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Quality Assurance Project Plan

Grayland Ditch: An Evaluation of Organophosphate Pesticides and Pesticide Test Kits

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Quality Assurance Project Plan

Grayland Ditch: An Evaluation of Organophosphate Pesticides and Pesticide Test Kits

July 2009

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SWRO – Southwest Regional Office
EIM – Environmental Information Management system
SCS – Statewide Coordination Section
WOS – Western Operations Section
EAP – Environmental Assessment Program

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Abstract

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

Between Grayland and North Cove along the Washington Coast, the Grayland Ditch is used to drain surface water and groundwater from cranberry growing operations and residential property. The Grayland Ditch is made up of two ditches: the Grays Harbor County ditch flowing north to Grays Harbor and the Pacific County ditch flowing south to Willapa Bay. Several Ecology studies have identified concentrations of three organophosphate pesticides (azinphos-methyl, chlorpyrifos, and diazinon) in water that did not meet water quality standards. Both ditches are currently on Washington State's 303(d) list for exceeding water quality criteria or recommended standards for multiple toxic pollutants.

To reduce pesticide levels in these drainages, local cranberry growers sponsored research and development of best management practices. After several years of design and implementation, Ecology conducted a study to evaluate the effectiveness of the best management practices. Results showed that there was some progress made, but concentrations of pesticides continued to exceed water quality standards during the growing season.

This Ecology study will provide another evaluation of current concentrations of the three organophosphate pesticides. Sampling will be conducted during the peak pesticide application period during June and July 2009. In conjunction with laboratory samples, field organophosphate pesticide test kits will also be evaluated as a sampling tool. If effective, commercially available organophosphate pesticide test kits could be used by cranberry growers to identify areas of concern.

Background

Between Grayland (Grays Harbor County) and North Cove (Pacific County), on the Washington Coast, is a major cranberry growing area. Grays Harbor County and Pacific County each manage a ditch system that drains these cranberry growing areas and residential property. These ditches originate in wetlands near the Grays Harbor/Pacific County line, west of Highway 105. Precipitation runoff from woodland areas east and upslope of the cranberry bogs also feeds into the ditches.

The Grays Harbor County ditch (GHCDD-1) flows north for about 2.8 miles, draining water from around the county line through the Grayland area, and discharges to South Bay in Grays Harbor. The Pacific County ditch (PCDD-1) flows south for about 5 miles, from around the county line and discharges to the North Cove of Willapa Bay. Figure 1 shows the location of GHCDD-1 and PCDD-1.

In Washington State, drainage ditches are designated as surface waters of the state. As with other surface water in Washington, water quality standards apply (Chapter 173-201A WAC). Currently, both ditches are listed as Category 5 on the federal Clean Water Act section 303(d) list as exceeding water quality criteria or recommended standards for multiple toxic pollutants. The 303(d) listings include chlorpyrifos, diazinon, as well as DDT and its metabolites (4,4'-DDD, 4,4'-DDE). DDT was banned from use in the United States in 1972 and is considered a legacy pesticide.

In 1994 and 1995, the Washington State Department of Ecology (Ecology) identified several pesticides that were frequently detected at concentrations exceeding Washington State or federal water quality criteria (Davis et al., 1997). To reduce pesticide levels in the Grayland and Pacific County ditches, local cranberry growers sponsored research and development of best management practices (BMPs) for their growing operations (Frantz et al., 1996).

To track progress, Ecology conducted studies to evaluate the reduction in pesticide concentrations (Anderson and Davis, 2000; Coots, 2003). Results of the studies showed that some improvement had been made, but concentrations of pesticides continued to exceed water quality standards (Table 1 and 2). The Larkin Road site used for comparison in Table 1 is an historic site and is located on Larkin Road approximately one third of a mile east of State Highway 105.

It was determined that the most effective way to make reductions was to continue supporting development and implementation of BMPs and to re-evaluate pesticide concentrations in future sampling. To help with implementation of BMPs the Natural Resource Conservation Service and other organizations have provided growers with technical assistance and grants.

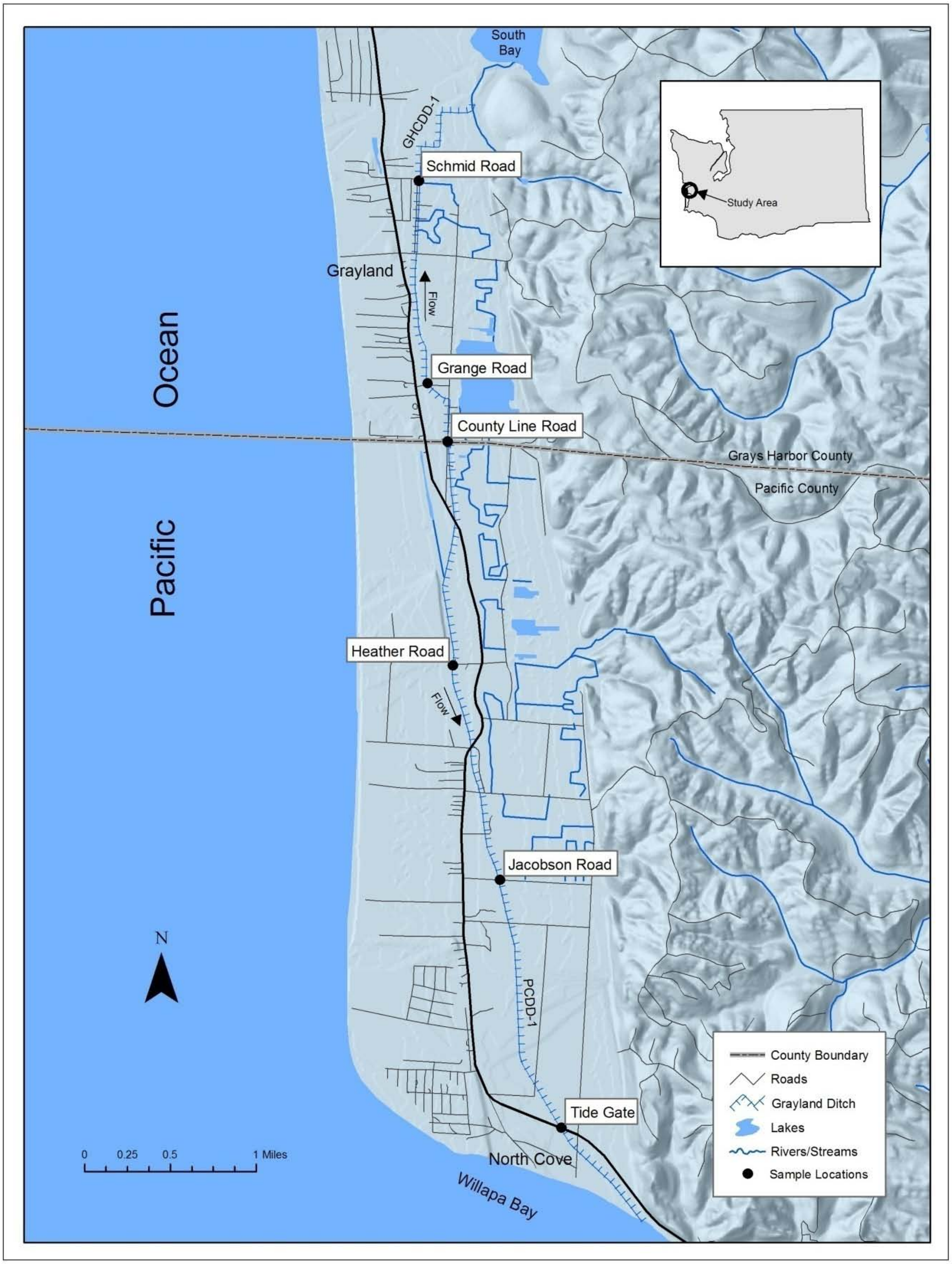

Figure 1. Grayland Ditch sampling locations.

Table 1. Summary of historic detections of azinphos-methyl, chlorpyrifos, and diazinon in Grays Harbor and Pacific County Drainage ditches from 1996-2002 (µg/L).

Location		1996	1998	2002
GHCDD-1 at Schmid Road				
Azinphos-methyl	mean range	**0.17** (n=17) 0.010-**0.73**	**0.26** (n=5) 0.004-**1.2**	**0.15** (n=2) **0.10-0.20**
Chlorpyrifos	mean range	0.008 (n=8) 0.008-0.016	**0.38** (n=5) 0.0095-**1.8**	0.008 (n=2) 0.0050-0.010
Diazinon	mean range	**0.86** (n=26) 0.026-**5.4**	**1.1** (n=5) 0.033-**4.4**	**0.17** (n=3) 0.018-**0.35**
PCDD-1 at Larkin Road				
Azinphos-methyl	mean range	**0.17** (n=26) 0.006-**0.74**	**0.33** (n=5) **0.012-1.4**	**0.050** (n=3) 0.0061-**0.13**
Chlorpyrifos	mean range	**0.44** (n=26) 0.003-**3.7**	**0.58** (n=5) 0.0.19-**1.3**	0.028 (n=3) 0.015-0.036
Diazinon	mean range	**0.29** (n=25) 0.008-**1.7**	**2.4** (n=5) 0.033-**7.0**	**0.48** (n=3) **0.20-0.64**

Bold values are greater than available water quality criteria.

Table 2. Available water quality criteria (µg/L).

Chemical	Type	Common Name	WAC		NRWQC	
			Acute	Chronic	CMC	CCC
Azinphos-methyl	Organophosphate	Guthion	--	--	--	0.01
Chlorpyrifos	Organophosphate	Lorsban	0.083	0.041	0.083	0.041
Diazinon	Organophosphate	(several)	--	--	0.17	0.17

WAC – Washington Administrative Code (Chapter 173-201A).
NRWQC – National Recommended Water Quality Criteria.
CMC – criteria maximum concentration.
CCC – criteria continuous concentration.

Project Description

Data collected for this 2009 study will be compared to data from previous studies to determine the progress in reducing organophosphate (OP) pesticide concentrations in the Grays Harbor and Pacific County drainage ditches. In addition to evaluating pesticide concentrations in both ditches, the cranberry growers have a desire to have a rapid screening tool for OP pesticides that would allow for rapid feedback on the effectiveness of BMPs. To address this, several commercially available OP pesticide test kits will be evaluated in the field. The OP pesticide test kits will be evaluated for ease of use, acceptable detection limits, and comparability to laboratory data.

Samples will be collected at three locations in each ditch system. The locations were selected using information from past reports and suggestions from the cranberry farmers. Sampling locations are shown in Figure 1 and are described in Table 3. Statistical comparisons will not be made due to small data sets.

Table 3. Sampling locations and descriptions for PCDD-1 and GHCDD-1.

Station Name	Latitude	Longitude	Description
GHCDD-1			
Schmid Road	46.8161	-124.0916	Upstream side of bridge on GHCDD-1
Grange Road	46.7991	-124.0891	Upstream side of bridge on GHCDD-1
County Line Road	46.7938	-124.0866	Upstream side of culvert on GHCDD-1
PCDD-1			
Heather Road	46.7758	-124.0777	Upstream side of bridge on PCDD-1
Jacobson Road	46.7580	-124.0777	Upstream side of bridge on PCDD-1
Tide Gate	46.7372	-124.0688	Upstream of tide gate on PCDD-1

Datum = NAD 83

Each site will be sampled three times. The first event will occur approximately one week prior to application of pesticides. The remaining two sampling events will occur during the peak application period and after all application has ended.

Objectives of the study are to:

- Assess current concentrations of azinphos-methyl, chlorpyrifos, and diazinon in the waters of Grays Harbor and Pacific County drainage ditches. Data will be compared to recommended water quality standards for the protection of aquatic life.
- Evaluate the effectiveness of implemented BMPs by comparing current pesticide concentrations to data collected in previous studies. The evaluation will provide a qualitative measure of the general effectiveness of the BMPs currently in use. Information gathered from the evaluation will be used to inform growers about the value of BMPs and to suggest areas that need increased use of BMPs.
- Evaluate OP pesticide test kits to determine if they will be useful as an investigative tool for use by growers. If proven practical for use, growers can better identify areas in need of BMP improvements.

Organization and Schedule

The names, titles, and responsibilities of the people involved in this project are summarized in Table 4. All are employees of the Washington State Department of Ecology. Table 5 shows the proposed schedule for project deliverables. Project costs for laboratory analysis and OP test kit purchase are shown in Table 6.

Table 4. Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Paul D. Anderson Toxics Studies Unit SCS Phone: (360) 407-7548	Project Manager/ Principal Investigator	Writes the QAPP, oversees field sampling and transportation of samples to the laboratory, conducts QA review of data, analyzes and interprets data, enters data into EIM, and writes the draft report and final report.
Tanya Roberts Toxics Studies Unit SCS Phone: (360)407-7392	Field Assistant	Helps collect samples and records field information.
David Rountry Water Quality Program Southwest Regional Office Phone: (360) 407-6276	Client	Clarifies scopes of the project, provides internal review of the QAPP, and approves the final QAPP.
Dale Norton Toxics Studies Unit SCS 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 SCS Phone: (360) 407-6698	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Bob Cusimano Western Operations Section Phone: (360) 407-6596	Section Manager for the Study Area	Reviews the project scope, approves the final QAPP, and reports progress to the regional water management team.
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.

EAP – Environmental Assessment Program.
QAPP – Quality Assurance Project Plan.
EIM – Environmental Information Management system.
SCS – Statewide Coordination Section.

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

Field and laboratory work	
Field work completed	July 2009
Laboratory analyses completed	September 2009
Environmental Information System (EIM) system	
EIM data engineer	Paul Anderson
EIM user study ID	PAND0002
EIM study name	OP Pesticides in Grayland Ditch
Data due in EIM	January 2010
Final report	
Author lead	Paul D. Anderson
Schedule	
Draft due to supervisor	October 2009
Draft due to client/peer reviewer	November 2009
Draft due to external reviewer(s)	December 2009
Final report due on web	January 2010

Table 6. Laboratory and test kit costs.

Expenditure Type	Parameter	Cost ($)
Laboratory	Organophosphate pesticides	5,500
	Total Suspended Solids	264
Test Kits	Organophosphate pesticides	1,125
	Total	6,889

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) assess the current concentrations of azinphos-methyl, chlorpyrifos, and diazinon in the Grayland Ditch; (2) compare them to current water quality standards; and (3) subjectively evaluate the effectiveness of implemented BMPs by comparing data from this study to data collected from previous studies. These objectives will be achieved through careful planning, sampling, and adherence to procedures described in this Quality Assurance (QA) Project Plan.

Field

Field meter measurements collected at each sampling site will conform to the measurement quality objectives (MQOs) summarized in Table 7.

Table 7. Measurement quality objectives for conventional parameters measured by field meters or determined by a standard method.

Parameter	Method/Equipment	Field Replicate MQO	Reporting Limits
Water Temperature	Hydrolab MiniSonde®/DataSonde®	±0.2°C	0.1°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

MQO – measurement quality objectives
RSD – relative standard deviation

Laboratory

Ecology's Manchester Environmental Laboratory (MEL) is performing the chemical analysis for the study. MEL is expected to meet all the quality control requirements of the analytical methods being used for this project. MEL's routine quality control tests for precision and accuracy will meet project needs. The analytical MQOs that will be used are shown in Table 7.

Quality objectives for the OP pesticide test kits have not been established. Establishing quality objectives will be part of the test kit evaluation process. The relative percent difference for laboratory analyzed OP replicate samples will be used to guide development of quality objectives for the OP pesticide test kits (Table 8).

Table 8. Laboratory measurement quality objectives.

Parameter	Laboratory Control Samples	Replicate Samples	Matrix Spikes Samples	Duplicate Samples	Surrogate Standards
	% recovery	RPD	% recovery	RPD	% recovery
OP pesticides	30-130	≤20	30-130	≤40	30-130
TSS	80-120	≤15	N/A	N/A	N/A

N/A – not applicable
OP – organophosphate
RPD – relative percent difference
TSS – total suspended solids

Sampling Process Design

Samples will be collected during three events at three locations in each of the GHCDD-1 and PCDD-1 ditch systems. Locations were chosen to correspond to previous studies. Use of historic sampling locations will ensure comparability with previous detections. The timing of the sampling will focus on the most intensive application of pesticides in the cranberry bogs. Intensive application of pesticides typically occurs during the middle of July.

Sampling will occur approximately one week before the onset of pesticide application. A second set of samples will be collected during or shortly after the peak of pesticide application. The third set of samples will be collected approximately two weeks after the start of pesticide application or after all application has ceased.

Due to the many factors that influence the start of pesticide application, exact timing of the sampling events will be determined closer to the application period. To achieve the target sample collection windows there will be frequent communication with the cranberry growers. In typical years pesticides are applied immediately after removal of honey bees, used for pollination. Removal of the bees is weather dependent, but in the past has occurred around the middle of July. Using prior studies as a guide, sampling likely will start during the first week of July. This sampling regime is similar to what has been used in previous studies.

In addition to collecting water samples for analysis by a laboratory, OP pesticide test kits will be used to evaluate comparability with pesticides detected by the laboratory. Quantitative results will not be used for comparison because the OP pesticide test kits only produce presence/absence results for a small number of chemicals. Three test kits will be used side by side to compare performance. These three test kits were selected from a small number of available test kits. Test kits were chosen based on cost and ability to be used in the field.

Sampling Procedures

Water Samples

All surface water samples will be collected by hand-compositing grab samples from quarter-point transects using a pole sampler or a U.S. Geological Survey DH-81 depth integrating sampler. Surface water sampling techniques will be consistent with Ecology standard operating procedures described in EAP003 *Sampling of Pesticides in Surface Waters* (Anderson, 2006) and EAP015 *Manually Obtaining Surface Water Samples* (Joy, 2006).

Recommended sample containers, preservation, and holding times are presented in Table 9.

Table 9. Recommended containers, preservations, and holding times.

Parameter	Container	Preservation	Holding Time
OP pesticides	1-liter narrow-mouth amber bottle with Teflon-lined cap	Cool to ≤6°C	7 days to extraction 40 days to analysis
Total Suspended Solids	1-liter wide-mouth polyethylene bottle	Cool to ≤6°C	7 days

All sample sites will be located using geographic coordinates from Ecology's Environmental Information Management (EIM) system and descriptions from past monitoring reports. Use of the GPS will follow Ecology standard operating procedure EAP013 (Janisch, 2006). If adjustments to the sampling locations are necessary, new position details including geographic coordinates (with datum) and a written description will be recorded.

Test Kits

Samples collected for analysis with test kits will be obtained using sample water collected as sequential replicates with the samples for laboratory analysis. Collection of the water used for analysis by the test kits will be consistent with the standard operating procedures referenced in the previous section. Samples will be held in coolers, on ice, until sampling operations are completed at the site. After sampling operations are completed, the water samples will be analyzed on site using the test kits.

Each test kit has a different recommended sampling procedure and list of detectable chemicals. Detailed information on each test kit selected for use is presented in Appendix A.

Invasive Species Decontamination

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

Measurement Procedures

Field

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

- EAP011 - Instantaneous Measurement of Temperature in Water (Nipp, 2006).
- EAP031 - Collection and Analysis of pH Samples (Ward, 2007a).
- EAP032 - Collection and Analysis of Conductivity Samples (Ward, 2007b).
- EAP033 - Hydrolab® DataSonde® and MiniSonde® Multiprobes (Swanson, 2007).

All field parameters will be measured at the sampling site by field staff. The expected range of results and reporting limits for field parameters are shown in Table 10.

Table 10. Expected range of results and reporting limits for field parameters.

Parameter	Expected Range of Results	Reporting Limits
Temperature	10-20 °C	0.02 °C
pH	6.5-7.5 s.u.	1-14 s.u.
Conductivity	100-300 µmhos/cm	0.1 µmhos/cm

Test Kits

All OP pesticide test kit samples will be analyzed in the field. Use of test kits in the field will best represent typical use by the cranberry growers. All three kits listed in Table 11 will be used at each site during each sample event. Samples will be analyzed using the manufacturer's instructions included with each test kit. The result from each kit will be recorded in a field notebook. Each kit will have a separate page to ensure that test results will not be incorrectly recorded. Notes on the performance of each test kit will be recorded with the result.

Performance measures will include:

- Pre-analysis set-up time.
- Ease of use (especially for someone with little or no laboratory experience).
- Time to complete each test.
- Ease of interpretation of test result(s).
- Accuracy (false positives versus false negatives).
- Number of tests per kit.

The cost of the test kit will also be considered.

Ease of use will be evaluated by (1) how well the included instructions direct the user through each test and (2) how much chemistry knowledge is required to perform each test.

Table 11. Organophosphate pesticide test kits.

Name of Test Kit	Manufacturer
Organophosphate/Carbamate Assay Kit	Abraxis
Agri-Screen Ticket®	Neogen
RaPID Assay® Organophosphate/ Carbamate Screen Kit	Strategic Diagnostics Inc.

Laboratory

All laboratory analyses for the study will be performed by MEL according to current standard operating procedures. Table 12 shows the expected range of results, required reporting limits, sample preparation methods, and analysis methods for laboratory parameters.

Table 12. Expected range of results, reporting limits, sample preparation methods, and analysis methods for laboratory parameters.

Parameter	Expected Range of Results	Reporting Limits	Sample Preparation Method	Analysis Method
OP pesticides	0.003-10 µg/L	0.01-1.0 µg/L	EPA 3535*	EPA 8270*
TSS	1-20 mg/L	1 mg/L	N/A	SM 2540D*

*SM, 1998; EPA, 1998; EPA, 2004
EPA – U.S. Environmental Protection Agency
N/A – not applicable
OP – organophosphate
SM – Standard Methods
TSS – total suspended solids

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 will be measured in the field using a Hydrolab MiniSonde® or DataSonde®, or a meter with equivalent measurement capabilities. All field parameters will be replicated once in each drainage ditch, during each sampling event. The location of the replicate measurements will be rotated through all six sampling sites. Precision for replicates will be expressed as percent relative standard deviation (RSD).

Any meter used to measure field parameters will be calibrated before use and post checked at the end of each day, using Ecology Standard Operating Procedures. Temperature will not be included in this procedure because it is factory calibrated. To check for drift in temperature calibration, field meters are compared to a National Institute of Standards and Technology (NIST) thermometer at the beginning and the end of each sampling season.

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 13.

Table 13. 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%

[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%.

Surface Water Samples

In addition to following standard operating procedures, field quality control samples will be collected. These field quality control samples will consist of transfer blanks and replicates (Table 14). Transfer blanks and replicates will be submitted blind to MEL using different sample numbers and sample site names.

Table 14. Field quality control samples and associated data quality objectives.

Analysis	Transfer Blank	Split Replicate	Data Quality Objective (RPD)
Organophosphate pesticides	3	3	±20
Total Suspended Solids	3	3	±15

RPD – relative percent difference

An equipment blank and replicate will be collected at one site during each sampling event. Each of the quality control samples will be collected at different sites within a sampling event. This will ensure adequate quality control sample coverage at all sites.

Equipment blanks evaluate potential contamination from sampling equipment and procedures, and transport to the laboratory. Blanks will be prepared using de-ionized, organics-free water from 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 separate sample containers from the same grab sample. The replicate will be labeled and stored in coolers, on ice, with the other samples.

Test Kits

Before using the OP pesticide test kits in the field, staff will read the included literature and instructions from the manufacturer. In addition, field staff will run a minimum of one practice analysis using each of the three test kits, prior to going in the field. Carefully following the use instructions for the test kits will ensure accurate and contamination-free test results. To augment these quality control procedures, at least ten percent of the organophosphate test kit samples will be replicated to assess the reproducibility of the result.

Laboratory

Manchester Environmental Laboratory will follow the methods listed in Table 6 and any associated laboratory standard operating procedures as described in their Quality Assurance Manual (MEL, 2006). Laboratory quality control will consist of laboratory control samples, method blanks, laboratory duplicates, matrix spike/matrix spike duplicates, and surrogate spikes (Table 15).

Total laboratory costs for the project are estimated at $5,814 (Table 16).

Table 15. Laboratory quality control samples.

Parameter	Lab Control Samples	Method Blank	Laboratory Duplicate	Matrix Spike	Matrix Spike Duplicate	Surrogate Spikes
OP pesticides	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

*A batch is defined as 20 or fewer samples
N/A – not applicable

Table 16. Estimated laboratory costs*.

Parameter	Number of Samples	Field QC Samples	Total Samples	Price per Sample ($)	Total Price ($)
OP pesticides	18	12	30	185	5,550
Total Suspended Solids	18	6	24	11	264
				Project Total	5,814

*Costs include 50% discount for Manchester Laboratory
QC – quality control

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 quality control 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 EIM system. 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

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

A report will be completed in January 2010 presenting the results of samples analyzed by MEL. Information on the effectiveness of the cranberry grower mitigation efforts at reducing pesticide concentrations in the Grays Harbor and Pacific County Drainage ditches will also be presented. The report may include observations and suggestions for helping the growers' better conduct or focus their BMPs. In addition, a comparison of the results from the OP pesticide test kits and samples analyzed by MEL will be presented.

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 OP pesticide field test kits to samples analyzed at MEL.
- Summary tables of the chemical and physical data.
- An evaluation of the significant findings as well as comparisons of historical data to current conditions.

Data Verification

Manchester Environmental Laboratory 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 quality control, 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 are calibrated within acceptance limits before and after field activities. If any field parameters are found to be outside of acceptance limits, data will be appropriately qualified or rejected.

Detailed Verification

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 quality control 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 also 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 report preparation will proceed. If data do not meet MQOs, the project manager will note any limitations on usability.

References

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Appendices

Appendix A. Information on Selected Organophosphate Pesticide Test Kits

Selection Process

The three OP pesticide test kits described in the following sections were selected from a small group of available kits. Selection criteria were:

1. Cost
2. Ability to detect target OP pesticides
3. Usability in the field

One of the most important selection criteria was cost. The equipment selected for testing could not be cost prohibitive. If an OP pesticide test kit is found to be viable for use, the cranberry farmers likely will be the ones purchasing the equipment. Equally important as cost is the ability of the OP pesticide test kit to detect the targeted OP pesticides. Finally, the OP pesticide test kit must be useable in the field. The cranberry farmers would be using the OP pesticide kits in the field, not in a lab or other controlled setting.

The available test kits all work as a colorimetric test based on the inhibition of the biological enzyme, acetyl cholinesterase. Organophosphate pesticides work in insects and other animals by inhibiting this same enzyme. In the absence of the ability to economically take the laboratory into the field, test kits have been developed to detect OP pesticides using acetyl cholinesterase.

Detection limits in OP pesticide test kits ranged widely and were most closely linked to cost. The more expensive the kit, the lower the detection limit. This scenario makes sense because in the laboratory the more sensitive the analysis, the more the technology will cost to achieve the result. With the restriction of cost, the sensitivity of detection is reduced.

The three OP pesticide test kits selected for evaluation were the best available within the restrictions of the selection criteria.

Abraxis Organophosphate/Carbamate Assay Kit

General Information

The Abraxis Organophosphate/Carbamate Assay Kit is capable of detecting a wide range of organophosphate and carbamate pesticides in water. Assay kits provide a qualitative result using a colorimetric assay based on the inhibition of acetyl cholinesterase. Various reagents are mixed in vials with a sample to form a color if no pesticide is present. If an OP and/or carbamate pesticide is present in the sample, color formation will be reduced or eliminated. The amount of reduction or elimination of color formation depends on the amount of pesticide(s) present in the sample.

Detection limits vary on a chemical-by-chemical basis depending on the ability of the specific chemical to inhibit acetyl cholinesterase. Most materials are provided with each kit. Materials not provided with each kit will need to be purchased from a separate vendor.

Detectable Compounds

A list of detectable compounds and their associated detection limit for the Abraxis Organophosphate/Carbamate Assay Kit are provided in Table A1.

Table A1. Detectable Compounds and Detection Limits (µg/L).

Compound	Detection Limit
Organophosphate	
Azinphos methyl	0.3
Chlorpyrifos methyl	0.4
Chlorpyrifos ethyl	0.5
Diazinon	0.6
Dichlorvos	0.5
Dicrotophos	2.4
Disulfoton	40
Ethion	0.6
Malathion	1.2
Parathion	0.8
Phorate	1
Phosmet	1.2
Carbamates	
Aldicarb	25
Carbaryl	206
Carbofuran	0.9

Neogen Agri-Screen Ticket®

General Information

Agri-Screen Ticket® can detect all major organophosphates and carbamates in many different types of samples (e.g., air, water, soil, produce, food). The test uses acetyl cholinesterase inhibition to produce a presence/absence (qualitative) result for OP and/or carbamate pesticides in the sample. Agri-Screen Ticket® uses a disc saturated with acetyl cholinesterase to determine if a pesticide is present in the sample. The sample is collected and mixed with activation chemicals. After activation, the disc is exposed to the sample. If there are no OP and/or carbamate pesticides present in the sample, the disc will change to a blue color. No color change will occur if an OP and/or carbamate pesticide is present in the sample.

Detection limits vary on a chemical-by-chemical basis depending on the ability of the specific chemical to inhibit acetyl cholinesterase. All materials are provided with each kit.

Detectable Compounds

An abbreviated list of detectable compounds and their associated detection limits for the Agri-Screen Ticket® are provided in Table A2.

Table A2. Detectable Compounds and Detection Limits (µg/L).

Compound	Detection Limit
Organophosphate	
Azinphos methyl	300
Chlorpyrifos methyl	700
Diazinon	2000
Dichlorvos	3000
Mevinphos	2000
Oxydemeton-methyl	20,000
Carbamates	
Carbaryl	7000
Carbofuran	100

Strategic Diagnostics Inc. RaPID Assay® Organophosphate/Carbamate Screen Kit

General Information

The Strategic Diagnostics Inc. RaPID Assay® Organophosphate/Carbamate Screen Kit is capable of detecting a wide range of organophosphate and carbamate pesticides in water, soil, crops, and foods. Rapid Assay® kits provide a qualitative result using a colorimetric assay based on the inhibition of acetyl cholinesterase. Various reagents are mixed in vials with a sample to form a color if no pesticide is present. If an OP and/or carbamate pesticide is present in the sample, color formation will be reduced or eliminated. The amount of reduction or elimination of color formation depends on the amount of pesticide(s) present in the sample.

Detection limits vary on a chemical-by-chemical basis depending on the ability of the specific chemical to inhibit acetyl cholinesterase. Most materials are provided with each kit. Materials not provided with each kit will need to be purchased from Strategic Diagnostics Inc. or other vendor.

Detectable Compounds

A list of detectable compounds and their associated detection limit for the Strategic Diagnostics Inc. RaPID Assay® Organophosphate/Carbamate Screen Kit are provided in Table A3.

Table A3. Detectable Compounds and Detection Limits (μg/L).

Compound	Detection Limit
Organophosphate	
Azinphos methyl	100
Chlorpyrifos	200
Chlorpyrifos methyl	300
Diazinon	20,000
Dichlorvos	3000
EPN	700
Fenitrothion	8000
Leptophos	700
Malathion	500
Methamidophos	20,000
Mevinphos	>50,000
Oxydemeton methyl	20,000
Parathion	3000
Parathion methyl	5000
Phorate	6000
Phosmet	1000
Carbamates	
Aldicarb	1000
Aldicarb sulfone	4000
Aldicarb sulfoxide	4000
Carbaryl	1000
Carbofuran	5000
Isoprocarb	3000
Methiocarb	1000
Methomyl	6000
Oxamyl	500
Propoxur	>50,000
Thiobencarb	30,000

Appendix B. Glossary, Acronyms, and Abbreviations

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.

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 Total Maximum Daily Load (TMDL; water cleanup) program.

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.

Grayland Ditch: Grayland Ditch is made up of two ditches: Grays Harbor County ditch (GHCDD-1) and Pacific County ditch (PCDD-1).

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.

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

Acronyms and Abbreviations

BMP	Best management practices
DDD	dichloro-diphenyl-dichloroethane
DDE	dichloro-diphenyl-trichloroethylene
DDT	dichloro-diphenyl-trichloroethane
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
GHCDD-1	Grays Harbor County ditch
GPS	Global Positioning System
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
OP	Organophosphate
PCDD-1	Pacific County ditch
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures

TSS	Total suspended solids
WAC	Washington Administrative Code

Units of Measurement

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