DEPARTMENT OF
ECOLOGY
State of Washington

Grayland Ditch

An Evaluation of Organophosphate Pesticides and Pesticide Test Kits

February 2010
Publication No. 10-03-012

Publication and Contact Information

This report is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/1003012.html.

Data for this project are available at Ecology's Environmental Information Management (EIM) website www.ecy.wa.gov/eim/index.htm. Search User Study ID, PAND0002.

Ecology's Study Tracker Code for this study is 09-206.

For more information contact:

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: (360) 407-6764

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

Grayland Ditch

An Evaluation of Organophosphate Pesticides and Pesticide Test Kits

by
Paul D. Anderson

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

Waterbody Number: WA-24-1030

This page is purposely left blank

Table of Contents

List of Figures and Tables

Page

Figures

Tables

Abstract

During 1996, 1998, and 2002, the Washington State Department of Ecology (Ecology) sampled for pesticides in surface water draining cranberry growing areas near Grayland on the Washington coast. Ecology found concentrations of three organophosphate pesticides which failed to meet water quality criteria: azinphos-methyl (guthion), chlorpyrifos (lorsban), and diazinon.

Cranberry farmers have been implementing best management practices (BMPs) to reduce concentrations of organophosphate pesticides. This 2009 study presents an evaluation of BMP effectiveness in reducing pesticide levels during peak application periods. Three sites were sampled in both Grays Harbor County Drainage Ditch No. 1 and Pacific County Drainage Ditch No. 1. Samples were collected one week prior to pesticide application, during the week of peak application, and two weeks following application.

Although it appears some improvements have been made, concentrations of chlorpyrifos and diazinon are still not meeting water quality standards. Most of the cranberry growers in the Grayland area have been using BMPs, but there are a small number of growers that have yet to implement them. Lack of detectable concentrations of azinphos-methyl, is likely in response to the cancellation of registered uses on cranberries. Increased usage of chlorpyrifos and diazinon, due to the loss of azinphos-methyl, did not always show increases in detectable concentrations.

Two organophosphate pesticide test kits were evaluated to determine if they could be used by growers as a less expensive tool for identifying areas in need of improvement by BMPs. Neither the Abraxis nor Neogen test kit was determined to be a viable tool for identifying areas in need of BMP improvements in the context of organophosphate pesticides.

Acknowledgements

The author of this report would like to thank the following people for their contribution to this study:

- Jim Cowles and Robin Schoen-Nessa from Washington Department of Agriculture for review of this report and information on pesticide application.
- Kevin Talbot from Ocean Spray for input on site selection, design of cranberry bog drainage systems, and pesticide application timing.
- Washington State Department of Ecology staff:
  - Dave Rountry for historical perspectives, assistance with project development, and review of the project plan and this report.
  - Dale Norton for review of the project plan and this report.
  - Randy Coots for peer review of this report.
  - Tanya Roberts and Janice Sloan for field assistance.
  - Stuart Magoon, Karin Feddersen, Dean Momohara, Bob Carrell, Jeff Westerlund, and other staff at Manchester Environmental Laboratory for analysis of samples and review of results.
  - Joan LeTourneau and Cindy Cook for editing and publishing this report.

Introduction

Study Area

A major cranberry growing area in Washington State is located between Grayland (Grays Harbor County) and North Cove (Pacific County) on the Washington Coast. Grays Harbor County and Pacific County each manage a ditch system, collectively known as Grayland Ditch, that drains these cranberry growing areas and residential properties. Precipitation runoff from woodland areas east and upslope of the cranberry bogs also feeds into the ditches. These ditches originate near the Grays Harbor/Pacific County line, west of Highway 105 (Figure 1).

Grays Harbor County Drainage Ditch No. 1 (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 of Grays Harbor. Pacific County Drainage Ditch No. 1 (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 locations of GHCDD-1 and PCDD-1.

Background

In Washington State, drainage ditches like GHCDD-1 and PCDD-1 are designated as surface waters of the state. As surface water, state water quality standards apply (Chapter 173-201A WAC). Washington State water quality standards are the basis for protecting and regulating the quality of surface waters. 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 – such as for drinking, recreation, aquatic habitat, or industrial use – are impaired by pollutants. Washington State Department of Ecology's (Ecology's) assessment of waters to be placed on the 303(d) list is guided by federal laws, state water quality standards, and state policy.

In 1994 and 1995, Ecology identified several pesticides that were frequently detected at concentrations not meeting (exceeding) Washington State or federal water quality standards in GHCDD-1 and PCDD-1 (Davis et al., 1997). The resulting 303(d) listings include chlorpyrifos, diazinon, as well as DDT and its metabolites (4,4'-DDD, 4,4'-DDE).[1]

Azinphos-methyl was found above federal water quality criteria, but there is not a corresponding state water quality criterion. As a result, azinphos-methyl was not put on the Washington State 303(d) list. However, due to the number of detections above the federal National Recommended Water Quality Criteria (NRWQC), azinphos-methyl was still considered a chemical in need of further investigation.

Local cranberry growers responded to these listings by sponsoring research and development of best management practices (BMPs) for their growing operations. Use of BMPs to reduce pesticide levels in GHCDD-1 and PCDD-1 began in 1994 (Pacific Conservation District and the Pacific Coast Cranberry Research Foundation, 1999).

[1] DDT was banned from use in the United States in 1972 and is considered a legacy pesticide.

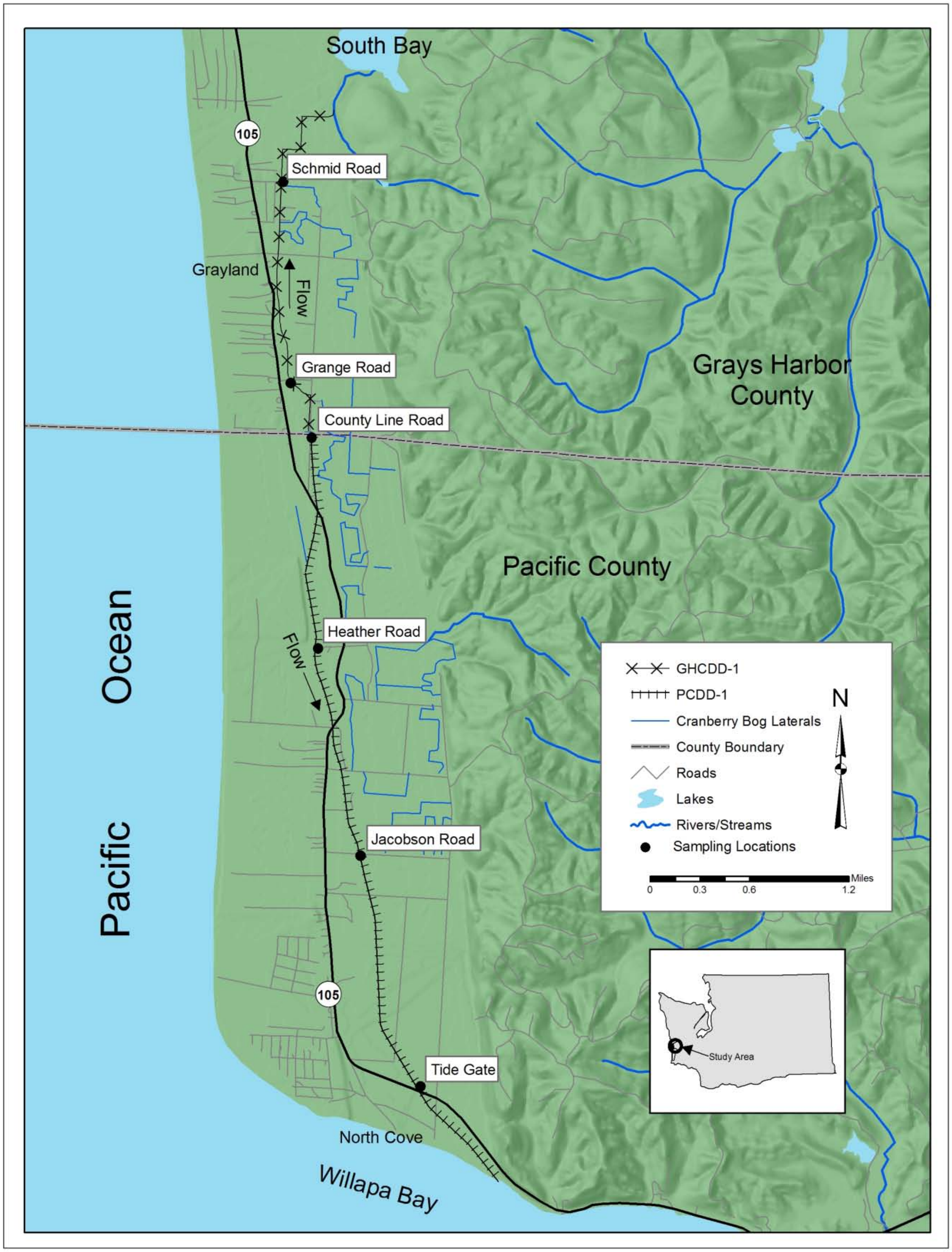

Figure 1. Area map and sampling locations for Grays Harbor and Pacific County Drainage Ditches.

A 1996 study conducted by Ocean Spray (Frantz et al., 1997) investigated the effectiveness of several different BMPs for use in the Grayland area cranberry bogs using rubidium chloride (RbCl) as a surrogate for pesticides. The study was able to show that lining (cribbing) and covering of ditches within and bordering cranberry bogs was the most effective BMP. Cribbing and covering reduced the interior and perimeter ditch concentrations of RbCl to non-detection levels at the study's detection limit of 100 µg/L.

At the time of the BMP effectiveness study, approximately one-half of the growers were implementing BMPs. By 2000, approximately 95% of the Grayland area cranberry growers were using at least one BMP for reducing pesticide pollution (Rountry, 2008).

To track the progress of the implemented BMPs, Ecology conducted studies to evaluate the reduction in pesticide concentrations (Anderson and Davis, 2000; Coots, 2003). Results of the studies showed that there were reductions in pesticide levels present in the ditches. However, the concentrations of pesticides continued to exceed water quality standards.

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, Pacific and Grays Harbor Conservation Districts, and other organizations have provided growers with technical assistance and grants.

Test Kit Evaluation

Laboratory testing for organophosphate (OP) pesticides is expensive and requires interpretation by trained staff. Relatively cheap test kits are now available for quick determination of OP and carbamate pesticide presence. While these test kits do not indicate the exact concentration of pesticides present, they do indicate if a pesticide is present above a certain threshold. The kits may be useful as a monitoring tool for cranberry growers. However, their effectiveness has not been tested in the cranberry ditch systems. If effective, these kits may provide growers with increased knowledge of BMP effectiveness without costly laboratory analyses.

Study Objectives

Results from this study are intended to:

- Assess current concentrations of azinphos-methyl, chlorpyrifos, and diazinon in the waters of GHCDD-1 and PCDD-1. Data will be compared to available Washington State water quality standards and NRWQC for the protection of aquatic life. While DDT and its metabolites are on the 303(d) list, management of the three chemicals listed above provide the greatest opportunity for water quality improvement. This improvement can be achieved by focusing on how pesticides are currently used.

- Evaluate the effectiveness of implemented BMPs by comparing current pesticide concentrations to data collected in previous studies.
    - Provide a qualitative measure of the general effectiveness of the BMPs currently in use.
    - Provide a comparison with previous studies on changes in pesticide concentrations.
    - Inform growers about the value of BMPs and suggest areas that need implementation or improvement to BMPs.

- Evaluate OP pesticide test kits to determine if they will be useful as a monitoring tool for the cranberry growers. If practical, growers can rapidly identify areas in need of BMP improvements for OP pesticides.

Methods

Sampling Design

During 2009, samples were collected at three locations in each of the GHCDD-1 and PCDD-1 systems during three separate events. Location selection corresponded to sites sampled in previous studies. Use of historic sampling locations ensured comparability with these earlier results.

Temperature, pH, and conductivity were measured in surface water. Organophosphate pesticides and total suspended solids (TSS) samples were collected for laboratory analysis. At times relationships can be identified between costly organic analyses and inexpensive conventional analytes such as TSS.

The timing of the sampling focused on the most intensive application of pesticides in the cranberry bogs. Due to the many factors that influence the start of pesticide application, the schedule of the sampling events was not determined until shortly before the application period. Frequent communication with a cranberry grower representative ensured accurate timing of sample collection. As in typical years, pesticides were applied in 2009 immediately after removal of honey bees, used for pollination. Intensive application of pesticides occurred during the middle of July.

To help in evaluating pesticide impacts and concentrations, 2009 samples were collected before, during, and after the intensive application period. The first sampling event occurred on July 8, five days before the onset of pesticide application. A second set of samples was collected on July 13, during the peak of pesticide application. The third set of samples was collected on July 27, approximately two weeks after the start of pesticide application. It was assumed that the majority of pesticide application had already occurred before the third and final sample collection.

Test Kits

In addition to collecting water samples for analysis by Manchester Environmental Laboratory (MEL), OP pesticide test kits were used to evaluate comparability with pesticides detected using laboratory methods. Quantitative results were not used for comparison because the test kits only produce presence/absence results.

The OP pesticide test kits used in this evaluation can detect organophosphate and carbamate pesticides by using the mode of action of these types of chemicals. In this case, the mode of action is the blocking of the brain chemical acetylcholinesterase. The tests use a change in color to show the presence of acetylcholinesterase-blocking chemicals. As with most chemical tests, there is a minimum amount of chemical that can be detected. A detailed description of how the test kits work can be found in Appendix C.

Two OP pesticide test kits were used side by side to compare their performance (Table 1). The basis for test kit selection included cost and usability in the field. During the design phase of this study, three OP pesticide test kits were selected from a small number available. Unfortunately, while finalizing study plans and ordering supplies, one of the three test kits was taken out of production. While other OP pesticide test kits existed to replace the third kit, insufficient time to select, order, and receive a replacement before the application season began resulted in the use of two instead of three kits.

Table 1. Organophosphate pesticide test kits.

Name of Test Kit	Manufacturer
Organophosphate/Carbamate Assay Kit	Abraxis
Agri-Screen Ticket®	Neogen

Sampling Sites

Sampling locations are shown in Figure 1 and are described in Appendix B, Table B-1. GHCDD-1 samples were collected from bridges on Schmid Road, Grange Road, and County Line Road. PCDD-1 samples were collected from bridges on Heather Road and Jacobson Road and from the bank at the tidegate on State Highway 105.

Field Procedures

Field measurements of temperature, pH, and conductivity were performed according to Ecology Standard Operating Procedures (SOP) (Nipp, 2006; Swanson, 2007; Ward, 2007a, 2007b). All field parameters were measured at the sampling site by field staff using a Hydrolab® MiniSonde® multiprobe.

All surface water samples were collected by hand-compositing grab samples from quarter-point transects using a pole sampler. Surface water sampling techniques were consistent with Ecology SOPs described in EAP003 *Sampling of Pesticides in Surface Waters* (Anderson, 2006) and EAP015 *Manually Obtaining Surface Water Samples* (Joy, 2006).

Test Kit Procedures

Sample water intended for analysis with OP pesticide test kits was collected as a sequential replicate with the samples for laboratory analysis. Collection of the water used for analysis by the OP pesticide test kits was consistent with the SOPs referenced in the previous section. Samples were held in coolers, on ice, until sampling operations were completed at the final site of the day.

The study was originally designed to have the OP pesticide test kits used at each site after samples were collected for laboratory analysis. During the first sampling event, test kits were used at several locations to assess usability for future sampling operations.

- It was determined that the Abraxis OP pesticide test kit would not be suitable for use at each site. This was due to each test taking about 60 minutes to complete. However, the kit was found to have the ability to run multiple tests simultaneously. The ability to run multiple tests made it possible for the test kit to be used at the end of the day after all sampling had been completed.
- Testing of the Neogen OP pesticide test kit showed that use at each site would be possible as was originally intended. The test kit only required a small amount of time, but running more than one test simultaneously was not practical.

Use of the OP pesticide test kits in the field best represented how the kits would be used by cranberry growers, if found to be practical tools. Samples were analyzed using the manufacturer's instructions included with each test kit. The result from each kit was recorded in a field notebook. Each kit was given a dedicated page to ensure that test results were correctly recorded. Notes on performance were recorded with each test during the first use of each kit.

Performance criteria included:

- Pre-analysis set-up time.
- Ease of use, particularly 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.
- Additional equipment needed.
- Cost.
- Sensitivity.

Detailed information on each test kit can be found in Appendix C.

Laboratory Procedures

MEL performed all laboratory analyses for the study according to current standard operating procedures. Table 2 shows each analyte and its required reporting limit, sample preparation method, and analysis method.

Table 2. Analytes, reporting limits, sample preparation methods, and analysis methods analyzed by Manchester Environmental Laboratory.

Analyte	Reporting Limits	Sample Preparation Method	Analysis Method
Organophosphate pesticides	0.01-1.0 µg/L	EPA 3535*	EPA 8270*
Total suspended solids	1 mg/L	N/A	SM 2540D*

*References: APHA, 2005 (SM); EPA, 1998; EPA, 2004.
EPA – U.S. Environmental Protection Agency.
N/A – not applicable.
SM – Standard Methods.

Data Quality Assessment

Quality assurance/quality control (QA/QC) results can be found in Appendix D.

Field Measurements

Two measures of quality were used to assess conventional parameter results collected using field meters.

1. Sequential replicate measurements were performed using the same field meter. Replication of field measurements assesses meter and environmental variability.
2. Meter calibration and post field checks were recorded. This information evaluates acceptability of field meter measurements.

Sequential field meter replicates were performed by taking a second set of measurements immediately following the first. All field meter replicates agreed within ±5% relative percent difference (RPD).

Field meter calibration was performed at the beginning of each sampling day, and post-checks were performed at the end of each sampling day. Calibrations and post-checks used commercially available pH and conductivity standards to evaluate performance. Differences between calibration and post-check values were small and well within acceptance criteria data quality objectives.

The data quality assessment indicated field meter data met measurement quality objectives outlined in the QA Project Plan (Anderson, 2009).

Laboratory

Results from MEL included case narratives describing QA/QC procedures used during analysis. These QA/QC results included holding times, instrument calibrations, method blanks, matrix spikes, laboratory duplicates, laboratory control samples, and surrogate spikes. Case narratives describing the quality of the data are available upon request.

No difficulties were encountered in the analysis of water samples, and all QC analyses were within established acceptance limits.

Qualification of Results

Data collected for this project are considered usable, with qualification, as reported. Data qualifiers give an indication of the degree of confidence that can be placed in the reported results. The absence of a data qualifier means the reported concentration was above the practical quantitation limit, and no analytical factors are present which may influence data use. The highest degree of confidence can be placed in unqualified results.

Data with a ‘J’ qualifier are defined as: the analyte is positively identified but the associated numerical result is an estimate (MEL, 2008). The use of ‘J’ qualified data in regulatory decision-making is acceptable with proper consideration of analytical confidence (EPA, 1991). Embrey and Frans (2003), of the United States Geological Survey, used estimated values for comparison to aquatic life standards.

‘NJ’ qualified data are defined as: the analysis indicates the presence of an analyte that has been “tentatively identified,” and the associated numerical value represents its approximate concentration (MEL, 2008). Designation of a result with an ‘NJ’ qualifier normally occurs when there is not an exact match in chemical signature. Data that are ‘NJ’ qualified are assigned a lower degree of confidence and are not treated as detections. EPA does not support the use of ‘NJ’ qualified data in regulatory decision-making (EPA, 1991 and 1994).

All data, including non-detects, are used in summary tables. When a result is considered a non-detect, half the detection limit was used in calculating means.

Water Samples

Split field replicates for laboratory analyses were used to provide an estimate of sampling and laboratory variability for the study. All split replicates agreed within ±15% RPD.

Transfer blanks were analyzed to evaluate the potential for contamination. Transfer blanks were prepared using blank water supplied by MEL. Laboratory water was transferred from its container to a new sample container. No target analytes were detected in transfer blanks.

The data quality assessment indicated results reported for analysis of water met measurement quality objectives outlined by the QA Project Plan (Anderson, 2009).

Test Kits

Two measures were used to assess the quality of data from the OP pesticide test kits.

1. Split replicates were analyzed to assess test kit variability.
2. Positive and negative control samples were used to assess the accuracy of test kit results (Abraxis only).

Split replicates were prepared by running two separate tests using water from the same grab sample. Replicates were performed on both the Abraxis and Neogen OP pesticide test kits. Results for the split replicates agreed for all tests.

Positive and negative control samples were analyzed with the Abraxis test kit. All control samples achieved expected results. No positive or negative control samples were provided with the Neogen test kit.

The measures used to assess the quality of data from the OP pesticide test kits showed that results from the kits are reliable for the conditions encountered during this study.

Results

Conventional Parameters

Results for conventional analysis of surface water samples are presented in Table 3.

Table 3. Conventional parameter results for water samples collected in Grays Harbor and Pacific County Drainage Ditches.

Site	Date	pH (s.u.)	Temperature (°C)	Conductivity (µmhos/cm)	TSS (mg/L)
GHCDD-1					
County Line Road	7/8/2009	6.6	13.4	195	8
	7/13/2009	6.6	12.8	182	10
	7/27/2009	6.7	18.2	331	7
Grange Road	7/8/2009	6.7	13.2	216	7
	7/13/2009	6.7	12.8	215	7
	7/27/2009	6.5	14.1	274	12
Schmid Road	7/8/2009	6.6	13.5	222	8
	7/13/2009	6.7	12.8	206	8
	7/27/2009	6.5	14.0	219	4
PCDD-1					
Heather Road	7/8/2009	6.4	13.9	167	12
	7/13/2009	6.4	13.6	152	8
	7/27/2009	6.4	15.9	154	8
Jacobson Road	7/8/2009	6.5	13.9	195	7
	7/13/2009	6.5	13.5	173	7
	7/27/2009	6.5	16.1	210	7
Tide Gate	7/8/2009	6.6	14.2	250	6
	7/13/2009	6.6	13.6	226	7
	7/27/2009	6.6	16.6	247	8

TSS – Total Suspended Solids.

Little variability was seen in pH measurements over the three sampling events. Temperature measurements in GHCDD-1 ranged from 12.8 to 18.2 ºC, and in PCDD-1 ranged from 13.5 to 16.6 ºC. The highest temperatures were recorded during the third (post-application) sampling event. Conductivity in GHCDD-1 ranged from 183 to 331 µmhos/cm, and in PCDD-1 ranged from 152 to 250 µmhos/cm. Total suspended solids in GHCDD-1 ranged from 4 to 12 mg/L, and in PCDD-1 ranged from 6 to 12 mg/L.

Organophosphate Pesticides

Results for OP pesticides are presented in Table 4. Out of the 24 OP pesticides analyzed, chlorpyrifos and diazinon were the only ones present in detectable quantities during the three sampling events. Chlorpyrifos and diazinon were detected in 78% of samples. Azinphos-methyl was not detected: the reporting limit is presented.

Table 4. Laboratory results for selected organophosphate pesticides in Grays Harbor and Pacific County Drainage Ditches (µg/L).

Site	Date	Azinphos-methyl	Chlorpyrifos	Diazinon
GHCDD-1				
County Line Road	7/8/2009	0.034 U	0.22	0.034 U
	7/13/2009	0.035 U	0.16	0.055
	7/27/2009	0.035 U	0.1	0.032 NJ
Grange Road	7/8/2009	0.034 U	0.21	0.034 U
	7/13/2009	0.034 U	0.13	0.050
	7/27/2009	0.033 U	0.089	0.094
Schmid Road	7/8/2009	0.034 U	0.13	0.034 U
	7/13/2009	0.035 U	0.082	2.2
	7/27/2009	0.034 U	0.051	0.058
PCDD-1				
Heather Road	7/8/2009	0.034 U	0.034 U	0.12
	7/13/2009	0.036 U	0.022 NJ	0.36
	7/27/2009	0.035 U	0.052	0.089
Jacobson Road	7/8/2009	0.035 U	0.041 NJ	0.096
	7/13/2009	0.033 U	0.035	0.42
	7/27/2009	0.034 U	0.082	0.099
Tide Gate	7/8/2009	0.034 U	0.035 NJ	0.099
	7/13/2009	0.034 U	0.027 J	0.22
	7/27/2009	0.034 U	0.18	0.085

U – The analyte was not detected at or above the reported sample quantitation limit.
NJ – The analyte has been tentatively identified, and the associated numerical value represents an approximate concentration.
J – The analyte was positively identified. The associated numerical result is an estimate.

In GHCDD-1, chlorpyrifos detections ranged from 0.051 to 0.22 µg/L and diazinon ranged from 0.034 to 2.2 µg/L. Detections of chlorpyrifos and diazinon in PCDD-1 ranged from 0.027 to 0.18 µg /L and 0.085 to 0.42 µg/L, respectively.

Chlorpyrifos detections in GHCDD-1 were consistently reported at higher concentrations than in PCDD-1. Chlorpyrifos was detected in GHCDD-1 in 100% of samples and decreased in concentration over the three sampling events. This decrease shows that application of chlorpyrifos is occurring prior to the first sampling event. For each of the three sampling events, concentrations of chlorpyrifos decreased from upstream to downstream. During the peak application sampling on 7/27/2009, chlorpyrifos concentrations in PCDD-1 increased from upstream to downstream and from peak-application to post-application sampling. The data overall show a considerable amount of pesticide application occurs prior to the peak period.

Diazinon was consistently detected at higher concentrations in PCDD-1 than in GHCDD-1, with the exception of the high concentration reported for Schmid Road on 7/13/2009 in GHCDD-1. Detections of diazinon in GHCDD-1 have no discernable pattern. In PCDD-1, diazinon was detected in 100% of samples and had the highest concentrations during peak application sampling. The detection pattern of diazinon seen in PCDD-1 is typical of what would be expected from this sampling design.

This page is purposely left blank

Discussion

Comparison to Water Quality Standards

Conventional Parameters

Washington State water quality standards for conventional water quality parameters are set forth in Chapter 173-201A of the WAC. Waterbodies are required to meet water quality standards based on the designated uses of the waterbody. When designated uses are not specified for a particular waterbody, then default designated uses are used to identify appropriate water quality criteria. GHCDD-1 and PCDD-1 do not have specified designated uses, so the default becomes (1) salmonid spawning, rearing, and migration, and (2) primary contact recreation. However, there is no documented use by, or presence of, any salmon species in Grayland Ditch (WDFW, 2010). The numeric pH criteria for the above designated uses should be within the range of 6.5 to 8.5, with a human-caused variation of less than 0.5 units.

Grab pH results were compared to water quality standards. At Heather Road, there were three excursions from the pH standard. The three results were 6.4 standard units (s.u.). While the pH results at Heather Road violate the water quality standard, the results are within the accuracy range of ±0.2 s.u. for the meter used to collect the measurement. In addition, all of the other pH results are at or near the lower end of the range of the water quality standard. Water in GHCDD-1 and PCDD-1 primarily comes from wetlands and bog drainage which are typically acidic (Mitsch and Gosselink, 2007). With pH results from all sampling sites in a similar range and water in GHCDD-1 and PCDD-1 coming from wetlands and bogs, it is likely that the data represent natural conditions. Therefore, GHCDD-1 and PCDD-1 should not be placed on the federal Clean Water Act Section 303(d) list for pH.

Organophosphate Pesticides

Water quality criteria for azinphos-methyl, chlorpyrifos, and diazinon were taken from Washington State water quality standards (Chapter 173-201A, WAC) and EPA's NRWQC (EPA, 2006). Available water quality criteria are presented in Table 5.

Table 5. 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.

Of the 14 detections of chlorpyrifos, 12 (86%) were above one of the available water quality criteria. The majority of detections were above both the state and federal chronic water quality criteria (Table 5). All of the detections of chlorpyrifos in GHCDD-1 were above the acute or chronic state and federal water quality criteria (Figure 2). In contrast, three detections of chlorpyrifos in PCDD-1 were above acute or chronic water quality criteria, and occurred during the last sampling event.

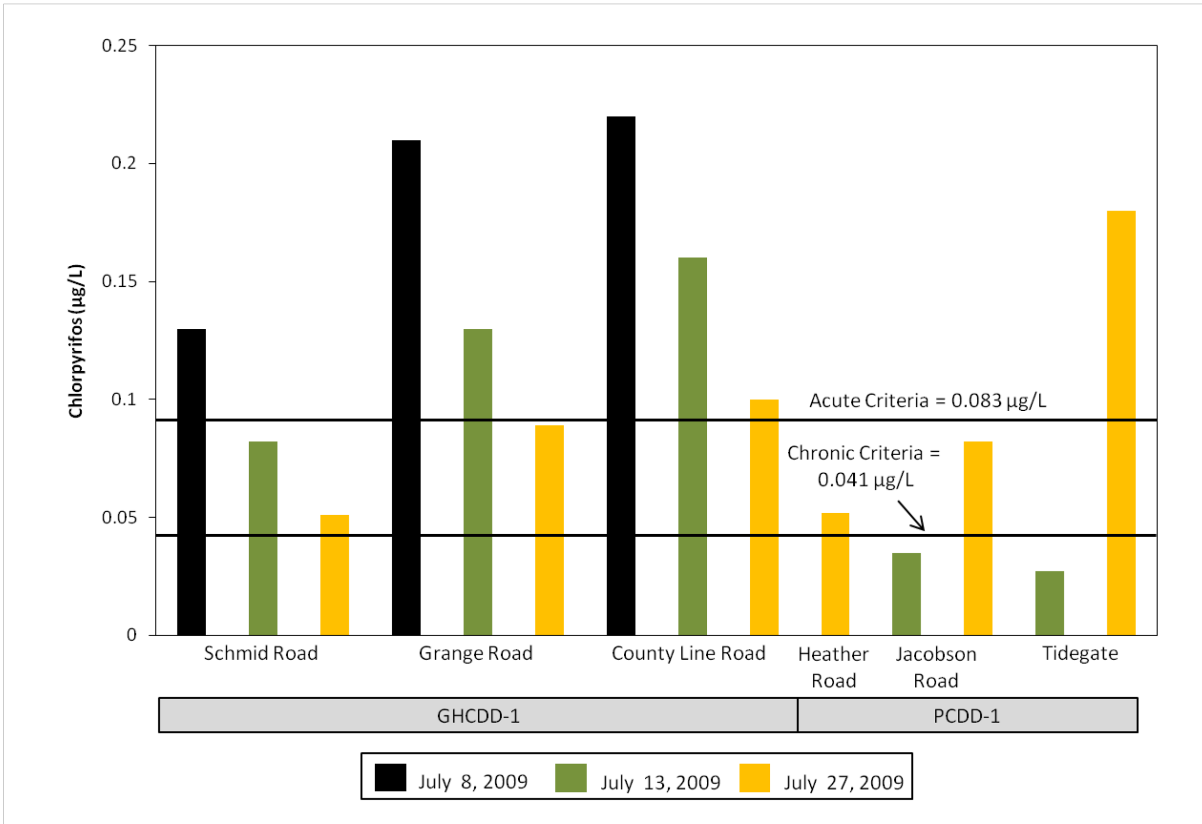

Figure 2. Detections of chlorpyrifos with acute and chronic water quality criteria for Grays Harbor and Pacific County Drainage Ditches.

Four of 14 detections (36%) of diazinon were above the federal NRWQC of 0.17 µg/L (Figure 3). Three of the four criteria exceedances occurred in PCDD-1. In GHCDD-1, one diazinon outlier exceeded NRWQC by approximately 13 times.

Chlorpyrifos and diazinon exceedances of state and federal water quality standards show that aquatic life are not being adequately protected in GHCDD-1 and PCDD-1. As a result, GHCDD-1 and PCDD-1 should continue to be on the federal Clean Water Act Section 303(d) list for exceedances of chlorpyrifos and diazinon.

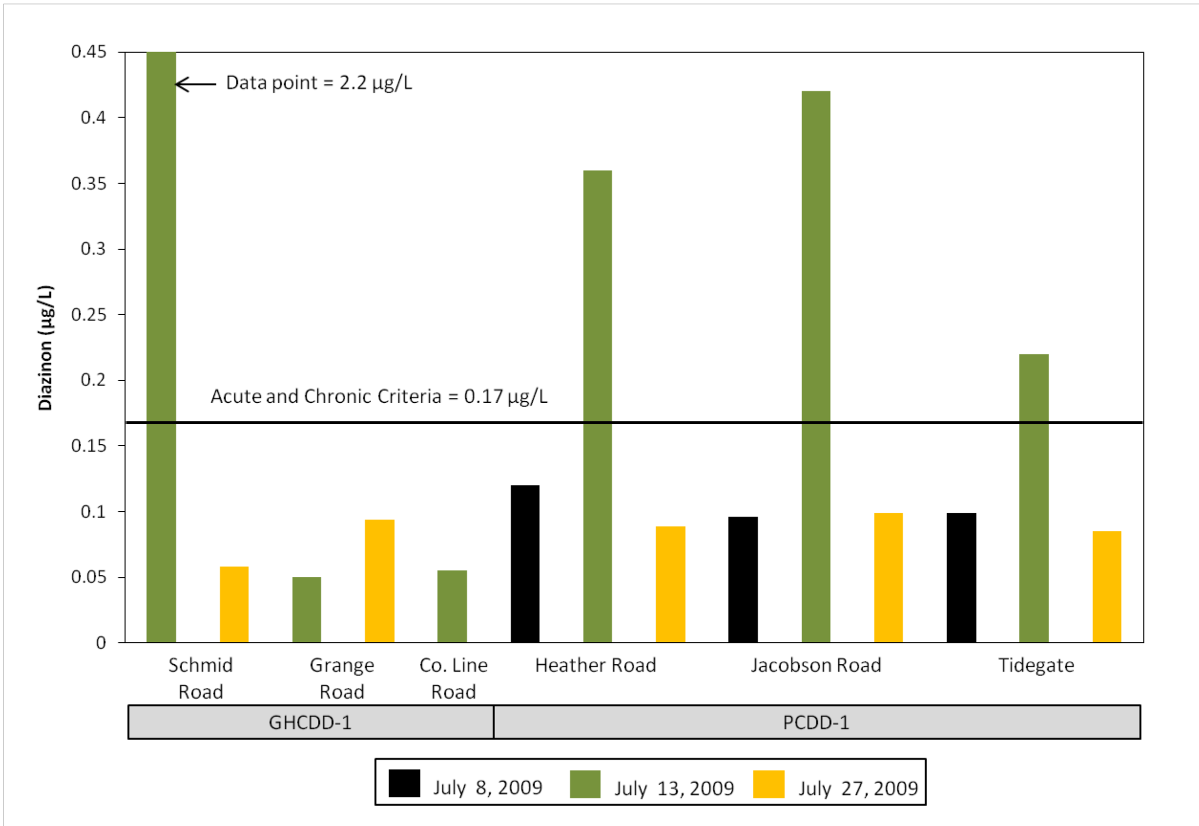

Figure 3. Diazinon detections shown with recommended acute and chronic water quality criteria for Grays Harbor and Pacific County Drainage Ditches.

To be placed on the state's 303(d) list, a pesticide must have a state water quality standard. Washington State does not have water quality criteria for diazinon. EPA, in its review of the 303(d) list, has the authority to require listings based upon federal water quality criteria if sufficient data are available. The decision to place diazinon on the 1998 303(d) list was made by EPA based on available data and federal recommended water quality criteria. Since 1998, updates have been made to the NRWQC. These updated recommended acute and chronic water quality criteria were used in this study and are listed in Table 5. The 2012 303(d) assessment should use the current recommended water quality criteria of 0.17 µg/L.

Comparison to Historical Data

Limitations

Data for the three target pesticides, azinphos-methyl, chlorpyrifos, and diazinon, from this 2009 study were compared to data from a 1996 study by Davis et al. (1997), a 1998 study by Anderson and Davis (2000), and a 2002 study by Coots (2003). When the three past studies were reviewed for comparison to this 2009 study, some issues were identified. There are differences in sites, timing of sample collection, total number of samples, and years between studies that make comparison complicated.

In general, the timing of pesticide application in cranberry bogs is based on initiators like degree days and the removal of the bees used for pollination. Ultimately, each individual cranberry grower decides when, what, and how much pesticide to apply. This is illustrated by the widely varying detection patterns seen in the 2009 data. Making a comparison between studies with different pesticide application patterns and sampling regimes can be problematic and make specific conclusions questionable. While specific conclusions can be uncertain, larger scale questions can be answered with a high degree of confidence.

An issue in the 1998 study by Anderson and Davis (2000) revealed in the 2002 study by Coots (2003) further complicated the comparison of data among all four studies. Concentrations of the three target pesticides from the 1998 study increased over the sampling period. The post-application samples were collected four days after the peak application samples. This likely did not allow enough time for peak pesticide loads to pass through the ditch system. The 1996 study by Davis et al. (1997) estimated that concentrations of OP pesticides in the ditches can take from one to two weeks to return to baseline levels.

A table summarizing all data common to past studies and this 2009 study can be found in Appendix E, Table E-1.

Table 6 presents summarized results from Ecology studies conducted between 1996 and 2009. Sampling locations at Schmid Road and Larkin Road were common to all studies with one exception: Larkin Road was not sampled in this 2009 study. Ideally, the same sampling location would be used to make a temporal comparison. In this situation, the two sampling locations used for comparison in PCDD-1 are located approximately 0.3 miles apart. There are approximately 42.5 acres of cranberry bogs between the Larkin Road and tidegate sites. Based on the small differences in concentrations between the sites in the 2002 study (Coots, 2003), the difference between the sites is not expected to have a large impact on the comparison.

Analysis

Azinphos-methyl was routinely detected in samples from both Schmid and Larkin Roads throughout the 1996, 1998, and 2002 studies. Many of the detections, and all of the means, from the three previous studies were above the EPA water quality criteria of 0.01 µg/L. There were no detections of azinphos-methyl in this 2009 study, suggesting significant improvement when compared to the other studies. Below the level of detection, results of azinphos-methyl in Grayland Ditch are likely due to the cancelation of registration for use on cranberries that was effective September 30, 2006 (Federal Register, 2006a; 2006b) rather than BMP implementation.

At Schmid Road, the 1996 and 2002 studies showed chlorpyrifos concentrations were low and did not exceed water quality criteria. The 1998 and 2009 studies routinely detected chlorpyrifos. Many of the detections in 1998, and all of the detections in 2009, exceeded water quality criteria. There does not seem to be an overall trend for chlorpyrifos detections at Schmid Road. However, there was an 11-fold increase in the mean concentration of chlorpyrifos from the 2002 study to the 2009 study.

Table 6. Comparison of azinphos-methyl, chlorpyrifos, and diazinon detected in Grays Harbor and Pacific County Drainage Ditches from 1996-2009 (µg/L).

Location		1996	1998	2002	2009
		Davis et al, 1997	Anderson and Davis, 2000	Coots, 2003	Current Study
GHCDD-1 at Schmid Road					
Azinphos-methyl	number	26	5	3	3
	detections	16	3	2	0
	mean	0.13	0.25	0.11	nd
	range	0.010-0.73	0.004-1.2	0.033-0.20	nd
Chlorpyrifos	number	26	5	3	3
	detections	7	5	2	3
	mean	0.021	0.38	0.008	0.09
	range	0.003-0.016	0.0095-1.8	0.0050-0.010	0.051-0.13
Diazinon	number	26	5	3	3
	detections	26	5	3	2
	mean	0.86	1.1	0.17	0.76
	range	0.026-5.42	0.033-4.4	0.018-0.35	0.034-2.2
PCDD-1 at Larkin Road[1]					
Azinphos-methyl	number	26	5	3	3
	detections	23	5	3	0
	mean	0.17	0.33	0.050	nd
	range	0.006-0.74	0.012-1.4	0.0061-0.13	nd
Chlorpyrifos	number	26	5	3	3
	detections	25	5	3	2
	mean	0.44	0.59	0.028	0.08
	range	0.003-3.7	0.019-1.3	0.015-0.036	0.027-0.18
Diazinon	number	26	5	3	3
	detections	25	5	3	3
	mean	0.28	2.4	0.48	0.13
	range	0.008-1.7	0.033-7.0	0.20-0.64	0.085-0.22

[1]2009 samples were collected approximately 0.3 miles downstream of Larkin at the tidegate on Highway 105.
nd = no data.

At Larkin Road, chlorpyrifos was frequently detected in the 1996 and 1998 studies, and many of the detections exceeded water quality criteria. In the 2002 and 2009 studies, there were several detections, but only one detection exceeded water quality criteria. Even with the decrease in the number of detections exceeding water quality criteria, there was a 3-fold increase in the mean chlorpyrifos concentration between the 2002 and 2009 studies.

Over the four studies, the frequency of diazinon detections has decreased at Schmid Road. The magnitude of detections improved over the 1996 to 2002 studies but increased with the 2009 study. The maximum detection in 2009 was 6 times greater than the maximum detection in 2002. Even with the decreased frequency of detections, there were still detections that exceeded EPA's NRWQC. The results for diazinon at Larkin Road were mixed but do show a decrease in magnitude over the four studies. However, there was still a 100% frequency of detection of diazinon across all four studies.

Summary

Diazinon results showed more improvement than chlorpyrifos, but a problem still exists. There were a number of detections that exceeded water quality criteria in this 2009 study. Of most concern was the detection at Schmid Road that was 13 times the recommended water quality criteria. In light of the concentrations as well as the rate of detection of diazinon, more BMP implementation is needed in both GHCDD-1 and PCDD-1.

The increase in chlorpyrifos concentrations and the continued 100% detection rate of diazinon likely can be explained by the cancellation of registered uses of azinphos-methyl on cranberries. With growers no longer being able to apply azinphos-methyl, most likely there is increased usage of diazinon and possibly chlorpyrifos (Kevin Talbot, personal communication, 2010). The resulting change in pesticide-use practices is one explanation for the differences in the timing and levels of the pesticides detected in GHCDD-1 and PCDD-1. Even with the detection rate of diazinon, the detected concentrations indicate that progress has been made at reducing diazinon concentrations.

Analysis of the data shows that while progress has been made at mitigating concentrations of azinphos-methyl, chlorpyrifos, and diazinon in Grayland Ditch, additional improvements are needed. With BMPs not being implemented at all cranberry farms, it will be impossible to meet water quality standards in GHCDD-1 and PCDD-1.

WSDA Response

Chlorpyrifos and diazinon have been continually detected above state water quality standards and federal NRWQC over the last 14 years. This requires that the Washington State Department of Agriculture (WSDA) follow guidance described in the *Washington State Pesticide Management Strategy for Water Quality Protection* (Cook and Cowles, 2009). WSDA is the State Lead Agency for pesticide registration in Washington as delegated by EPA under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).

As a State Lead Agency, WSDA reviews pesticides that occur in surface and groundwater at concentrations that approach or exceed human health or ecological reference points. If the pesticide(s) are determined to pose a risk to surface water and/or groundwater quality, management measures are required to be developed and implemented. A response matrix detailing WSDA's approach to assessing pesticide detections in surface and groundwater is provided in Appendix One of the *Washington State Pesticide Management Strategy for Water Quality Protection* (Cook and Cowles, 2009).

For the cranberry growing area of Grayland, response levels 1 and 2 of the response matrix have already been covered. This places the response at level 3 which may result in implementation of mandatory BMPs. As is stated in Bicki et al. (2003), ditch lining and covering BMPs are effective when implemented.

Under the *Washington State Pesticide Management Strategy for Water Quality Protection*, WSDA will coordinate with Ecology and, if needed, Washington State Department of Health to implement the management strategies.

Evaluation of Organophosphate Pesticide Test Kits

Performance Analysis

Each of the two OP pesticide test kits was assessed using nine performance criteria. Table 7 summarizes the performance criteria.

Table 7. Summary of assessment criteria for the organophosphate pesticide Abraxis and Neogen test kits.

Performance Criteria	Test Kit	
	Abraxis	Neogen
Pre-analysis set-up time	10-15 minutes	1-2 minutes
Ease of use	Directions are easy to follow. Large number of steps that require exact volumes. Not for someone unfamiliar with laboratory procedures.	Directions slightly confusing. Little to no laboratory or chemical knowledge needed.
Time to complete each test	Approximately 60 minutes	>20 minutes
Ease of result interpretation	Obvious change in color but result could easily be subject to differences in color interpretation.	Result is obvious. Little room for misinterpretation.
Accuracy	Passed control tests	No control samples available. All replicate sample results matched.
Number of tests per kit	96	Packages of 25 and 50.
Additional equipment needed	yes	no
Cost*	$225	$200
Limit of detection	Lowest detection limit = 0.3 µg/L. Able to detect pesticides close to target concentrations.	Lowest detection limit = 300 µg/L. Not able to detect pesticides at target concentrations.

*The amount shown does not include the cost for additional equipment needed to run each test.

The Abraxis and Neogen OP pesticide test kits performed well, but each had limitations and drawbacks. Both kits were comparable in price, ease of operation, and interpretation of results. The instructions that accompanied each test kit were complete and easy to follow. However, the Abraxis kit instructions required a familiarity with laboratory techniques to complete the test. Each test kit used a color change to indicate the presence of acetylcholinesterase-blocking pesticides. Results from the Abraxis kit were easy to interpret but left room for user error when not using a colorimeter. Color changes in the Neogen kit were obvious and left no room for interpretation error by the user.

The largest differences between the two test kits included: time to complete each test, the need to purchase additional equipment, availability of control samples, and limit of detection. Each Abraxis test took more than 60 minutes to complete, although it has the capability of running multiple tests simultaneously. The Neogen test took less than 20 minutes. The Abraxis test kit comes only with the reagents needed to run the test, requiring additional purchases. The Neogen test kit has an option to buy a starter kit that has all needed equipment to run the tests**.**

In terms of quality assurance, one major difference is the lack of available control samples in the Neogen test kit. The Abraxis test kit contains both positive and negative control samples. These samples allow the person running the tests to account for the rate of false positives and negatives.

A second major difference is in the limits of detection of the two test kits. The Abraxis kit detection limits for OP pesticides range from 0.3 for to 40 µg/L, while the Neogen kit detection limits range from 300 to 20,000 µg/L.

Comparison to Laboratory Analyzed Data

Overview

The initial examination and set-up, prior to field use, of the Abraxis and Neogen OP pesticide test kits identified several differences. These differences showed that the Neogen kit had the potential to be an ideal tool for cranberry farmers to use in identifying areas in need of BMP improvement. The Abraxis kit also had the potential to be a very useful tool, but would require a large amount of time and a familiarity with laboratory procedures and equipment. Further comparison of the two test kits showed that the Abraxis kit was more sensitive than the Neogen kit, illustrated by the large differences in detection limits (Appendix C, Tables C-1 and C-2).

The OP pesticide test kits work on an additive basis. This means that any chemicals that can be detected by the kit are measured together and show a positive result at the lowest detection limit for the kit. Unlike the test kits, MEL can identify specific chemicals and has a detection limit at or below environmentally relevant concentrations.

Abraxis and Neogen OP pesticide test kit results and summed OP pesticide laboratory results are shown in Table 8. During the pre-spray sampling event on July 8, the Abraxis kit was used only at the Schmid Road and Tidegate sites. This was due to the length of time needed to use the Abraxis kit.

Analysis

When comparing MEL results to the Abraxis test kit results, all available results show a detection with the exception of the pre-spray (7/8/2009) sampling at Schmid Road and the peak application (7/13/2009) sampling at Grange Road. At these sites, MEL shows detection while the Abraxis test kit does not. None of the Neogen test results match the MEL results.

Table 8. Comparison of organophosphate pesticide results for Abraxis and Neogen test kits to summed laboratory results from samples collected in Grays Harbor and Pacific County Drainage Ditches.

Site	Date	Test Kit		Sum of Lab OP Detections (µg/L)
		Abraxis	Neogen	
GHCDD-1				
County Line Road	7/8/2009	NA	non-detect	0.22
	7/13/2009	detection	non-detect	0.22
	7/27/2009	detection	non-detect	0.1
Grange Road	7/8/2009	NA	non-detect	0.21
	7/13/2009	non-detect	non-detect	0.18
	7/27/2009	detection	non-detect	0.183
Schmid Road	7/8/2009	non-detect	non-detect	0.13
	7/13/2009	detection	non-detect	**2.3**
	7/27/2009	detection	non-detect	0.109
PCDD-1				
Heather Road	7/8/2009	NA	non-detect	0.12
	7/13/2009	detection	non-detect	**0.36**
	7/27/2009	detection	non-detect	0.141
Jacobson Road	7/8/2009	NA	non-detect	0.096
	7/13/2009	detection	non-detect	**0.46**
	7/27/2009	detection	non-detect	0.181
Tide Gate	7/8/2009	detection	non-detect	0.099
	7/13/2009	detection	non-detect	0.05
	7/27/2009	detection	non-detect	0.27

Bold indicates a summed laboratory detection that was above the lowest available detection limit for the Abraxis test kit (0.3 µg/L).
NA= Not analyzed.

When the difference in detection limits is accounted for, the similarity in the Abraxis test kit and MEL results no longer exists. Summed MEL detections only matched three of the Abraxis detections when compared to the kit's lowest available detection limit of 0.3 µg/L. The relatively few MEL detections above the lowest Abraxis detection limit called into question the legitimacy of the Abraxis results.

Upon further examination, the disparity was found to go beyond differences in detection limits. The difference can be accounted for by the carbamate portion of the OP/carbamate pesticide test kit. Carbamates are registered for use on cranberries and likely were applied to fields during the growing season. If carbamate pesticides were applied during the sampling periods for this 2009 study, the Abraxis test kit likely detected them. The laboratory testing for this 2009 study was limited to OP pesticides. It is possible that MEL reported results below the Abraxis test kit detection limits, that Abraxis showed as detections, may be reflecting carbamates not analyzed for the study.

After comparing results from each of the two OP pesticide test kits and MEL, it became clear that the Neogen test kit would not be a viable option. There were no detections for samples analyzed using the Neogen test kit. Combined levels of pesticides would need to be orders of magnitude higher to be detected by the Neogen kit. Therefore, results from the Neogen kit did not provide any insight into pesticide levels at concentrations found in GHCDD-1 and PCDD-1.

Findings

While the Abraxis test kit can detect OP and carbamate pesticides near environmentally relevant concentrations, the kit would not be a useful tool because it is not specific to OP pesticides. To make a true comparison between the Abraxis test kit and MEL, samples for carbamates would need to be included. In addition, to acquire meaningful results, the user would need to be trained in the operation of the test kit. This training would need to cover clean sampling techniques; equipment decontamination procedures; proper use of a micro-pipette; precise measurement, preparation, and mixing of reagents; clean analysis techniques; and interpretation of results.

Conclusions

Target Pesticides

The concentrations of three (OP) pesticides, azinphos-methyl, chlorpyrifos, and diazinon, in Grayland Ditch were the focus of this 2009 study.

Chlorpyrifos and diazinon were found at all sampling sites and in the majority of samples. Many samples were found to have concentrations of chlorpyrifos and diazinon at levels that failed to meet (exceeded) state or federal water quality criteria. These two pesticides should continue to be on the federal Clean Water Act Section 303(d) list.

Earlier studies of Grayland Ditch have reported azinphos-methyl at concentrations exceeding federal water quality criteria. In this 2009 study, there were no detections of azinphos-methyl. The change can be attributed to the cancellation by EPA (September 2006) of all registered uses of azinphos-methyl on cranberries. While results from this study show an improvement in water quality for azinphos-methyl in Grayland Ditch, much work still needs to be done.

Chlorpyrifos results showed an increase in the number of detections and exceedances of water quality criteria. The relative amount of each detection also increased. This change in chlorpyrifos detections may be explained by increased usage due to the cancellation of registered uses of azinphos-methyl on cranberries.

Diazinon showed some improvement over past study results. As with chlorpyrifos, diazinon is likely being used as a replacement chemical for azinphos-methyl. However, the data do not appear to show an increase in diazinon concentrations despite increased usage. This lack of increase in diazinon concentrations is most likely related to cranberry growers implementing best management practices (BMPs).

The data show that while some progress has been made at mitigating concentrations of azinphos-methyl, chlorpyrifos, and diazinon in Grayland Ditch, there is still work to be done. Cancellation of azinphos-methyl has resulted in reductions of pesticides levels. However, it is unlikely that the cancellation of azinphos-methyl for use on cranberries has reduced overall pesticide use. During 2009, cranberry growers likely used other pesticides in place of the ones no longer available (Grayland Cranberry Growers Board, personal communication, January 2010).

With detections of chlorpyrifos and diazinon not meeting water quality standards and the use of pesticides, it is apparent that there continues to be a problem. The problem likely will persist until BMPs are fully implemented at all cranberry farms.

WSDA Response

Due to the detections of chlorpyrifos and diazinon above water quality standards and the continued placement of GHCDD-1 and PCDD-1 on the 303(d) list, the Washington State Department of Agriculture (WSDA) will take action as specified in the 2009 *Washington State*

Pesticide Management Strategy for Water Quality Protection. WSDA will coordinate with the Washington State Department of Ecology (Ecology) to implement the response matrix for surface water quality described in the above document.

Test Kits

Two OP pesticide test kits were evaluated to determine viability as an investigative tool for use by Cranberry growers to identify areas in need of BMP improvement. Due to the known use of OP and carbamate pesticides, the Abraxis and Neogen pesticide test kits would not be useful tools for identifying areas in need of BMP improvement for OP pesticides alone. However, the Abraxis test kit would be an effective tool to track overall surface water concentrations of OP and carbamate pesticides.

Recommendations

Based on the data collected and analyzed for this 2009 study, the following recommendations are made:

- Based on the history of OP pesticide detections not meeting water quality criteria and voluntary implementation of BMPs, WSDA and Ecology should implement the response matrix for surface water quality. This matrix is described in Appendix One of the *Washington State Pesticide Management Strategy for Water Quality Protection* (Cook and Cowles, 2009). Begin with mandatory BMPs that require maintenance of existing and newly installed mitigation equipment.

- Cranberry growers should further explore the use of alternative pesticide products and pest management strategies.

- The Abraxis pesticide test kit could be useful in tracking overall surface water concentrations of acetylcholinesterase inhibiting compounds in GHCDD-1 and PCDD-1 greater than 0.3 µg/L. The kit could be used by a cranberry grower representative who is familiar with laboratory techniques and procedures.

- The 303(d) listing of GHCDD-1 and PCDD-1 for diazinon should be updated, using the 2006 EPA National Recommended Water Quality Criteria of 0.17 µg/L for criteria maximum concentration (CMC) and criteria continuous concentration (CCC). Past 303(d) listings of diazinon were based on CMC and CCC values calculated by the California Department of Fish and Game using EPA guidelines for the development of numerical water quality criteria (Menconi and Cox, 1994).

- Ditches GHCDD-1 and PCDD-1 should remain on the federal Clean Water Act Section 303(d) list for chlorpyrifos and diazinon.

This page is purposely left blank

References

Anderson, P., 2006. Standard Operating Procedure (SOP) for Sampling of Pesticides in Surface Waters, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP003. www.ecy.wa.gov/programs/eap/quality.html.

Anderson, P., 2009. Quality Assurance Project Plan: Grayland Ditch: An Evaluation of Organophosphate Pesticides and Pesticide Test Kits. Washington State Department of Ecology, Olympia, WA. Publication No. 09-03-115. www.ecy.wa.gov/biblio/0903115.html.

Anderson, P. and D. Davis, 2000. Evaluation of Efforts to Reduce Pesticide Contamination in Cranberry Bog Drainage. Washington State Department of Ecology, Olympia, WA. Publication No. 00-03-041. www.ecy.wa.gov/biblio/0003041.html.

APHA, 2005. Standard Methods for the Analysis of Water and Wastewater, 21st Edition. Joint publication of the American Public Health Association, American Water Works Association, and Water Environment Federation. www.standardmethods.org/.

Cook, K.V. and J. Cowles, 2009. Washington State Pesticide Management Strategy: Water Quality Protection, Version 2.22. Washington State Department of Agriculture, Olympia, WA.

Coots, R., 2003. Pesticide Reduction Evaluation for Cranberry Bog Drainage in the Grayland Area. Washington State Department of Ecology, Olympia, WA. Publication No. 03-03-034. www.ecy.wa.gov/biblio/0303034.html.

Davis, D., D. Serdar, and A. Johnson, 1997. Assessment of Cranberry Bog Drainage Pesticide Contamination. Washington State Department of Ecology, Olympia, WA. Publication No. 97-329. www.ecy.wa.gov/biblio/97329.html.

Embrey, S.S. and L.M. Frans, 2003. Surface-Water Quality of the Skokomish, Nooksack, and Green-Duwamish Rivers and Thornton Creek, Puget Sound Basin, Washington, 1995-98. U.S. Geological Survey, Water-Resources Investigation Report 02-4190. http://pubs.usgs.gov/wri/wri024190/pdf/wri024190.pdf.

EPA, 1991. Guidance for Data Usability in Risk Assessment. (Part A). EPA/540/R-92/003. U.S. Environmental Protection Agency, Washington, D.C.

EPA, 1994. Using Qualified Data to Document an Observed Release. EPA/540/F-91/028. U.S. Environmental Protection Agency, Washington, D.C.

EPA, 1998. Method 8270. Semivolatile Organic Compounds by GC/MS, Revision 4.0. U.S. Environmental Protection Agency, Office of Solid Waste. www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8270d.pdf.

EPA, 2004. Method 3535. Solid-Phase Extraction for Organic Analytes, Revision 6.0. U.S. Environmental Protection Agency, Office of Solid Waste. www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3535a.pdf.

EPA, 2006. National Recommended Water Quality Criteria. U.S. Environmental Protection Agency, Office of Water and Office of Science and Technology. www.epa.gov/waterscience/criteria/wqctable/.

Federal Register, 2006a. Environmental Protection Agency: Azinphos-methyl; Order to Amend Registrations to Terminate Certain Uses. March 29, 2006. Volume 71, Number 60: 15731-15732. Document ID: fr29mr06-77.

Federal Register, 2006b. Environmental Protection Agency: Azinphos-methyl; Amending Existing Stocks Provisions of Distribution for Cranberry Growers. July 5, 2006. Volume 71, Number 128: 38148-38149. Document ID: fr05jy06-46.

Frantz, W. T., T. Bicki, K. Talbot, and E. Unruh, 1997. Determining the Effectiveness of Surface Water Best Management Practices (BMPs) for Grayland, WA Cranberry Bogs. Cranberry Institute, Wareham, Massachusetts.

Grayland Cranberry Growers Board, 2010. Personal communication at the January 2010 board meeting regarding the use of other pesticides in place of azinphos-methyl. Markham, WA. Last communication January 2010.

Joy, J., 2006. Standard Operating Procedure (SOP) for Manually Obtaining Surface Water Samples, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP015. www.ecy.wa.gov/programs/eap/quality.html.

MEL, 2008. Manchester Environmental Laboratory Lab Users Manual, Ninth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Menconi, M. and C. Cox, 1994. Hazard Assessment of the Insecticide Diazinon to Aquatic Organisms in the Sacramento-Jan Joaquin River System. State of California Department of Fish and Game, Environmental Services Division, Pesticide Investigations Unit, Rancho Cordova, CA. Administrative Report 94-2. www.cdpr.ca.gov/docs/emon/surfwtr/hazasm/hazasm94_2.pdf.

Mitsch, W.J. and J.G. Gosselink, 2007. Wetlands, 4th edition. John Wiley & Sons, Inc., Hoboken, NJ.

Nipp, B., 2006. Standard Operating Procedure (SOP) for Instantaneous Measurements of Temperature in Water, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP011. www.ecy.wa.gov/programs/eap/quality.html.

Pacific Conservation District and Pacific Coast Cranberry Research Foundation, 1999. BMPs for Cranberry Agriculture. Washington State Conservation Commission.

Rountry, D., 2008. Grayland Cranberry Growers Get Pesticides Out of Water and Reduce Costs. Washington State Department of Ecology, Olympia, WA. Publication No. 08-10-087. www.ecy.wa.gov/biblio/0810087.html.

Swanson, T., 2007. Standard Operating Procedure (SOP) for Hydrolab® DataSonde® and MiniSonde® Multiprobes, Version 1.0. Washington State Department of Ecology, Olympia, WA. SOP Number EAP033. www.ecy.wa.gov/programs/eap/quality.html.

Talbot, Kevin, 2010. Personal communication regarding types and amounts of pesticides used in Grayland cranberry bogs. Ocean Spray, Markham, WA. Last communication January 2010.

WAC 173-201A. Water Quality Standards for Surface Waters in the State of Washington Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/laws-rules/ecywac.html.

Ward, W., 2007a. Standard Operating Procedure for the Collection and Analysis of pH Samples, Version 1.3. Washington State Department of Ecology, Olympia, WA. SOP Number EAP031. www.ecy.wa.gov/programs/eap/quality.html.

Ward, W., 2007b. Standard Operating Procedure for the Collection and Analysis of Conductivity Samples, Version 1.3. Washington State Department of Ecology, Olympia, WA. SOP Number EAP032. www.ecy.wa.gov/programs/eap/quality.html.

WDFW, 2010. SalmonScape interactive mapping application. Washington Department of Fish and Wildlife, Olympia, WA. http://wdfw.wa.gov/mapping/salmonscape/index.html.

This page is purposely left blank

Appendices

This page is purposely left blank

Appendix A. Glossary, Acronyms, and Abbreviations

Glossary

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.

Acetylcholinesterase: An enzyme that hydrolyzes the neurotransmitter acetylcholine: its action is blocked by nerve gases and certain drugs.

Carbamate insecticides: N-methyl carbamate insecticides are similar to organophosphate insecticides in that they are nerve agents that inhibit cholinesterase enzymes. However they differ in action from the organophosphate compounds in that the inhibitory effect on cholinesterase is brief. Carbamates degrade rapidly in the environment.

Clean Water Act: A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

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.

Exceeds criteria: Fails to meet criteria.

Grab sample: A discrete sample from a single point in the water column or sediment surface.

Organophosphate pesticides: Organophosphate pesticides are all derived from phosphoric acid. They are nerve poisons which kill the target pest (usually insects). The mechanism of action is similar to carbamate insecticides, both are neurotoxins, inhibiting the enzyme acetylcholinesterase by inhibiting cholinesterase. They break down relatively quickly in the environment.

Parameter: Water quality constituent being measured (analyte). A physical, chemical, or biological property whose values determine environmental characteristics or behavior.

Pesticide: A pesticide is any substance or mixture of substance intended for preventing, destroying, repelling or mitigating any pest. Pests include nuisance microbes, plants, fungus, and animals.

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.

Total Maximum Daily Load (TMDL): Water cleanup plan. A calculated or managed distribution of a substance in a waterbody designed to protect it from exceeding water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a Margin of Safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids: The suspended particulate matter in a water sample as retained by a filter.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

BMP	Best management practices
CCC	Criteria Continuous Concentrations
CMC	Criteria Maximum Concentration
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
GHCDD-1	Grays Harbor County Drainage Ditch No. 1
MEL	Manchester Environmental Laboratory
NAD	North American Datum
NOAA	National Oceanic and Atmospheric Administration
NRWQC	National Recommended Water Quality Criteria
OP	Organophosphate
PCDD-1	Pacific County Drainage Ditch No. 1
QA	Quality Assurance
QC	Quality Control
RPD	Relative percent difference
SOP	Standard operating procedures
TSS	Total Suspended Solids
WAC	Washington Administrative Code
WSDA	Washington State Department of Agriculture

Units of Measurement

°C	degrees centigrade
mg/L	milligrams per liter
s.u.	standard unit
µg/L	micrograms per liter (parts per billion)
µmhos/cm	micromhos per centimeter

Appendix B. Locations and Descriptions of Sampling Sites

Table B-1. Sampling locations and descriptions for ditches GHCDD-1 and PCDD-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.

Appendix C. Information on Selected Organophosphate Pesticide Test Kits

Selection Process

The two OP pesticide test kits described below 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.

The equipment selected for testing must 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. Also, the OP pesticide test kit must be able 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 laboratory or other controlled setting.

The available test kits all work as a colorimetric test, based on the inhibition of the biological enzyme, acetylcholinesterase. OP pesticides work in insects and other animals by inhibiting this 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 acetylcholinesterase.

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.

The two test kits selected for evaluation were the best available, considering the limits of the three selection criteria.

1. Abraxis Organophosphate/Carbamate Assay Kit

General Information

The Abraxis OP/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 acetylcholinesterase. Various reagents are mixed in vials with a sample to form a color if no pesticide is present. If OP and/or carbamate pesticides are present in the sample, color formation will be reduced or eliminated.

The Abraxis test kit works on an additive principal. The combined concentrations of all detectable compounds are measured and show a positive result at the lowest detection limit. Detection limits vary on a chemical-by-chemical basis depending on the ability of the specific chemical to inhibit acetylcholinesterase.

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 OP/Carbamate Assay Kit are provided in Table C1.

Table C-1. Detectable pesticides and detection limits (µg/L) using the Abraxis test kit.

Pesticides	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
Carbamates	
Aldicarb	25
Carbaryl	206
Carbofuran	0.9

2. Neogen Agri-Screen Ticket®

General Information

The Neogen 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 acetylcholinesterase 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 acetylcholinesterase to determine if a pesticide is present in the sample. The sample is collected and mixed with activation chemicals. The disc is then exposed to the activated 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 acetylcholinesterase. 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 C-2.

Table C-2. Detectable pesticides and detection limits (µg/L) using the Neogen Agri-Screen test kit.

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

Appendix D. Quality Assurance/Quality Control Data

Field Measurements

Table D-1. Field meter replicate results for pH (s.u.), temperature (°C), and conductivity (µmhos/cm).

Parameter	Sample	Replicate	RPD (%)
pH	6.6	6.6	0.00
	6.6	6.6	0.00
	6.5	6.5	0.00
	6.5	6.5	0.00
		mean =	0.00
temperature	14.2	14.2	0.00
	12.8	12.8	0.00
	13.5	13.5	0.00
	14.0	14.2	1.42
		mean =	0.35
conductivity	250.0	250.0	0.00
	182.9	183.6	0.38
	173.5	176.0	1.43
	219.1	218.8	0.14
		mean =	0.49

RPD – relative percent difference.

Table D-2. Field meter post-check results for pH (s.u.) and conductivity (µmhos/cm).

Parameter	Calibration	Post-Check	Difference	Assessment
pH				
Point 1	6.98	6.97	0.01	Accept
	6.98	6.93	0.05	Accept
	6.97	6.96	0.01	Accept
		mean =	0.02	
Point 2	4.10	4.08	0.02	Accept
	4.10	4.05	0.05	Accept
	4.10	4.08	0.02	Accept
		mean =	0.03	
Conductivity	998.0	1000.0	0.2%	Accept
	998.0	990.0	-0.8%	Accept
	998.0	997.0	-0.1%	Accept
		mean =	-0.2%	

Water Samples

Table D-3. Field replicate results for chlorpyrifos (µg/L), diazinon (µg/L), and total suspended solids (mg/L).

Parameter	Sample	Replicate	RPD (%)
Chlorpyrifos	0.13 0.052	0.14 0.053	7 2
		mean =	5
Diazinon	0.096 0.05 0.089	0.089 0.057 0.084	8 13 6
		mean =	9
Total Suspended Solids	7 7 8	7 6 9	0 15 12
		mean =	9

RPD – relative percent difference.

Table D-4. Matrix spike/matrix spike duplicate results for water samples (%).

Parameter	MS	MSD	RPD (%)
Azinphos-methyl	118 132 111	110 126 115	7 5 4
		mean =	5
Chlorpyriphos	101 104 78	99 84 88	2 21 12
		mean =	12
Coumaphos	134 139 121	123 135 132	9 3 9
		mean =	7
Diazinon	99 110 94	92 100 103	7 10 9
		mean =	9
Dichlorvos	105 108 78	90 99 101	15 9 26
		mean =	17
Disulfoton	95 106 86	87 95 99	9 11 14
		mean =	11

Parameter	MS	MSD	RPD (%)
Ethoprop	120	115	4
	122	112	9
	111	121	9
		mean =	7
Fenamiphos	119	114	4
	142	128	10
	117	121	3
		mean =	6

MS – matrix spike.
MSD – matrix spike duplicate.
RPD – relative percent difference.

Test Kits

Table D-5. Organophosphate pesticide test kit replicate results.

Date	Kit	Sample	Replicate
7/8/2009	Abraxis	non-detect	non-detect
	Neogen	non-detect	non-detect
7/13/2009	Abraxis	non-detect	non-detect
	Neogen	non-detect	non-detect
	Abraxis	detect	sample error
	Neogen	non-detect	non-detect
7/27/2009	Abraxis	detect	detect
	Neogen	non-detect	non-detect
	Abraxis	detect	detect
	Neogen	non-detect	non-detect

Table D-6. Abraxis test kit control sample results.

Date	Positive Control	Negative Control
7/8/2009	detection	no detection
7/13/2009	detection	no detection
7/27/2009	detection	no detection

Appendix E. Summarized Study Results from Common Sampling Sites, 1996-2009.

Table E-1. Summarized study results from 1996, 1998, and 2009 sampling sites.

Location			1996	1998	2002	2009
GHCDD-1						
Schmid Road	Azinphos-methyl	number	26	5	3	3
		detections	16	3	2	0
		mean	0.13	0.25	0.11	nd
		range	0.010-0.73	0.004-1.2	0.033-0.20	nd
	Chlorpyrifos	n	26	5	3	3
		detections	7	5	2	3
		mean	0.021	0.38	0.008	0.09
		range	0.003-0.016	0.0095-1.8	0.0050-0.010	0.051-0.13
	Diazinon	n	26	5	3	3
		detections	26	5	3	2
		mean	0.86	1.1	0.17	0.76
		range	0.026-5.42	0.033-4.4	0.018-0.35	0.034-2.2
Grange Road	Azinphos-methyl	n	-	-	3	3
		detections	-	-	3	0
		mean	-	-	0.13	nd
		range	-	-	0.019-0.020	nd
	Chlorpyrifos	n	-	-	3	3
		detections	-	-	3	3
		mean	-	-	0.013	0.14
		range	-	-	0.0065-0.023	0.089-0.21
	Diazinon	n	-	-	3	3
		detections	-	-	3	2
		mean	-	-	1.9	0.054
		range	-	-	0.033-5.7	0.034-0.094
County Line Road	Azinphos-methyl	n	-	-	3	3
		detections	-	-	3	0
		mean	-	-	0.18	nd
		range	-	-	0.020-0.30	nd
	Chlorpyrifos	n	-	-	3	3
		detections	-	-	2	3
		mean	-	-	0.012	0.16
		range	-	-	0.0067-0.020	0.1-0.22
	Diazinon	n	-	-	3	3
		detections	-	-	3	1
		mean	-	-	0.80	0.029
		range	-	-	0.036-2.0	0.032-0.055

Table E-1 cont'd. Summarized study results from 1996, 1998, 2002, and 2009 sampling sites.

Location			1996	1998	2002	2009
PCDD-1						
Heather Road	Azinphos-methyl	number	-	-	3	3
		detections	-	-	3	0
		mean	-	-	0.11	nd
		range	-	-	0.048-0.22	nd
	Chlorpyrifos	number	-	-	3	3
		detections	-	-	3	1
		mean	-	-	0.027	0.027
		range	-	-	0.019-0.039	0.022-0.052
	Diazinon	number	-	-	3	3
		detections	-	-	3	3
		mean	-	-	0.16	0.19
		range	-	-	0.079-0.31	0.089-0.36
Jacobson Road	Azinphos-methyl	number	-	-	3	3
		detections	-	-	3	0
		mean	-	-	0.08	nd
		range	-	-	0.0079-0.22	nd
	Chlorpyrifos	number	-	-	3	3
		detections	-	-	3	2
		mean	-	-	0.39	0.046
		range	-	-	0.034-0.59	0.035-0.082
	Diazinon	number	-	-	3	3
		detections	-	-	3	3
		mean	-	-	0.31	0.21
		range	-	-	0.11-0.69	0.096-0.42
Larkin Road	Azinphos-methyl	number	26	5	3	-
		detections	23	5	3	-
		mean	0.17	0.33	0.050	-
		range	0.006-0.74	0.012-1.4	0.0061-0.13	-
	Chlorpyrifos	number	26	5	3	-
		detections	25	5	3	-
		mean	0.44	0.59	0.028	-
		range	0.003-3.7	0.019-1.3	0.015-0.036	-
	Diazinon	number	26	5	3	-
		detections	25	5	3	-
		mean	0.28	2.4	0.48	-
		range	0.008-1.7	0.033-7.0	0.20-0.64	-
Tidegate	Azinphos-methyl	number	-	-	3	3
		detections	-	-	3	0
		mean	-	-	0.06	nd
		range	-	-	0.0067-0.15	nd
	Chlorpyrifos	number	-	-	3	3
		detections	-	-	3	2
		mean	-	-	0.025	0.08
		range	-	-	0.014-0.030	0.027-0.18
	Diazinon	number	-	-	3	3
		detections	-	-	3	3
		mean	-	-	0.53	0.13
		range	-	-	0.18-0.71	0.085-0.22

This page is purposely left blank