

Quality Assurance Project Plan

Potholes Reservoir Assessment of Dieldrin and Other Chlorinated Contaminants

by Brandee Era-Miller

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

February 2008

Publication Number 08-03-101

This plan is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0803101.html.

Quality Assurance Project Plan

Potholes Reservoir Assessment of Dieldrin and Other Chlorinated Contaminants

February 2008

303(d) Listings Addressed in this Study

Potholes Reservoir (WA-41-9280) - Dieldrin

Project Code: 08-068

Any use of product or firm names in this publication is for descriptive purposes only and does not imply endorsement by the author or the Department of Ecology.

If you need this publication in an alternate format, call Carol Norsen at 360-407-7486. Persons with hearing loss can call 711 for Washington Relay Service. Persons with a speech disability can call 877- 833-6341.

Quality Assurance Project Plan

Potholes Reservoir Assessment of Dieldrin and Other Chlorinated Contaminants

February 2008

Approvals

Signature ¹ :	Date: February 2008
Jon Jones, Client, WQP ² , Eastern Regional Office	
Signature:	Date: January 2008
Dave Knight, Unit Supervisor, WQP, Eastern Regional Office	5
Signature:	Date: January 2008
Jim Bellatty, Section Supervisor, WQP, Eastern Regional Office	
Signature:	Date: January 2008
Brandee Era-Miller, Project Manager and Environmental Information	
Management System Data Engineer, EAP ³	
Signature:	Date: January 2008
Dale Norton, Unit Supervisor, EAP	
Signature:	Date: January 2008
Will Kendra, Section Manager, EAP	
Signature:	Date: January 2008
Stuart Magoon, Director, Manchester Environmental Laboratory	
Signature:	Date: January 2008
Bill Kammin, Ecology Quality Assurance Officer	

 ¹ Signatures are not available on the Internet version
 ² Water Quality Program
 ³ Environmental Assessment Program

Table of Contents

	<u>Page</u>
Abstract	5
Background Study Area Description Basin Contaminant History	5 5 7
Project Description	9
Organization and Schedule Organization Schedule	10 10 10
Quality Objectives	11
Sampling Design Fish SPMDs Sediments	12 12 13 14
Sampling Procedures Fish Tissue SPMD Sediments Decontamination Procedures	15 16 17 18
Measurement Procedures	19
Quality Control Procedures Fish Tissue SPMD Sediments	21 21 21 22
Data Management Procedures	23
Audits and Reports Audits Reports	
Data Verification	24
Data Quality (Usability) Assessment	24
References	25
Appendix A. Acronyms	27
Appendix B. Dieldrin Fish Tissue 303(d) Listing for Potholes Reservoir	

Abstract

Potholes Reservoir in Grant County has been listed by Washington State under Section 303(d) of the federal Clean Water Act for dieldrin in edible fish tissue. The U.S. Environmental Protection Agency requires each state to address 303(d)-listed waterbodies by establishing Total Maximum Daily Loads (TMDLs) for each waterbody.

This study will assess Potholes Reservoir for dieldrin, other chlorinated pesticides, and PCBs. Sampling will include fish tissue, surface sediments, and water. The results will be used to (1) evaluate the extent and significance of dieldrin contamination in Potholes Reservoir and (2) make recommendations for a TMDL study (water cleanup plan), if warranted. The fish tissue data will be provided to the Washington State Department of Health for determination of risk to human health from consuming fish from the reservoir.

Each study conducted by the Washington State Department of Ecology (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 those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Background

Potholes Reservoir has been listed by Washington State under Section 303(d) of the federal Clean Water Act for dieldrin in edible fish tissue. (See Appendix B for listings.) The U.S. Environmental Protection Agency (EPA) requires each state to address 303(d)-listed waterbodies by establishing Total Maximum Daily Loads (TMDLs) for each waterbody.

The Washington State Department of Ecology (Ecology) Water Quality Program, Eastern Regional Office, has requested a screening-level study of the reservoir. More information about the extent and significance of dieldrin contamination in Potholes Reservoir is needed to make recommendations for a future TMDL technical study, if warranted.

Study Area Description

Potholes Reservoir is located in north central Grant County (Figure 1). It was formed by two distinct events. The first occurred during the massive flooding from glacial Lake Missoula (12,000 years ago) when huge depressions were carved out of the earth. During the 1950s, the depressions were filled with water by the creation of O'Sullivan Dam. The dam was built by the U.S. Bureau of Reclamation to provide irrigation water for farming as part of the Columbia Basin Irrigation Project.



Figure 1. Potholes Reservoir.

The northern half of the reservoir, particularly the western side, is shallow. The deepest section of the reservoir is on the southeast side near O'Sullivan Dam at about 70 feet (Rogowski and Davis, 1999).

Potholes Reservoir collects excess irrigation water from farmland in the northern part of the Columbia Basin Irrigation Project for reuse in the southern part. The reservoir receives irrigation-return flows from Winchester Wasteway, Frenchman Hills Wasteway, and Lind Coulee. Water also enters the reservoir from Moses Lake and from groundwater. Irrigation-return flows usually peak during the summer and taper off by fall.

Agriculture in Grant County is mainly irrigated wheat crops followed by hay, alfalfa, corn (grain and silage), beans, potatoes, and barley (USDA, 2006).

Potholes Reservoir is a popular fishing destination. The fish community in Potholes is diverse. The most common species include walleye, yellow perch, black crappie, lake whitefish, and smallmouth bass. According to the Potholes Reservoir walleye survey conducted by the Washington Department of Fish and Wildlife (WDFW) in 2006, 75% of all the fish caught were walleye and yellow perch. Other species captured in smaller numbers included brown bullhead, bluegill, channel catfish, carp, yellow bullhead, and burbot (WDFW, 2007). Largemouth bass and rainbow trout have also been reported.

Basin Contaminant History

Potholes Reservoir is located in Water Resource Inventory Area (WRIA) 41: Lower Crab Creek. WRIA 41 has edible fish tissue listings on the EPA water quality impaired list or 303(d) list. Listed parameters include dieldrin, DDE, PCBs, and TCDD (dioxin).

The most upstream listings in WRIA 41 are for TCDD and PCBs in Moses Lake (Seiders and Kinney, 2004). Although these concentrations are high enough to be listed, they are relatively low compared to concentrations in fish in other areas of Washington State.

Potholes Reservoir is listed for dieldrin, based on Serdar et al. (1994). Frenchman Hills Wasteway, a tributary, also has a dieldrin listing in its upper section (Frenchman Hills Lake) based on the EPA National Lake Fish Tissue Study (EPA, 2005). There are no additional toxics 303(d) listings for Potholes or upstream waterbodies, other than Moses Lake as mentioned above.

The dieldrin data that have been collected on fish in the Potholes drainage are summarized in Table 1. This area has had some of the highest dieldrin concentrations reported for Washington. The listing criterion for dieldrin is 0.65 ug/Kg^4 (parts per billion) in edible (fillet) tissue.

Study	Sampling Date	Location	Species	Tissue	No. in Composite Sample	Dieldrin (ug/Kg ww)
Hopkins	1989	Winchester WW	LMB	Fillet	3	<16
(1991)		"	LSS	Whole	2	<15
Serdar et al.	1992	Potholes Reservoir	LMB	Fillet	5	~5
(1994)		"	LWF	"	5	32
		"	LSS	Whole	5	37
Munn & Gruber	1992	Lind Coulee	CARP	Whole	5	260
(1997)		Winchester WW	CARP	"	5	53
EPA National	1999	Potholes Reservoir	WALL	Fillet	5	<1
Study (2005)		"	CARP	Whole	5	13
		Frenchman Hills Lake	LMB	Fillet	5	7
		"	CARP	Whole	5	27
Seiders & Kinney	2002	Moses Lake	LMB	Fillet	10	ND
(2004)		"	WALL	"	9	ND
		"	RBT	"	6	ND

Table 1. Historical Data on Dieldrin Levels in Fish from the Potholes and Moses Lake A
--

WW=Wasteway

ND = not detected

LMB = largemouth bass; LSS = largescale sucker; LWF = lake whitefish; CARP = common carp; WALL = walleye; RBT = rainbow trout

⁴ Criteria for the protection of human health are applied to the state through the EPA National Toxics Rule (NTR) [40 CFR 131.36(14)]

Lind Coulee appears to be a major source of dieldrin to Potholes. In addition to the high concentration reported in whole carp (260 ug/Kg ww), U.S. Geological Survey detected dieldrin in 13 of 38 water samples from Lind Coulee, compared to 3 or fewer detections in other Central Columbia Plateau waterbodies (Greene et al., 1994). The detection limit was not provided in Green et al.

Downstream of Potholes there are edible fish tissue 303(d) listings for dieldrin, DDE, and/or PCBs in Red Rock Lake, Royal Lake, Scooteney Reservoir, and Lower Crab Creek. The dieldrin concentrations are similar to Potholes (Table 2). The DDE and PCB levels in some of these waterbodies are much higher than in the Potholes/Moses Lake area (data not tabulated).

Study	Sampling Date	Location	Species	Tissue	Dieldrin (ug/Kg ww)
Davis & Johnson					
(1994)	1992	Lower Crab Creek	MWF	Fillet	ND
		"	LSS	Whole	ND
Munn & Gruber					
(1997)	1994	Royal Lake	CARP	Whole	35
		Lower Crab Creek	"	"	ND
Davis et al.					
(1998)	1995	Red Rock Lake	LMB sm	Fillet	4.1
		"	LMB lg	"	8.6
		Royal Lake	SMB	"	8.2
		"	CARP	Whole	42
		Scooteney Reservoir	LMB sm	Fillet	ND
		"	LMB lg	"	0.7
		"	SMB sm	"	ND
		"	SMB lg	"	2.8
		"	CARP	Whole	28
		"	CARP	"	19
Seiders et al.					
(2006)	2003	Scooteney Reservoir	CH CAT	Fillet	2.4
		"	WALL	"	2.3
		"	YP	"	ND

Table 2. Historical Data on Dieldrin Levels in Fish Downstream of Potholes Reservoir.

ND = not detected

MWF = mountain whitefish; LMB = largemouth bass; SMB = smallmouth bass; LSS = largescale sucker; CARP = common carp; CH CAT = channel catfish; YP = yellow perch; WALL = walleye

Project Description

Ecology will assess Potholes Reservoir for dieldrin, other chlorinated pesticides, and PCBs. Dieldrin is the focus of the study. The results will be used to evaluate the extent and significance of dieldrin contamination in Potholes Reservoir and to make recommendations for future work for a TMDL technical study, if warranted. The fish tissue data will be provided to the Washington State Department of Health (WDOH) for determination of risk to human health from consuming fish from the reservoir.

Sampling will include fillet tissue from up to ten fish species, surface sediments, and passive water samplers called SPMDs (semi-permeable membrane devices). SPMD sampling will occur from mid-November through mid-December 2007 after the irrigation season, and again in April 2008 at the onset of the irrigation season. Fish will be collected in October and November 2007. Sediments will be collected in April 2008.

The study objectives are as follows:

- 1. Assess current levels of dieldrin and other chlorinated contaminants in fish, water, and sediments by comparing data to Washington State and national standards.
- 2. Assess the relative importance of the water column and sediments as contaminant pathways to fish.
- 3. Identify seasonal patterns of chlorinated pesticides in the lake water column and inflows.
- 4. Evaluate differences in contaminant levels among the various fish species and among different size classes of fish.
- 5. Provide fish tissue data to WDOH to assess a need for a fish consumption advisory.
- 6. Prioritize reservoir inflows as sources of dieldrin.
- 7. Recommend how and where to focus work for a TMDL technical study, if warranted.

Organization and Schedule

Organization

The following people are involved in this project.

Name	Organization	Phone No.	Role
Brandee Era-Miller	EAP	360.407.6771	Project Manager
Randy Coots	EAP	360.407.6690	Field Lead
Dan Dugger	EAP	509.454.4183	Field Assistance
Dave Serdar	EAP	360.407.7104	Field Assistance
Dale Norton	EAP	360.407.6765	Unit Supervisor
Jon Jones	ERO - WQP	509.329.3481	Client
Terri Spencer	Environmental Sampling	816 232 8860	SPMD Preparation
	Technologies	010.252.0000	and Extraction
John Weakland	Manchester Laboratory	360.871.8820	Organics Supervisor
Dean Momohara	Manchester Laboratory	360 871 8808	Inorganic Chemistry
Dean Womonara	Wallenester Edoblatory	500.071.0000	Unit Supervisor
Stuart Magoon	Manchester Laboratory	360.871.8801	Lab Director
Karin Feddersen	Manchester Laboratory	360.871.8829	Contract Lab Services
Bill Kammin	EAP	360.407.6964	Quality Assurance Officer

EAP=Environmental Assessment Program ERO=Eastern Regional Office

WQP=Water Quality Program

Schedule

Environmental Information Management System (EIM) Data Set						
EIM Data Engineer	Brandee Era-Miller					
EIM User Study ID	BERA0005					
EIM Study Name	Potholes Reservoir Assessment					
	of Dieldrin and other					
	Chlorinated Contaminants					
EIM Completion Due	December 2008					
Final Report						
Author Lead	Brandee Era-Miller					
Schedule						
Draft Due to Supervisor	August 2008					
Draft Due to Client/Peer Reviewer	September 2008					
Draft Due to External Reviewer	October 2008					
Final Report Due	December 2008					

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality and quantity so that the data can be used to (1) evaluate the extent and significance of contamination by dieldrin and other chlorinated compounds in Potholes Reservoir and (2) determine the need for a fish consumption advisory in Potholes Reservoir. These objectives will be achieved through careful sampling and by following the *Sampling Procedures* and *Quality Control Procedures* described in this Quality Assurance Project Plan.

Ecology's Manchester Environmental Laboratory (MEL) is performing the chemical analysis for the study (with the exception of sediment grain size, which will be performed by a contract laboratory). MEL is expected to meet all the quality control (QC) requirements of the analytical methods being used for this project. MEL's routine QC tests for precision and accuracy will meet project needs. The analytical measurement quality objectives (MQOs) that will be used are shown in Table 3.

Parameter	Laboratory Control Samples	Duplicate Samples	Matrix Spikes	Matrix Spike Duplicates	Surrogate Standards
	% recovery limits	RPD	% recovery limits	RPD	% recovery limits
Fish Tissue					
Percent lipids	n/a	≤ 20	n/a	n/a	n/a
PCB aroclors	50-150	\leq 50	50-150	\leq 50	30-130
Chlorinated Pesticides	50-150	≤ 50	50-150	≤ 50	20-130
Sediments					
TOC	75-125	≤15	n/a	n/a	n/a
PCB aroclors	50-150	\leq 50	50-150	\leq 50	50-150
Chlorinated Pesticides	50-150	≤ 50	50-150	≤ 40	50-150
Grain size	n/a	≤15	n/a	n/a	n/a
SPMDs					
Chlorinated Pesticides	50-150	≤ 50	50-150	≤ 50	50-150
Water (for SPM	Ds)				
TOC	80-120	≤ 20	75-125	≤ 20	n/a
TSS	80-120	≤ 20	n/a	n/a	n/a
Nitrate/Nitrite	80-120	≤ 20	75-125	≤ 20	n/a
Conductivity	80-120	≤ 20	n/a	n/a	n/a

Table 3. Analytical Measurement Quality Objectives.¹

¹Quality Control (QC) limits from personal communication with MEL. RPD = Relative RPD = Rela

RPD = Relative Percent Difference

The percent recoveries of the laboratory control samples (LCS), matrix spikes, and surrogate standards provide and indication of bias in the analytical system due to calibration or matrix effects. Surrogate standards are added to every sample prior to extraction, while matrix spikes are added to only one sample within a sample batch. The relative percent differences (RPD) of laboratory duplicates and matrix spike duplicates are a measure of analytical precision.

Sampling Design

The field sampling schedule for the Potholes Reservoir study is given in Table 4. Figure 2 shows where the SPMD and sediment locations will be. Fish will be collected throughout the reservoir.

Table 4.	Sampling Schedule	
----------	-------------------	--

	Analysis										
Sampling	Location	Dieldrin & other Chlorinated Pesticides	PCB Aroclors	Lipids	Hd	Temperature	Conductivity	Nitrate/Nitrite	SSL	TOC	Sampling Dates
Fish Tissue	entire lake	Х	Х	Х							Oct-07 & Nov-07
SPMD	inflows (4) lake (2)	Х									Nov-07 & Apr-08
Water (for SPMDs)	inflows (4) lake (2)				Х	Х	Х	Х	Х	Х	Nov-07 & Apr-08
Sediment	Inflows (4) lake (3)	X	Х							Х	Apr-08

Fish

Chlorinated pesticides, PCB aroclors, and lipids will be analyzed in three to six composite fillets from each of ten fish species. Targeted species include walleye, black crappie, lake whitefish, yellow perch, smallmouth bass, largemouth bass, bluegill, rainbow trout (net pen reared), brown bullhead, and carp.

To assess the potential for a size effect, walleye, largemouth bass, and lake whitefish will be analyzed in three composites each of small and large individuals; a total of three composites would be analyzed for the other seven species. Samples will be collected at the end of the peak fishing period (mid-summer through fall) in late October and November 2007.

Comparison to Human Health Criteria

The fish tissue results will be compared to statewide data and to the EPA National Toxics Rule (NTR) criteria (40 CFR 131.36(14)). These criteria are based on water column criteria for human health and EPA's bio-concentration factors; the criteria apply to edible fish tissue only.



Figure 2. SPMD and Sediment Sampling Locations.

SPMDs

SPMDs will be deployed twice during the study. The first deployment will occur in mid-November through mid-December 2007 after the end of the irrigation season. During this time of year, irrigation wasteway flows are primarily supplied by groundwater (Ebbert and Jones, 1997). The second set will be deployed in April 2008 during the first half of the irrigation season.

SPMDs will be deployed at the four major inflows to Potholes Reservoir: Winchester Wasteway, Frenchman Hills Wasteway, Lind Coulee, and Crab Creek as well as at a water column site in the reservoir. At the water column site, two SPMDs will be deployed: one within 20 feet of the surface (above thermocline) and one just above the bottom of the lake.

SPMDs will be analyzed for chlorinated pesticides and include water grabs for total suspended solids, total organic carbon, nitrate/nitrite, and conductivity. Nitrate/nitrite and conductivity will help delineate the relative importance of surface water and groundwater inputs. These parameters are typically higher in groundwater than surface water.

PCBs will not be analyzed in SPMDS because PCB levels in Potholes Reservoir are relatively low. PCB congener analysis, which is more sensitive and expensive than PCB aroclor analysis, is typically used to measure low-level PCBs. PCBs are not the focus of this study and therefore the additional cost is not justified.

Water column concentrations of chlorinated pesticides will be calculated using the most recent version of the SPMD Water Calculator spreadsheet developed by USGS. Currently this is v5_10Jan07.xls, David Alvarez, Columbia Environmental Research Center. The spreadsheet uses an empirical uptake model described in Huckins et al. (2006).

Comparison to Water Quality Criteria

The pesticide concentrations estimated from the SPMDs will be compared to Washington State water quality standards (WAC 173-201A). Water quality standards include freshwater acute and chronic criteria for the protection of aquatic life as well as criteria for the protection of human health from fish and water consumption.

Sediments

Surface sediment samples will be collected from seven sites: at a depositional area near each of the four inflows to Potholes Reservoir and at three additional sites. The three additional sites will be located in deep/depositional areas of the reservoir. Sediments will be analyzed for chlorinated pesticides, PCB aroclors, and TOC.

Comparison to Sediment Criteria

Numerical criteria have not been established for freshwater sediments in Washington. Freshwater Sediment Standards (WAC 173-204-340) state that Ecology "will determine on a case-by-case basis the criteria, methods, and procedures necessary to meet the intent of this chapter." Avocet Consulting (2003) proposed a set of sediment quality standards (SQS) and cleanup screening levels (CSL) as part of Ecology's effort to develop sediment criteria for Washington.

Sediment chemistry data for the study will be compared to statewide data and to Avocet's SQS and CSL levels for chlorinated pesticides and PCBs in freshwater sediments. Sediment criteria from other states and from Canada may also be used, if appropriate.

Sampling Procedures

Fish Tissue

Collection

Ecology will work with the WDFW Region 2 Warmwater Survey team to collect the majority of fish needed for study. WDFW will be conducting a walleye survey in Potholes Reservoir in late October 2007. Their fish collection will be primarily through the use of gill nets. Ecology will take the netted fish once WDFW has processed them. The rest of the fish needed for the study will be collected by Ecology, primarily by electrofishing.

Electrofishing will be conducted with a Smith-Root 16' electrofishing boat with an isolated cathode array. Fish collected will be held in an aerated live well until sampling is completed; fish not selected for further analysis will be released.

Fish selected as samples will be sacrificed in the field, assigned a unique identification number, and measured for total length and weight. Fish will be wrapped in aluminum foil and polyethylene bags, placed on ice for up to 72 hours while in the field, and then frozen at -20 F until processed for laboratory analysis.

Preparation of Tissue Samples

Preparation of fish tissue samples will follow *Ecology Standard Operating Procedures for Resecting Finfish Whole body, Body Parts, Or Tissue Samples* (Sandvik, 2007) and will take place at Ecology's Headquarters building in Lacey, Washington.

Samples for analysis will be prepared by partially thawing the fish to remove the foil wrapper and rinsing in deionized water to remove adhering debris. The entire fillet from one or both sides of each fish will be removed with stainless steel knives or scalpels and homogenized in a Kitchen-Aide or Hobart commercial blender. The fillets will be scaled and analyzed skin-on, except skin-off for brown bullhead since the skin is not typically eaten.

Composite samples will be made up of equal-weight aliquots from each of three to five fish. The samples will be homogenized to uniform color and consistency and placed in jars, specifically cleaned for pesticides and PCB analyses. The samples will then be sent to Manchester Environmental Laboratory. Recommended sample jars, preservations, and holding times are shown in Table 5. Excess sample will be retained from each composite and stored frozen in the event that additional analysis is required.

The sex of each fish will be recorded during processing. Upon request from WDFW, fin clips may be collected for possible future DNA analysis.

Table 5.	Recommended	Containers,	Preservations,	and Holding	Times fo	r Fish T	Tissue,	Water,
and Sedi	ment Analysis. ¹			-				

Analyte	Container	Container Preservation	
Fish Tissue Chemistry			
Chlorinated Pesticides, PCBs and Lipids	Certified 4 oz glass jar Teflon lid liner	14 day Extraction 40 day Analysis (1 year if frozen)	
Water Chemistry (for .	SPMDs)		
Nitrate/Nitrite	125 mL wide mouth polyethylene bottle	H2SO4 to pH<2; refrigerate, 4°C	28 days
ТОС	60 mL narrow mouth polyethylene bottle	1:1 HCl to pH<2; refrigerate, 4°C	28 days
TSS	1 liter wide mouth polyethylene bottle	Refrigerate, 4° C	7 days
Conductivity	500 mL wide mouth polyethylene bottle	Refrigerate, 4° C	28 days
Sediment Chemistry			
Chlorinated Pesticides and PCBs	Certified 8 oz glass jar Teflon lid liner	Refrigerate, 4° C	14 day Extraction 40 day Analysis (1 year if frozen)
Grain Size ²	8 oz polyethylene jar	Refrigerate, 4° C	6 months
тос	Certified 2 oz glass jar Teflon lid liner	Refrigerate, 4° C	14 days (6 months if frozen)

¹ = Information taken from the Manchester Laboratory Lab Users Manual (MEL, 2005)

 2 = Gravel, sand, silt, and clay fractions

SPMD

Deployment and retrieval procedures for the SPMDs will follow the guidance in Huckins et al. (in press) and *Ecology's Standard Operating Procedures for SPMDs* (Johnson, 2007). Standard SPMDs (91 x 2.5 cm membrane containing 1 mL of 99% pure triolein) and the stainless steel canisters (16.5 x 29 cm) and spider carrier devices that hold the membranes during deployment will be obtained from Environmental Sampling Technologies Inc (EST). The SPMDs are preloaded onto the carriers by EST in a clean room and shipped in solvent-rinsed metal cans under argon atmosphere.

Three SPMD membranes will be used for each sample to ensure that sufficient residues are obtained for chemical analysis. The membranes will be deployed in a single canister. The SPMDs will be kept frozen until deployed.

SPMDs will be spiked with performance reference compounds (PRCs) prior to their being deployed in the field. PCB-4 and PCB-29 will serve as PRCs for this project. These PCB congeners are used to derive an exposure adjustment factor (EAF) to calibrate the effects of temperature, water velocity, and biofouling that can occur while SPMDs are deployed in the environment.

On arrival at the sampling site, the cans will be pried open, spider spindles slid into the canisters, and the device suspended from a surface structure or anchored to the bottom. Field personal will wear nitrile gloves and not touch the membranes. The SPMDs will be located out of strong currents and placed deep enough to allow for fluctuations in water level. Because SPMDs are potent air samplers, this procedure will be done as quickly as possible. For the deepwater site in the middle of the reservoir, one SPMD will be positioned near the bottom and the other in the top 20 feet of the water column, above thermocline. They will be anchored and have a float at the water surface.

The SPMDs will be deployed for approximately 28 days as recommended by USGS and EST. During a 28-day deployment, chemical uptake by an SPMD is assumed to be linear and there are no significant losses of accumulated residues. A 28-day deployment has provided useful results in past Ecology studies. The retrieval procedure is essentially the opposite of the deployment. The cans holding the SPMDs must be carefully sealed and maintained at or near freezing until they arrive at EST for extraction.

At the beginning, middle, and end of each deployment period, TOC, TSS, nitrite/nitrate, and conductivity samples, as well as temperature and pH measurements, will be taken at each monitoring site. Recommended water sample containers, preservations, and holding times are shown in Table 5.

Sediments

Sediments will be collected using a stainless steel petite ponar (0.05 m^2) sampler. Each sample will be a composite, consisting of three individual grabs. Sampling locations will be recorded from GPS, and a field log describing the quality of each grab will be maintained.

Fine-grained sediments (silt) will be targeted over large-grained sediments (sand), to represent depositional areas. Subsamples will be taken from the top 2 cm of sediment and removed with a stainless steel spoon and placed in a large stainless steel bowl. Sediments touching the sidewalls of the grab will not be taken. Once all three replicate grabs have been collected, sediments will be homogenized by stirring. Homogenized sediment will then be placed in jars specifically cleaned for pesticide analysis. Recommended sample jars, preservations, and holding times are shown in Table 5.

Stainless steel implements used to collect and manipulate sediments will be cleaned as described below. Between-sample cleaning of the petite ponar will consist of a thorough brushing with on-site water.

Sediment samples will be placed on ice immediately after collection and transported to MEL within two business days. Excess sample will be retained from each sample and stored frozen in the event that additional analysis is required by the laboratories.

Decontamination Procedures

Precautions will be taken to minimize contamination during both sample collection and sample processing. Persons collecting and preparing samples will wear non-talc nitrile gloves and change them between each sample.

Sample processing equipment for sediments and fish tissue resecting instruments will be washed thoroughly with Liquinox detergent and hot tap water, followed by rinses with de-ionized water, acetone, and hexane. Instruments will then be dried in a fume hood before use. After drying, sediment processing equipment will be wrapped in foil to keep clean prior to field use.

For fish tissue resection, work surfaces will be covered with heavy grade aluminum foil. Gloves, aluminum foil, and dissection tools will be changed between composite samples.

Measurement Procedures

The majority of the laboratory analyses for the study will be performed by Manchester Environmental Laboratory. SPMDs will be prepared and extracted at Environmental Sampling Technologies Inc. (EST). EST is the sole commercial supplier of SPMDs. Sediment grain size will be analyzed at a contract laboratory selected by MEL. Table 6 shows the expected range of results, required reporting limits, and sample preparation and analysis methods.

Analysis	Expected Range of Results	MEL Reporting Limits	Sample Preparation Method	Analytical Method
Fish Tissue (wet	weight)			
Dieldrin	<1 - 10 ug/Kg	0.6 - 3 ug/Kg	EPA 3540/3620/3665	EPA 8081/8270
Chlorinated pesticides	<1 - 25 ug/Kg	1 - 5 ug/Kg	n	:
PCB aroclors	<1-10 ug/Kg	5 - 25 ug/Kg	EPA 3540	EPA 8082
Lipids	<1-10 %	0.01%	extraction	EPA-600 8-80-038
SPMD				
Dieldrin	1 - 500 ng	10 ng/SPMD	dialysis/GPC*	EPA 8081/8270
Chlorinated pesticides	"	"	"	"
Water				
TSS	1 - 10 mg/L	1 mg/L	N/A	EPA 160.2
TOC	1 - 5 mg/L	1 mg/L	N/A	EPA 145.1
Nitrate/Nitrite	<1 - 40 mg/L	0.01 mg/L	N/A	SM 4500-NO3 ⁻ I
Conductivity	200 - 1000 μmhos/cm at 25°C	1 μmhos/cm at 25°C	N/A	SM 2510B & EPA 120.1
Sediment (dry we	right)			
Dieldrin	<1 - 10 ug/Kg	1 - 5 ug/Kg	EPA 8081	EPA 8081/8270
Chlorinated pesticides	<1 - 25 ug/Kg	2 - 10 ug/Kg	"	"
PCB aroclors	<1 - 25 ug/Kg	15 - 25 ug/Kg	EPA 8082	EPA 8082
TOC	<1 - 3%	0.1%	PSEP, 1986/1996	PSEP, 1986/1997
Grain Size	N/A	0.1%	PSEP, 1986	PSEP, 1986

Table 6.	Laboratory	Reporting	Limits and	Analytical	Methods.
	2			2	

*EST Laboratory SOPs E14, E15, E19, E21, E33, E44, E48

N/A = not applicable

SM=standard method

EST will extract the SPMDs (referred to as dialysis), perform gel permeation chromatography (GPC) cleanup on the extracts, and ship them to MEL for chlorinated pesticide analysis. The dialysis method used by EST is a patented procedure, described in Huckins et al. (in press). EST Laboratory dialysis and GPC methods are documented in SOPs which are on file at Ecology.

The SPMD results will be reported as total nanograms (ng) in the entire extract. The performance reference compounds (PCB-4 and PCB-29) will be quantified during the chlorinated pesticide analysis.

The total laboratory cost for the project is estimated at \$28,155 (Table 7).

Analysis	Number of Samples	Field Replicate/QC Samples ¹	Total Number of Samples	Price Per Unit (\$)	Total Price (\$)
Fish Tissue					
Chlorinated pesticides/PCBs	39	0	39	325	12,675
Lipids	39	0	39	31	1,209
SPMD					
Chlorinated Pesticides	12	3*	15	200	3,000
Water					
TSS	36	6	42	10	420
TOC	36	6	42	30	1,260
Nitrate/Nitrite	36	6	42	12	504
Conductivity	36	6	42	8	336
Sediment					
Chlorinated pesticides/PCBs	7	1	8	225	1,800
TOC	7	1	8	39	312
Grain Size	7	1	8	85	680

Table 7. Estimate of Project Laboratory Costs.

 Laboratory Costs:
 \$ 22,196[†]

 EST Costs:
 \$ 5,959

 Project Total:
 \$ 28,155

¹ Does not include laboratory QC samples

* QC for SPMD samples includes one field blank in both deployments and one replicate for the project † Costs include 50% discount for Manchester Environmental Laboratory

Quality Control Procedures

The field sampling and decontamination procedures described in the *Sampling Procedures* section of this QA Project Plan will be carefully followed to avoid contamination of samples. A copy of the QA Project Plan will be taken into the field for reference. Laboratory quality control samples for all study matrices are shown in Table 8.

Parameter	Method Blank	Lab Duplicate	Check Std./LCS	Matrix Spike	Matrix Spike Duplicate	Surrogate Spikes
Fish Tissue						
Chlorinated pesticides/PCBs	1/batch*	1/batch	1/batch	1/batch	1/batch	All Samples
Lipids	1/batch	1/batch				
SPMD						
Chlorinated Pesticides	1/batch		1/batch	1/batch	1/batch	All Samples
Water						
TSS	1/batch	1/batch	1/batch			
TOC	1/batch	1/batch	1/batch			
Nitrate/Nitrite	1/batch	1/batch	1/batch			
Conductivity	1/batch	1/batch	1/batch			
Sediment						
Chlorinated pesticides/PCBs	1/batch	1/batch	1/batch	1/batch	1/batch	All Samples
TOC	1/batch	1/batch	1/batch			
Grain Size		1/batch				

Table 8. Laboratory Quality Control Samples.

* A batch is defined as 20 or fewer samples

Fish Tissue

Natural variability in chlorinated pesticide and PCB concentrations in fish will be addressed by analyzing samples as composites and as replicates of three samples per species and age class.

SPMD

Field replicates will provide estimates of total variability in the SPMD data (field + laboratory). One SPMD field replicate will be deployed for the project. Because SPMDs can be potent air samplers, a field blank will be used for both sampling periods. The field blank will be exposed to the air for the average amount of time that all of the sample SPMDs are exposed to air during deployment and retrieval. Total exposure time is typically two minutes or less.

Prior to deployment, EST will spike each SPMD membrane with PRCs PCB-4 and PCB-29. These PRCs are suitable for this project because they have similar properties to chlorinated pesticides, are not present in significant amounts in the environment, and have shown appropriate rates of loss in past Ecology studies (loss rates should be 20-80%). MEL will supply the PRCs to EST.

EST Laboratory will add surrogate compounds to each SPMD sample prior to dialysis. The surrogates for the chlorinated pesticide analysis will be tetrachloro-m-xylene, 4,4- dibromooctafluorobiphenyl, and dibutylchlorendate. MEL will supply the spiking solution for their respective surrogates.

MEL will analyze their own method blanks with each batch of samples. EST Laboratory will prepare the following method blanks for each SPMD deployment:

- *Spiking-blank SPMD* exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST Laboratory and later dialyzed with project samples.
- *Day-zero SPMD blank* to serve as a reference point for PRC loss to represent background during dialysis and cleanup.
- *Fresh Day-zero SPMD blank*, spiked with the PRC compounds when the exposed SPMDs are being dialyzed. It serves as a verification of the archived day zero blank.
- *Reagent blank* to assess contamination independent of the SPMDs.

Water Samples (for SPMDs)

In addition to laboratory Quality Control analysis for water samples, the following field Quality Control samples will be analyzed: Field Quality Control samples will include two replicates per deployment and one transfer blank per deployment.

Sediments

Natural variability in chlorinated pesticide and PCB concentrations in surface sediments will be addressed by analyzing samples as composites of three single grabs at each site. One composite sample will also be split and analyzed separately as a field duplicate.

Data Management Procedures

Field data and data from fish tissue processing will be recorded on printed data sheets and then carefully transferred to electronic data sheets.

The data package from MEL will include a case narrative discussing any problems encountered in the analysis, corrective actions taken, and an explanation of data qualifiers. The project manager will then review the data package to determine if project MQOs (method blanks, check standards/LCS samples, surrogate compounds, matrix spikes, and laboratory duplicates) were met.

Data for the study will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal data review process where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

Audits and Reports

Audits

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

Reports

The project manager will provide a fish tissue data report to WDOH in *April 2008*. Their review and any associated formal reports will be provided separate from the Ecology technical report. A date for the completion of the WDOH review has yet to be determined.

The Ecology draft technical report will be provided to the client, internal Ecology reviewers, and other interested parties by August 2008. The final technical report will be completed and published by *December 2008*. Data will be completed in EIM by December 2008.

Data Verification

The project manager will review MEL's data package and data verification report. Based on these assessments, the data will either be accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

To determine if project MQOs have been met, the project manager will compare results of the field and laboratory QC samples to MQOs. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects to determine if any values exceed the lowest concentration of interest.

Formal (third party) validation of the data will not be necessary for this project.

Data Quality (Usability) Assessment

Once the data have been reviewed and verified, the project manager will determine if the quality and quantity of the data are useable for the purposes of the study. The project manager will review laboratory data by determining if study MQOs were met.

References

Avocet, 2003. Development of Freshwater Sediment Quality Values for Use in Washington State. Phase II Report: Development and Recommendations of SQVs for Freshwater Sediments in Washington State. Prepared for Washington State Department of Ecology, Toxics Cleanup Program, Olympia, WA. Avocet Consulting, Kenmore, WA.

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

Davis, D. D. Serdar, and A. Johnson, 1998. Washington State Pesticide Monitoring Program: 1995 Fish Tissue Sampling Report. Washington State Department of Ecology, Olympia, WA. Publication No. 98-312. <u>www.ecy.wa.gov/biblio/98312.html</u>

Ebbert, J.C. and J.L. Jones, 1997. Sampling Irrigation Wasteways, Surface and Subsurface Drains to Monitor Ground-Water Quality in the Quincy and Pasco Basins, Washington. Second Symposium on the Hydrogeology of Washington State, Aug. 25-27, 1997.

EPA, 2005. National Lake Fish Tissue Study. U.S. Environmental Protection Agency, Office of Water, Washington D.C. First through Fourth Year (1999-2004) Results: Data Released to States. <u>www.epa.gov/waterscience/fishstudy/overview.htm</u>

Greene, K.E., J.C. Ebbert, and M.D Munn, 1994. Nutrients, Suspended Sediment, and Pesticides in Streams and Irrigation Systems in the Central Columbia Plateau in Washington and Idaho, 1959-1991. U.S. Geological Survey, Water-Resources Investigations Report 94-4215.

Hopkins, B., 1991. Basic Water Monitoring Program: Fish Tissue and Sediment Sampling for 1989. Washington State Department of Ecology, Olympia, WA. Publication No. 91-e14. www.ecy.wa.gov/biblio/91e14.html

Huckins, J.N., J.D. Petty, and K. Booij, 2006. Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices. Springer Science and Business Media, New York, NY. 223 pp.

Huckins, J.N. et al. (in press). A Guide to the Use of Semipermeable Membrane Devices (SPMDs) as Samplers for Waterborne Hydrophobic Organic Contaminants. USGS Columbia Environmental Research Center, Columbia MO. Am Petrol. Inst. 4690

Johnson, A., 2007. Standard Operating Procedure for Using Semipermeable Membrane Devices to Monitor Hydrophobic Organic Compounds in Surface Water. Washington State Department of Ecology, Olympia, WA.

www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_ForUsingSemipermealableMembrane Devices_v2_0.pdf

MEL, 2005. Manchester Environmental Laboratory Lab Users Manual, Eighth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Munn, M. and S.J. Gruber, 1997. The Relationship Between Land Use and Organochlorine Compounds in Streambed Sediments and Fish in the Central Columbia Plateau, Washington and Idaho, USA. Environ. Toxicol. Chem. 16:1877-1887.

Rogowski, D. and D. Davis, 1999. Potholes Reservoir Pesticide Survey, 1998. Washington State Department of Ecology, Olympia WA. Publication No. 99-331. www.ecy.wa.gov/biblio/99331.html

Sandvik, P., 2007. Ecology Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts, or Tissue Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP EAP007.

Seiders, K. and K. Kinney, 2004. Washington State Toxics Monitoring Program: Toxic Contaminants in Fish Tissue and Surface Water in Freshwater Environments, 2002. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-040. www.ecy.wa.gov/biblio/0403040.html

Seiders, K., C. Deligeannis, and K. Kinney, 2006. Washington State Toxics Monitoring Program: Toxic Contaminants in Fish Tissue and Surface Water in Freshwater Environments, 2003. Washington State Department of Ecology, Olympia, WA. Publication No. 06-03-019. www.ecy.wa.gov/biblio/0603019.html

Serdar, D., A. Johnson, and D. Davis, 1994. Survey of Chemical Contaminants in Ten Washington Lakes. Washington State Department of Ecology, Olympia, WA. Publication No. 94-154. <u>www.ecy.wa.gov/biblio/94154.html</u>

USDA, 2006. Washington Statistics for 2005 through 2006. United States Department of Agriculture - National Agricultural Statistics Service. <u>http://www.nass.usda.gov/Statistics_by_State/Washington/index.asp</u>

WDFW, 2007. Results of the 2006 WDFW Fall Walleye Index Netting (FWIN) Surveys. Washington Department of Fish and Wildlife – Warmwater Enhancement Program. http://wdfw.wa.gov/fish/warmwater/library/walleye_fwin06.pdf

Appendix A. Acronyms

Following is a list of acronyms used frequently in this QA Project Plan:

DDE	Dichloro-diphenyl-dichloroethylene
EPA	U.S. Environmental Protection Agency
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management System (Ecology)
EST	Environmental Sampling Technologies, Inc.
LCS	Laboratory control samples
MEL	Manchester Environmental Laboratory (Ecology)
MQO	Management quality objective
QA	Quality assurance
QC	Quality control
PCBs	Polychlorinated biphenyls
PRC	Performance reference compounds
SOP	Standard operating procedure
SPMD	Semi-permeable membrane device
TMDL	Total Maximum Daily Load
TOC	Total organic carbon
TSS	Total suspended solids
USGS	U.S. Geological Survey
WDFW	Washington Department of Fish and Wildlife
WDOH	Washington State Department of Health
WW	Wet weight

Appendix B. Dieldrin Fish Tissue 303(d) Listing for Potholes Reservoir

Water Quality Assessment for Washington

2002/2004 Candidate List

Water Body Name:	POTHOLES RESERVOIR	Listing ID #:	8945
Parameter:	Dieldrin	Township:	
Medium:	Tissue	Range:	
Category:	5	Section:	
Listed 98?:	Y	Latitude:	46.995
Listed 96?:	Y	Longitude:	119.175

Basis Serdar, et al. 1994. excursions beyond the criterion in edible fish tissue (Largemouth Bas

Water Quality Assessment for Washington

2002/2004 Candidate List

Water Body Name:	POTHOLES RESERVOIR	Listing ID #:	8946
Parameter:	Dieldrin	Township:	
Medium:	Tissue	Range:	
Category:	5	Section:	
Listed 98?:	Y	Latitude:	46.985
Listed 96?:	Y	Longitude:	119.345

ъ		•
в	as	15
~		20

Serdar, et al. 1994. excursions beyond the criterion in edible fish tissue (Lake Whitefish)	*
	Ŧ