will be analyzed by gas chromatography/electron capture detection (GC/ECD), optimized for toxaphene. Past experience has shown this approach can be used to detect and quantify toxaphene at the sub-parts per trillion level, with low equipment blanks and minimal analytical interferences.

SPMDs will be deployed in 9 lakes that were treated with toxaphene between 1957 and 1969 and in 15 streams and irrigation returns downstream of animal feeding operations in existence prior to the toxaphene ban in 1990. Sampling will be conducted during the fall (2010) and spring (2011) when the highest toxaphene concentrations are anticipated.

This project was initiated by the Toxics Studies Unit of the Ecology Environmental Assessment (EA) Program. The Toxics Studies Unit will conduct the study and prepare the project report. SPMDs will be obtained from and extracted by Environmental Sampling Technologies (EST www.est-lab.com/index.php). The extracts will be analyzed by the Ecology Manchester Environmental Laboratory (MEL). The results will be compared to water quality criteria and the data provided to other resource agencies and the Washington State Department of Health, as appropriate. This QA Project Plan follows the Ecology guidance in Lombard and Kirchmer (2004).

Water Quality Criteria

Washington State’s water quality criteria for toxaphene are shown in Table 1 (WAC 173-201A).

Table 1. Water Quality Criteria for Toxaphene (ng/L; parts per trillion).

Protection of Aquatic Life (WAC 173-201A)		Protection of Human Health (EPA National Toxics Rule)	
Freshwater		Fish	Water & Fish
Chronic	Acute	Consumption	
0.2	730	0.75	0.73

Chapter 173-201A WAC establishes water quality standards for surface waters consistent with the maintenance and protection of uses such as public health, public enjoyment, aquatic life, and wildlife resources. Water quality criteria are designed to provide full protection for these uses.

The chronic aquatic life criterion for toxaphene is a 4-day average concentration not to be exceeded more than once every three years on average. The acute criterion is for a 1-hour average concentration not to be exceeded more than once every three years on average.

The human health water quality criteria for toxaphene are for a 10^{-6} excess lifetime cancer risk (1 in 1,000,000). Unlike most other carcinogens, toxaphene has a lower (more restrictive) aquatic life criterion (0.2 ng/L, parts per trillion) than the human health criteria (0.73-0.75 ng/L).

To assess human health risk from chemical contaminants in edible fish tissue, Ecology uses values derived from the human health water quality criteria in Table 1 and EPA bioconcentration factors (BCFs). The BCF predicts the chemical concentration in fish that would be expected to result for a given concentration in the water column. For a 10^{-6} cancer risk where both water and fish are consumed, the fish tissue criterion for toxaphene is 9.6 ug/Kg wet weight (parts per billion; BCF = 13,100). In essence, the fish tissue criteria are the human health water quality criteria expressed in tissue form.

Toxaphene Uses of Interest

Fisheries

Toxaphene was introduced in the late 1940s as an insecticide on cotton. It was first used to eliminate undesirable fish species in lakes, streams, and ponds in the mid-1950s (Eisler and Jacknow, 1985). By 1966 it was the chemical of choice in fish eradication programs in Canada and second in the United States after rotenone (Lennon et al., 1970). The practice was especially prominent in the northern states.

Records provided by the Washington Department of Fish and Wildlife (WDFW) show that 94 Washington lakes were treated with toxaphene or a combination of toxaphene and rotenone between 1954 and 1969. There were 111 toxaphene treatments overall. Four lakes were also treated with pentachlorophenol. WDFW stopped using toxaphene (and pentachlorophenol) after 1969 because the persistent residues killed planted trout (Hisata, 2002).

Upper Goose Lake in Grant County is an example of a lake that was treated toward the end of the program. The lake has a surface area of 112 acres and average depth of 40 feet. It was treated with toxaphene in 1960 and again in 1969 (the lake was rotenoned in 1965). The intent of the 1969 application was to remove carp, pumpkinseed, yellow perch, and largemouth bass. The lake was to be restocked with rainbow trout in 1971. Ninety gallons (720 pounds) of toxaphene were applied from 30 gallon drums mounted on a boat. The target treatment level was 1 part toxaphene to 19 million gallons of water by weight (0.05 ppm). The success of this treatment was characterized by WDFW as “fair”.

The dominant fate process for toxaphene in aquatic environments is sorption to sediments (Callahan et al., 1979). Loss rates from sediment are typically higher in shallow, eutrophic waterbodies. Long-term persistence is generally associated with deep, soft-water lakes where trout fisheries are important (Hughes and Lee, 1973).

Toxaphene may persist for over three decades in the sediments of lakes where it was applied (Miskimmin et al., 1995; Donald et al., 1998). During this time it undergoes changes in composition due to preferential loss of the less chlorinated components. Toxaphene residues in subsurface sediments, however, may continue to resemble the technical mixture (Miskimmin et al., 1995).

Livestock

The primary use of toxaphene in the U.S., estimated at 70-90% of total U.S. production, was on insect pests of cotton and soybeans in the southeast (ATSDR, 1996). Less than 1% was used on agriculture in the Midwest and Western states (Von Rumker et al., 1975). Toxaphene does not appear to have been an important pesticide on agricultural crops in Washington, but the true extent of its use here is unknown.

The second largest use, 7-15% of U.S. production, was to control parasites and other insect pests on livestock and poultry (Glassmeyer et al., 1997; ATSDR, 1996; Knipling and Westlake, 1966). There is a circumstantial link between use on animals and water quality concerns in Washington streams, as described below.

Water Quality Criteria Exceedances

Walla Walla River

Ecology's first effort to analyze toxaphene at water quality criteria levels was in the Walla Walla River drainage where SPMDs were deployed in 2002-03 as part of a Total Maximum Daily Load (TMDL) study for pesticides and PCBs (Johnson et al., 2004). Significant contamination was discovered in Pine Creek, where a toxaphene concentration of 40 ng/L was measured during the early part of the irrigation season, exceeding the 0.2 ng/L chronic aquatic life criterion by more than two orders of magnitude. Concentrations decreased to approximately 2 ng/L by the fall - still, however, substantially above criteria.

The same study analyzed fish collected in the Walla Walla mainstem near Pine Creek. Toxaphene concentrations in fillets ranged from 10 – 58 ug/Kg (wet weight), exceeding the 9.6 ug/Kg human health criterion by up to a factor of 6.

The inability of the 2002-03 study to detect toxaphene elsewhere in the Walla Walla drainage or to detect very low levels suggests a unique source within Pine Creek, as opposed to widespread use on crops. When these data were presented at a public meeting in Walla Walla, several landowners implicated an animal feedlot on Pine Creek as a possible source of contamination. This claim has not been confirmed.

Toxaphene continues to be a water quality concern in the Walla Walla River. SPMDs have been deployed twice a year in the lower river beginning in 2007 as part of an Ecology statewide trend monitoring program for persistent, bioaccumulative, and toxic chemicals. Toxaphene levels of 0.4 – 1.2 ng/L are reported for 2007 through 2009 (Sandvik, 2010).

Yakima River

A similar effort to analyze toxaphene was undertaken in the Yakima River in 2006-08, again as part of a pesticide/PCB TMDL (Johnson et al., 2007, 2010). Results from SPMD deployments in the mainstem and selected tributaries are shown in Figure 2. The sampling sites are arranged in downstream order, left to right. The mainstem sites are the diversion dams (Easton Dam, Easton Diversion, Roza Dam, etc.).

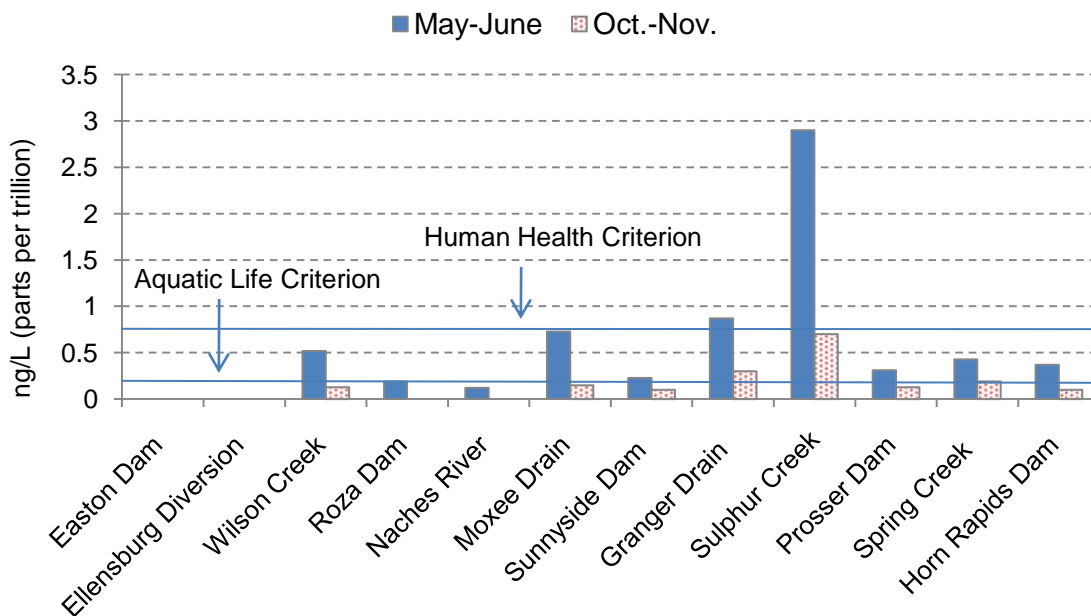


Figure 2. Estimates of Toxaphene Concentrations in the Yakima River Drainage during and after the 2007 Irrigation Season (Johnson et al., 2010).

As can be seen in the figure, toxaphene levels gradually increased in the mainstem Yakima River moving downstream from Easton to Horn Rapids Dam near the river mouth. During the irrigation season, toxaphene was below detection limits down to at least Ellensburg. Wilson Creek, which enters the Yakima just below Ellensburg, had an elevated toxaphene concentration of 0.52 ng/L. Further downstream, mainstem levels rose to 0.19 ng/L at Roza Dam, and 0.23 ng/L by Sunnyside Dam just below the city of Yakima, slightly exceeding the chronic aquatic life criterion. Between Sunnyside Dam and Horn Rapids (Wanawish Dam), toxaphene nearly doubled to 0.37 ng/L. After the end of the irrigation season (October-November data), toxaphene continued to exhibit increased concentrations in the lower river, but remained within criteria.

Toxaphene substantially exceeded the chronic aquatic life criterion in Wilson Creek, Moxee Drain, Granger Drain, and especially Sulphur Creek Wasteway. This occurred primarily during the irrigation season, when the 0.2 ng/L criterion was exceeded by a factor of 2- 4 in Wilson Creek, Moxee Drain, and Granger Drain, and by more than a factor of 10 in Sulphur Creek Wasteway (2.9 ng/L). Concentrations decreased markedly in all the four drains after the end of irrigation, but remained elevated in Sulphur Creek, exceeding the criterion by a factor of 3. Toxaphene was at or above human health criteria (0.73-0.75 ng/L) in two of these returns.

Fish tissue samples collected from the Yakima mainstem in 2006 showed a strong trend toward increasing toxaphene concentrations moving downstream, consistent with the location of sources (Figure 3). Several species exceeded human health criteria in the lower river, including mountain whitefish, largescale suckers, and carp. Concentrations in fillets ranged from 11 – 55 ug/Kg, similar to earlier findings for Walla Walla River fish.

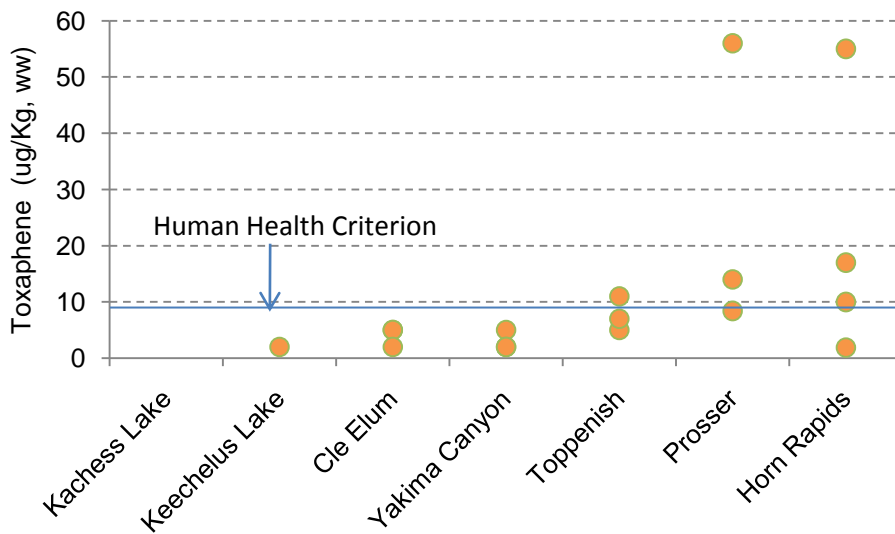


Figure 3. Mean Toxaphene Concentrations in Composite Fish Fillet Samples Collected from the Yakima River in 2006 (Johnson et al., 2007).

The link between elevated levels of toxaphene in the Yakima drainage and its use on livestock is, again, circumstantial. Sulphur Creek Wasteway and Granger Drain both have an unusually high concentration of dairies and feedlots in their watersheds; 5% of the land is confined animal feeding operations, not including pasture. A map showing how dairies are concentrated in this part of the lower Yakima basin and elsewhere in Washington is shown in Figure 4.

A large cattle feedlot (Shaake) was historically located in Ellensburg along Wilson Creek. Its runoff discharged to Wilson Creek via Tjossem Ditch (Bohn, 2010). Potential sources to Moxee Drain are less obvious. A large dairy (although recently established) and a medium-sized seasonal sheep operation (40-50 years old) are located upstream, in addition to the many hobby farms common to the Yakima area.

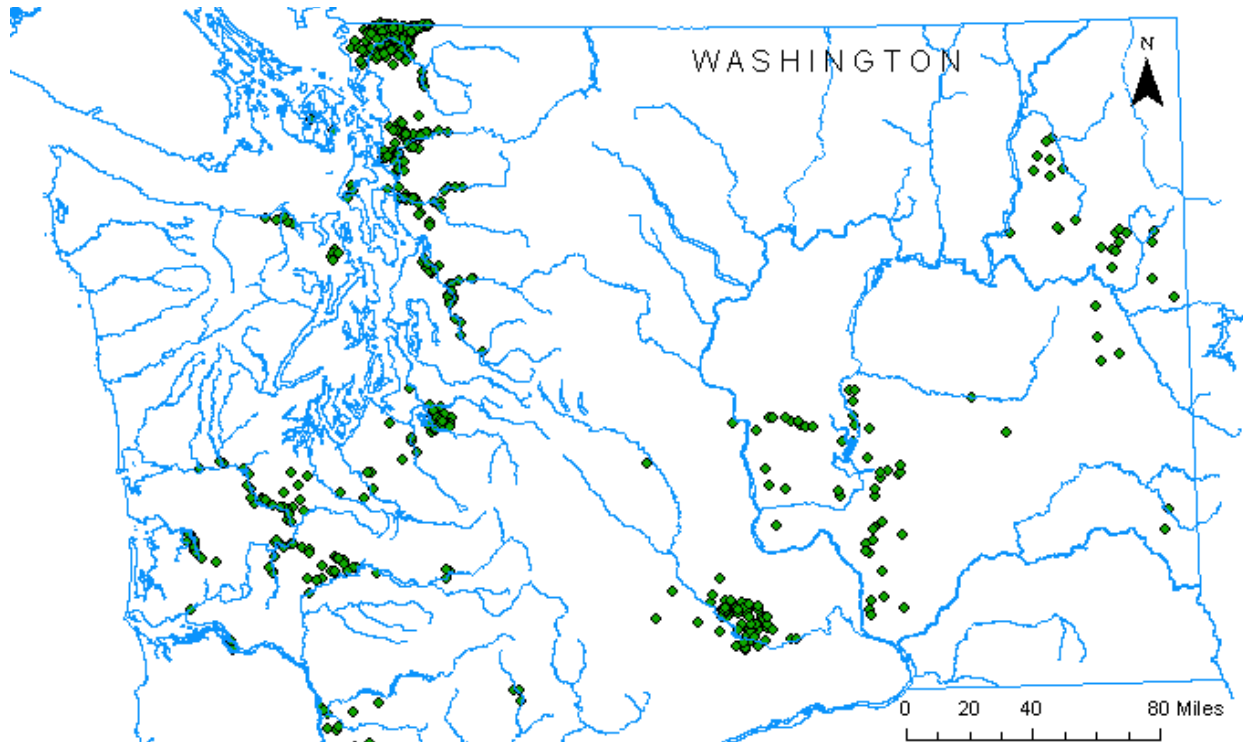


Figure 4. Location of Dairy Farms in Washington as of 2003.

Other Waterbodies

The Washington State Toxics Monitoring Program (WSTMP), initiated by the EA Program in 2000, monitors fish tissue statewide on an annual basis. Historically, reporting limits for toxaphene have been 18-20 ug/Kg. Improved reporting limits of 5-20 ug/Kg have been achieved more recently, allowing some waterbodies to be assessed for criteria compliance (Seiders et al., 2007, 2008; Seiders and Deligeannis, 2009). A separate fish tissue survey conducted by the EA Program in Vancouver Lake analyzed toxaphene at a reporting limit of approximately 9 ug/Kg (Coots; 2007). Between the WSTMP and Coots studies, ten additional lakes and rivers have been identified as exceeding the toxaphene human health criteria in edible fish tissue (Table 2).

Of the six lakes listed above, WDFW records only show toxaphene having been applied to Fish Lake, which was treated in 1964. The data suggest higher concentrations in Vancouver Lake, which apparently was not treated. However, fish are free to move between Vancouver Lake and the Columbia River, which has a number of known or potential toxaphene sources. For the most part, the concentration difference seen in Table 2 are relatively small and could be heavily influenced by the species analyzed, time of year, or other factors unrelated to ambient toxaphene levels.

Table 2. Recent Exceedances of Human Health Criteria for Toxaphene (9.6 ug/Kg) in Edible Fish Tissue Samples Analyzed by the EA Program (ug/Kg, wet weight).

Waterbody	Year Sampled	Species	Concentrations
Fish Lake	2008	BNT, LMB	13 - 20
Goodwin Lake		RBT	13
Merrill Lake		CTT	9.9
Stevens Lake		KOK	11
Klickitat River		MWF	16
Snoqualmie River		MWF	10 - 13
Meridian Lake	2006	LMB, KOK	11 - 15
Vancouver Lake		LMB	28
Queets River	2004	CHNK	9.7
Snake River		CHCAT	19

Sources: Seiders and Deligeannis (2009); Seiders et al. (2007, 2008); Coots (2007).
 BNT - brown trout, LMB - largemouth bass, RBT - rainbow trout,
 MWF - mountain whitefish, CTT - cutthroat trout, KOK - kokanee,
 CHNK - chinook salmon, CHCAT - channel catfish.

303(d) Listings

Section 303(d) of the Clean Water Act requires states to prepare a list every two years of waterbodies that do not meet water quality standards. The Act requires that a TMDL be developed for every waterbody and pollutant on the list. The TMDL determines the loading capacity of the waterbody and allocates that pollutant load among the various sources.

Based on findings from the Seiders and Coots studies, Vancouver Lake, Meridian Lake, and the Snake River have been placed on the 303(d) list as being water quality limited for toxaphene. The remaining waterbodies with fish tissue exceedances for toxaphene, including the Yakima River, will likely be added during the next listing cycle. A TMDL has already been established for toxaphene and other chlorinated pesticides in the Walla Walla River.

Passive Sampling

As previously noted, toxaphene is a complex mixture of hundreds of chlorinated compounds which are difficult to analyze. Methods are available to detect toxaphene at very low levels in whole water samples (e.g., high resolution gas chromatography/mass spectrometry) but analyzing enough samples to obtain representative data is expensive. This study will use SPMD passive samplers to concentrate sufficient toxaphene residues for analysis by the less expensive GC/ECD method.

A SPMD is composed of a thin-walled, layflat polyethylene tube filled with a neutral lipid material, triolein, (Figure 5). When placed in water, dissolved lipophilic compounds like toxaphene diffuse through the membrane and are concentrated over time. The typical deployment period is about one month, after which the membranes are retrieved, extracted, and analyzed for the chemicals of interest. The large chemical residues accumulated in a SPMD give a strong analyte signal, which translates into parts per trillion detection limits or lower. Because SPMDs measure the long-term average concentration of a chemical, random fluctuations are smoothed and representativeness of the data improved.



Figure 5. Standard SPMD Membrane Mounted on a Spider Carrier.

SPMDs were developed by the USGS Columbia Environmental Research Center, Columbia, MO and are now of standardized design, patented, and commercially available through Environmental Sampling Technologies (EST), St. Joseph, MO (www.est-lab.com/index.php). Details of SPMD theory, construction, and applications can be found at wwwaux.cerc.cr.usgs.gov/spmd/index.htm and in Huckins et al. (2006).

The use and practicality of SPMDs for environmental monitoring is now well established. Studies have shown that chemical concentrations derived from SPMDs are comparable to other more complicated preconcentration methods such as solid-phase and liquid-liquid extraction, generally agreeing within a factor of two (Ellis et al., 1995; Rantalainen et al., 1998; Hyne et al., 2004).

The amount of chemical absorbed by a SPMD is proportional to the local water column concentration. Therefore, contaminant levels among sites can be assessed by directly comparing absorbed amounts over the monitoring period.

SPMDs can also provide an estimate of the time-weighted average concentration for the chemicals of interest. Water column concentrations are derived using Permeability/Performance Reference Compounds (PRCs) spiked into deployed SPMDs. PRCs are analytically non-interfering compounds with moderate to high tendency to escape and do not occur in significant concentrations in the environment. The rate of PRC loss while exposed during a sampling period is related to the uptake of the target compound. PRCs calibrate for the effects of water velocity, temperature, and biofouling on chemical uptake.

For the present study, SPMD membrane parameters, toxaphene residue amounts, starting and ending PRC concentrations, and a toxaphene Log K_{ow} (octanol-water partition coefficient) will be entered into the SPMD Water Concentration Calculator spreadsheet. This spreadsheet was developed by USGS to estimate the average chemical concentration over the deployment period (www.cerc.usgs.gov/Branches.aspx?BranchId=8). This spreadsheet is based on an empirical uptake model described in Huckins et al. (2006). More information about how the USGS model estimates water concentrations and the function of PRCs can be found at wwwaux.cerc.cr.usgs.gov/spmd/index.htm and in Huckins et al. (2006).

Sampling Design

Waterbodies Selected for Sampling

Lakes

The WDFW records on historical toxaphene treatments were reviewed to identify lakes for sampling. Most of the applications (92 vs. 19) were in Eastern Washington lakes. Western Washington lakes were only treated during the early years of the program (1954-1963). The counties with the most treatments were Grant (30), Adams (13), Spokane (13), and Stevens (10) (Figure 6).

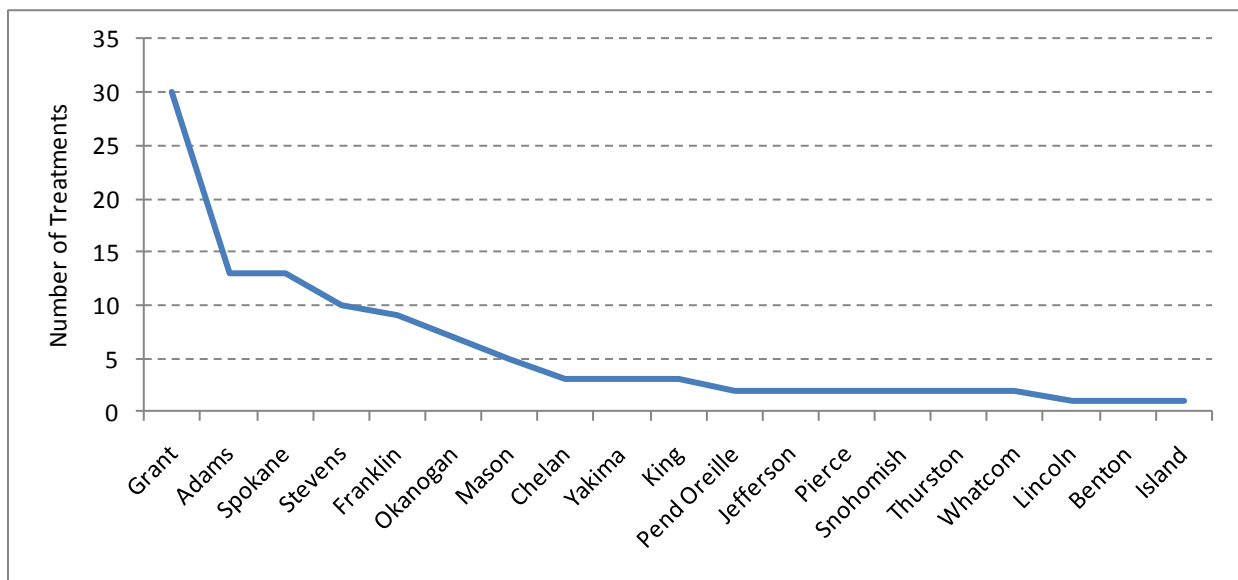


Figure 6. Frequency of Toxaphene Treatments in Washington, by County.

Nine lakes with characteristics that should favor toxaphene persistence were tentatively selected from among the 94 lakes treated during 1954 – 1969 (Table 3, Figure 7). Lakes were selected based on these factors. They were:

- Treated most recently.
- Treated twice.
- Either deep or located in cooler climates.

To minimize the field effort, lakes were selected that were close to one another within four geographic areas: Columbia National Wildlife Refuge, Medical Lake/Spokane area, Quincy Wildlife Area, and South Puget Sound. A shallow lake was included for comparison with the deeper lakes in each area.

Table 3. Treated Lakes Proposed for Sampling.

Lake	County	Year Treated	Acres	Maximum Depth	Location
Columbia National Wildlife Refuge					
Canal	Grant	59 / 68	76	120	6.5 miles N of Othello
Upper Goose		60 / 69	112	95	9.2 miles N of Othello
Lyle	Adams	59 / 69	22	15	5.3 miles N of Othello
Medical Lake/Spokane					
Silver	Spokane	59 / 67	559	80	1.1 miles E of Medical Lake
Ring		57 / 64	23	12	1.0 miles SE of Medical Lake
Quincy Wildlife Area					
Burke	Grant	66	73	33	7.5 miles SW of Quincy
H		62 / 67	7	17	6.7 miles SW of Quincy
South Puget Sound					
Star	King	62	34	50	3 miles SW of Kent
Lawrence	Thurston	63	339	26	6 miles S of Yelm

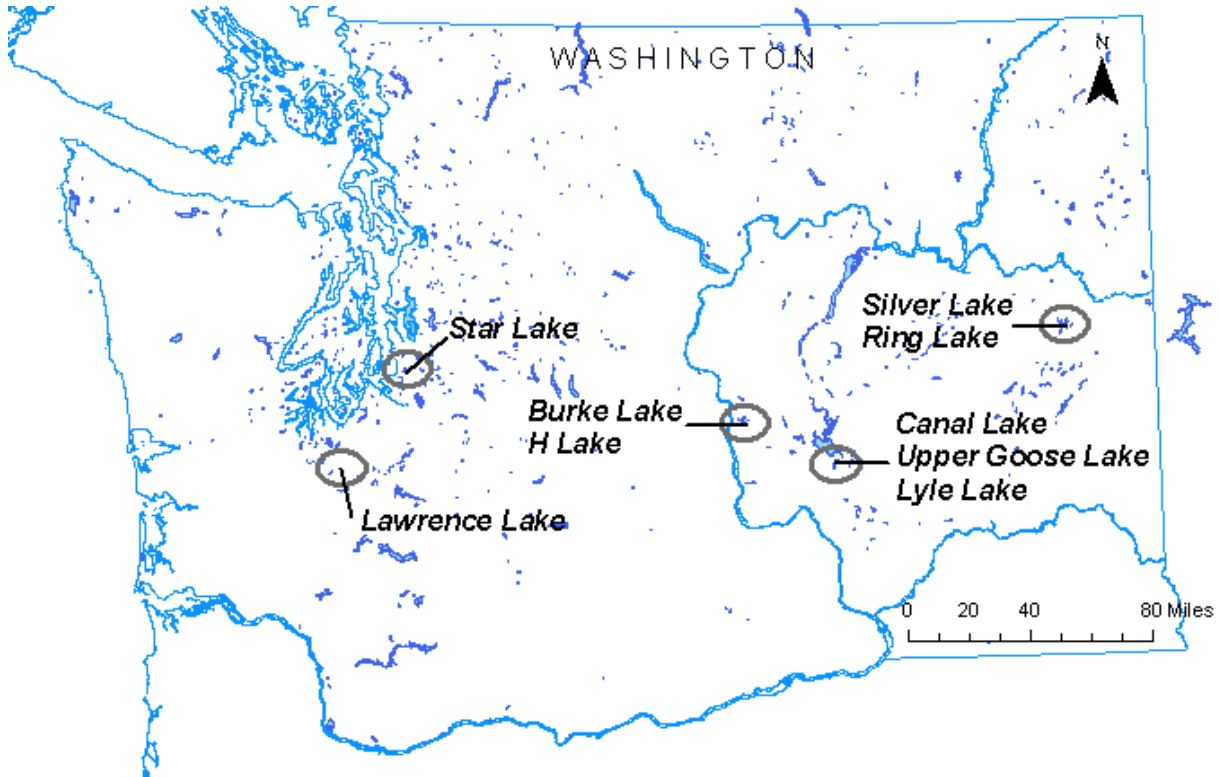


Figure 7. Approximate Lake Locations.

Streams

Ecology regulates animal feeding operations under the Concentrated Animal Feeding Operation (CAFO) National Pollutant Discharge Elimination System (NPDES) and State Waste Discharge General Permit (www.ecy.wa.gov/programs/wq/permits/cafo/cafofinalpermit06.pdf).

CAFOs are a specific category of Animal Feeding Operations (AFOs) based on the number of animals at the facility and whether or not they are discharging. Any CAFO that is discharging to waters of the state is required to obtain coverage under the general permit or obtain an individual permit.

AFOs and CAFOs are located throughout Washington. Ecology is in the process of mapping all the CAFOs, but GIS coverage is currently available for dairies only (refer to Figure 4). The locations of many of the smaller animal operations are poorly known.

In view of incomplete mapping information, Ecology staff knowledgeable on water quality issues related to animal feeding operations were asked to recommend creeks or irrigation returns they considered vulnerable to runoff from these types of facilities. It was stipulated that at least some of the facilities in question were in operation prior to the toxaphene ban in 1990.

Fifteen waterbodies were tentatively selected for sampling from among those recommended (Table 4, Figure 8). More agricultural streams are proposed for sampling than treated lakes because the extent and location of historical toxaphene use in Washington is largely unknown. It is recognized that the detection of toxaphene in a stream would not conclusively demonstrate that the source is use on livestock, given other potential sources within these drainages.

Table 4. Agricultural Streams Proposed for Sampling.

Stream	County	WRIA	In Vicinity of	Rationale for Sampling
Western Washington				
Fishtrap Creek	Whatcom	1	Lynden	Dairies; John Jennings HQ WQP/ Joe Joy EAP recommendation.
Bertrand Creek	Whatcom	1	Lynden	Dairies; John Jennings HQ WQP/ Joe Joy EAP recommendation.
Big Ditch	Skagit	3	Mt. Vernon	Diverse agriculture; Sally Lawrence NWRO/ John Jennings HQ WQP recommendation.
South Fork	Lewis	23	Boistfort	Dairies; Joe Joy EAP recommendation.
Newaukum Creek	King	10	Enumclaw	Dairies; Joe Joy EAP recommendation.
Eastern Washington				
Tjossem Ditch	Kittitas	39	Ellensburg	Toxaphene > WQ criteria 2007 (Wilson Creek); historic feedlot; Jon Merz CRO recommendation.
Granger Drain	Yakima	37	Granger	Toxaphene > WQ criteria 2007; dairies, feedlots.
Sulphur Creek	Yakima	37	Sunnyside	Toxaphene > WQ criteria 2007; dairies, feedlots.
Blue Stem Creek	Lincoln	41	Davenport	Pasture/range-based operations; Chad Atkins CRO recommendation.
Cow Creek	Adams	34	Hooper	Pasture/range-based operations; Chad Atkins CRO/ Jim Ross ERO recommendation.
Steptoe Creek	Whitman	35	Clarkston	Pasture/range-based operations; Chad Atkins CRO recommendation.
Pine Creek	Walla Walla	32	Touchet	Toxaphene > WQ criteria 2002-03; feedlot?
Deadman Creek	Garfield	35	Central Ferry	Pasture/range-based operations; Chad Atkins CRO recommendation.
Asotin Creek	Asotin	35	Clarkston	Pasture/range-based operations; Chad Atkins CRO recommendation.
Couse Creek	Asotin	35	Clarkston	Pasture/range-based operations; Chad Atkins CRO recommendation.

WRIA - Water Resources Inventory Area.
 HQ WQP - Headquarters Water Quality Program.
 EAP - Environmental Assessment Program.
 ERO - Eastern Regional Office.
 CRO - Central Regional Office.

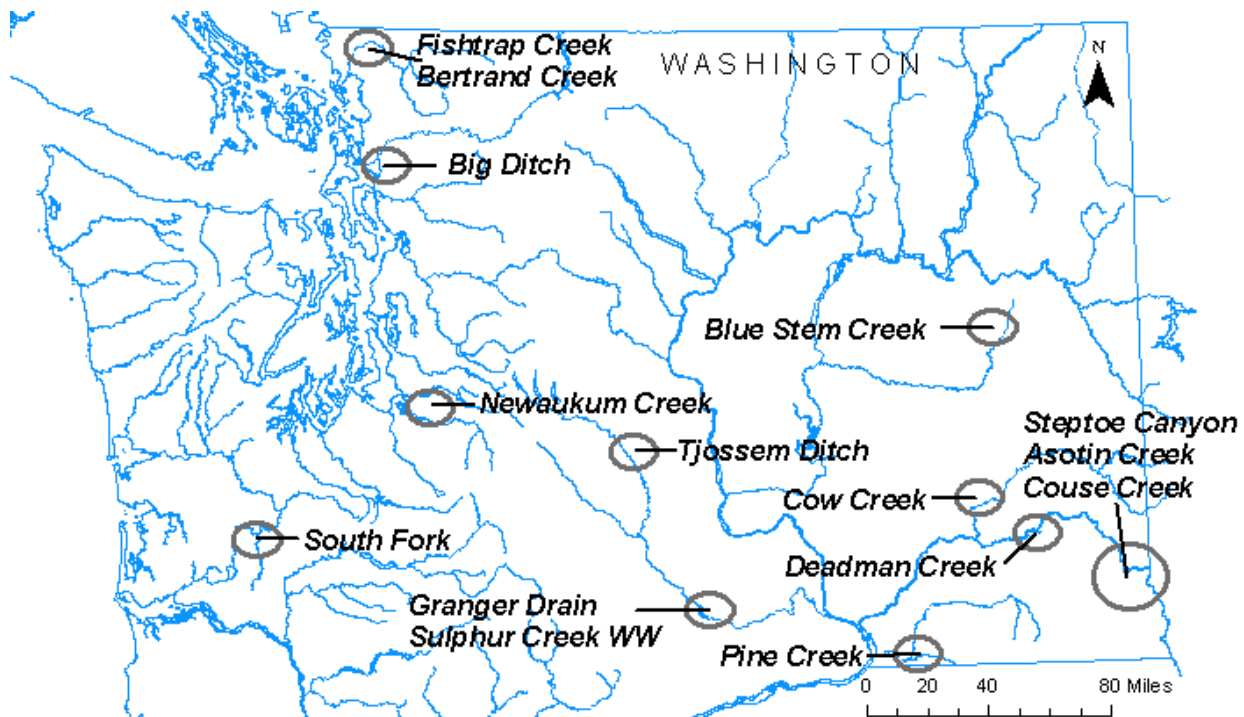


Figure 8. Approximate Stream Locations.

Timing, Location, and Number of Samples

Lakes

Most of the toxaphene remaining from historical applications to lakes would be expected to reside in the bottom sediments, some fraction of which would continually partition into the water column. Formation of the summer thermocline restricts exchange between surface and bottom water. This would act to bring about relatively higher toxaphene concentrations near the bottom during the summer months. When the thermocline breaks down in the fall, mixing should equalize concentration throughout the water column. This type of seasonal cycle has been observed in local lakes and reservoirs for other chlorinated organic compounds that reside in the sediments (Serdar and Lubliner, 2010; Coots and Era-Miller, 2005).

In an effort to obtain results that are representative of each lake as a whole, the SPMDs will be deployed in late September or October after the fall overturn. The samplers will be located toward the outflow end of the lake (or lake center if no outlet) and suspended in the water column. Each deployment will last about 30 days to give a time-weighted average toxaphene concentration over one month.

The budget for this project allows for one SPMD deployment per lake. A replicate sampler will be set out in two lakes to provide an estimate of the variability associated with measurement of toxaphene in a lake environment.

Streams

USGS has reviewed data on the occurrence of legacy and current-use pesticides in Pacific Northwest surface waters and concluded that the type of runoff was the major controlling factor. Pesticide detections in the west and in urban areas were dominated by rainfall runoff in the winter and spring and in the east were dominated by the irrigation season in the spring and summer (Anderson et al., 2005). Stream sampling for toxaphene will therefore focus on these runoff periods. For Western Washington streams, SPMDs will be deployed in early October during the onset of the rainy season. Deployments for Eastern Washington streams will take place in April-May when runoff typically peaks due to snowmelt and onset of the irrigation season.

As with lakes, there will be one SPMD deployment in each agricultural stream. Five streams will be sampled in Western Washington and ten in Eastern Washington. Greater effort is being devoted to Eastern Washington due to already known instances of significant toxaphene contamination. Replicate samplers will be deployed in two streams to assess the variability associated with data on toxaphene in streams.

Quality Objectives

The goal of this project is to obtain data of sufficient quality so that uncertainties are minimized and results are comparable to Washington water quality criteria and similar data from previous studies. These objectives will be achieved through careful attention to the sampling, measurement, and quality control (QC) procedures described in this plan.

Measurement Quality Objectives

EST and MEL are expected to meet all QC requirements of the methods and SOPs being used for sample preparation, extraction, and analysis. Measurement quality objectives (MQOs) for the project are shown in Table 5.

Table 5. Measurement Quality Objectives.

Analysis	Surrogates (% recov.)	Matrix Spikes (% recov.)	Spiked Blanks (% recov.)	Field Replicates (RPD)	Lowest Concentration of Interest
Toxaphene	30-130%	50-150%	50-150%	≤20%	≤25 ng/SPMD

RPD - relative percent difference.

Surrogates are compounds with characteristics similar to target compounds and are added to all samples prior to extraction. Recovery of the chlorinated pesticide surrogates tetrachloro-m-xylene and dibromooctafluorobiphenyl - which elute prior to toxaphene - and hexabromobiphenyl - which elutes after toxaphene - will be used to estimate recovery of native toxaphene in the SPMDs. Toxaphene will be spiked into freshly prepared SPMDs to assess bias due to characteristics of the SPMD matrix. As a cost savings measure, matrix spike duplicates will not be analyzed. Blank water spiked with a known amount of toxaphene and analyzed in duplicate will be used to assess bias due to sample preparation and calibration.

The MQOs for surrogate, matrix spike, and spiked blank recoveries are MEL's acceptance limits for analyzing chlorinated pesticides by GC/ECD. It is recognized that success in meeting these MQOs is equally a function of performance at EST laboratory in preparing, spiking, and extracting the SPMD membranes. The respective roles of the two laboratories are described later in this plan.

Field replicates (separately deployed SPMDs) will be used to assess the total variability (field + laboratory) associated with the data obtained through this project. Laboratory duplicates (split samples) will not be requested. The MQO for field replicates is based on what has been achieved in similar SPMD projects conducted by the Toxics Study Unit in the recent past.

The lowest concentration of interest shown in Table 5 is MEL's current reporting limit for toxaphene in SPMD extracts. This has been adequate to quantify toxaphene concentrations in local waterbodies with trace levels of contamination.

Organization and Schedule

The following people are involved in this project. All are employees of Washington State Department of Ecology, Environmental Assessment Program (EAP) unless otherwise noted.

Table 6. Organization of Project Staff and Responsibilities.

Staff	Title	Responsibilities
Art Johnson Toxics Studies Unit Statewide Coordination Section (360) 407-6766	Principal Investigator	Writes the QAPP, coordinates field work and chemical analyses, conducts QA review of data, analyzes and interprets data, writes the project report.
Brandee Era-Miller Toxics Studies Unit Statewide Coordination Section (360) 407-6771	Environmentalist	Assists with field work.
Kristin Carmack Toxics Studies Unit Statewide Coordination Section (360) 407-6690	Environmentalist	Assists with field work.
Michael Friese Toxics Studies Unit Statewide Coordination Section (360) 407-6737	Environmentalist	Enters project data into EIM.
Dale Norton Toxics Studies Unit Statewide Coordination Section (360) 407-6765	Unit Supervisor	Provides internal review of the QAPP, approves the budget, approves the final QAPP, reviews and approves the project report.
Will Kendra Statewide Coordination Section (360) 407-6698	Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Robert F. Cusimano Western Operations Section (360) 407-6596	Section Manager for Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Gary Arnold Eastern Operations Section (509) 454-4244	Section Manager for Study Area	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Terri Spencer Environmental Sampling Technologies (816)232-8860	Chemist	Contact for SPMD preparation and extraction.
John Weakland Ecology Manchester Environmental Laboratory (360) 871-8820	Chemist	Organics unit supervisor.
Stuart Magoon Ecology Manchester Environmental Laboratory (360) 871-8801	Director	Approves the final QAPP.
Bill Kammin (360) 407-6964	QA Officer	Reviews the draft QAPP and approves the final QAPP.

EAP – Environmental Assessment Program

EIM – Environmental Information Management system

QAPP – Quality Assurance Project Plan

Table 7. 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	October 2010 and June 2011	Art Johnson
Laboratory analyses completed	September 2011	
Environmental Information System (EIM) database		
EIM user study ID	AJOH0062	
Product	Due date	Lead staff
EIM data loaded	December 2011	Michael Friese
EIM quality assurance	January 2012	Michael Friese
EIM complete	February 2012	Michael Friese
Final report		
Author lead / Support staff	Art Johnson	
Schedule		
Draft due to supervisor	December 2011	
Draft due to client/peer reviewer	January 2012	
Final (all reviews done) due to publications coordinator (Joan)	February 2012	
Final report due on web	March 2012	

Sampling Procedures

Deployment and retrieval procedures for SPMDs will follow the EA Program SOP for SPMDs (Johnson, 2007). Standard SPMDs (91 x 2.5 cm membrane containing 1 mL triolein) and the stainless steel canisters (16.5 x 29 cm) and spindle devices that hold the membranes during deployment will be obtained from EST. The SPMDs are preloaded onto the spindles by EST in a clean-room and shipped in solvent-rinsed metal cans under argon atmosphere. Three SPMDs will be used in each canister, with one canister per sampling site. The SPMDs will be kept frozen until deployed.

EST will spike each SPMD membrane with PRCs prior to their being deployed in the field, including the field trip blank and day-zero blank (see Quality Control). PCB-4, -29, and -50 will serve as PRCs for this project. These congeners have shown appropriate rates of loss (20-80%) in past Ecology studies. PCBs can be used to adjust SPMD uptake rates for a wide range of hydrophobic chemicals including toxaphene and other chlorinated pesticides (Huckins et al., 2006). The spiking level will be 0.2 ug of each congener per SPMD membrane (0.6 ug per sample). MEL will provide the PRC spiking solution to EST.

On arriving at the sampling site, the cans will be pried open, spindles slid into the canisters, and the device anchored and tethered in the lake or stream. Because SPMDs are potent air samplers, this procedure should be done as quickly as possible. Field personnel will wear nitrile gloves and not touch the membranes. The SPMDs will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for anticipated fluctuations in water level.

The latitude and longitude of each sampling site will be recorded from a GPS. The location of the SPMD array and dates/times of deployment/retrieval will be noted in a field book.

The SPMDs will be deployed for approximately 28 days, as recommended by USGS and EST. The retrieval procedure is essentially the opposite of deployment. The cans holding the SPMDs must be carefully sealed and the SPMDs maintained at or near freezing. The SPMDs will be shipped with a chain-of-custody record to EST by overnight Federal Express, in coolers with blue ice or ice in poly bottles.

Laboratory Procedures

EST will extract the SPMDs and clean up the extracts by Gel Permeation Chromatography (GPC) following the SOPs referenced below. The extracts will be transferred to vials and shipped to MEL. MEL will analyze the extracts by GC/ECD following EPA method 8081 and associated MEL SOP. The analysis will include PCB-4, -29, and -50.

The results will be reported as ng/SPMD (ng/sample). Excess extract will be saved at MEL.

Table 8. Laboratory Procedures.

Analysis	Approx. Number of Samples*	Expected Range of Results (field samples)	Reporting Limit	Sample Prep Method	Analytical Method
Toxaphene, PCB-4, -29, and -50	31	100-1,000 ng	25 ng	dialysis/GPC [†]	EPA 8081*

*Includes field blanks, and field replicates.

[†]EST SOPs E14, E15, E19, E21, E33, E44, E48.

**MEL SOP 730091 (micro-florisil cleanup) and 730002 (analysis by dual column GC).

Quality Control Procedures

Field

Because SPMDs sample vapors while exposed to air, a field trip blank is needed to determine potential toxaphene accumulation during deployment, retrieval, and transport. The field blank SPMD is opened to the air for the average amount of time it takes to open and place the SPMD array in the water; the blank is then resealed and refrigerated. The blank is stored frozen and taken back into the field and opened and closed again to mimic the retrieval process. The blank is prepared, processed, and analyzed the same as deployed SPMDs. There will be one SPMD field blank consisting of three membranes for each of the three deployment periods.

As previously stated, field replicates will provide estimates of the variability in the toxaphene data (field + laboratory). Three SPMD samples will be collected in replicate - one lake sample and two stream samples. Each replicate pair (field sample and replicate sample) will consist of two separate SPMD arrays set out in close proximity to one another.

Laboratory

Table 9. Laboratory Quality Control Samples.

Prepared by	Method Blanks	Surrogate Spikes	Matrix Spike	Spiked Blank & Duplicate	Laboratory Duplicates†
EST	4/batch*	all samples	1/batch	none	none
MEL	2/batch	--	none	1/batch	none

*See details below.

†Field replicates will be submitted by project lead.

EST will prepare the following method blanks for each SPMD deployment:

- Day-zero dialysis blank serves as a reference point for chemical compound loss and potential background contamination during preparation of SPMDs for field, storage, post-field processing, spiking of membranes, dialysis, and GPC cleanup. This blank will contain the same amount of membranes as in the field samples (3) and manufactured at the same time.
- Fresh day-zero blank SPMD is prepared just prior to dialysis. It contains a single membrane and serves as a control during extraction and dialysis. This blank may help in determining the sources and levels of contamination if apparent.
- Spiking blank is a single membrane exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples.
- Solvent blank is assesses contamination of the solvent used in GPC. This blank is prepared at the same time the exposed SPMDs are processed. It is spiked with PRCs and surrogates and goes through GPC along with the samples.

The extracts from these EST blanks will be held frozen at MEL and analyzed in the event there is evidence of significant contamination in the field blank or other problems needing further investigation. MEL will analyze their own method blanks with each batch of samples.

EST will add surrogate compounds to one membrane in each SPMD sample prior to dialysis. MEL's standard surrogate mix for chlorinated pesticide analysis - tetrachloro-m-xylene, dibromooctafluorobiphenyl, and hexabromobiphenyl - will be provided to EST for spiking. The pesticide surrogates will be spiked at 100 ng per membrane.

For each dialysis batch, EST will do a toxaphene matrix spike of one field quality SPMD membrane. The spiking level will be 500 ng, using MEL’s standard matrix spike mix. MEL will supply EST with the solution for the matrix spike. A duplicate matrix spike will not be prepared.

MEL will analyze their own spiked blank and spiked blank duplicate (reagent water).

Duplicate analysis of field samples will not be requested.

Laboratory Cost Estimate

Table 10. Laboratory Cost Estimate.

Deployment	Number of Sites	Replicate Samples	Field Blanks	Matrix Spikes	SPMD Extracts Analyzed	EST Cost	MEL Cost per Sample	Cost Subtotals
Lakes	9	2	1	1	13	\$5,176	\$110	\$6,606
Streams (fall)	5	1	1	1	8	\$3,019	\$110	\$3,899
Streams (spring)	10	1	1	1	13	\$5,176	\$110	\$6,606
Total Lab Cost =								\$17,111

The cost estimate includes the 50% discount for MEL.

Data Verification

EST will provide documentation describing the spiking, dialysis, and GPC procedures used on project samples. PRC spikes, pre-dialysis condition, identification, dialysis, cleanup, and any problems encountered with SPMD processing will be described for each sample. A copy of the chain-of-custody form will be returned to MEL along with the SPMD extracts.

The data package from MEL will include a case narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether the MQOs were met. The data package should include results for all method blanks, spiked blanks, surrogate compounds, and matrix spikes included in the sample batch.

Data Management Procedures

Field data and observations will be recorded in a bound notebook of waterproof paper. Hard copies of the EST documentation and MEL case narratives and data reports will be held on file at the EA Program at Ecology headquarters.

Modeled results for dissolved water concentrations from SPMDs may be put into EIM once they are reviewed by the project manager. Data entered into EIM follow a formal data review procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Water column concentrations of toxaphene will be estimated by the project team using the most recent version of the SPMD Water Calculator spreadsheet developed by USGS. Currently, this is version 5 www.cerc.usgs.gov/Branches.aspx?BranchId=8. The user will verify that the most current version of the calculator is being used and be certain to lock the spreadsheet to prevent accidental changes to underlying formulae. Before each use, the spreadsheet will be tested with a set of verified SPMD parameters and results to ensure that consistent and accurate data are being obtained throughout the project.

Based on past experience, blank correcting the data is not anticipated for this study. However, if blank contamination appears to be an issue, the Ecology QA Officer will be consulted before correcting any data. Corrected data will be flagged accordingly.

The bulk of project data will be stored in an electronic depository at Ecology. These data include: SPMD residue results, laboratory case narratives, QC results, membrane manufacturing and processing history, spiking history for each membrane, extract splits and multipliers for results, PRC results, log K_{ow}s used, TidbiT™ data, temperature and conductivity grab sample results, date and time of deployments, field trip blank exposure records, and other field or laboratory notes.

Data Quality (Usability) Assessment

Once the data have been verified, the project lead will determine if they can be used to make the calculations and determinations for which the project was conducted. If the MQOs have been met, the data should be useable for meeting project objectives and data analysis and report preparation will proceed.

Excel and Systat will be used to identify water quality criteria exceedances and construct graphs comparing concentrations with criteria. Summary tables of the data, criteria comparisons, and other findings will be prepared.

Audits and Reports

Laboratory Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request.

EST has patented and proprietary procedures for the manufacture, preparation, post-deployment processing, and extraction of SPMDs. EST has made SOPs available. Questions about their procedures have been addressed satisfactorily to date by Ecology and, therefore, deemed to not require accreditation and audits under Ecology's Environmental Laboratory Accreditation Program.

Project Reports

On or before January 2012 a draft report will be prepared for peer and client review. The draft report will include:

- Maps of the study area showing sampling sites.
- Coordinates and detailed descriptions of each sampling site.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical data.
- Comparisons with toxaphene water quality criteria.
- Conclusions as to evidence for significant contamination in each waterbody and likely sources.
- Recommendations for source tracing or other follow-up work as appropriate.

A final project report is anticipated by March 2012. The responsible staff member for the report is Art Johnson.

Some project data will be stored in an organized structure as previously described. Some project results will be entered into EIM. Access to the final report and data in EIM will be available through Ecology's internet homepage (www.ecy.wa.gov). Access to other project records and data will be made available upon request. Project data entered into EIM will be done on or before March 2012. The responsible staff member is Michael Friese.

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Appendix. 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.

Eutrophic: Nutrient- rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

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

Thermocline: A subsurface layer in a lake or other waterbody where temperature changes more rapidly with depth than it does in the layers above or below.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody designed to protect it from 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.

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

AFO	Animal Feeding Operation
CAFO	Concentrated Animal Feeding Operation
BCF	Bioconcentration factor
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EA Program	Environmental Assessment Program
EPA	U.S. Environmental Protection Agency
EST	Environmental Sampling Technologies

GC/ECD	Gas chromatography/electron capture detection
GPC	Gel permeation chromatography
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NPDES	(See Glossary above)
PCB	Polychlorinated biphenyls
PRC	Performance reference compound
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
SPMD	Semipermeable membrane device
SOP	Standard operating procedures
TMDL	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WRIA	Water Resources Inventory Area
WSTMP	Washington State Toxics Monitoring Program

Units of Measurement

ng/L	nanograms per liter (parts per trillion)
ug/Kg	micrograms per kilogram (parts per billion)