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State of Washington

Quality Assurance Project Plan

Skagit-Samish Watershed Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams

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Author and Contact Information

Paul D. Anderson and Debby Sargeant
P.O. Box 47600
Environmental Assessment Program
Washington State Department of Ecology
Olympia, WA 98504-7710

For more information contact: Carol Norsen, Communications Consultant
Phone: 360-407-7486

Washington State Department of Ecology - www.ecy.wa.gov/

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Yakima 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

Quality Assurance Project Plan

Skagit-Samish Watershed
Intensive Surface Water Sampling for Pesticides in Salmonid-Bearing Streams

August 2009

Approved by:

Signature: _____ Date: July 2009
Jim Cowles, Client, Natural Resources Assessment Section, WSDA

Signature: _____ Date: August 2009
Kirk Cook, Natural Resources Assessment Section Coordinator, WSDA

Signature: _____ Date: August 2009
Ted Maxwell, Pesticide Management Division, WSDA

Signature: _____ Date: July 20009
Debby Sargeant, Author/Project Manager, EAP

Signature: _____ Date: July 2009
Paul D. Anderson, Author/Principal Investigator/EIM Data Engineer, EAP

Signature: _____ Date: July 2009
Dale Norton, Author's Unit Supervisor, EAP

Signature: _____ Date: July 2009
Will Kendra, Author's Section Manager, EAP

Signature: _____ Date: August 2009
Robert F. Cusimano, Section Manager for Project Study Area, EAP

Signature: _____ Date: July 2009
Stuart Magoon, Director, Manchester Environmental Laboratory, EAP

Signature: _____ Date: August 2009
Bill Kammin, Ecology Quality Assurance Officer

Signatures are not available on the Internet version.
EAP - Environmental Assessment Program
EIM - Environmental Information Management system
WSDA - Washington State Department of Agriculture

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Abstract

The Washington State Department of Ecology (Ecology) has conducted a surface water monitoring program for pesticides in salmonid habitat since 2003. This program has included weekly monitoring at 16 sites in five index watersheds statewide: Thornton Creek, Longfellow Creek, Lower Yakima River, Wenatchee River, and Entiat River.

In 2008, the National Oceanic and Atmospheric Administration National Marine Fisheries Service (NOAA-Fisheries) released a biological opinion for three organophosphate pesticides: chlorpyrifos, diazinon, and malathion. The biological opinion recommended seven consecutive days of monitoring in at least three seven-day events during the typical pesticide application season. In Washington, this usually occurs from March through September.

The current 2009 study will incorporate daily monitoring during a seven-day period into the weekly monitoring program to evaluate comparability of the results generated from these sampling frequencies. Sampling will be conducted at four sites in the Skagit River delta which is an important salmonid-rearing area in Puget Sound. In addition to conventional water sampling on a weekly and daily basis, a new continuous sampling technique will be evaluated using Continuous Low-Level Aquatic Monitor (CLAM™) devices.

Understanding short-term variability of pesticides in surface waters will assist the Washington State Department of Agriculture, U.S. Environmental Protection Agency, and NOAA-Fisheries in evaluating pesticide risks to salmonids.

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

Background

The Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) have conducted a monitoring program to characterize pesticide concentrations in salmonid-bearing streams since 2003. The study targets the typical pesticide-use season (March – September).

Data from the program is being used to develop accurate pesticide exposure assessments for Endangered Species Act (ESA) listed salmonid species. The data are provided to the U.S. Environmental Protection Agency (EPA) and NOAA-Fisheries for ESA consultations on pesticides and salmonids. WSDA uses the monitoring data for pesticide registration decisions and to determine if pesticide mitigation efforts are successful.

Sites are monitored weekly in two urban areas (Thornton Creek, Water Resource Inventory Area (WRIA) 8; and Longfellow Creek, WRIA 9) and four agricultural areas (Skagit-Samish, WRIA 3; Lower Yakima, WRIA 37; Wenatchee, WRIA 45; and Entiat, WRIA 46).

Currently, monitoring is conducted weekly for a minimum of three years per site. Watersheds were chosen due to the intensity of cropping, salmonid presence, and diversity of agriculture within the watershed. Monitoring locations evaluate specific land-use practices.

In 2008, NOAA-Fisheries released a biological opinion on three organophosphate insecticides - chlorpyrifos, diazinon, and malathion-under consultation with EPA (NOAA-Fisheries, 2008). Both chlorpyrifos and diazinon are not registered for homeowner use, but all three are registered for select agricultural uses. EPA is currently reviewing this biological opinion for its application to pesticide re-registration.

In the biological opinion, NOAA-Fisheries recommended a monitoring regime for chlorpyrifos, diazinon, and malathion to help evaluate impacts to salmonids. The recommendation included targeting one site in each state where juvenile ESA-listed salmon migrate to the Pacific Ocean. Monitoring at each site should include daily surface water sampling for at least three periods of seven consecutive days each during the pesticide application season.

Project Description

The focus of the current 2009 study will be to collect pesticide monitoring data over a seven-day period in the Skagit-Samish WRIA. This intensive sampling effort will allow Ecology to study the utility of the data generated by seven consecutive days of sampling while EPA is reviewing the NOAA-Fisheries biological opinion.

The Skagit-Samish WRIA is the largest freshwater input to Puget Sound. The WRIA is an important salmonid-rearing area that is intensively cultivated by agriculture, making it an ideal candidate for study.

In addition to daily intensive monitoring, Ecology has the opportunity to experiment with the use of a new technology called the CLAM™ made by Aqualytical. The CLAM™ sampler will provide continuous sampling over the seven-day period. This will allow comparison with the seven-day intensive sampling regime and the weekly grab sampling regime.

Four sites in the Skagit-Samish WRIA will be sampled for this 2009 study. Two of these sites will be sampled using CLAM™ devices. These sites were chosen based on registered use of chlorpyrifos, diazinon, and malathion.

This 2009 study will evaluate the variability of pesticide occurrence and magnitude by sampling on three temporal frequencies. Temporal variation will be evaluated by continuous, daily, and weekly monitoring. Understanding short-term variability of pesticides in surface waters will assist WSDA, EPA, and NOAA-Fisheries in evaluating pesticide risks to salmonids. In addition to evaluating variability of pesticide occurrence, data collected for this project will be compared to the same assessment endpoints used in the existing monitoring program (Burke et al., 2006). Any exceedances of the endpoints may be used by WSDA or EPA to make pesticide re-registration decisions.

Intensive sampling will be conducted at four sites in the Skagit-Samish WRIA. Samples for chlorinated pesticides, organophosphate pesticides, pyrethroids, nitrogen-containing pesticides, herbicides, carbamates, and total suspended solids will be sent to the laboratory for analysis. Dissolved oxygen, pH, conductivity, temperature, and streamflow will be measured in the field. Sampling and analysis methods are the same methods used for weekly sampling in the existing monitoring project (Johnson and Cowles, 2003; Burke and Anderson, 2006; Anderson and Sargeant, 2009). This will allow for direct comparison of daily- and weekly-derived exposure estimates.

CLAM™ devices will be deployed to investigate the comparability of continuous data to the daily and weekly grab samples. CLAM™ devices and grab samples both collect whole water and give total fraction results. This allows for direct comparison of results. However, the CLAM™ sampling technology has not yet been fully verified. Results from the CLAM™ will be considered experimental and will only be used to compare seven-day average values to daily and weekly sampling results.

Organization and Schedule

The names, titles, and responsibilities of the people involved in this project are summarized in Table 1. Table 2 shows the proposed schedule for project deliverables.

Table 1. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Jim Cowles Washington State Department of Agriculture Phone: (360) 902-2066	Client	Clarifies the scope of the project. Provides internal review of the QAPP and approves the final QAPP.
Debby Sargeant Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6139	Project Manager	Writes the QAPP, oversees field sampling and transportation of samples to the laboratory. Conducts QA review of data and analyzes and interprets data. Writes the draft report and final report.
Paul D. Anderson Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-7548	Principal Investigator	Writes the QAPP. Conducts field sampling and prepares samples for transport to laboratory. Enters data into EIM and assists with analysis and interpretation of data. Assists with writing of draft report and final report.
Michael Friese Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6737	Field Assistant	Helps collect samples and records field information.
Dale Norton Toxics Studies Unit Statewide Coordination Section Phone: (360) 407-6765	Unit Supervisor for the Project Manager	Provides internal review of the QAPP. Approves the budget and approves the final QAPP.
Will Kendra Statewide Coordination Section Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget and tracks progress. Reviews the draft QAPP and approves the final QAPP.
Robert F. Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope and budget and tracks progress. Reviews the draft QAPP and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory Phone: (360) 871-8801	Director	Approves the final QAPP.
William R. Kammin Phone: (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

QAPP – Quality Assurance Project Plan.
EIM – Environmental Information Management system.

Table 2. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	
Field work completed	June 11, 2009
Laboratory analyses completed	October 2009
Environmental Information System (EIM) system	
EIM data engineer	Paul D. Anderson
EIM user study ID	DSAR0005
EIM study name	Pesticides in Salmonid-Bearing Streams, Skagit-Samish Intensive Sampling
Data due in EIM	May 2010
Final report	
Author lead	Debby Sargeant
Schedule	
Draft due to supervisor	December 2009
Draft due to client/peer reviewer	February 2010
Draft due to external reviewer(s)	March 2010
Final report due on web	May 2010

Quality Objectives

Quality objectives for this project are to obtain data of sufficient quality and quantity so that the data can be used to meet the objectives and data quality requirements of the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams* (Johnson and Cowles, 2003; Burke and Anderson, 2006; Dugger et al., 2007; Anderson and Sargeant, 2009). These objectives will be achieved through careful planning, sampling, and adherence to procedures described in this Quality Assurance (QA) Project Plan.

Field

Instantaneous or continuous field meter measurements collected at each of the four sampling sites will conform to the measurement quality objectives (MQOs) summarized in Table 3.

Table 3. Measurement quality objectives for conventional parameters measured by field meters or determined by a standard method.

Parameter	Method/Equipment	Field Replicate MQO	Reporting Limits
Discharge Volume	Marsh-McBirney Flow-Mate Flowmeter	10% RSD	0.1 ft/s
Water Temperature	Hydrolab MiniSonde®/DataSonde®/TidbiT®	±0.2°C	0.1°C/0.2°C
Conductivity	Hydrolab MiniSonde®/DataSonde®	10% RSD	0.1 µmhos/cm
pH	Hydrolab MiniSonde®/DataSonde®	10% RSD	0.1 s.u.
Dissolved Oxygen	Hydrolab MiniSonde®/DataSonde®	10% RSD	0.1 mg/L
Dissolved Oxygen	SM4500C	±0.2 mg/L	0.1 mg/L

RSD – relative standard deviation.

Laboratory

Ecology's Manchester Environmental Laboratory (MEL) will perform the chemical analysis for the study. 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 MQOs that will be used are shown in Table 4. These MQOs apply to daily, weekly, and continuous water sample results.

Table 4. Laboratory measurement quality objectives.

Parameter	Laboratory Control Samples (LCS)	Replicate Samples	Matrix Spikes	Matrix Spike Duplicates	Surrogate Standards
	% recovery	RPD	% recovery	RPD	% recovery
PESTMS*	30-130	≤20	30-130	≤40	30-130
Carbamate	50-150	≤20	50-150	≤40	30-140
Herbicides	40-130	≤20	40-130	≤40	40-130
TSS	80-120	≤15	N/A	N/A	N/A

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.
N/A – not applicable.
RPD – relative percent difference.
TSS – total suspended solids.

Sampling Process Design (Experimental Design)

Over a seven-day period from June 5-11, 2009, surface water grab samples will be collected once daily at four sites in the Skagit-Samish WRIA. These sites are: Brown Slough, upper and lower Big Ditch, and Indian Slough. Sites were previously established by this program based on use by salmonids, rate of detection of target compounds, and proximity to agricultural land use practices. Analysis will include chlorinated pesticides, organophosphate pesticides, pyrethroids, nitrogen-containing pesticides, herbicides, carbamates, and total suspended solids (TSS). During the same time period, CLAM™ devices will be deployed to sample for chlorinated pesticides, organophosphate pesticides, pyrethroids, nitrogen-containing pesticides and carbamates at lower Big Ditch and Indian Slough.

One time during the June 5-11 sampling period, a regularly scheduled weekly grab sample will be collected as a daily sample. Locations, descriptions, and types of sampling for each site are provided in Table 5. The locations of sampling sites in the Skagit-Samish WRIA are shown in Figure 1.

To augment laboratory data, temperature, pH, conductivity, streamflow, and dissolved oxygen will be measured in the field. Field measurements will be conducted during daily, weekly, and continuous sampling.

Table 5. Locations, descriptions, and types of sampling for Brown Slough (BS-1), downstream Big Ditch (BD-1), upstream Big Ditch (BD-2), and Indian Slough (IS-1).

Site	Latitude	Longitude	Location Description	CLAM™	Daily	Weekly
BS-1	48.3406	-122.4140	Downstream of the tidegate on Fir Island Road.	No	Yes	Yes
BD-1	48.3086	-122.3473	Upstream side of the bridge at Milltown Road.	Yes	Yes	Yes
BD-2	48.3887	-122.3329	Upstream side of the bridge at Eleanor Lane.	No	Yes	Yes
IS-1	48.4506	-122.4651	On the upstream side of tidegate at Bayview-Edison Road.	Yes	Yes	Yes

Datum = North American Datum 1983 (NAD 83).

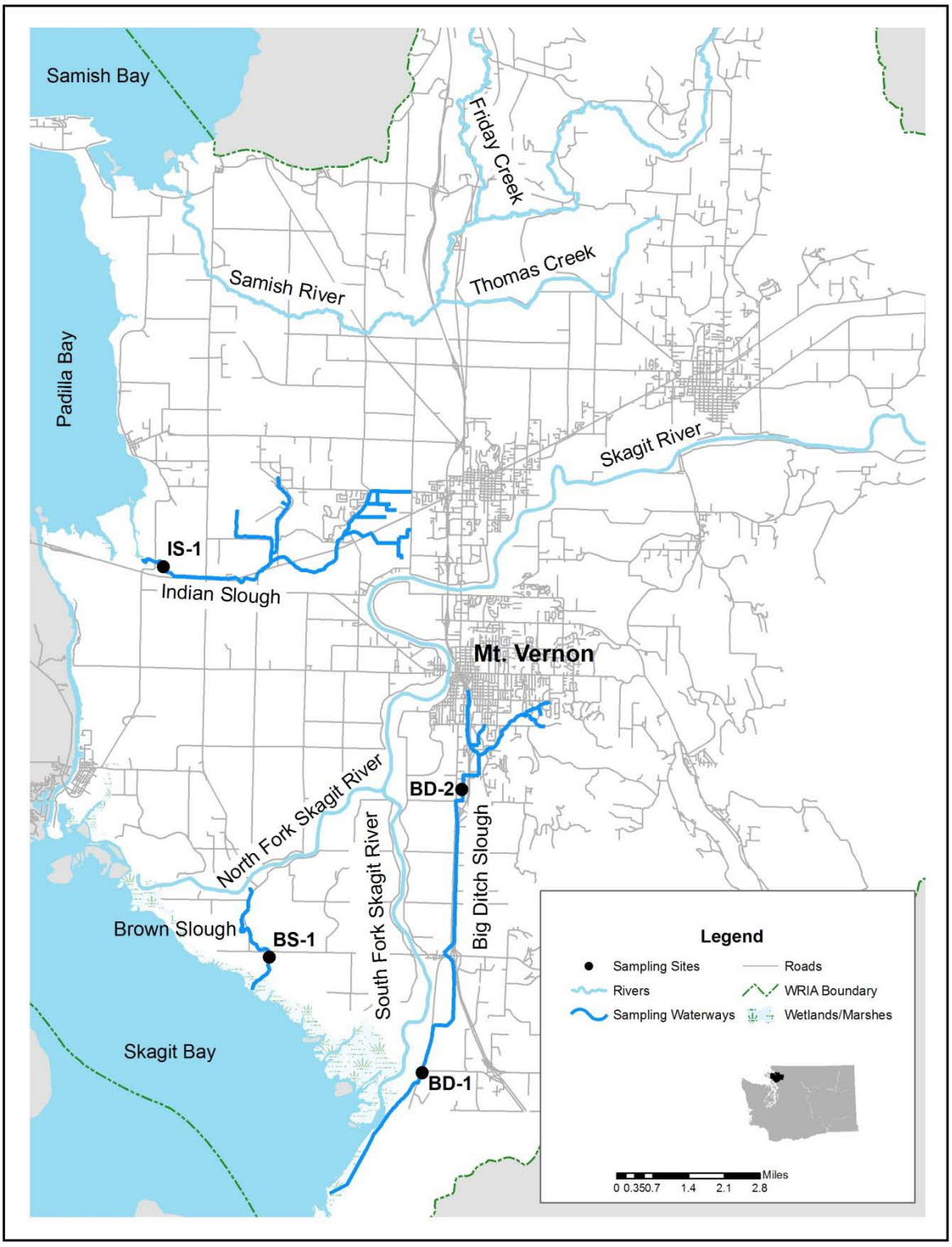

Figure 1. Location of Brown Slough, Big Ditch, and Indian Slough sampling sites in the Skagit-Samish watershed.

All four of the sites selected for sampling with one exception (upper Big Ditch) are tidally influenced. Brown Slough, Lower Big Ditch, and Indian Slough all have tide gates to control tidal influx of marine waters. The influence of tide gates ranges from backing up of water to complete obstruction of water flow. In order to maximize the ability to collect comparable data, daily and weekly sampling will occur during the period of the tidal cycle that water is actively flowing.

Due to the nature of the CLAM™ devices, timing of sampling will not be an issue. The continuous sampling provided by the CLAM™ will allow the study to investigate what occurs during the period of the tidal cycle when water is backed up or obstructed from flowing.

Sampling Procedures

Grab Sampling

All surface water samples will be collected by hand-compositing grab samples from quarter-point transects using a pole sampler or a United States Geological Survey DH-81 depth integrating sampler. Surface water sampling techniques and equipment will be consistent with Ecology standard operating procedures described in EAP003 *Sampling of Pesticides in Surface Waters* (Anderson, 2006).

Samples will be labeled with a laboratory identification number, name of the project, location identification, date and time of sample collection, and parameter for analysis. Photographs will be taken to document sampling procedures. After collection, all samples will be stored in coolers, on ice, until transported to the laboratory for analysis. Before samples are transported to the laboratory, a chain-of-custody seal will be placed on each cooler. Chain-of-custody will be maintained throughout collection and transport to laboratory.

Recommended sample containers, preservation, and holding times are presented in Table 6.

Table 6. Recommended containers, preservations, and holding times.

Parameter	Container	Preservations	Holding Time
PESTMS*	1 L narrow-mouth amber bottle with Teflon-lined cap	Cool to ≤ 6°C	7 days to extraction 40 days to analysis
Carbamates	250 mL wide-mouth amber bottle with Teflon-lined cap	Cool to ≤ 6°C, potassium dihydrogen citrate	28 days if preserved
Herbicides	1 L narrow-mouth amber bottle with Teflon-lined cap	Cool to ≤ 6°C	7 days to extraction 40 days to analysis
Total Suspended Solids	1 L wide-mouth polyethylene bottle	Cool to ≤ 6°C	7 days

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.

Continuous Sampling

Overview

On the first day of sampling, CLAM™ devices will be deployed at two of the four sites chosen for intensive monitoring. Only two of the sites were selected due to the number of available CLAM™ devices. Each CLAM™ device can hold one collection disk. The collection disk is placed at the end of the device where a pump draws water through at a specific rate. This pump rate is based on the desired length of deployment. In the case of this project, the pump rate will be set to 10 mL/minute to yield a volume of water less than or equal to 100 liters.

Two CLAM™ devices plus a replicate CLAM™ will be deployed at Indian Slough and lower Big Ditch (BD-1). One CLAM™ will be used to sample for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides while the other CLAM™ will be used to sample for carbamates. At Indian Slough, the replicate CLAM™ will sample for pesticides. At lower Big Ditch, the replicate CLAM™ will sample for carbamates.

Preservation methods and holding times for water will be used because they are not defined for collection disks (Table 7).

Table 7. Collection disks, preservation, and holding times for pesticides and carbamates.

Parameter	Collection Media	Preservation	Holding Time
PESTMS*	H2O-Phobic DVB	Cool to ≤ 6°C	7 days to extraction 40 days to analysis
Carbamates	Oasis® HLB	Cool to ≤ 6°C	7 days to extraction 40 days to analysis

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.

Collection Disks

The collection disks used for the CLAM™ devices were originally designed to be used in the laboratory and are commercially available from different manufacturers. Collection disks are made of a proprietary manufactured material that chemicals are adsorbed onto. Disks are designed to adsorb specific chemicals of interest. At MEL, each analysis method has a specific method used for extracting chemicals from the collection disks. Only certain collection disks work with the methods used for extraction and analysis. Due to the design of the CLAM™, the specificity of the collection disks, and restrictions at the laboratory, a single collection disk cannot be used.

For this project, two collection disks from different manufacturers will be used. Pesticides analyzed by gas chromatography/mass spectrometry (GCMS) will be sampled using an H20-Phobic DVB collection disk made by J.T. Baker. Carbamates analyzed by liquid chromatography/mass spectrometry (LCMS) will be sampled using an Oasis® HLB collection disk made by Waters. A detailed description of the collection disks is provided in Appendix B.

The collection disks will be supplied by the manufacturer of the CLAM™. CLAM™ devices will be set up and deployed using manufacturer instructions and recommendations. All of the pieces of the CLAM™ and collection disks will be handled while wearing non-talc nitrile gloves.

Deployment

Each CLAM™ will be deployed at the sampling site suspended in the water column. To suspend the sampling device, a concrete block, rope, and a float will be used. The concrete block will be placed on the bottom. The rope will be attached to the anchor threaded through an attachment point on the CLAM™ and tied to the float. To ensure that the CLAM™ device does not move

up or down the rope, knots will be tied on either side of the attachment point. Figure 2 shows how the CLAM™ devices will be deployed. To help prevent clogging, the water intake will be placed away from the direction of flow.

Both sites, Indian Slough and lower Big Ditch are tidally influenced. The tidal influence causes water levels to raise and lower over the daily tidal cycle. When suspending CLAMs™ in the water column, care will be taken to ensure that the sampling device does not contact bottom sediment or water near bottom sediment.

The CLAM™ devices selected will have a pump rate of 10 mL/min. This pump rate was selected based on the manufacturer recommendation not to draw more than 100 liters of water through the collection media. If the pump rate stays constant over the seven-day deployment period, the volume of water passing through the collection disk will not exceed 100 liters. To ensure pump rates stay constant, a pre- and post-deployment measurement will be conducted. The procedure for checking pump rates is described in the *Quality Control Procedures* section of this QA Project Plan.

It is not known what will occur if the volume of water passed through the collection disk exceeds 100 liters. It is possible that breakthrough of the disk could occur. Breakthrough is defined as the point at which the collection disk can no longer hold any more material that the disk was designed to capture. At the point of breakthrough, material intended to be captured by the collection disk will pass through the disk. This occurrence would cause results to be biased low.

Breakthrough is possible even if less than 100 liters of water passes through the collection disk. This would only occur if more material is captured on the collection disk than the disk was designed to handle. After results are determined by MEL, a total amount of material collected by the CLAM™ devices will be estimated and compared to available breakthrough values. This will give a rough estimation of whether or not breakthrough occurred during deployment.

Retrieval

At the end of the June 5-11 sampling period, the CLAM™ devices will be retrieved and collection disks removed. Each disk will be removed using nitrile gloves and then placed in an organics-free glass container. Each container will be labeled with a laboratory identification number, name of the project, location identification, date and time of sample collection, and parameter for analysis. Photographs will be taken to document sampling procedures and placement of each CLAM™. After retrieval, collection disks will be stored in coolers, on ice, until transported to the laboratory for analysis. Before samples are transported to the laboratory, a chain-of-custody seal will be placed on each cooler. Chain-of-custody will be maintained throughout removal of collection disk and transport to laboratory.

Invasive Species Decontamination

Field staff will follow draft decontamination standard operating procedures described in Ward (2009).

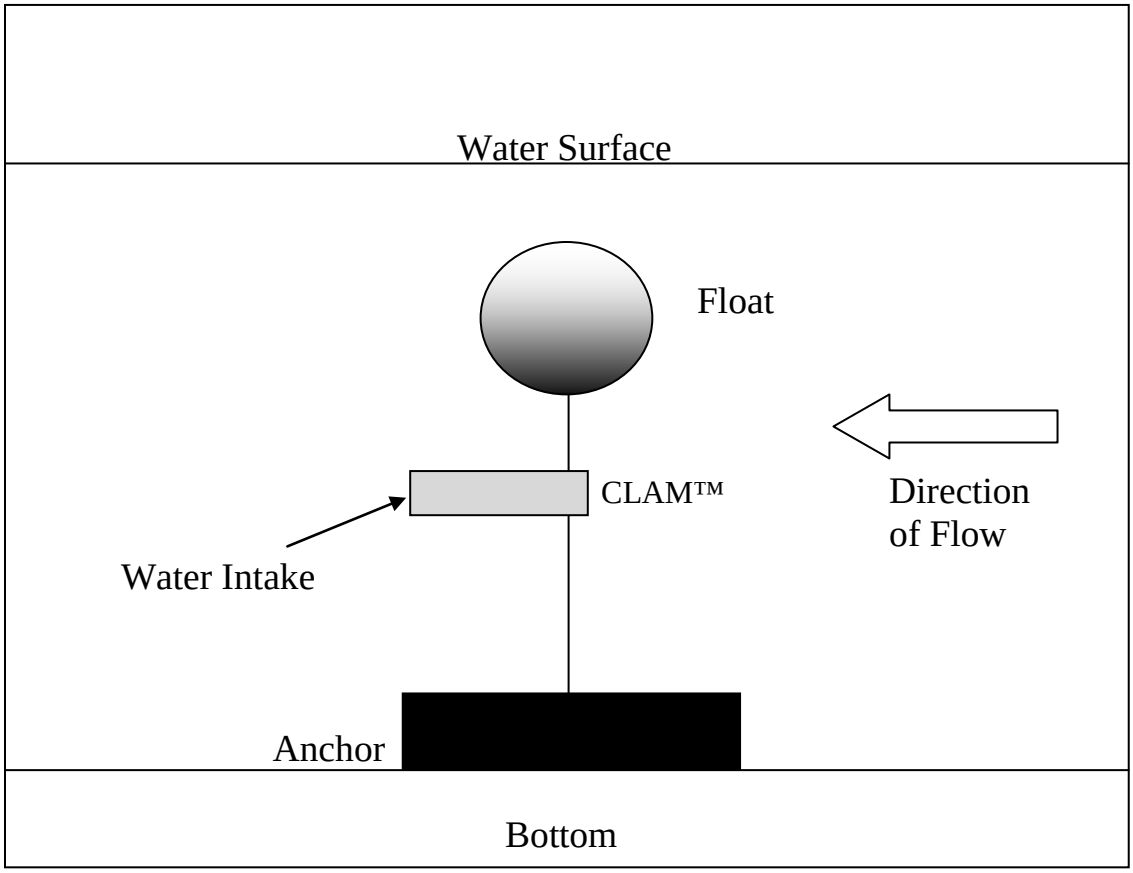

Figure 2. CLAM™ sampler deployment.

Measurement Procedures

Field

Field measurement of temperature, streamflow, pH, dissolved oxygen, and conductivity will be consistent with the following Ecology standard operating procedures:

- EAP011 - Instantaneous Measurement of Temperature in Water (Nipp, 2006).
- EAP023 - Collection and Analysis of Dissolved Oxygen (Winkler Method) (Ward, 2007a).
- EAP024 - Estimating Streamflow (Sullivan, 2007).
- EAP031 - Collection and Analysis of pH Samples (Ward, 2007b).
- EAP032 - Collection and Analysis of Conductivity Samples (Ward, 2007c).
- EAP033 - Hydrolab® DataSonde® and MiniSonde® Multiprobes (Swanson, 2007).

In addition to instantaneous field measurements, continuous field measurements will be collected. Continuous field measurements of pH, conductivity, and dissolved oxygen will be collected using Hydrolab DataSondes®. Measurements of continuous temperature will be collected using previously installed TidbiT® temperature loggers. The Hydrolabs DataSondes® will be deployed at all four sampling sites during the seven-day sampling period.

Laboratory

All of the laboratory analyses for the study will be performed by MEL according to current standard operating procedures. Table 8 shows the expected range of results, required reporting limits, sample preparation methods, and analysis methods for grab sample parameters.

Table 8. Expected range of results, reporting limits, sample preparation methods, and analysis methods for grab sample parameters.

Parameter	Expected Range of Results	Reporting Limits	Sample Extraction Method	Analysis Method
PESTMS*	0.02 - 1.0 µg/L	0.01 - 1.0 µg/L	EPA 3535[1]	EPA 8270[1]
Herbicides	0.02 - 1.0 µg/L	0.01 - 1.0 µg/L	EPA 3535[1]	EPA 8270[1]
Carbamates	0.02 - 0.4 µg/L	0.2 to 0.1 µg/L	EPA 3535[1]	EPA 8321A[1]
Total Suspended Solids	1 - 80 mg/L	1 mg/L	N/A	SM 2540D[1]

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.
[1]APHA et al. 1998; EPA, 1996; EPA, 1998; EPA, 2004.
N/A – not applicable.
SM – Standard Methods.

The collection disks used in the CLAM™ devices are the same disks used by MEL for the extraction of water samples. Since the collection disks are the same, MEL can use the same extraction and analysis methods used for water samples. The expected range of results cannot be provided for CLAM™ data because sampling with this technology has not been conducted at these sampling sites.

After sample results have been determined, an average concentration can be calculated using the volume of water that passed through the collection media. This volume is determined by multiplying the pump rate of the CLAM™ device by the exact duration of deployment. In addition, a daily average concentration can be calculated using the same information.

Quality Control Procedures

The standard operating procedures listed in the *Sampling Procedures* section of this QA Project Plan will be carefully followed to avoid contamination of samples. Copies of the QA Project Plan and standard operating procedures will be taken into the field for reference.

Field Parameters

All field parameters except streamflow will be measured in the field using a Hydrolab MiniSonde® or DataSonde®, or a meter with equivalent measurement capabilities. Streamflow will be measured using a Marsh-McBirney® or equivalent flow meter.

All field parameters will be replicated four times over the seven-day sampling period. Field parameter replicates are performed by measuring all parameters two consecutive times at the selected site. The location of the replicate measurements will be rotated through all sample sites. Precision for replicates will be expressed as percent relative standard deviation (RSD). For dissolved oxygen, two Winkler method samples will be collected per day: one at the beginning of the sampling day and one at the end.

Any meter used to measure field parameters will be calibrated before use and post checked at the end of each day, using conductivity/pH buffer solutions and the air saturation calibration method for dissolved oxygen. Temperature on field meters will not be included in this procedure because it is factory calibrated. To check for drift in temperature calibration, field meters will be compared to a National Institute of Standards and Technology (NIST) thermometer at the beginning and the end of each sampling season. Streamflow meters will be set to zero velocity at the beginning of each sampling day.

All calibration and post-check data will be recorded on a calibration sheet kept with the field meters or in the sampling vehicle. Post-check values will be assessed for acceptance, qualification, or rejection based on the data quality objectives for field meter post checks summarized in Table 9.

Table 9. Field meter post check data quality objectives for Hydrolab MiniSonde®/DataSonde® or equivalent field meters.

Parameter	Units	Accept	Qualify	Reject
pH	standard units	≤ ± 0.25	> ± 0.25 and ≤ ± 0.5	> ± 0.5
Conductivity[1]	µmhos/cm	≤ ± 5%	> ± 5% and ≤ ± 15%	> ± 15%
Dissolved oxygen[2]	% saturation	≤ ± 5%	> ± 5% and ≤ ± 15%	> ± 15%

[1]Criteria expressed as a percentage of readings. For example, buffer = 100.2 µmhos/cm and Hydrolab = 98.7 µmhos/cm; (100.2-98.7)100.2 = 1.49% variation, which would fall into the acceptable data criteria of less than 5%.

[2]When Winkler data are available, they will be used to evaluate acceptability of data in lieu of percent saturation criteria (Mathieu and Sargeant, 2008).

Grab Samples

In addition to following standard operating procedures, field quality control (QC) samples will be collected, including transfer blanks and replicates (Table 10). Transfer blanks and replicates will be submitted blind to MEL using different sample numbers and sample site names. Each sampling site will have at least one blank or one replicate per parameter over the seven-day period. This will ensure adequate QC sample coverage at all sites.

Table 10. Field quality control samples for surface water parameters.

Parameter	Transfer Blank	Split Replicate
PESTMS*	3	3
Herbicides	3	3
Carbamates	3	3
Total suspended solids	3	3
Total	12	12

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.

Equipment blanks evaluate potential contamination from sampling procedures and transport to the laboratory. Blanks will be prepared using de-ionized, organic-free water prepared at MEL. Laboratory water is transferred from its container to the sample transfer (collection) bottle. While at the selected sampling site, blank water is put into a new sample container from the transfer bottle. The blank is then labeled and stored in coolers, on ice, with the other samples.

Split replicates will be used to provide an estimate of sampling and laboratory variability. These replicates will be prepared by filling two sample containers from the same grab sample. The replicate will be labeled and stored in coolers, on ice, with the other samples.

Continuous Samplers

In the absence of standard operating procedures, field staff will follow manufacturer instructions and use field blanks, field replicates, and pump rates to ensure collection of quality data. Field staff will also become familiar with the operation of the CLAM™ device before using it in the field.

Table 11 shows field blanks and replicates for the seven-day sampling period. One field blank and replicate each will be collected for chlorinated pesticides, organophosphate pesticides, pyrethroids, nitrogen-containing pesticides, and carbamate analysis.

Table 11. Field quality control samples for CLAM™ collection disk parameters.

Parameter	Field Blank	Field Replicate
PESTMS*	1	1
Carbamates	1	1

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.

Field blanks will be used to assess contamination from the CLAM™ device before sample water passes through the collection disk. The field blanks will be collected by exposing clean, un-used, collection disks to air. Each disk will be exposed to air two times. One exposure will occur after the CLAM™ device is placed in the water, and the second will occur after the CLAM™ device is retrieved. The length of each blank exposure will be based on the time the collection disk is exposed to air. Before, after, and between exposures, the disk will be stored in a pre-labeled, organics-free glass container. After the second exposure at the end of the seven-day sampling period, the disk will be sent to the laboratory for extraction and analysis.

Field replicates will be used to assess sampling and laboratory variability. Collection of field replicates will consist of side-by-side deployment of two CLAM™ sampling devices with the same type of collection disks. At the end of the deployment period, the replicate collection disk will be removed from the CLAM™ devices, placed in a pre-labeled, organics-free glass container, and sent to the laboratory for analysis.

Pump rates will be measured before and after deployment. Measuring the pump rates will assess any reduction in pumping efficiency over the sampling period. Reduction in pump rates will affect the calculation of pesticide loading at the sampling sites. Pump rates will be measured by pumping 100 mL of organics-free blank water through each CLAM™ device and collecting the exit water in a graduated cylinder. The fill rate of the graduated cylinder will be timed and recorded in a field notebook.

Laboratory

MEL will follow the methods listed in Table 8 and any associated standard operating procedures as described in their quality assurance manual (MEL, 2006). Laboratory QC will consist of laboratory control samples, method blanks, laboratory duplicates, matrix spike/matrix spike duplicates, and surrogate spikes (Table 12).

The total laboratory cost for the project is estimated at $27,520 (Table 13).

Table 12. Laboratory quality control samples.

Parameter	Lab Control Samples	Method Blank	Laboratory Duplicate	Matrix Spike	Matrix Spike Duplicate	Surrogate Spikes
PESTMS*	1/batch[1]	1/batch	1/batch	1/batch	1/batch	All Samples
Herbicides	1/batch	1/batch	1/batch	1/batch	1/batch	All Samples
Carbamates	1/batch	1/batch	1/batch	1/batch	1/batch	All Samples
TSS	1/batch	1/batch	1/batch	N/A	N/A	N/A

*Refers to a single analysis which analyzes for chlorinated pesticides, organophosphate pesticides, pyrethroids, and nitrogen-containing pesticides.
[1]A batch is defined as 20 or fewer samples.
N/A – not applicable.
TSS – total suspended solids.

Table 13. Estimated laboratory costs*.

Parameter	Number of Samples[1]	QC Samples	Total Samples	Price per Sample ($)	Total Price ($)
Surface Water Samples					
Pesticides	24	6	30	425	12,750
Herbicides	24	6	30	195	5,850
Carbamates – low level	24	6	30	185	5,550
Total suspended solids	24	6	30	11	330
Totals	96	24	120	816	24,480
Continuous Water Samples (extraction of collection disk only)					
Pesticides	2	2	4	410	1,640
Herbicides[2]	2	2	4	180	720
Carbamates – low level	2	2	4	170	680
Totals	6	6	12	760	3,040
				Project Total:	27,520

*Costs include 50% discount for MEL.
QC – Quality control.
[1]The actual number of samples will be seven per site. Six samples are listed here. One sample is not included in this estimate because it is already accounted for in the weekly sampling regime.
[2]This cost will only be incurred if MEL is able to split the extract from the pesticide samples and then acidify the portion to be used in herbicide analysis.

Data Management Procedures

Case narratives included with the data package from MEL will discuss any problems encountered with the analysis, corrective action taken, changes to the requested analytical method, and a glossary for data qualifiers.

Laboratory data and QC results, with any qualifiers noted, will be included in the data package. This information will be used to evaluate data quality and will act as acceptance criteria for the project data.

Field and laboratory data will be entered into Ecology's Environmental Information Management system (EIM). Laboratory data will be downloaded directly into EIM from MEL's Laboratory Information Management System. All data will be reviewed by the project manager and then entered into EIM by the data engineer.

Audits and Reports

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

A final report will be completed in May 2010 presenting the results of samples analyzed by MEL. Information on the effectiveness of the weekly sampling regime to obtain representative results for western Washington agricultural practices will also be presented. In addition, a comparison of the results from the daily, weekly, and continuous samples will be included.

The report will contain at a minimum:

- A map of the study area showing sites and significant features.
- Coordinates of each sampling location.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of problems encountered.
- A table comparing results from daily, weekly, and continuous sampling.
- Summary tables of the chemical and physical data.
- An evaluation of the performance of the CLAM™ devices and recommendations for future use by Ecology.

Data Verification

MEL will conduct a review of all laboratory data for this project. MEL will verify that (1) methods and protocols specified in this QA Project Plan were followed; (2) all calibrations, checks on QC, and intermediate calculations were performed for all samples; and (3) the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of instrument calibration, procedural blanks, check standards, recovery and precision data, and appropriateness of any data qualifiers assigned. MEL will prepare written data verification reports based on the results of their review. A case summary can meet the requirements for a data verification report.

Field data will be verified by conducting a review of field meter calibration records. The project manager will verify that all parameters calibrated within acceptance limits before and after field activities. If any field parameters are found to be outside of acceptance limits, then data will be appropriately qualified or rejected.

The project manager will review the laboratory data packages and data verification reports. To determine if project MQOs have been met, results for check standards, lab control samples, duplicate samples, surrogates, and matrix spikes will be compared to QC limits. Method blank results will be examined to verify there was no significant contamination of the samples. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects and to determine if any values exceed the lowest concentration of interest.

Data Quality (Usability) Assessment

After the data have been verified, the project manager will determine if they can be used to make the determinations for which the project was conducted. If the MQOs have been met, the quality of the data should be useable for meeting project objectives, and the report will be written. If data do not meet MQOs, the project manager will note any limitations on usability.

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Appendices

Appendix A. Glossary, Acronyms, and Abbreviations

Carbamate: An insecticide.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Dissolved oxygen: A measure of the amount of oxygen dissolved in water.

Endpoint: An explicit expression of the environmental value that is to be protected.

Herbicide: A substance or preparation for killing plants.

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

Pesticide: A substance or preparation used to kill pests. Pesticides include fungicides, herbicides, insecticides, and rodenticides.

pH: A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (7 to 14) indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.

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

Total suspended solids: Portion of solids retained by a filter.

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

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

CLAM™	Continuous Low-Level Aquatic Monitor
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database (Ecology)
EPA	U.S. Environmental Protection Agency
ESA	Endangered Species Act
Fisheries	National Marine Fisheries Service (NOAA)
GCMS	Gas Chromatography Mass Spectrometry
LCMS	Liquid Chromatography Mass Spectrometry
MEL	Manchester Environmental Laboratory (Ecology)

MQO	Measurement Quality Objective
NOAA	National Oceanic and Atmospheric Administration
QA	Quality Assurance
QC	Quality Control
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
TSS	Total Suspended Solids
WSDA	Washington State Department of Agriculture
WRIA	Water Resources Inventory Area

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
ft/s	feet per second
mg/L	milligrams per liter (parts per million)
mL	milliliters
mL/min	milliliters/minute
s.u.	standard units
µg/L	micrograms per liter (parts per billion)
umhos/cm	micromhos per centimeter

Appendix B. Information on CLAM™ Collection Disks

H2O-Phobic DVD by J.T.Baker

The H2O-Phobic Di-Vinyl-Benzene (DVB) disk was designed by J.T. Baker for use in SPE in the laboratory. Prior to use, the disk requires laboratory conditioning. Sorbent media in the disk is effective with a wide range of analytes, from slightly polar to non-polar (Mallinckrodt Baker, 2009). The H20-Phobic DVB disk can handle dirty samples while maintaining high-speed laminar flow.

H2O-Phobic DVB disks are made from a patented microparticulate sorbent that is packed between two screens and two filters (Mallinckrodt Baker, 2009). The configuration maximizes laminar flow, capacity, adsorption, speed, and resists clogging.

For this study the H2O-Phobic DVB disk will be used for collecting a wide range of pesticides and herbicides. After being used in the field in conjunction with the CLAM™, the H2O-Phobic DVB disk will be extracted using EPA Method 3535 (EPA, 2004). The H2O-Phobic DVB is currently in use by MEL to extract water samples, collected in the field, for analysis by GC/MS. After extraction, samples will be analyzed using EPA Method 8270 (EPA, 1998).

Oasis® HLB Disk by Waters

The Oasis® Hydrophobic-Lipophilic-Balanced (HLB) disk was designed by Waters for use in solid-phase extraction (SPE) in the laboratory. The disk requires little to no laboratory conditioning prior to use, and does not dry out when air is drawn through. The sorbent media in the disk is effective with a large range of analytes, especially polar compounds (Waters, 2009). The Oasis® HLB disk can handle large sample volumes and has increased capacity for dirty samples.

The Oasis® HLB disk is made from a specific ratio of two monomers, hydrophilic N-vinylpyrrolidone and lipophilic divinylbenzene (Waters, 2009). This combination of two monomers provides a large reverse-phase capacity for improved retention of polar analytes.

For this study the Oasis HLB disk will be used for collecting carbamates. After its use in the field with the CLAM™, the Oasis® HLB disk will be extracted using EPA Method 3535 (EPA, 2004). The Oasis® HLB disk is currently in use by MEL to extract water samples, collected in the field, for analysis using the LCMS. After extraction, samples will be analyzed using EPA Method 8321A (EPA, 1996).