

Quality Assurance Project Plan

Pesticide Reduction Evaluation for Cranberry Bog Drainage in the Grayland Area

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303(d) Listings Addressed in this Study:

Grays Harbor Drainage Ditch (AB55IV) – Azinphos-methyl, Carbaryl, Diazinon, Parathion
Pacific County Drainage Ditch (YF44AK) – Azinphos-methyl, Carbaryl, Diazinon, Chlorpyrifos
Both above numbers included in waterbody number: 1240346467226 (WA 24-1030)

Ecology EIM Number: RCOO0003

Approvals:

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Abstract

Along Washington's coast, the Grayland to North Cove area uses two ditch systems to drain surface and ground water from cranberry growing operations and run-off from residential property. Both ditches originate in wetlands around the Grays Harbor/Pacific County line. The Grays Harbor County ditch flows north for about 2.8 miles, discharging into Grays Harbor's South Bay; while the Pacific County ditch flows south, for about 5 miles, and discharges to the North Cove of Willapa Bay. A number of studies conducted during the cranberry growing season have identified concentrations of three organophosphorus pesticides (*i.e.*, azinphos-methyl, chlorpyrifos, and diazinon) and carbaryl, a carbamate pesticide, in water that exceeded recommended water quality standards. Currently, both ditches are listed on the states 303(d) list as not meeting water quality standards for multiple toxic pollutants. Efforts by cranberry growers are underway to reduce the discharge of pesticides to the ditches, through implementation of BMPs. This Quality Assurance (QA) Project Plan will direct a study to evaluate the progress made by growers, to reduce pesticides entering the ditches. Organophosphorus pesticides and carbamate samples will be collected at three sites in the Grays Harbor County ditch, six sites in the Pacific County ditch, and one reference site not impacted by cranberry bog drainage. The timing of the study will focus around the most intensive application period of the growing season. Samples will be collected in June and July of 2002 for a comparison to data from 1996 and 1998 studies, and recommended water quality standards.

Background/Problem Statement

South of Grays Harbor, along the Washington coast, the Grayland to North Cove area uses ditch systems to drain surface and ground water from cranberry growing operations and run-off from residential property (Figure 1). Grays Harbor County and Pacific County each manage a ditch system that originates in wetlands near the Grays Harbor/Pacific County line, west of Highway 105. 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 Grays Harbor's South Bay. 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. During the cranberry growing-season, concentrations of three organophosphorus (OP) pesticides (*i.e.*, azinphos-methyl [guthion], chlorpyrifos [lorsban], and diazinon), have been reported at levels in water from one or both ditches that exceeded recommended water quality standards (Davis *et.al.*, 1997; Anderson and Davis, 2000). In addition carbaryl, a carbamate pesticide, has also been identified as causing water quality concerns. Cranberry growers have been implementing BMPs for some time and there is a need to document the effectiveness of these measures. Currently, both ditches are on the states 303(d) list for not meeting water quality standards or recommended standards for multiple toxic pollutants. The 303(d) listings proposed for study in the GHCDD-1 ditch are: azinphos-methyl, carbaryl, diazinon, and parathion. The 303(d) listed parameters to be addressed for the PCDD-1 ditch are: azinphos-methyl, carbaryl, chlorpyrifos, and diazinon. Both ditches are also listed for the chlorinated pesticide 4,4'DDD. A legacy chemical, 4,4'DDD is a metabolite of DDT, which was banned from use in the United States in 1972. Due to budget constraints chlorinated pesticides will not be evaluated during this study.

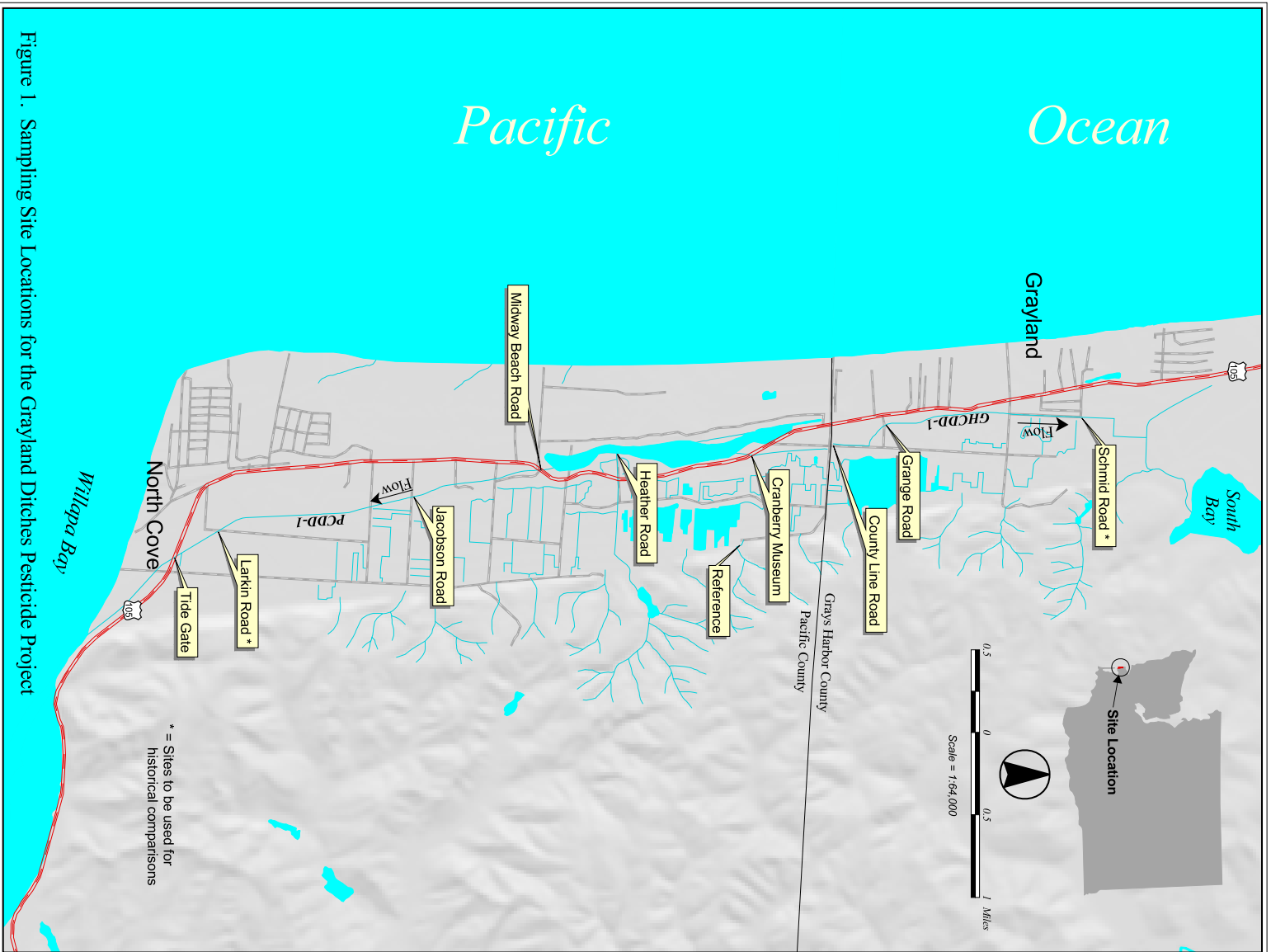


Figure 1. Sampling Site Locations for the Grayland Ditches Pesticide Project

Ecology studies conducted during the cranberry growing season in 1996 and 1998, have shown chlorpyrifos, diazinon, and azinphos-methyl measured in the ditch below cranberry farms frequently exceed water quality criteria for protection of aquatic life. Tables 1 and 2 that follow, summarize results from samples collected in 1996 by Davis *et.al.*, (1997) and in 1998 by Anderson and Davis, (2000), while Table 3 shows the available and recommended water quality standards that will be used for comparison of pesticide data.

Table 1. Pesticide Results from the Grayland Ditches in 1996 (Range and Mean)

<u>GHCDD-1</u>			<u>PCDD-1</u>		
<u>Schmid Road</u>			<u>Larkin Road</u>		
		(ug/L, ppb)			(ug/L, ppb)
chlorpyrifos	range	0.003J – 0.016J	chlorpyrifos	range	0.003J – 3.7
	mean	0.008 (n=8)		mean	0.44 (n=26)
diazinon	range	0.026J – 5.4	diazinon	range	0.008J – 1.7J
	mean	0.86 (n=26)		mean	0.29 (n=25)
azinphos-methyl	range	0.015J – 0.73J	azinphos-methyl	range	0.006J – 0.74J
	mean	0.16J (n=17)		mean	0.17 (n=26)
carbaryl	mean	0.028J (n=2)	carbaryl	mean	0.036J (n=2)

J = The analyte was positively identified. The associated numerical result is an estimate.

Bolded values are greater than available standards.

Table 2. Pesticide Results from the Grayland Ditches in 1998 (Pre-Spray, Post-Spray, and Mean)

<u>GHCDD-1</u>				<u>PCDD-1</u>			
<u>Schmid Road</u>				<u>Larkin Road</u>			
	(ug/L, ppb)				(ug/L, ppb)		
	Pre-Spray	Post-Spray	Mean		Pre-Spray	Post-Spray	Mean
chlorpyrifos	0.017 (n=2)	0.62 (n=3)	0.38 (n=5)	chlorpyrifos	0.038 (n=2)	0.95 (n=3)	0.58 (n=5)
diazinon	0.13 (n=2)	1.8 (n=3)	1.1 (n=5)	diazinon	0.11 (n=2)	3.9 (n=3)	2.4 (n=5)
azinphos-methyl	0.028 (n=2)	0.41 (n=3)	0.26 (n=5)	azinphos-methyl	0.038 (n=2)	0.53 (n=3)	0.33 (n=5)

Bolded values are greater than available standards.

Table 3. Comparative Water Quality Criteria for Pesticides

Pesticide	Aquatic Life Standards (<i>ug/L, ppb</i>)		
	Acute	Chronic	RMC ¹
azinphos-methyl		0.01 ²	
carbaryl			0.02 ³
chlorpyrifos	0.083 ⁴	0.041 ⁴	
diazinon	0.08 ⁵	0.04 ⁵	

1 - RMC = recommended maximum concentration

2 - USEPA – Gold Book (1986)

3 - National Academy of Sciences-NAS 1973

4 - Washington State Water Quality Standards, WAC 173-201A

5 - California Department of Fish and Game – Menconi and Cox, 1994

Other programs that have aimed at reduction or evaluation of the pesticide levels in the Grayland Ditches include a program sponsored by cranberry growers for the research and development of BMPs (Frantz *et.al.*, 1997). The NRCS (USDA) has provided technical assistance and equipment cost-share grants for several years to help growers reduce pesticide releases to the ditches. At the same time, a multi-year program to develop a “reduced risk” pest management program was initiated (Booth *et.al.*, 2000).

The Pacific County Conservation District also administered a program to provide cranberry farmers technical assistance and cost-share to implement BMPs, through a Clean Water Act Section 319 Grant. This program was also intended to document effectiveness of the BMPs. There is also a study being developed by WSU Long Beach Research and Extension Unit to evaluate the ability of new BMPs along with other BMPs to be effective on an individual farm scale to maintain pesticide residues below water quality criteria necessary to protect aquatic life (Patten, in progress).

Goals/Objectives

The study will compare current data on 303(d) listed pesticides to data from past studies to determine the progress in reducing pesticide concentrations in the Grays Harbor and Pacific County drainage ditches, related to cranberry growing operations in the area. Statistical comparisons will not be made due to small data sets, so comparisons will be subjective. Specific objectives of the study are:

- Assess current levels of azinphos-methyl, chlorpyrifos, carbaryl, diazinon, and parathion in the two ditch systems. These data will allow comparisons to recommended water quality standards for the protection of aquatic life.
- Evaluate the effectiveness of BMPs implemented by the cranberry growers by comparing mean pesticide levels in water from the ditches before and after pesticide application to mean baseline data collected in previous studies.

Responsibilities

The following individuals and organizations will be involved in the project:

David Rountry and Janet Boyd (Ecology): Client and staff contact for the Southwest Regional Office. Responsible for reviewing the QA Project Plan and draft study report, write-up of the report to the Governor's Office as an environmental performance measure, field sampling, and coordinating basin planning activities (360/407-6276 and 407-0245).

Randy Coots (Ecology): Contaminant Studies Unit. Develops the project objectives, scope, and study design. Responsible for preparation of the project *QA Project Plan*, and write-up of study findings. Provides technical assistance to regional staff on field sampling techniques as needed (360/407-6690).

Stuart Magoon and Manchester Environmental Laboratory (MEL) Personnel (Ecology): Responsible for review of the QAPP pertaining to laboratory analyses, and the analysis and reporting of project data to principal investigators for samples submitted to the Ecology Manchester Environmental Laboratory (360/871-8860).

Dale Norton (Ecology): Contaminant Studies Unit Supervisor. Responsible for review of the project QA Project Plan and draft study report (360/407-6765).

Cliff Kirchmer (Ecology): Quality Assurance Officer responsible for review of the project QA Project Plan (360/895-4649).

Carolyn Lee (Ecology): Contaminant Studies Unit. Responsible for entering project data into the EIM database system (360/407-6430).

Schedule and Budget

The timing of the study will be focused around pesticide application in the cranberry bogs, in late June and early July. This is the most intensive application period of the growing season and has resulted in the highest concentrations of pesticides in ditch water (Davis *et.al.*, 1997). Three sample surveys will be conducted. One sample set will be collected prior to pesticide application. The second sample set will be collected during the week of pesticide application. A third sample set will be collected two weeks after the start of pesticide application. The exact timing of the surveys will be determined by the activities of the growers. Typically pesticides have been applied immediately following removal of honey bees, used for pollination of the crops. Removal of the bees is weather dependant, but in the past this has occurred around the middle of July.

Analytical cost for the study will be \$13,194. This includes laboratory analysis of the OP pesticides, carbamates, and TSS samples. There will be no analytical cost associated with the field measurements for temperature, pH, and flow, by thermometer and field meters. Listed below is Table 4 showing the total number of samples per analysis and the associated cost.

Table 4. Sample Numbers and Analytical Cost

Analyte	Total Samples*	Cost per Sample	Subtotal
Organophosphorus Pesticides	45	184	8280
Carbamates	24	186	4464
TSS	45	10	450

* = Includes QA samples

Total = \$13,194

Data Quality Objectives and Decision Criteria

Two Ecology surveys from the Washington State Pesticide Management Program (WSPMP) used Method 8085 for OP pesticide analysis and reported excellent accuracy and precision (Davis and Johnson, 1994; and Davis, 1996). In these two studies, matrix spike recoveries ranged from 69% to 110%, with an average of 89%, while the relative percent difference (RPD) between spiked duplicates averaged 11%. Listed below in Table 5 are the measurement quality objectives (MQOs) for the OP pesticides and TSS.

Table 5. MQOs for the OP Pesticides and TSS

Compound	Precision Target (RSD)	Bias Target	Accuracy (2P+B)	Required Reporting Limit
Azinphos-methyl	10%	+10%	30%	0.1 ug/L
Chlorpyrifos	10%	+20%	40%	0.06 ug/L
Diazinon	10%	+10%	30%	0.06 ug/L
Parathion	7%	+10%	24%	0.06 ug/L
TSS	3%	+6%	12%	1 mg/L

Study Design

Water samples will be analyzed from three locations in the GHCDD-1, six locations in the PCDD-1, and one reference site in a natural stream flowing into the PCDD-1 from the eastern hillslopes, that does not receive drainage water from cranberry growing operations (Figure 1). The reference site samples will be analyzed for the same suite of parameters as the Schmid Road and Larkin Road sites. Sampling will measure pollutants from the upper, middle, and lower drainage areas. The Schmid Road site in GHCDD-1 and the Larkin Road site in PCDD-1 coincide with the downstream sites sampled in studies completed in 1996 and 1998 (Davis *et.al.*, 1997; Anderson and Davis, 2000). Sample locations for GHCDD-1 will be: Schmid Road, Grange Road, and County Line Road. Sample locations for PCDD-1 will be: Tide Gate at Highway 105, Larkin Road, Jacobson Road, Midway Beach Road, Heather Road, and the Cranberry Equipment Museum at Highway 105.

Water samples will be collected on three occasions: during the last part of June and first part of July. The exact timing of sample collection will be determined by pesticide application in the cranberry bogs. This period coincides with the most intensive pesticide application period of the growing season and, in the past, resulted in the highest pollutant concentrations in the ditches (Davis *et al.*, 1997). Samples will be collected at each site on three occasions: 1) prior to pesticide application, 2) immediately following the pesticide application by most growers, and 3) two weeks following the pesticide application. Samples will be collected and analyzed for target analytes (Table 6) on the states 303(d) list. Pesticide analysis will include OP pesticides and carbamates (Table 7 and 8) for samples collected at the Schmid Road, Larkin Road, and reference site. Other study sites will have samples analyzed for OP pesticides only. The TSS samples will be collected at all sites, in addition to field measurements for pH and temperature. Flow will be measured at sites accessible by wading, to allow calculation of pollutant loads. Immediately following collection, water samples will be placed on ice, in a chain of custody cooler, for transport to the lab.

Table 6. Summary of Station Location and Analysis

<u>GHCDD-1</u>	<u>Laboratory</u>	<u>Field</u>
Reference Site	Organophosphorus Pesticides, TSS Carbamates	Temperature, pH, flow
Schmid Road	Organophosphorus Pesticides, TSS Carbamates	Temperature, pH, flow
Grange Road	Organophosphorus Pesticides, TSS	Temperature, pH, flow
County Line Road	Organophosphorus Pesticides, TSS	Temperature, pH, flow
 <u>PCDD-1</u>		
Tide Gate at Highway 105	Organophosphorus Pesticides, TSS	Temperature, pH, flow
Larkin Road	Organophosphorus Pesticides, TSS Carbamates	Temperature, pH, flow
Jacobson Road	Organophosphorus Pesticides, TSS	Temperature, pH, flow
Midway Beach Road	Organophosphorus Pesticides, TSS	Temperature, pH, flow
Heather Road	Organophosphorus Pesticides, TSS	Temperature, pH, flow
Cranberry Museum	Organophosphorus Pesticides, TSS	Temperature, pH, flow

Target Pesticides List

**Table 7. Target List for Water Analyses – Organophosphorus Pesticides
SW846 Method 8085**

Analyte	Quantitation Limit ¹ (ug/L)		Analyte	Quantitation Limit ¹ (ug/L)
Acephate	0.30		fenosulfothion	0.075
Azinphos-ethyl	0.12		fenthion	0.055
Azinphos-methyl	0.12		fonophos	0.045
Carbophenothion	0.80		imidan	0.080
Chlorpyrifos	0.055		malathion	0.060
chlorpyrifos-methyl	0.040		merphos	0.12
coumaphos	0.090		methamidophos	0.30
DEF	0.11		mevinphos	0.075
demeton-O	0.055		paraoxon-methyl	0.15
demeton-S	0.060		parathion	0.060
diazinon	0.060		parathion-methyl	0.055
dichlorvos	0.060		phorate	0.055
demethoate	0.060		phosphamidan	0.18
dioxathion	0.12		propetamphos	0.15
disulfthion	0.045		ronnel	0.055
EPN	0.075		sulfotepp	0.045
Ethion	0.055		sulprofos	0.055
ethoprop	0.060		temephos	0.70
fenamiphos	0.12		tertachlorvinphos	0.15
fenitrothion	0.055			

¹Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample.

Method Developed by the California Department of Food and Agriculture
(Methylene Chloride Extraction, HPLC)

**Table 8. Target List for Water Analyses – Carbamates
SW846 Method 8318 – Modified**

Analyte	Quantitation Limit ¹ (ug/L)		Analyte	Quantitation Limit ¹ (ug/L)
1-naphthol	0.05		carbofuran	0.28
3-hydroxycarbofuran	0.15		methiocarb	0.5
Aldicarb	0.5		methomyl	0.15
Aldicarb sulfone	0.15		oxamyl	0.15
Aldicarb sulfoxide	0.15		propoxur (baygon)	0.3
Carbaryl	0.28			

¹Quantitation limits are approximate and are often different for each sample; these values are representative of a typical sample.

Willapa Bay has a tidal influence on the discharge for the lower drainage sites in PCDD-1. To avoid these influences, the Tide Gate at Highway 105 and Larkin Road sites require samples be collected during low tide. Prior to sample surveys, tide tables for Willapa Bay will be reviewed to determine the window for sample collection at these two sites.

Representativeness

The QA Project Plan has been developed to ensure data are representative of conditions in the Grayland Ditches before, during, and after peak pesticide application in the cranberry bogs. The sampling methods, equipment, and collection timing will ensure representativeness. Pesticide samples will be depth integrated.

Completeness

The amount of useable data obtained through this study will be maximized by careful planning and coordination of field surveys, and employing standardized protocols for sample collection and analysis. All personnel involved with sample collection will be familiar with Environmental Assessment (EA) Program routine procedures for pesticide sampling in water (Davis *et.al*, 1997) and the WAS field sampling and measurement protocol manual (WAS, 1993).

Comparability

Sampling, quality assurance, and analytical methods were selected to generate results that would be consistent and comparable with previous studies conducted in the Grayland Ditches that evaluated run-off from pesticide application.

Field Procedures

Water samples collected for pesticide analysis will be depth and width integrated. A USGS DH-81 depth-integrated sampler (with a D-77 cap and wading rod) will be used that allows sample water to contact only Teflon or glass. Samples will be collected by slowly lowering the sampler to the bottom and immediately raising it back to the surface in a smooth motion. Sub-samples will be collected at each site from three positions across the transect (quarter-point). If the ditch water is less than one foot deep, an attempt will be made to integrate depth by hand collection. Sample water will be composited at each site by hand splitting into individual sample bottles. Sample containers will be one-third filled by each of the three quarter-point sub-samples. OP pesticide samples will be collected in one-gallon glass bottles, while carbamate samples will be collected in 125 mL amber glass bottles, containing preservative. Grab samples for TSS will be collected in 1000 mL poly bottles. Samples will be placed in coolers on ice, immediately following collection, until delivered to Manchester Environmental Laboratory (MEL) the following day.

Temperature will be measured *in situ* by alcohol thermometer. The pH will be measured by hand-held meter pre-calibrated with low ionic strength standards of 4.0 and 7.0 pH units. At sample sites that are wadable, flow will be measured using a Marsh-McBirney 201 velocity meter and standard top-setting wading rod. Operating procedures for determining discharge will follow those described in WAS (1993). Sample site locations will be determined by hand-held GPS unit and recorded in field log books.

During a reconnaissance of sample sites, it was noted that water in PCDD-1 at the Cranberry Museum was slowly moving to the north. This may not be typical for this site (Boyd, Personnel Communication). During sample events, the direction of flow should be recorded in field books for this site, along with all other pertinent field information like date, time, weather conditions, site name, field personnel, sample identification, and flow data.

Laboratory Procedures

The Manchester Environmental Laboratory will conduct all sample analysis. OP pesticides will be analyzed using SW846 Method 8085. This method uses capillary gas chromatography by atomic emission detector (AED). The carbamates will be analyzed using SW846 Method 8318 – modified. A methylene chloride extraction is used, with high performance liquid chromatography (HPLC). The target pesticides list, analytical methods, and quantitation limits are presented in Tables 7 - 8. Analytical methods and quantitation limits for pesticide analysis are such that comparison to previous studies can be made. For the analysis of TSS samples, EPA Method 160.2 will be used with a practical quantitation limit of 1 mg/L.

Decontamination Procedures

All samples collected for OP pesticides and carbamate analysis will be placed in organic free glass containers having teflon lined lids, with certificate of analysis. Sampler bottles used for water collection will be supplied by MEL pre-cleaned. The depth integrating sampler will be cleaned prior to the sample event and between samples in the field by washing with laboratory-grade detergent (Liqui-Nox/Aqua-Nox), rinsing with deionized water, and rinsing with pesticide-grade acetone.

Quality Control Procedures

Field Quality Control

Field quality assurance samples will include replicates (splits), duplicates, and bottle blanks. For each of the three sample events, one split sample, one bottle blank, and one duplicate will be submitted to the laboratory for OP pesticides and carbamate analysis.

One site per survey day will be selected for the split sample to estimate the total variability of the analysis (*i.e.*, field and sampling plus analytical variability).

The bottle blank will be supplied by the MEL containing organic-free water and transported throughout the survey in the sample vehicle. It will be submitted blind to the laboratory to verify the absence of target analytes from the sample containers. Bottle blank samples will be treated like all other samples and analyzed for OP pesticides and carbamates.

The TSS samples will be duplicated (*i.e.*, a second sample or measurement collected within five minutes), at one site per survey day, to estimate total variability of the analysis. Field measurements for pH and temperature will also be duplicated at one site per survey day for estimation of field variability.

Immediately following collection, samples will be placed in coolers on ice, until delivered to MEL the following day.

Lab Quality Control

The MEL will follow standard operating procedures for quality control as described in the *Quality Assurance Manual for the Washington State Department of Ecology Manchester Environmental Laboratory* (MEL, 2001). Matrix spike and matrix spike duplicate samples will be analyzed for each sample survey. These samples will be collected in separate bottles at one site and used to evaluate potential interferences from the sample matrix and estimate analytical bias and precision. A method blank will be analyzed with each sample set.

Data Review and Validation

Manchester Environmental Laboratory's standard operating procedures for data reduction, review, and reporting will meet the needs of the project. Data packages including QC results for pesticide analysis conducted by MEL will be assessed by laboratory staff using the EPA Functional Guidelines for Organic Data Review. All data generated during the project will be entered into the EIM database.

Relying on QA results from the Washington State Pesticide Management Program and a need for a high degree of confidence in pesticide data, matrix spike recoveries will be considered questionable when <75% recoveries are reported by the laboratory. Data associated with spiked recoveries between 69 and 75% will be qualified as estimates. Results will be rejected, for data associated with spiked recoveries below 69%. Affected data will be qualified as an estimate when the RPDs for duplicated pesticide analysis fall between 50 and 100%. All pesticide data associated with RPDs greater than 100% will be rejected.

Reporting

A report will be completed in December of 2002 presenting the significant findings of the study by the EA Program, in conjunction with SWRO staff. The report will include:

- 1) A map of the study area showing sampling sites and significant features
- 2) Coordinates of each sample site
- 3) Descriptions of field and laboratory methods
- 4) Discussion of data quality and the significance of any problems encountered
- 5) Results of the OP pesticides and carbamates related to recommended standards
- 6) Summary tables of the chemical and physical data
- 7) An evaluation of the significant findings and comparisons of historical data to current conditions
- 8) Complete set of chemical and physical data and the Manchester QA review as an Appendix.

Data Quality Assessment

Precision and Bias

The data from the laboratory's standard quality control procedures and replicate field samples will provide information to determine if data quality objectives have been met.

Standard protocols for data and sample collection will be followed throughout the study to limit sources of bias. Sources of bias from sampling procedures and sample handling will be minimized by adhering to EA Program routine procedures for sampling pesticides in water (Davis *et.al.*, 1997).

Results from duplicate spiked samples will be used as an estimate of analytical bias. To evaluate bias due to contamination, bottle blanks will be submitted to the laboratory and analyzed for pesticides along with other field samples. Possible sources of bias due to contamination are (MEL, 2000):

- Sample containers
- Sampling equipment
- Sample site surroundings
- Transportation or storage practices
- Other samples
- Laboratory analysis

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