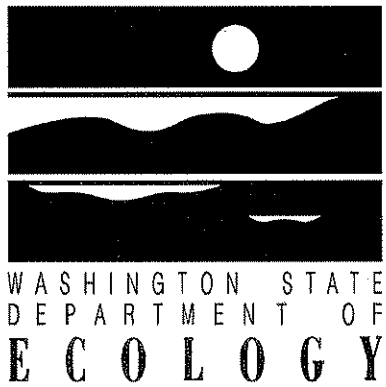

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Results from Chemical Analyses of Surface Water, Tissue, and Sediment Samples Collected in 1996

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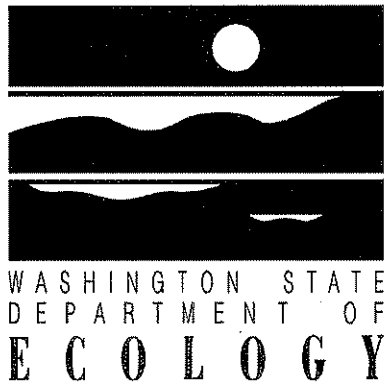

Assessment of Cranberry Bog Drainage Pesticide Contamination

Results from Chemical Analyses of Surface Water, Tissue, and Sediment Samples Collected in 1996

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by
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Table of Contents

List of Figures and Tables

Abstract

High concentrations of multiple pesticides detected in Grays Harbor County Drainage Ditch No.1 (GHCDD-1) in 1994 and 1995 by the Washington State Department of Ecology prompted an intensive survey of water, sediment, and fish and shellfish potentially impacted by drainage from cranberry bogs in the Grayland/North Cove area. The objective of the survey was to determine the extent and severity of pesticide contamination from cranberry farming, and to establish a baseline of pesticide concentrations to assess effectiveness of best management practices (BMPs). GHCDD-1 drains bogs in the Grayland area, and discharges into South Bay of Grays Harbor. Pacific County Drainage Ditch No.1 (PCDD-1) drains bogs south of the county line, and discharges into Willapa Bay.

Water samples were collected from each ditch once per week throughout the growing season, and once per day for five days following peak pesticide applications in 1996. Most water samples were analyzed for organophosphorus pesticides only. One of the samples from each ditch collected during the five days after pesticide applications was analyzed for an expanded list of 150 compounds that included most pesticides that are being or have been used on cranberries. One set of tissue and sediment samples was collected in the last week of August 1996. Tissue samples were analyzed for 48 pesticides and PCBs, and sediment samples were analyzed for 133 compounds.

High concentrations of multiple insecticides were detected in water samples collected throughout the growing season. Nearly all detections of three highly toxic organophosphorus insecticides -- azinphos-methyl (Guthion), chlorpyrifos (Lorsban), and diazinon -- exceeded water quality criteria for the protection of aquatic life. Many detections were above LC_{50} values for some aquatic invertebrates. Azinphos-methyl, chlorpyrifos, and diazinon were found at the highest concentrations ever recorded in state waters.

While these data document a pesticide contamination problem in the drainage ditches, there is little information to determine environmental pathways. More information is needed to identify the routes that transport pesticides into the drainage ditches so appropriate prevention measures can be developed.

Few or no pesticides were detected in tissue samples of shellfish that might be regularly consumed by humans. DDE, a breakdown product of DDT, was found in three samples at low concentrations. PCB-1260 was also found in two samples at low concentrations. Levels of total DDT and total PCBs in these samples exceeded human health screening values calculated based on expected consumption for subsistence fishermen based on a risk level of $1x10^{-6}$. Sticklebacks, a non-food fish, contained moderate concentrations of several pesticides and breakdown products, but none exceeded criteria for protection of fish-eating wildlife. Several pesticides were detected in each of the sediment samples collected from the drainage ditches, but only two organophosphorus insecticides -- azinphos-methyl and diazinon -- were found at elevated concentrations.

Recommendations include (1) additional water sampling to identify the routes that transport pesticides into the main drainage ditches, and (2) after steps have been taken to reduce pesticide levels, water samples should be collected to confirm effectiveness of BMPs.

Acknowledgments

Numerous people contributed to the development or implementation of this study. A list of the key participants is included here:

Karl Arne	USEPA, Region 10
Tom Bicki	Ocean Spray Cranberries
Joe Blazevich	USEPA, Manchester Laboratory
Joyce Carr	Department of Agriculture, Yakima Chemical and Hop Laboratory
Randy Cummings	USEPA, Manchester Laboratory
Robert Cutler	USEPA, Region 10
Jere Downing	The Cranberry Institute
Brady Engvall	Coalition of Coastal Fishers
Merri Erickson	Washington Cranberry Alliance
Bill Frantz	Ocean Spray Cranberries
Jennifer Hagen	Shoalwater Bay Indian Tribe
Dave Howard	Department of Ecology
Kahle Jennings	Department of Ecology
Stuart Magoon	Department of Ecology, Manchester Laboratory
Mike Marsh	USEPA, Region 10
Norman Olson	Department of Ecology, Manchester Laboratory
Kim Patten	Washington State University Cooperative Extension Service
Royal Schoen	Department of Agriculture, Yakima Chemical and Hop Laboratory
Kevin Talbot	Ocean Spray Cranberries
Will White	Department of Ecology, Manchester Laboratory
Ann Wick	Department of Agriculture

The following persons deserve special recognition for their contributions to this study:

- Rick Cordel, cranberry grower - for granting access to his property adjacent to GHCDD-1 for collection of sediment samples (GHCDD-1 Site 1).
- Doug Davis, commercial fisherman - for collection of dungeness crabs, and assistance in collection of razor and piddock clam samples.
- Brady Engvall, Brady's Oysters - for access to and assistance in collection of oyster samples.
- Merri Erickson, Washington Cranberry Alliance - for assistance with numerous grower-related questions and issues.
- Art Larson, Department of Ecology - for assistance in collection of sediment and tissue samples.
- Ralph Larson and Jim Middleton, Laidlaw Gun Club - for granting access to club property near the discharge of GHCDD-1 for sample collection.
- Larry Goldstein and Dale Norton, Department of Ecology - for providing valuable review comments for the draft report.

Summary

High concentrations of multiple insecticides were detected in water samples collected throughout the four-month growing season in 1996 from two ditches draining cranberry bogs in the Grayland/North Cove area. Nearly all detections of three highly toxic organophosphorus insecticides used in cranberry culture -- azinphos-methyl (Guthion), chlorpyrifos (Lorsban), and diazinon -- exceeded water quality criteria for the protection of aquatic life. Many detections were above LC_{50} values for some aquatic invertebrates. These three pesticides were found in all samples except one collected from Pacific County Drainage Ditch No.1 (PCDD-1), and in most samples from Grays Harbor County Drainage Ditch No.1 (GHCDD-1). High concentrations of parathion were also detected in six samples collected from GHCDD-1 in May as a result of illegal use. Azinphos-methyl and diazinon were found in both drainage ditches and chlorpyrifos was found in PCDD-1 at the highest concentrations ever recorded in state waters for these pesticides. These data indicate that some aquatic life within these ditches are probably being adversely impacted by pesticide contamination from cranberry farming.

While these data document that a serious pesticide contamination problem exists in the drainage ditches, there is little information to determine environmental pathways. Water flow in the ditches increases rapidly in response to heavy rainfall, and drops shortly after the rain stops, indicating that water moves through the bogs quickly. Peak pesticide concentrations do not appear to be associated with rainfall or flow, but levels also decrease quickly after application suggesting that the pesticides are traveling in surface water and not in runoff. More information is needed to identify the routes that transport pesticides into the main drainage ditches so appropriate prevention measures can be developed.

Few or no pesticides were detected in tissue samples of shellfish that might be regularly consumed by humans. None of the detected compounds are currently used on cranberries. DDE, a breakdown product of DDT, was found in three samples at low concentrations. PCB-1260 was also found in two samples at low concentrations. There is probably little risk to human health associated with consumption of these shellfish. However, levels of total DDT and total PCBs in three samples exceeded calculated human health screening values based on expected consumption for subsistence fishermen using a risk level of $1x10^{-6}$. Additional sampling and an assessment by the Washington State Department of Health is necessary before considering any possible consumption restrictions.

Pesticide levels in crabs and oysters were similar to concentrations reported in shellfish from Willapa Bay and Puget Sound. Compared to levels in fin fish from Washington, California, and national studies, pesticide concentrations were much lower in shellfish impacted by cranberry bog drainage.

Sticklebacks were the only fish or shellfish that could be found within the drainage ditches. A sample of sticklebacks from GHCDD-1 contained moderate concentrations of several pesticides and breakdown products. Sticklebacks are not eaten by humans, but are likely to be consumed regularly by wildlife, such as great blue herons. None of the individual pesticide levels found in

the stickleback sample exceeded wildlife criteria, but the combination of these chemicals may result in effects that are more harmful than would be expected for individual compounds. Tissue concentrations were not high enough to directly affect stickleback productivity.

Several pesticides were detected in each of the sediment samples collected from the drainage ditches, but most were in low concentrations. Samples from two sites, one in GHCDD-1 and one in PCDD-1, had moderately high levels of total DDT. None of the detected chlorinated pesticides was above sediment quality guidelines for protection of sediment-dwelling organisms, but all detections of azinphos-methyl and diazinon exceeded sediment criteria set by New York State to protect aquatic ecosystems.

There is no direct evidence from this study, but the high concentrations of pesticides seen in water samples and moderate levels in sediments may be preventing other fish and shellfish from colonizing the drainage ditches. Results from bioassays show that pesticide levels in the ditches are high enough to cause acute mortality to indigenous aquatic organisms (Wood, 1997), and if pesticides are causing a significant reduction in microfauna populations that are a food source for many fish, then it may not be possible for other fish to colonize the ditches. However, results from a survey of benthic invertebrates (Wood, 1997) suggest that habitat modifications necessary to maintain drainage ditches may result in low productivity regardless of contamination. More information is needed to determine how the pesticides are affecting ditch fauna.

Recommendations

Water

While there is clearly a pesticide contamination problem in the main drainage ditches, there is no information available to establish how the pesticides are getting into the ditches. Two possible routes, perennial streams and shallow ground water, should be investigated initially.

- Sample at mouths of perennial streams in the summer when other ditches are dry to compare the pesticide load in the streams to the total load in the main ditch.
- Assess pesticides in shallow ground water within the cranberry bogs to determine if pesticides detected in the main ditches may be partially attributed to transport through ground water.

Tissue

Only breakdown products of DDT and PCB-1260 were found at low concentrations in shellfish tissue likely to be consumed by humans. There is probably little risk to most consumers, but there may be some concern for subsistence fishermen. If it is determined that additional sampling is necessary to assess the risk to subsistence fishermen, then sampling should be limited to oysters and crabs. Other species of shellfish, such as razor and littleneck clams, should not be used for an assessment of contamination due to their lack of significant uptake of organic chemicals.

- Collect samples of dungeness crabs and pacific oysters from various sites in Willapa Bay and Grays Harbor to assess the extent of contamination, and to identify background concentrations and areas with reduced concentrations.

Sediment

Concentrations of chlorinated pesticides in sediment from the ditches are probably not high enough to be a concern for aquatic organisms. However, levels of some organophosphorus insecticides appear to be elevated and may be affecting some sediment-dwelling invertebrates. To assess this impact, some sampling and analysis modifications should be employed.

- Collect one liter of sediment from each site and centrifuge to remove most of the water, which will improve detection limits as well as accuracy and precision.
- Analyze samples for organophosphorus insecticides only, to reduce analytical expenses.
- Assess toxicity of sediments using laboratory bioassays.

Bioassessment

A complete bioassessment of the drainage ditch system, including suitable reference sites, should be completed to gain a better understanding of ditch biology, so pesticide impacts can be quantified.

- Use a multihabitat approach, sampling each microhabitat in the ditches to obtain a complete picture of the resident faunal assemblage.
- Sample before and/or after the growing (pesticide application) season to determine the degree of impacted fauna recovery.

Assessment of BMP Effectiveness

After BMPs have been implemented in a majority of the cranberry bogs, samples should be collected from the main drainage ditches to determine if the BMPs have been effective in reducing pesticide concentrations to acceptable levels.

- Collect water samples from each ditch immediately after peak pesticide applications in May, July, and August.
- Analyze samples for organophosphorus insecticides only.

Introduction

Water draining from cranberry bogs and residential property in the Grayland/North Cove area south of Westport, Washington collects in a ditch system that discharges to the south into Willapa Bay and to the north into South Bay of Grays Harbor (Figure 1). Both the north and south ditches originate from a wetland area just south of the Grays Harbor/Pacific County line and west of Highway 105 in Grayland. The ditches essentially parallel Highway 105, collecting runoff from about 900 acres of cranberry bogs. Both ditches also receive water from several small streams that run down from the hills east of the cranberry bogs, and probably directly from shallow ground water within the bogs, as theses typically have a static level from just a couple of inches to a few feet below the soil surface (personal observation). The north ditch is called Grays Harbor County Drainage Ditch No.1 (GHCDD-1), and the south ditch is called Pacific County Drainage Ditch No.1 (PCDD-1).

Although these drainage ditches have been constructed to drain the land in the Grayland/North Cove area, and are periodically dredged and otherwise kept free from debris, drainage ditches have been designated by the State Attorney General (1969) as waters of the state. As such, these waters are subject to Washington State Water Quality Standards (Chapter 173-201A WAC).

In 1994, water from GHCDD-1 was collected at Schmid Road in Grayland (Figure 1B) in April, June, and October as a part of the Department of Ecology (Ecology) Washington State Pesticide Monitoring Program (WSPMP). No pesticides were detected above Washington State or federal water quality criteria, but the high number and frequency of detections prompted additional sampling in April, June, August, and October of 1995 at the same site. Pesticides detected in 1995 were similar to those found in 1994, but concentrations in 1995 were substantially higher. Three insecticides -- azinphos-methyl (Guthion), chlorpyrifos (Lorsban), and diazinon -- were found at levels exceeding state or federal water quality criteria. Concentrations of chlorpyrifos, diazinon, and carbofuran (another insecticide) detected in August 1995 were the highest ever seen in the state. In addition, DDE and DDD, breakdown products of DDT, were identified in all water samples collected in 1995 at levels above state criteria. DDT was banned in 1972, but it and its breakdown products are extremely persistent and are commonly found in areas with historical use.

Detections of chlorpyrifos and DDE/DDD in 1995 meet the requirements for Clean Water Act 303(d) water quality limited listing (Washington State, 1993). Ecology is required to take some form of action to resolve the contamination issue so that the waterbody can be removed from the list.

While performing a water quality needs assessment for the Western Olympic watershed in the fall of 1995, Ecology's Environmental Investigations Program identified the pesticides issue in GHCDD-1 as a significant problem, and recommended additional sampling to determine the extent and effects of the contamination (Jennings, 1996). In December 1995, Dr. Kim Patten, with the Washington State University (WSU) Cooperative Extension Service, organized a meeting with cranberry growers in the Grayland area, the U.S. Environmental Protection Agency

Assessment of Cranberry Bog Drainage Pesticide Contamination

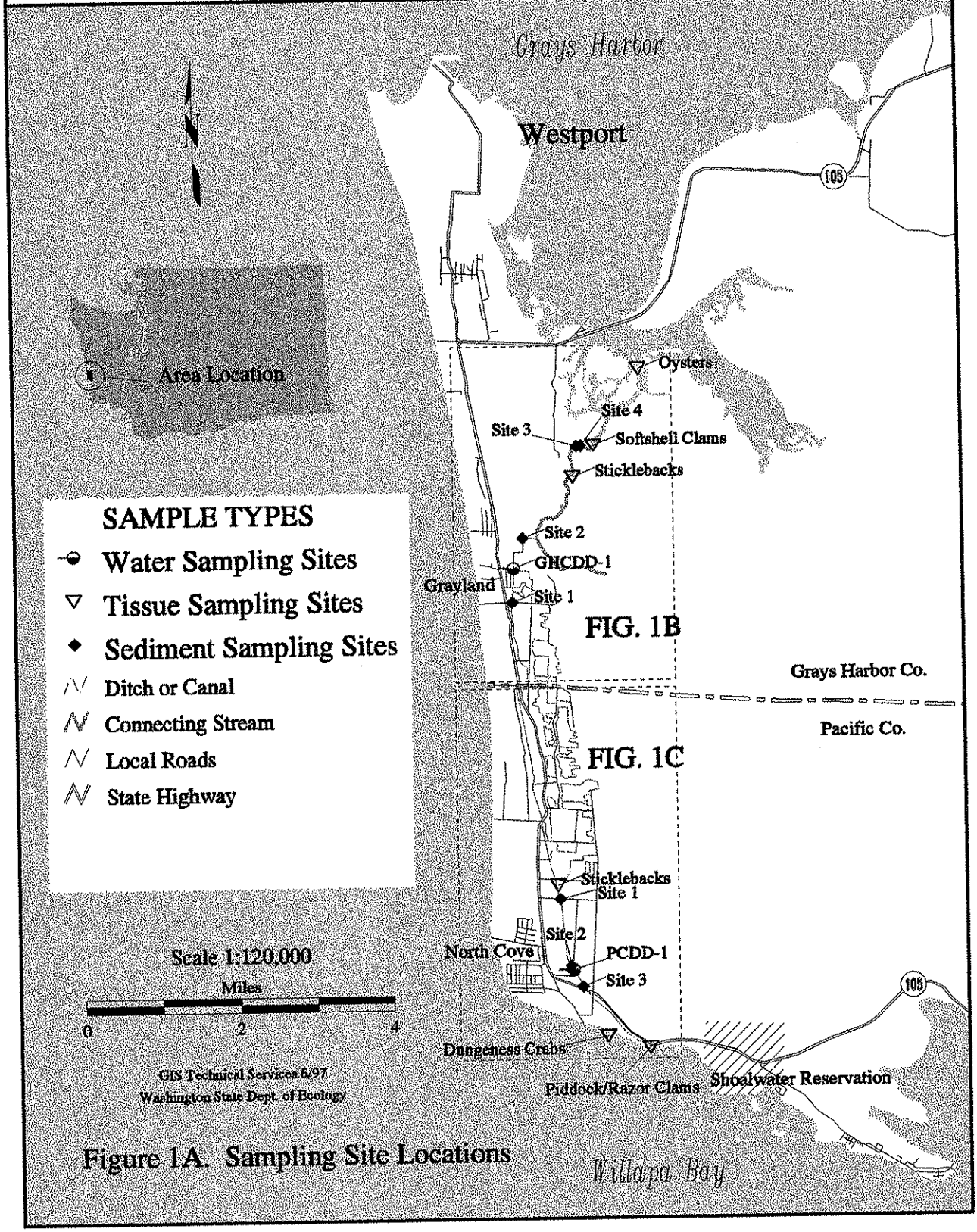


Figure 1A. Sampling Site Locations

Fig. 1B Sampling Site Locations, Grays Harbor Co. Drainage Ditch #1

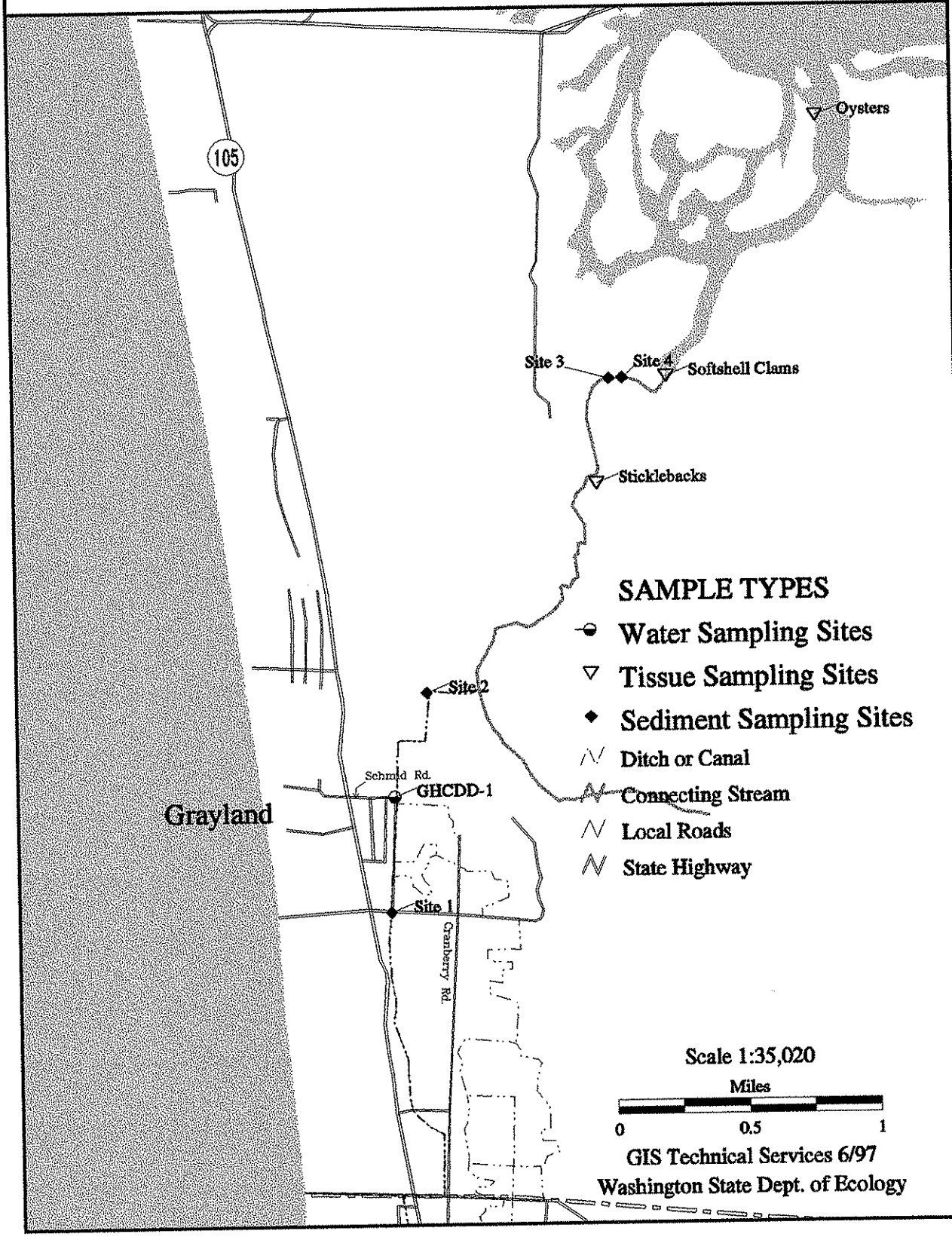
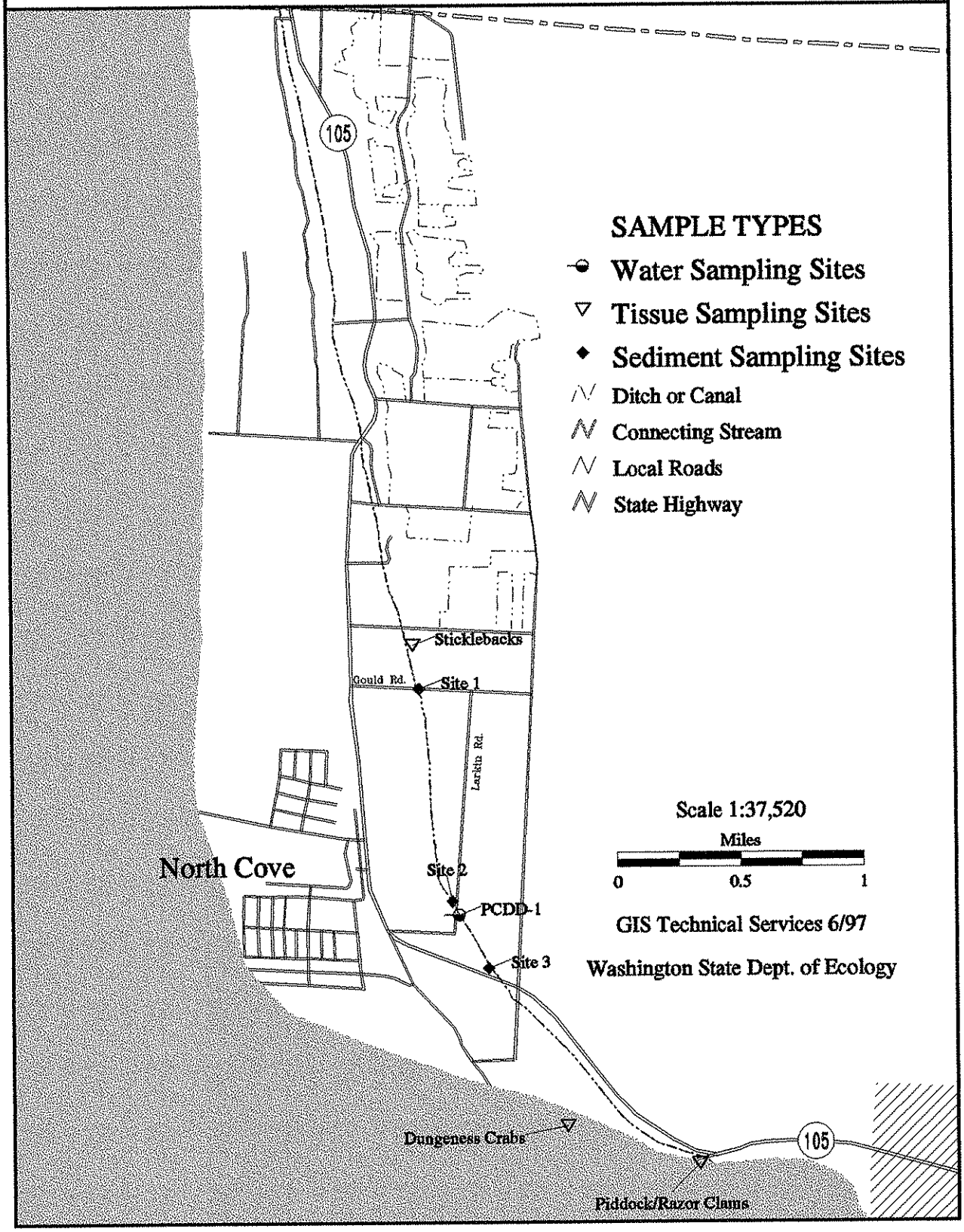


Fig. 1C Sampling Site Locations, Pacific Co. Drainage Ditch #1



(USEPA, Region 10), the Conservation Commission, and Ecology to discuss the pesticide contamination problem.

Another meeting was held in February 1996 to discuss monitoring options. All participants agreed that anticipated sampling of cranberry bog drainage for the 1996 WSPMP would be insufficient to: 1) assess pesticide contamination trends, 2) determine the extent and severity of contamination, or 3) determine if the pesticides were adversely affecting fauna in the ditches. The WSPMP was designed to be a screening tool, and not to answer site-specific, fate and transport questions. It was decided that sampling plans should be prepared to address the concerns of all interested parties.

An advisory committee was formed with representatives from the Shoalwater Bay Indian Tribe, the Cranberry Alliance, the USEPA, the WSU Cooperative Extension Service, and Ecology to develop the sampling plans. Davis and Serdar (1996a) identified three primary objectives and presented multiple monitoring options. The objectives were as follows:

- Determine the extent and severity of pesticide contamination from cranberry farming in the Grayland/North Cove area.
- Determine if pesticide contamination from cranberry farming is adversely affecting aquatic life and/or wildlife.
- Evaluate the effectiveness of measures implemented by cranberry growers to reduce concentrations of pesticides in the drainage ditches.

To determine the full extent and severity of contamination, collection of water, tissue, and sediment samples was considered necessary, and water samples needed to be collected at regular intervals throughout a complete growing season to establish a reliable baseline. To fulfill these needs, joint efforts between Ecology and the USEPA (Davis and Arne, 1996; Davis and Cutler, 1996) resulted in this study and report.

To determine if pesticide contamination is adversely affecting aquatic life and/or wildlife, bioassays were performed on drainage ditch water, and sediment samples were collected for assessment of benthic assemblages. This work was conducted by Barbara Wood, a graduate student with Dr. John Stark of WSU. Preliminary results from the bioassays and bioassessment are presented by Stark and Wood (1996a,b).

To evaluate the effectiveness of best management practices (BMPs) implemented by growers to reduce pesticide concentrations in the ditches, a study was proposed by the Cranberry Institute and cooperating growers (Frantz *et al.*, 1996). The industry planned to apply a non-toxic surrogate chemical using the same chemigation techniques as for pesticide applications. Effectiveness of BMPs implemented by growers could be assessed quickly and easily by measuring the concentration of the surrogate chemical. Results of the BMP effectiveness study will be released in a report by the industry (Frantz, 1997 - personal communication).

Methods

Methods Details

Details of all methods are presented in the following appendices:

- Appendix A - Sampling Site Positions
- Appendix B - Target Pesticides
  - > B-1 - Water
  - > B-2 - Tissue
  - > B-3 - Sediment
  - > B-4 - Distribution of Compounds Eluted from Florisil Columns
- Appendix C - Sample Collection and Processing Procedures
- Appendix D - Analytical Methods
- Appendix E - Quality Assurance/Quality Control
- Appendix F - Data Review
  - > F-1 - Duplicate Analysis Results for Water Samples (USEPA Lab)
  - > F-2 - Duplicate Analysis Results for Water Samples (WSDA Lab)
  - > F-3 - Duplicate Analysis Results for Tissue and Sediment Samples
  - > F-4 - Matrix Spike Recoveries for Water Samples (USEPA Lab)
  - > F-5 - Matrix Spike Recoveries for Water Samples (WSDA Lab)
  - > F-6 - Matrix Spike Recoveries for Tissue Samples
  - > F-7 - Matrix Spike Recoveries for Sediment Samples
  - > F-8 - Field Spike Results
  - > F-9 - Interlaboratory Comparison of Results from Split Samples
- Appendix G - Data Validation Reports for Water Analyses

Sampling Design

While the objectives for sampling water, tissue, and sediment were essentially the same, the sampling designs were much different. Pesticide concentrations in water can change quickly in a short period of time, requiring numerous samples at regular intervals to document the changes. In contrast, the concentration of pesticides that accumulate in tissues and sediment is unlikely to change substantially over time. Pesticides that bioaccumulate adsorb to fatty tissues in animals and organic matter in sediment, and can accumulate to levels much higher than those seen in the water column. A single set of samples collected when the concentrations are likely to be highest is generally sufficient for tissue and sediment.

Water Sampling

Samples were collected from two sites that are representative of water draining from the cranberry bogs. One site was where samples were collected for the WSPMP on GHCDD-1 (Figure 1B). This site was at the bridge on Schmid Road, which is downstream of all bog drainages that flow into GHCDD-1. The other site was at the bridge on Larkin Road, just upstream from the tide gates on PCDD-1, and downstream of all bog drainages except one (Figure 1C). Latitude, longitude, and state plane coordinates are listed for each site in Appendix A.

Timing for water sampling was centered around three peak insecticide application periods: the first in early May, the second in mid July, and the last in early August. These dates vary somewhat from year to year depending on a number of variables, such as weather conditions. Applications in July 1996 were later than usual due to cold weather at the end of June.

Samples were collected at both water sampling sites once each week beginning on the week of May 13 to the week of August 19, 1996. Samples were collected on Monday or Tuesday to give the laboratory time to extract the samples before the weekend. In addition to the weekly sampling, samples were collected daily for four or five consecutive days immediately after peak pesticide applications. The first intensive sampling took place during the week of May 20 (May 20-24), the second during the week of July 15 (July 15-19), and the last took place from August 12 through 15.

Three organophosphorus insecticides -- azinphos-methyl, chlorpyrifos, and diazinon -- are currently used pesticides that were most often detected above water quality standards in cranberry bog drainage, and are the greatest potential hazard to aquatic life. Therefore, most water samples were analyzed for organophosphorus pesticides only. Only one set of samples collected for the intensive sampling events was analyzed for the complete list of target analytes as used for the WSPMP. This included analyses for chlorinated pesticides, organophosphorus pesticides, nitrogen-containing pesticides, sulfur-containing pesticides, pyrethrins, and chlorinated herbicides -- a total of 150 compounds (Appendix B-1). A separate sample for carbamate analysis was not collected, but carbofuran and carbaryl were included as target compounds along with the other pesticide analyses.

Samples were also collected at each site to analyze for total suspended solids (TSS) and total organic carbon (TOC). Field measurements included temperature, pH, conductivity, and flow.

Tissue and Sediment Sampling

Two composite tissue samples were collected near the mouth of each drainage ditch (Figure 1). Samples collected near the mouth of GHCDD-1 included pacific oysters (*Crassostrea gigas*) and eastern softshell clams (*Mya arenaria*). Razor clams (*Siliqua patula*) and pilsbry piddock clams (*Zirphoea pilsbryi*) were collected near the mouth of PCDD-1. Dungeness crabs (*Cancer magister*) were also collected just off shore from the mouth of PCDD-1 in Willapa Bay. One composite sample of three-spine sticklebacks (*Gasterosteus aculeatus*) was collected from each

ditch. Sticklebacks were the only animals that were found within the ditches, and other species would have been preferred for data comparison purposes, so only the sample from GHCDD-1 was analyzed.

Pesticides that accumulate in sediments are particularly attracted to fine organic material (USEPA, 1982). Three depositional areas in each ditch where fine organic material has accumulated were identified in February 1996 during a reconnaissance of the ditches. Four sediment samples were collected from GHCDD-1 and three were collected from PCDD-1 at these depositional areas (Figure 1). Site 1 on GHCDD-1 was located just upstream of the bridge at Cranberry Road near the end of Schmid Road, Site 2 was about a mile down stream from the bridge at Schmid Road, and Sites 3 and 4 were in an area where the ditch widens out just behind the tide gates. The two samples at Sites 3 and 4 were collected to assess sample variability; the two sites were about 50 meters apart. Site 1 on PCDD-1 was at the bridge on Gould Road, Site 2 was at the bridge on Larkin Road, and Site 3 was on the north side of Highway 105, just behind the tide gates.

To simplify and reduce field time for tissue and sediment sampling, sample collection was scheduled around low tides, which were necessary for shellfish collection. Minus 1.8 tides in the last week of August were the first exceptionally low tides that occurred after the last insecticide applications to cranberry bogs. All samples except crabs were collected on August 27 through August 29, 1996. Crabs were collected on September 9, 1996.

Tissue samples were analyzed for 43 pesticides and breakdown products, and 5 polychlorinated biphenyls (PCBs) (Appendix B-2). Sediments were analyzed for a total of 133 compounds, which included chlorinated pesticides and PCBs, organophosphorus pesticides, nitrogen-containing pesticides, chlorinated herbicides, pyrethroid pesticides, and propargite, a sulfur-containing pesticide (Appendix B-3).

No field measurements were collected for tissue or sediment samples, except site positions, which are listed in Appendix A. Conventional analyses included percent total lipid (fat) for tissue samples, as well as percent solids, percent total organic carbon (TOC), and grain size for sediment samples.

Data Review Summary

Assessment of quality assurance/quality control (QA/QC) results for water analyses indicates that the data are of very high quality. Few results required qualification due to analytical problems. Many of the results, especially for azinphos-methyl and chlorpyrifos, were qualified as estimates by the laboratory because detected concentrations were below quantitation limits. No results were rejected, and all data were usable as qualified.

Quality of data from tissue analyses was also high, but few pesticides were detected, and most concentrations were low. Results for the most frequently detected compound, 4,4'-DDT, were qualified as estimates due to a high relative percent difference (RPD) between duplicate analysis results.

Analytical difficulties in sediment samples, due to unusually high proportions of water, resulted in qualification of nearly all pesticide detections. Three compounds -- 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT -- were the most frequently detected sediment analytes, but the QA/QC results for these compounds were very poor, and required qualification of all results. Accuracy and precision of most sediment data were poor, but there is evidence that some pesticides are present in substantial concentrations.

Results and Discussion

Water Sampling

Pesticides Detected

Eight organophosphorus (OP) pesticides were detected in water samples collected from GHCDD-1 and PCDD-1 in 1996 (Table 1A). Six of these compounds -- acephate, azinphos-methyl, chlorpyrifos, diazinon, malathion, and methamidophos -- were found in both drainage ditches. Parathion was found only in samples from GHCDD-1 collected in May, and sulfotep only in PCDD-1 in July. Azinphos-methyl, chlorpyrifos, and diazinon were the most frequently detected pesticides in both ditches.

Acephate was detected in all samples collected in the first two weeks of the study, but was found in only one sample from GHCDD-1 in July. Malathion was found only once in each ditch in July. Methamidophos, a breakdown product of acephate that is more toxic than the parent compound, was detected in several samples from each drainage ditch in May and July.

Fifteen additional pesticides -- three insecticides and 12 herbicides -- were detected in the four samples analyzed for the complete list of target analytes (Table 1B). Carbaryl and carbofuran were found only in samples collected in May and July from both drainage ditches. Samples collected in May and July from GHCDD-1 also contained 4,4'-DDD, and 4,4'-DDD was found in all four samples from PCDD-1. Herbicides that were detected in all four samples from both ditches include napropamide, norflurazon, and 2,4-D. MCPP was found in three of the samples from both sites, and dichlorprop was detected in three of the samples from GHCDD-1.

Results from split samples analyzed by the Washington State Department of Agriculture (WSDA) Laboratory are presented in Table 2. Samples collected on July 22, 24, and 25 were not splits and were analyzed only by the WSDA Laboratory. Data were collected on these three days to assess pesticide contamination for the *in situ* bioassays that were in place during these dates (Wood, 1997). Results from the WSDA Laboratory are compared to Manchester Environmental Laboratory results in Appendix F-9. There was generally good similarity between results from the two laboratories.

Comparisons to Water Quality Criteria

Water quality criteria were obtained from several sources, and are summarized for detected pesticides in Table 3. There are no numeric criteria available for detected pesticides that are not listed in Table 3. All listed criteria were developed for the protection of freshwater aquatic life. Multiple sources were used because no single source includes all of the detected pesticides. State water quality standards have been established for only four detected compounds, chlorpyrifos, DDD, parathion, and pentachlorophenol (PCP). State standards were adopted from criteria developed by the USEPA (1986), which are available for only one other detected pesticide,

Table 1A. Organophosphorus Pesticides Detected in Water Samples Collected from Grayland and North Cove Cranberry Bog Drainage Ditches in 1996 (µg/L, ppb)
Samples Analyzed by the Manchester Environmental Laboratory

GHCDD-1

	acephate	azinphos-methyl	chlorpyrifos	diazinon	malathion	metham-idophos	parathion
13-May	0.14 J		0.005 NJ	[2]4.4		0.069	
20-May	0.013 J	[1]0.21 J	0.006 J	[2]0.32		0.019 NJ	[3]0.10 J
21-May	0.013 J	[1]0.092 J		[2]0.37		0.029 NJ	[3]0.056 J
22-May	0.032 J	[1]0.18 J		[2]0.51		0.067 NJ	[3]0.048 J
23-May	0.010 J	[1]0.077 J		[2]0.14		0.013 NJ	[3]0.04 J
24-May	0.32 J	[1]0.049 J	0.012 J	[2]0.077		0.007 NJ	[3]0.019 J
28-May		[1]0.025 J		[2]0.4			[3]0.014 J
4-Jun		[1]0.015 J		[2]5.42			
11-Jun				[2]0.45			
18-Jun				[2]0.07			
24-Jun				[2]0.056			
1-Jul				[2]0.12			
9-Jul				0.026 J			
15-Jul		[1]0.12 J		[2]0.7			
16-Jul		[1]0.25 J		[2]0.15			
17-Jul		[1]0.66 J		[2]0.28	0.005 NJ	0.001 NJ	
18-Jul		[1]0.11 J	0.005 J	[2]0.45		0.012 J	
19-Jul	0.012 J	[1]0.73 J	0.005 J	[2]1.7		0.13 J	
23-Jul		[1]0.11 J		[2]0.35		0.012 J	
30-Jul		[1]0.069 J	0.016 J	[2]0.053 J			
6-Aug		[1]0.094 J	0.009 J	[2]0.055 J			
12-Aug		[1]0.016 NJ	0.003 J	[2]2.3 J			
13-Aug				[2]1.5			
14-Aug		0.010 J		[2]1.1 J			
15-Aug				[2]0.86 J			
20-Aug				[2]0.41 J			

Shaded values exceed water quality criteria

The highest concentration detected for each pesticide is outlined.

A blank indicates that the target analyte was not detected.

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

NJ = There is evidence that the analyte is present. The associated numerical result is an estimate.

[1] - Exceeds USEPA (1986) Quality Criteria for Water (Gold Book).

[2] - Exceeds California Department of Fish and Game Water Quality Criteria (Menconi and Cox, 1994).

[3] - Exceeds Washington State Water Quality Standards, WAC 173-201A.

Table 1A (cont.). Organophosphorus Pesticides Detected in Water Samples Collected from Grayland and North Cove Cranberry Bog Drainage Ditches in 1996 (µg/L, ppb)
Samples Analyzed by the Manchester Environmental Laboratory

PCDD-1

	acephate	azinphos-methyl	chlorpyrifos	diazinon	malathion	metham-idophos	sulfotep
13-May	0.091 J	[1]0.056 J	0.010 NJ	[3]0.56		0.0085	
20-May	0.032 J	[1]0.74 J	[2]0.13 J	[3]0.057			
21-May	0.061 J	[1]0.62 J	[2]0.13 J	[3]1.62		0.007 NJ	
22-May	0.079 J	[1]0.56 J	[2]0.055 J	[3]0.56		0.008 NJ	
23-May	0.025 J	[1]0.26 J	0.039 J	[3]0.29		0.006 NJ	
24-May	0.018 J	[1]0.22 J	[2]0.042 J	[3]0.9		0.003 NJ	
28-May		[1]0.14 J	0.018 J	[3]0.25			
4-Jun		[1]0.04 J	0.013 J	[3]0.22			
11-Jun		[1]0.019 J	0.013 J	0.027 J			
18-Jun		[1]0.024 J	0.021 J				
24-Jun		0.013 NJ	0.009 J	0.022 J			
1-Jul		0.01 NJ	0.006 J	0.014 J			
9-Jul		0.012 NJ	0.003 J	0.01 J			
15-Jul		0.006 J	[2]3.7	0.008 J			0.019 J
16-Jul		0.007 J	[2]1.9	0.01 J			0.004 J
17-Jul		[1]0.018 J	[2]1.3	0.01 J			0.003 J
18-Jul		[1]0.50 J	[2]1.3	0.035 J		0.007 J	0.003 J
19-Jul		[1]0.13 J	[2]1.3	[3]0.39	0.008 NJ	0.012 J	0.004 J
23-Jul		[1]0.10 J	[2]0.54	[3]0.075		0.005 NJ	
30-Jul		[1]0.021 J	[2]0.38 J	[3]0.34 J			
6-Aug		[1]0.38 J	[2]0.14 J	[3]1.7 J			
12-Aug		[1]0.18 J	[2]0.064 J	[3]0.046 J			
13-Aug		[1]0.2	[2]0.11	[3]0.056			
14-Aug		[1]0.096 J	[2]0.069 J	[3]0.069 J			
15-Aug		[1]0.05 J	[2]0.078 J	[3]0.051 J			
20-Aug		[1]0.015 J	[2]0.054 J	[3]0.048 J			

Shaded values exceed water quality criteria

The highest concentration detected for each pesticide is outlined.

A blank indicates that the target analyte was not detected.

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

NJ = There is evidence that the analyte is present. The associated numerical result is an estimate.

[1] - Exceeds USEPA (1986) Quality Criteria for Water (Gold Book).

[2] - Exceeds Washington State Water Quality Standards, WAC 173-201A.

[3] - Exceeds California Department of Fish and Game Water Quality Criteria (Menconi and Cox, 1994).

Table 1B. Carbamate and Chlorinated Insecticides, and Herbicides Detected in Water Samples Collected from Cranberry Bog Drainage Ditches in 1996 (µg/L, ppb)
Sample Analyzed by the Manchester Environmental Laboratory

	20-May	11-Jun	15-Jul	13-Aug
GHCDD-1				
Insecticides				
carbaryl	[1]0.030 J		[1]0.026 J	
carbofuran	0.12 J		0.021 J	
4,4'-DDD	[2]0.0080 J		[2]0.0041 J	
Herbicides				
dichlobenil		0.20		0.087 J
2,6-dichlorobenzamide		0.20 J		0.24 J
dichlorprop	0.072	0.012 J		0.010 J
diuron			0.042 J	
MCPP		0.014 J	0.018 J	0.018 J
napropamide	0.48	0.068 J	0.12 J	0.095 J
norflurazon	0.44 J	0.066 J	0.052 J	0.054 J
prometon			0.0038 J	
simazine	0.006 J			
terbacil	0.040 J			
2,4-D	0.28	0.075	0.046	0.054
PCDD-1				
Insecticides				
carbaryl	[1]0.029 J		[1]0.042 J	
carbofuran	0.078 J		0.01 J	
4,4'-DDD	[2]0.011 J	[2]0.008 J	[2]0.027 J	[2]0.012 J
Herbicides				
dichlobenil		1.5		0.34
2,6-dichlorobenzamide		0.11 J		0.15 J
dichlorprop	0.017 J			0.017 J
MCPP		0.013 J	0.014 J	0.017 J
napropamide	0.28	0.63	0.042 J	0.076 J
norflurazon	0.82 J	0.11 J	0.054 J	0.20 J
simazine				
terbacil				
2,4-D	0.36	0.12	0.039 J	0.09
pentachlorophenol	0.025			

Shaded values exceed water quality criteria

A blank indicates that the target analyte was not detected.

[1] - Exceeds National Academy of Sciences (1973) Recommended Maximum Concentration.

[2] - Exceeds Washington State Water Quality Standards, WAC 173-201A.

Table 2. Pesticides Detected in Field Split Water Samples Collected from Grayland and North Cove Cranberry Bog Drainage Ditches in 1996 (µg/L, ppb)
Samples Analyzed by the WSDA Chemical and Hop Laboratory, Yakima, WA

	GHCDD-1				PCDD-1			
Date	acephate	diazinon	chlorpyrifos	azinphos-methyl	acephate	diazinon	chlorpyrifos	azinphos-methyl
20-May	[1]0.14 NJ	[1]0.28 J		[1]0.15 J	0.46 NJ	0.063 J	0.12	0.62 J
22-May	0.278 NJ	0.59 J	0.012	0.17 J	[1]0.652 NJ	[1]0.51 J	[1]0.082	[1]0.508 J
24-May	0.063 NJ	0.108 J	0.023 J	0.05 J		0.991 J	0.061	0.195 J
28-May	[1]0.139 NJ	[1]0.45 J	[1]0.01 J	[1]0.05 J		0.241 J	0.028 J	0.129 J
4-Jun		5.2 J				0.293 J	0.021 J	0.053 J
11-Jun		0.361 J				[1]0.026 J	[1]0.02 J	
18-Jun		0.059 J					0.025 J	
24-Jun		[1]0.046 J				0.014 J		
9-Jul		[1]0.02 J			0.051 NJ	0.02 J		
15-Jul	0.09 NJ	0.107		0.036 J		0.012 J	5.1	0.06 J
17-Jul		[1]0.294		1.31 E		0.022 J	2.03	
19-Jul	0.216 NJ	1.99		1.53	0.081 NJ	0.342	1.1	0.303
22-Jul	0.056 NJ	0.553		0.263		0.159	0.499	0.176
23-Jul	0.074 NJ	0.403		0.179		0.077	0.582	0.205
24-Jul		0.233		0.093 J		0.036 J	0.428	0.133
25-Jul		0.081		0.059 J		0.029 J	0.264	0.073 J
30-Jul		0.055	0.021 J	0.067 J		0.309	0.344	
5-Aug		0.056		0.106 J		[1]1.72	[1]0.11	[1]0.366
12-Aug		2.60				0.048	0.063	0.252
14-Aug	[1]0.051 NJ	[1]0.935				0.045 J	0.053	0.088 J
20-Aug		0.319				[1]0.047 J	[1]0.043 J	

A blank indicates that the target analyte was not detected.

[1] - Values are means of duplicate analyses.

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

NJ = There is evidence that the analyte is present. The associated numerical result is an estimate.

E = The concentration of the associated value exceeds the known calibration range.

azinphos-methyl (Guthion). Recommended maximum concentrations established by the National Academy of Sciences (1973) are widely used and accepted, and have been included here when there are no other criteria available, although they are over 20 years old and sometimes considered too conservative. Another source was Canadian water quality guidelines (CCREM, 1987). Criteria from all of these sources have been summarized by Nowell and Resek (1994).

Table 3. Water Quality Criteria for Detected Pesticides (µg/L, ppb)

		Aquatic Life Standards		
Common Name	Trade Names	Acute	Chronic	RMC[1]
azinphos-methyl	Guthion		[2] 0.01	
carbaryl	Sevin			[3] 0.02
carbofuran	Furadan			[4] 1.75
chlorpyrifos	Lorsban, Dursban	[5] 0.083	[5] 0.041	
DDT and metabolites		[5] 1.1	[5] 0.001	
diazinon	Diazinon	[6] 0.08	[6] 0.04	
dichlobenil	Casoron, Norosac			[3] 37
diuron	Karmex			[3] 1.6
malathion	Malathion		[2] 0.1	
parathion	Parathion	[5] 0.065	[5] 0.013	
pentachlorophenol	Permatox	[5] 20 [a]	[5] 13 [a]	
simazine	Princep			[4] 10
2,4-D	several			[3] 3

[1] - RMC = Recommended Maximum Concentration
[2] - USEPA (1986), Quality Criteria for Water (Gold Book)
[3] - National Academy of Sciences (1973)
[4] - CCREM (1987), Canadian Water Quality Guidelines
[5] - Washington State Water Quality Standards, WAC 173-201A
[6] - Menconi and Cox (1994), California Department of Fish and Game
[a] - Criteria are pH dependent, values shown are calculated at a pH of 7.8

Azinphos-Methyl - All but one of the concentrations of azinphos-methyl found in samples from GHCDD-1, and 21 of 26 detections from PCDD-1, exceeded the USEPA (1986) water quality criterion of 0.01 µg/L (parts per billion). Detected concentrations from two GHCDD-1 samples and three PCDD-1 samples were the highest recorded in state waters.

Chlorpyrifos - None of the chlorpyrifos detections in samples from GHCDD-1 exceeded state water quality standards. Concentrations of chlorpyrifos found in samples from PCDD-1 were much higher. Seventeen of 26 detections were above Washington State water quality standards; 11 of the 17 exceeded the acute standard of 0.083 µg/L, and the other six were above the chronic standard of 0.041 µg/L. Five values in July were over 1 µg/L, and are the highest concentrations of chlorpyrifos ever detected in state waters.

Diazinon - There are no state or federal water quality criteria for the protection of aquatic life established for diazinon. Criteria used here are maximum (acute) and continuous (chronic) concentrations of 0.08 µg/L and 0.04 µg/L respectively, as calculated by the California Department of Fish and Game (CDFG) using USEPA guidelines (Menconi and Cox, 1994).

Twenty-five of 26 detections in samples from GHCDD-1, and 17 of 25 from PCDD-1 exceeded the CDFG chronic criterion. Some of these values are the highest concentrations ever recorded in state waters for diazinon. Twenty detections from GHCDD-1 and ten from PCDD-1 were above the CDFG acute criterion.

Parathion - Parathion detections in six samples collected from GHCDD-1 in May exceeded Washington State water quality standards for the protection of aquatic life. The concentration of the first detection on May 20 was above the state acute criterion of 0.065 µg/L, and the remaining five values exceeded the chronic criterion of 0.013 µg/L. Parathion is no longer registered for use on cranberries in Washington State. All available evidence indicates that the levels of parathion contamination identified in GHCDD-1 were the result of illegal application by a single grower on May 15, 1996 to bogs that are over two miles upstream from the sample site at Schmid Road (Boyd, 1997).

Malathion - The two malathion detections, one in GHCDD-1 and one in PCDD-1, were well below the USEPA (1986) criterion of 0.1 µg/L.

Other Pesticides - There are no water quality criteria available for methamidophos or sulfotep, but both are highly toxic, comparable to azinphos-methyl and chlorpyrifos. Neither of these two compounds is registered for use on cranberries. As indicated above, methamidophos is probably present as a breakdown product of acephate, but the source of sulfotep is unknown.

Of the 15 additional pesticides detected in samples analyzed for the complete list of target analytes, only two -- carbaryl and 4,4'-DDD -- exceeded water quality criteria. Detected concentrations of carbaryl on May 20 and July 15 from both drainage ditches were above the National Academy of Sciences (NAS) recommended maximum concentration of 0.02 µg/L. Levels of 4,4'-DDD in samples from GHCDD-1 collected on May 20 and July 15, and in all four samples from PCDD-1, exceeded the Washington State water quality chronic standard of 0.001 µg/L. None of the detected herbicides was found at levels above water quality criteria.

Human Health Criteria

USEPA human health criteria assume that the water is used for drinking, but the ditches are probably not used as a drinking water source. In addition, criteria available for detected pesticides are expressed as lifetime health advisory levels that are calculated based on a lifetime of 70 years consuming two liters of contaminated water per day. Some detected concentrations of diazinon exceeded the criterion of 0.6 µg/L, but most were lower. Human health criteria are not available for the other organophosphorus pesticides found in the ditches, and other detected pesticides were lower than applicable criteria.

Comparisons to LC_{50}s

Acute toxicity data provide an estimate of the concentration of a chemical that will result in 50% mortality (LC_{50}) to a test organism that is exposed to a chemical for a specified time period. Several detected concentrations of organophosphorus insecticides were higher than LC_{50} values

for a variety of organisms (Johnson and Finley, 1980; USEPA, 1996). LC_{50} values for the three most frequently detected insecticides are presented in Table 4. The four invertebrates and four fish that are listed in Table 4 were selected because data for all three insecticides were available for these species. Of these eight species, only sticklebacks are known to inhabit the ditches, but the invertebrates are likely to be representative of microfauna that reside in the ditches. Several detected concentrations of azinphos-methyl and chlorpyrifos exceeded LC_{50} values for all four invertebrates in Table 4. LC_{50} values for diazinon were higher, and only the value for *Gammarus fasciatus* fell below detected levels. All concentrations of the three insecticides were lower than LC_{50} values for the fish, although the highest level of chlorpyrifos was very close to the LC_{50} for bluegill. Much more toxicity data are available for most of the pesticides that were detected, and these data can be used to evaluate the impact on ditch fauna as more is learned about which species are or should be present.

Table 4. Comparison of Acute Toxicity of Three Detected Insecticides (µg/L, ppb)

		96 Hour LC_{50}		
Scientific Name	Common Name	azinphos-methyl	chlorpyrifos	diazinon
Chironomus tentans	midge	0.37	0.47	5.4
Gammarus fasciatus	amphipod (scud)	0.18	0.32	0.2
Gammarus lacustris	amphipod (scud)	0.14	0.11	185
Mysidopsis bahia	opossum shrimp	0.24	0.05	6.4
Cyprinodon variegatus	sheepshead minnow	2.3	182	810
Gasterosteus aculeatus	3-spine stickleback	8.5	8.5	not available
Lepomis macrochirus	bluegill	5.7	4.5	302
Oncorhynchus mykiss	rainbow trout	6.0	8.8	1040

LC_{50} values are from the USEPA AQUIRE (Aquatic Toxicity Information Retrieval) Database

Conventional Parameters

Results from field measurements are presented in Table 5A, and results from samples collected for analysis of total organic carbon (TOC) and total suspended solids (TSS) are listed in Table 5B. Values of all conventional parameters were within acceptable levels and state criteria. Temperature throughout the summer remained below state criteria for a class A stream (18 °C). Peat bogs are often acidic, but the pH of water in the ditches was consistently neutral (near pH 7.0). There are no state numerical water quality criteria for TOC or TSS, but the levels reported here are not elevated compared to data from other sites in Washington, which include values from agricultural drainage ditches (Davis and Johnson, 1994a; Davis, 1996). According to the NAS (1973), suspended solids concentrations below 25 mg/L result in a high level of protection for aquatic communities.

Stream flow is plotted with rainfall (daily measurements by the NOAA National Weather Service, Long Beach Experimental Station) in Figures 2 and 3. It is important to note that rainfall measurements were recorded daily, but flow was measured only when water samples were collected. Flow in both drainage ditches appears to respond about the same to rainfall. Flow levels fell quickly in May and early June as spring rains began to diminish. A steady decline in

Table 5A. Cranberry Bog Drainage Water Quality Assessment (1996)
Conventional Parameters

	GHCDD-1				PCDD-1			
Date	Flow (CFS)	Temperature (°C)	pH	Conductivity (µmho/cm)	Flow (CFS)	Temperature (°C)	pH	Conductivity (µmho/cm)
16-Apr	12	10.8	6.7	114	8.9	10.7	6.8	117
13-May	11.7	13.7	6.7	DNC	19.9	13.0	6.7	DNC[1]
20-May	9.2	13.0	6.6	158	18.8	12.1	7.0	174
21-May	9.4	11.3	6.5	114	14.8	10.9	7.1	129
22-May	11.7	11.5	6.7	102	16.1	11.5	6.4	108
23-May	8.2	11.7	6.6	115	11.7	11.5	6.7	123
24-May	6.4	13.5	6.6	123	5.4	13.1	6.4	196
28-May	4.7	16.3	6.8	182	6.8	14.2	6.9	203
4-Jun	4.2	13.5	6.6	DNC	7.3	13.0	6.8	DNC
11-Jun	2.9	17.3	6.4	212	6.3	14.7	6.6	240
18-Jun	1.8	12.5	6.5	DNC	5.3	13.5	6.5	DNC
24-Jun	5.2	15.0	6.3	184	6.6	14.5	6.4	212
1-Jul	1.9	14.1	6.8	220	4.9	14.2	7.1	230
9-Jul	1.3	14.6	7.1	210	4.2	15.1	7.3	235
15-Jul	0.4	14.5	6.8	243	3.2	14.2	7.1	258
16-Jul	1.9	13.8	7.0	215	2.7	13.8	7.2	254
17-Jul	2.1	13.9	6.9	211	3.3	13.1	7.1	242
18-Jul	2.9	13.6	6.5	194	8.2	13.5	6.6	178
19-Jul	5.1	14.3	6.6	202	9.8	14.4	6.4	205
22-Jul	3.8	14.4	6.6	204	6.2	15.1	6.9	238
23-Jul	2.4	14.4	6.6	211	5.1	15.8	6.7	244
24-Jul	1.9	14.4	6.6	220	4.8	15.9	6.7	252
30-Jul	1.5	13.8	6.3	230	4.6	13.4	6.5	238
6-Aug	2.2	16.0	6.8	169	5.1	15.0	6.9	200
12-Aug	1.8	16.0	6.7	165	4.1	16.8	6.8	194
13-Aug	1.3	14.1	6.6	158	3.7	13.5	6.7	236
14-Aug	1.4	13.5	6.6	211	3.2	12.4	6.7	243
15-Aug	0.9	13.8	6.6	228	3.6	13.7	6.7	250
20-Aug	0.8	14.1	6.7	188	3.4	14.5	6.4	229

[1] - DNC = Data Not Collected

Table 5B. Cranberry Bog Drainage Water Quality Assessment (1996)
Total Organic Carbon (TOC) and Total Suspended Solids (TSS) (mg/L)

	GHCDD-1		PCDD-1	
Date	TOC	TSS	TOC	TSS
16-Apr	14.6	7	15.2	11
13-May	12.1	10 U	14.6	11.0
20-May	13.1	5.0 U	15.5	5.0 U
21-May	14.1	8.0	15.5	5.0 U
22-May	16.0	5.0	16.9	7.0
23-May	13.8	10	15.2	14
24-May	12.3	10	13.4	9.2
28-May	11.5	10.8	10.3	9.1
4-Jun	9.1	6.3	10.4	7.5
11-Jun	8.3	8	9.7	5
18-Jun	6.7	7.0	9.5	5.5
24-Jun	8.6	13.0	7.6	10.8
1-Jul	8.2	6.6	9	4.0 U
9-Jul	6.5	4.0 U	8.2	5.2
15-Jul	6.1	5.8	8.6	4.8
16-Jul	6.5	7.0	8.7	6.0
17-Jul	7.7	10.2	9.5	8.0
18-Jul	7.7	6.0	9.1	9.2
19-Jul	8.1	5.6	9.1	6.8
23-Jul	9.8	5.6	9.0	7.6
30-Jul	6.6	4.0 U	7.9	4.0 U
6-Aug	6.3	4.0 U	9.3	20
12-Aug	5.0	4.0 U	9.3	5.6
13-Aug	6.4	2 U	8.4	2 U
14-Aug	5.2	4.0 U	9.7	5.6
15-Aug	2.0	4.8	5.4	6.8
20-Aug	4.7	4.0 U	4.5	4.4

U = Undetected at or above the reported value.

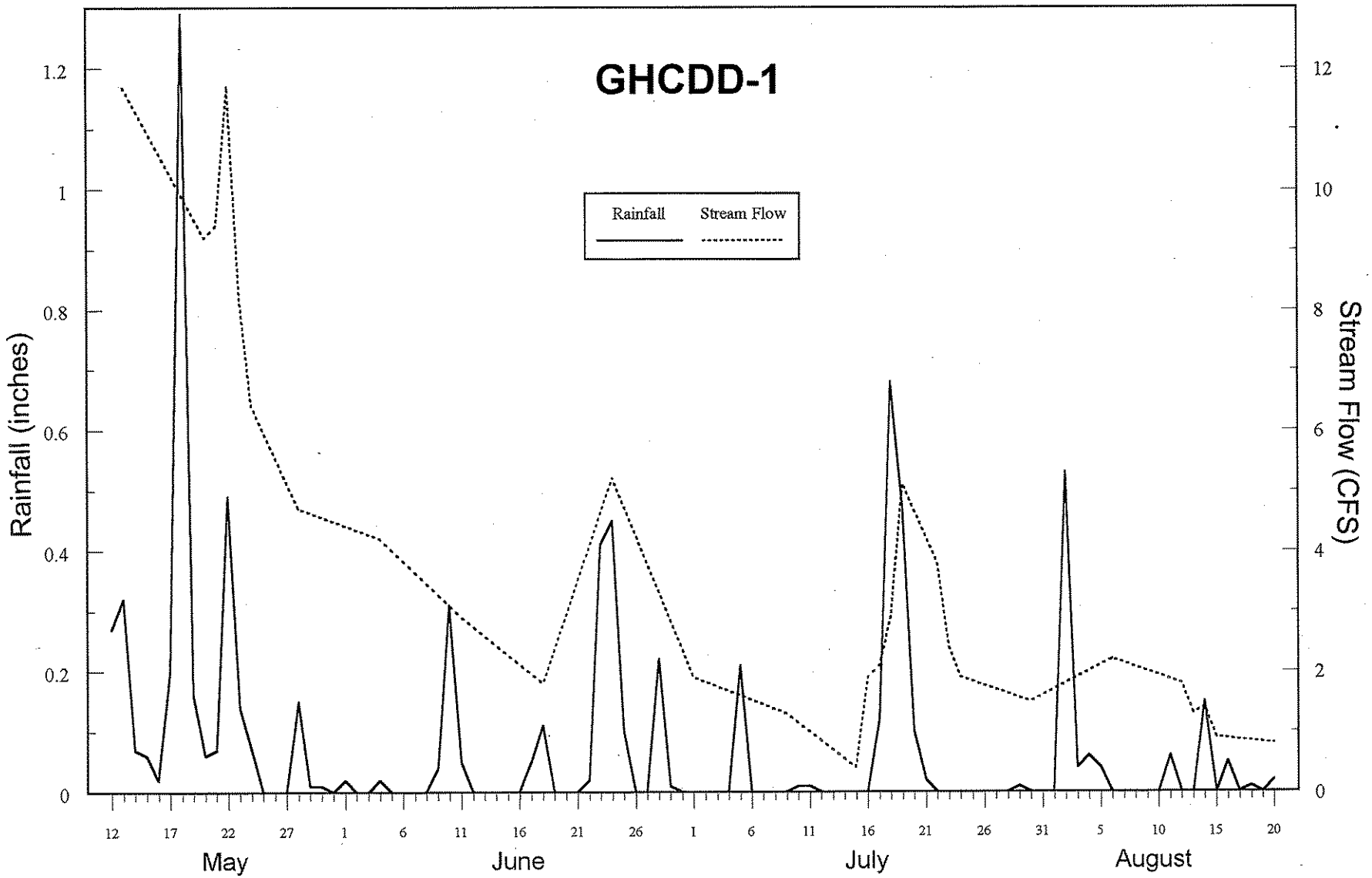


Figure 2. Comparison of Rainfall in Pacific County to Stream Flow Measurements from GHCDD-1 (1996)

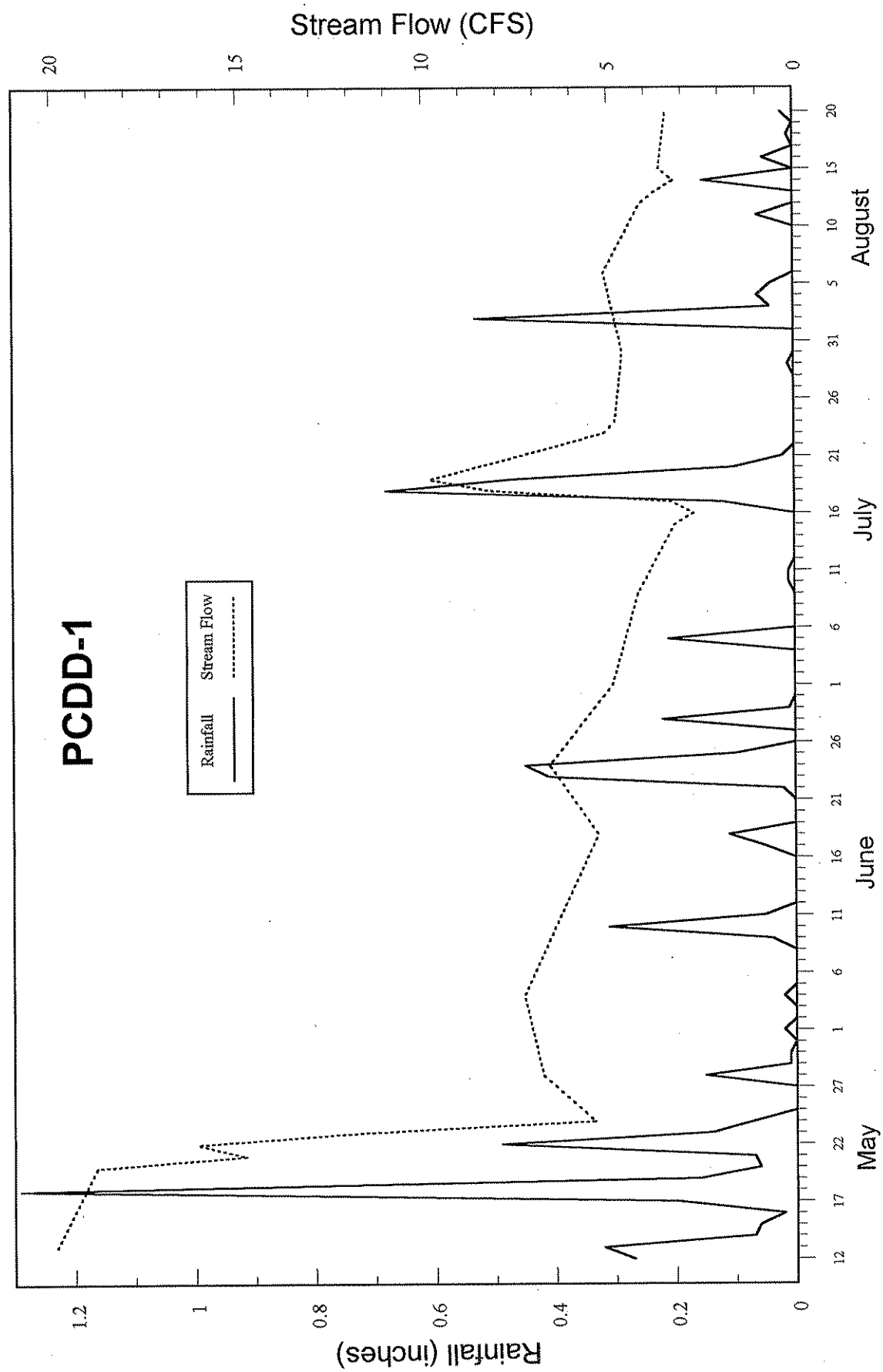


Figure 3. Comparison of Rainfall in Pacific County to Stream Flow Measurements from PCDD-1 (1996)

flow was briefly interrupted in late June by a storm event from June 22 through 25. Flow reached a low on July 15 and then increased rapidly in response to a storm from July 17 through 21. After the storm, levels dropped quickly and then remained nearly the same to the end of August, with a small increase in early August from a brief storm event.

Stream flow was not affected substantially unless the rain continued for four or more days and 24 hour accumulations were greater than 0.4 inches. Flow appears to respond to heavy rainfall quickly. For the two storm events in June and July, flow peaked about one day after the heaviest rainfall and returned to normal two to four days after the storms.

Discussion

Concentrations of organophosphorus pesticides in both drainage ditches remained high enough throughout the entire study period to potentially adversely impact some aquatic life. At least one pesticide was detected in each sample at a concentration that exceeded water quality criteria for protection of aquatic life, and most samples contained multiple pesticides above criteria. Levels of several detections were one to three orders of magnitude higher than the criteria. Many detected concentrations of organophosphorus insecticides exceeded LC_{50} values.

Water quality criteria and LC_{50} values are determined for individual compounds only. Very little is known about the effects due to combinations of pesticides, but some are additive or synergistic, potentially resulting in more environmental damage than would be expected (Macek, 1975; Faust *et al.*, 1994). In addition, criteria and LC_{50}s are generally calculated based on exposure times of a few days or less. LC_{50} values that are calculated based on longer exposure times are almost always lower. Organisms in the Grayland/North Cove cranberry bog drainage ditches are being exposed to multiple highly toxic insecticides for the entire four-month growing season. These data indicate that some aquatic life within these ditches are probably being adversely impacted by pesticide contamination from cranberry farming.

While these data document that a pesticide contamination problem exists in the drainage ditches, there is little information to determine how the pesticides make their way into the ditches. Stream flow and rain measurements (Figures 2 and 3) show that rainwater entering the bogs tends to move through the system quickly. Figures 4 and 5 compare pesticide concentrations in the ditches with flow. In general, peak flows do not occur at the same time as peak pesticide concentrations, suggesting that the pesticides are not entering the system primarily from rain runoff. However, once the pesticides get in the system, the concentration of a chemical in water tends to decrease in one to two weeks to a level below the detection limit, indicating that the pesticides are moving through rapidly with the water.

Parathion detections give an indication of pesticide movement through the bogs. As previously noted, evidence shows that parathion was applied on May 15 to a single bog over two miles from the GHCDD-1 sample site and was detected on May 20 through 28 (no samples were collected from May 15 through 19). Heavy rain on May 18 may have aided in its rapid movement, but Figures 4 and 5 indicate that the pesticides do not need rainfall to be transported. These data

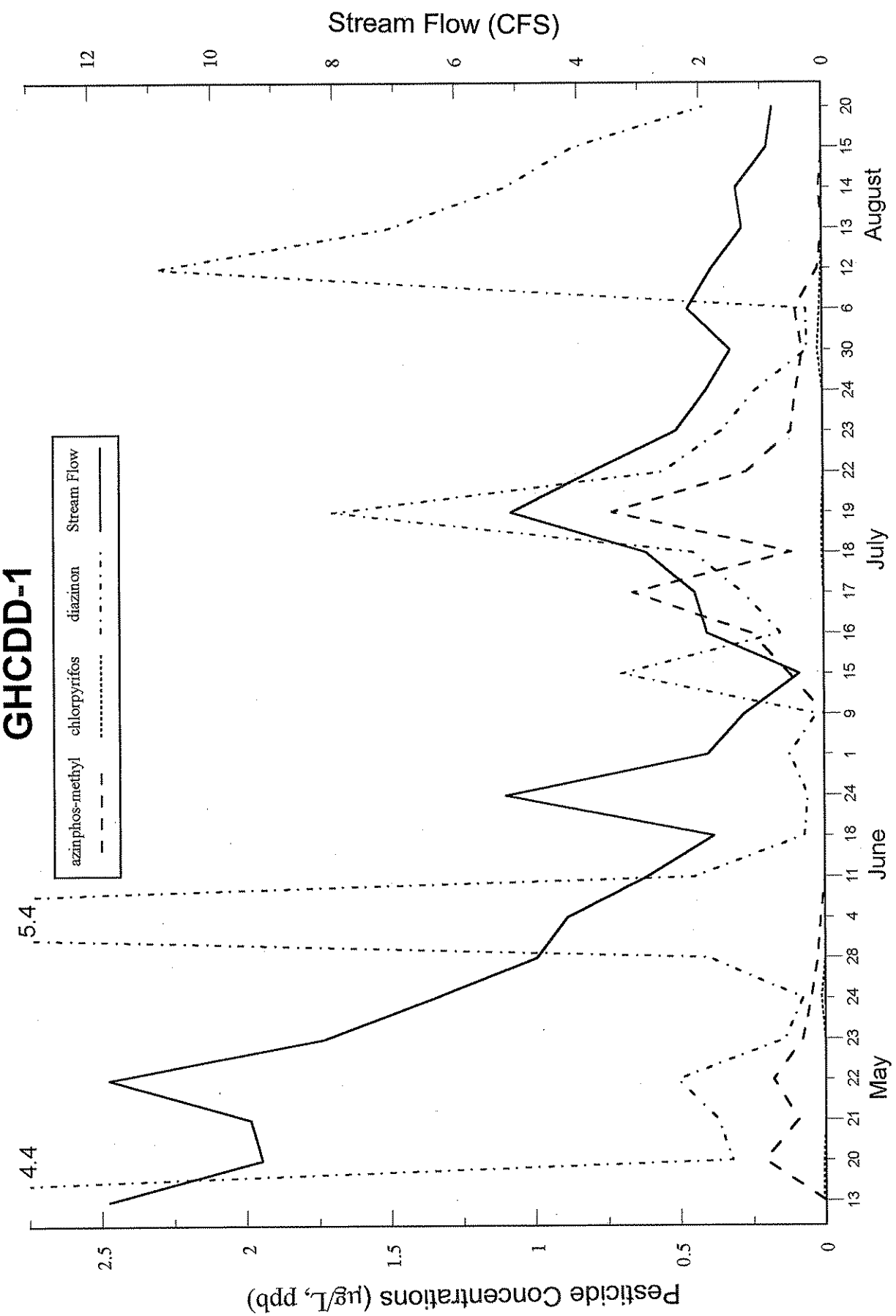


Figure 4. Comparison of Pesticide Concentrations to Stream Flow in GHCDD-1 (1996)

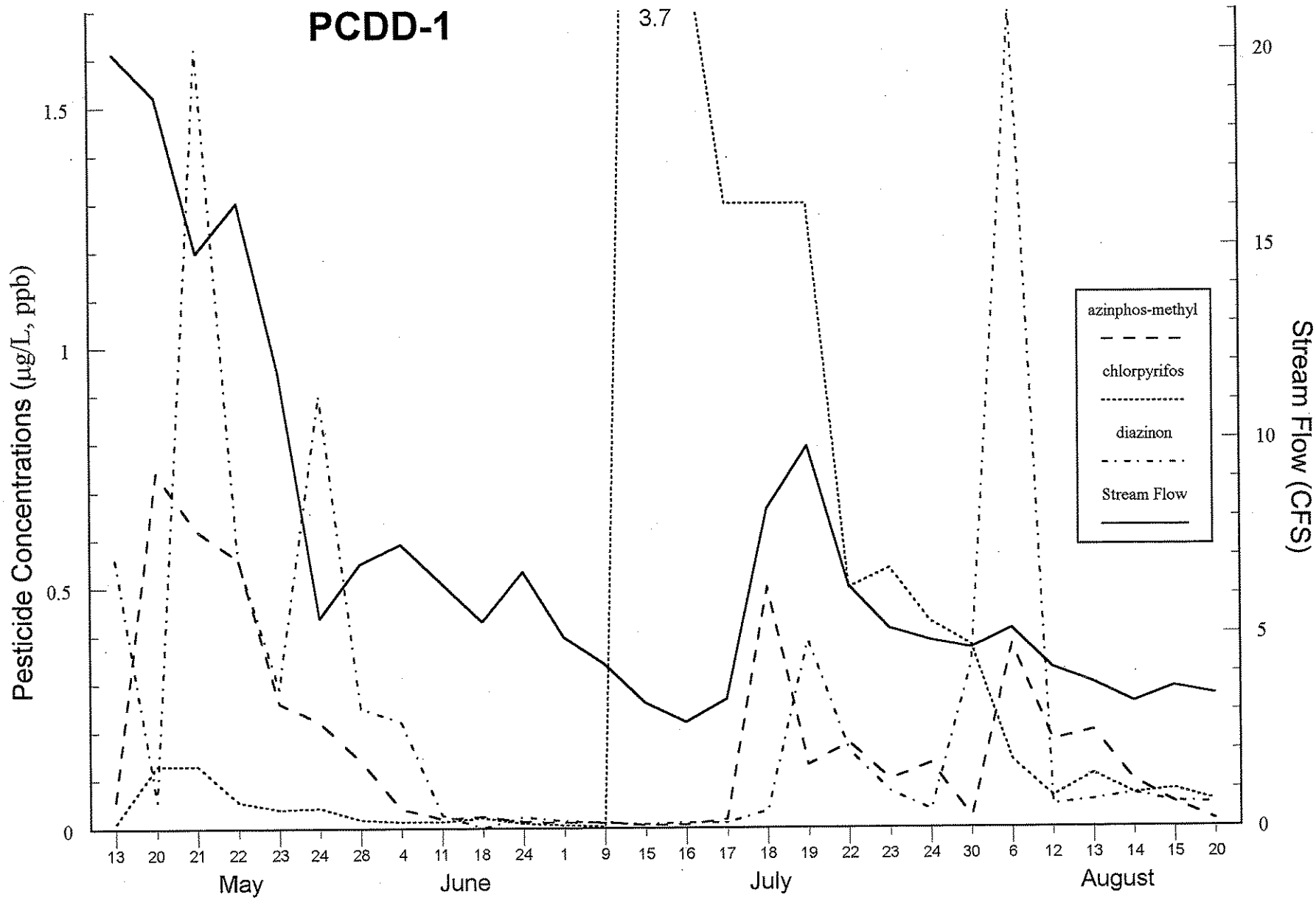


Figure 5. Comparison of Pesticide Concentrations to Stream Flow in PCDD-1 (1996)

suggest that it takes about two weeks for organophosphorus pesticides to move through the bog system. The data from this report combined with application records from individual growers may give a better indication of where the pesticides are coming from, and how long they take to move through the bogs.

Pesticide detections in July and August give some insight into how the pesticides are getting into the water. From personal observations while collecting samples, I noted that most side ditches draining cranberry bogs into GHCDD-1 and PCDD-1 (the main ditches) began drying up in early July. When pesticides were applied in July and August, there was no water flowing through most of these side ditches. Even during heavy rainfall that resulted in substantial flow increases in the main ditches, there was very little (a trickle) or no flow in the side ditches. The only side ditches that were flowing during this time were three or four that carry small perennial streams from the hills east of the bogs. These streams appear to be the only route for pesticide contamination to get into the main ditches from direct runoff when the other side ditches are dry.

Another possible entry point for pesticide contamination is through the ground water. Ground water within the cranberry bogs is very shallow, typically a couple inches to a few feet from the surface even during the summer (personal observation). Pesticides may be moving with water from irrigation (most pesticides are applied through chemigation) into a shallow ground water layer that is flowing directly into the main ditches. There is no direct evidence of this happening, but ground water flow may explain why flow in the main ditches increases substantially during rain storms even when there is no flow in most side ditches.

Tissue Sampling

Shellfish were collected to assess potential human health and wildlife impacts. Sticklebacks are not consumed by humans and were collected to assess wildlife impacts only.

Pesticides Detected

Eight pesticides and/or breakdown products, as well as one polychlorinated biphenyl (PCB) mixture, were detected in six tissue samples collected from or near GHCDD-1 and PCDD-1 (Table 6). Low concentrations of 4,4'-DDE were found in oysters, softshell clams, and dungeness crabs; 4,4'-DDD was also detected in oysters. Very low levels of PCB-1260 were tentatively identified in oyster and crab tissue. All eight compounds were detected in the stickleback sample, including moderately high levels of 4,4'-DDE and dieldrin.

Comparisons to Criteria

Human Health Screening Values

Tissue sampling for this study fits the definition of a screening survey. Data from screening surveys are not adequate for making decisions regarding fish and shellfish consumption by humans, but the USEPA recommends evaluating detected chemical contaminants with screening values to prioritize problem areas. Sites with concentrations exceeding screening values are an

Table 6. Pesticides Detected in Tissue Samples Collected from Cranberry Bog Drainage Ditches and Receiving Waters in 1996 (µg/kg, ppb - wet weight)

	GHCDD-1 and Vicinity			PCDD-1 and Vicinity		
	Pacific Oysters[1]	Softshell Clams	Stickle-backs	Dungeness Crabs	Razor Clams	Piddock Clams
% Lipid	1.00	0.37	2.08	0.11	0.64	0.62
4,4'-DDE	3.2 J	0.8 J	57 J	3.5 J		
4,4'-DDD	1.9 J		14			
2,4'-DDD			3.9			
4,4'-DDT			5.8			
total DDT	5.1	0.8	81	3.5		
DDMU			10			
dieldrin			5.2			
hexachlorobenzene			0.2 NJ			
pentachloroanisole			0.7 J			
PCB-1260	5 NJ			4 NJ		

A blank indicates that the target analyte was not detected.

[1] - Values are means of duplicate analyses.

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

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

indication that there is a potential problem, and that more intensive monitoring should be conducted. These sites would be evaluated based on a variety of parameters that include, but are not limited to, the level of exceedance, local fish and shellfish consumption patterns and alternative foods, and toxicity of the contaminant. The following summarizes factors that were used to calculate screening values for this study as outlined by the USEPA (1995).

Calculation of Screening Values

Screening values for carcinogenic compounds are calculated using a risk level. All compounds detected in tissues except pentachloroanisole are carcinogenic. A risk level is a value that predicts the increased number of cancer cases caused by a specific or multiple contaminant(s); a risk level of $1x10^{-6}$ is the probability that one person in a million will contract cancer as a result of long-term exposure to the contaminant(s) through consumption of contaminated food. Washington State has adopted $1x10^{-6}$ as its acceptable risk level under the State Water Quality Standards (173-201A-040 WAC) and the Model Toxics Control Act (173-340-730 WAC). The following formula was used to calculate screening values:

$$SV = [(RL/SF) \times BW]/CR$$

where

SV = Screening Value
RL = Maximum acceptable Risk Level ($1x10^{-6}$)
SF = Oral Slope Factor (a carcinogenicity potency factor)
BW = Body Weight of the population of concern (70 kg)
CR = Consumption Rate

Exposure assumptions used to calculate screening values include a body weight of 70 kg and a fish and shellfish tissue consumption rate of 6.5 grams per day (g/d). These values represent the mean body weight for all adults and the average consumption rate for the general U.S. population (USEPA, 1995). The body weight of 70 kg is widely used and accepted, but a consumption rate of 6.5 g/d is often considered too low, particularly for some Native American, Hispanic, and Asian populations. A more realistic number for the general population in western Washington is 26 g/d, which is based on a survey of anglers in Puget Sound (Landolt *et al.*, 1985). A recent consumption survey of the Tulalip and Squaxin Island Tribes in the Puget Sound area (Toy *et al.*, 1996) provides a reasonable estimate of fish and shellfish consumption by Shoalwater Bay Indians, and should be protective of other populations in the area that frequently consume fish and shellfish. Mean consumption of all fish and shellfish for both tribes combined was 62 g/d, and mean consumption of shellfish only was 19 g/d.

Screening values are for use with data from edible tissue only, so results from whole-fish analysis of sticklebacks were not used for assessment of effects on human health. Levels of total DDT (DDT+DDE+DDD) and PCB-1260 in oysters and dungeness crabs exceeded the human health screening value, using a consumption rate of 62 g/d. Using the lower rate of 19 g/d for consumption of shellfish only (oysters and crabs are shellfish), levels of total DDT were lower than the screening value, but PCB concentrations still exceeded the screening value.

The consumption rates used above are for average adult consumers. Children with lower body weights than adults who consume similar quantities of contaminated shellfish would accumulate higher concentrations of contaminants per kilogram of body weight. Similarly, adults who regularly consume higher quantities of shellfish than the average (e.g., subsistence fishermen) would accumulate more contaminants.

Because of the uncertainty associated with the consumption rate, it may be more meaningful to calculate a maximum consumption rate based on concentrations detected in the tissues tested. This is done by using the formula for calculating screening values and solving for the consumption rate based on a screening value equal to the contaminant concentration in the tissue. Based on detected concentrations of total DDT, maximum consumption rates would be 40 g/d for pacific oysters, 257 g/d for softshell clams, and 59 g/d for dungeness crabs (1 ounce = ~28 grams). Consumption rates based on PCB levels would be 1.8 g/d for oysters and 2.3 g/d for crabs. These consumption rates would theoretically result in a $1x10^{-6}$ (one in a million) risk of increased cancer, but it is important to remember that the consumption rates listed above apply to the detected concentrations in Table 6 only. In addition, these consumption rates are provided as an example only, to help clarify the concept of screening values, and do not represent a formal consumption recommendation or advisory.

Reproductive and Developmental Effects

In a recent report by the Washington and Oregon State Health Departments to assess chemical contaminants in lower Columbia River fish (Laflamme and Gilroy, 1996), reproductive and developmental effects rather than cancer were used as endpoints to evaluate the toxicity of total DDT and PCBs to humans. An action level of 61 µg/kg for total DDT in fish fillets was established based on neurodevelopmental effects on rodents from exposure soon after birth, and was derived using a consumption rate of 200 g/d. People eating less than 200 g/d or tissue with lower levels of contamination should not be affected. A Health Protective Value (HPV) derived by the Great Lakes Sport Fish Advisory Task Force was used to assess reproductive and developmental health risks from PCB contamination. Using a consumption rate of 140 g/d, the HPV for total PCBs in fish fillets was equivalent to 50 µg/kg. Concentrations of total DDT and PCBs in pacific oysters and dungeness crabs analyzed for this study were well below the action level and HPV used by the Department of Health assessment.

Water Quality Limited List

When calculated with a risk level of $1x10^{-6}$, a body weight of 70 kg, and a consumption rate of 6.5 g/d, screening values have the same numerical value as National Toxics Rule (NTR) criteria (40 CFR part 131) that are used to assess sites for possible addition to the water quality limited list (section 303(d) of the federal Clean Water Act). The 303(d) list contains state water bodies that do not meet water quality standards, and is used to help set priorities for addressing water pollution from a variety of sources. Sites are added to the list if there is one or more NTR criterion exceeded for a five (or more) fish composite of edible tissue (Washington State Water Quality Policy 1-11, 1993).

The detection limit for PCBs is higher than the NTR criterion of 1.4 µg/kg, so any detection of PCBs in a tissue composite sample could result in addition of the sample site water body segment to the 303(d) list. However, the PCBs found in oyster and crab samples were at very low concentrations and were only tentatively identified. Confirmation samples should be collected and analyzed before these sites are added to the list. Although levels of 4,4'-DDE and dieldrin in sticklebacks exceeded NTR criteria, these fish were analyzed whole. NTR criteria are compared to contaminant concentrations in edible tissue (e.g., fillets) only, which tend to have lower levels of contaminants than whole fish.

Wildlife Criteria

There are no Washington State or national pesticide or PCB criteria that have been adopted for protection of wildlife. Tissue results for this report are compared to wildlife criteria developed by Newell *et al.* (1987) for contaminants found in Niagara River fish to protect piscivorous (fish-eating) wildlife. The methodology used by Newell *et al.* to calculate criteria has been selected to develop Canadian tissue residue guidelines for protecting wildlife (Environment Canada, 1994-draft).

Wildlife criteria were compared to concentrations of contaminants found in whole-animal samples only. None of the contaminant levels found in these tissue samples exceeded wildlife criteria.

Comparison of Results to Other Data

Pacific oysters were used to monitor 19 sites in western Washington for organochlorine pesticides as a part of the National Pesticide Monitoring Program: two sites in Grays Harbor, seven in Willapa Bay, and ten in Puget Sound (Butler, 1973). Samples were collected from each site monthly from October 1965 through December 1968. DDT residues were detected in only 11% of the samples, and dieldrin was found in one sample. DDT residues were found at all the sites in Willapa Bay, at one site in South Bay of Grays Harbor, and at only four of the sites in Puget Sound. Concentrations of total DDT were generally higher at sites in Willapa Bay, and the highest was 176 µg/kg in a sample from Stony Point. Most detections at all sites were near the quantitation limit of 10 µg/kg. From a national perspective (in 1973), the report concluded that these areas were remarkably free from DDT contamination.

A single composite sample of Japanese littleneck clams was collected from Shoalwater Bay tribal tideflats in 1989 by Ecology (Cubbage, 1989). The sample was analyzed for chlorinated pesticides and PCBs, as well as organophosphorus pesticides, but none were detected.

Littleneck clams were also used in a study by the Washington State Department of Health (DOH) to assess chemical contamination of shellfish in Puget Sound (Patrick, 1996). Native littlenecks were collected from 29 sites in 1992 and 1993, and analyzed for an extensive list of chemicals that included chlorinated pesticides and PCBs; none were detected. Report recommendations included discontinuation of organic chemical monitoring in littleneck clams due to lack of significant organic chemical uptake by this species.

Native and Japanese littleneck clams were used by Ecology to assess accumulation of chemical contaminants in marine organisms from Sinclair and Dyes Inlets in Puget Sound near Bremerton (Cubbage, 1992). Clams were collected from eight sites in the fall of 1989 and five sites in 1990, and analyzed for chlorinated pesticides and PCBs. No pesticides or PCBs were detected in any of the samples with detection limits of 2 µg/kg for most chlorinated pesticides and 20 µg/kg for PCBs. Several samples of fish (five species of sole) were also analyzed, and the only pesticide detected was a low level of DDE in one sample.

Native and Japanese littleneck clams were collected from four sites, and dungeness crabs from eight sites, in Bellingham Bay by Ecology in 1990 (Cubbage, 1991). Samples were analyzed for chlorinated pesticides, PCBs, chlorpyrifos, and pentachlorophenol. No pesticides or PCBs were detected with detection limits similar to the Sinclair and Dyes Inlets study described above.

Dungeness crabs were collected from two contaminated sites in Commencement Bay and from a reference site in Discovery Bay by the USEPA in 1981 to assess potential health risks from eating crabs (Gahler *et al.*, 1982). Samples were analyzed for the full list of EPA Priority Pollutants, which included chlorinated pesticides and PCBs. Low concentrations of DDT residues were found in samples from all three sites, and PCBs were detected in samples from Commencement Bay, but not from the reference site. Total DDT levels ranged from 4 to 7 µg/kg, and PCBs averaged 60 µg/kg. Detection limits were very low, 1 µg/kg for DDT residues and 10 µg/kg for PCBs.

Low concentrations of DDE were found in dungeness crab leg muscle tissue collected from six sites near the IONA deep-sea sewage outfall in the Strait of Georgia in 1993 (GVRD, 1994). The average DDE concentration for the six samples was 1.4 µg/kg. PCBs were not detected above the detection limit of 4 µg/kg.

Dungeness crabs were also collected and analyzed for chlorinated pesticides as a part of the Fraser River Estuary Monitoring Program. In 1993, eleven crab samples were collected from Boundary Bay and Roberts Bank (Swain and Walton, 1994). Dieldrin was the only pesticide detected.

Two reports summarize fish and shellfish contamination data from Puget Sound. Table 7 compares mean concentrations and ranges of total DDT and PCBs from these reports to levels found in oysters and crabs from the study area. One report summarizes existing data to assess the health risk from consumption of contaminated seafood (Tetra Tech, 1988), and the other summarizes data related to chemicals of concern in Puget Sound as a reference manual (PTI, 1991). Both summarized shellfish data separately from fin fish, and data are representative of most areas within Puget Sound, including many of the most contaminated spots, as well as reference sites. A mean value was calculated by Tetra Tech in addition to the range, but only the range was reported by PTI for fish and shellfish. Results from both studies were based on data from analysis of edible portions only. The mean total DDT concentration in shellfish was 1.6 µg/kg with a range of 0.15 to 5.6 µg/kg, and the mean concentration of total PCBs was 45 µg/kg with a range of 1.0 to 177 µg/kg. The range reported by PTI for total DDT in shellfish was 0.15 to 11 µg/kg, and 1.0 to 480 µg/kg for total PCBs. Concentrations in fin fish were

substantially higher. The mean calculated by Tetra Tech for total DDT was 11 µg/kg, and 138 µg/kg for total PCBs. Ranges were 0.9 to 28 µg/kg, and 1.8 to 320 µg/kg respectively. The range for total DDT in fin fish reported by PTI was <0.1 to 415 µg/kg, and <5 to 2,060 µg/kg for total PCBs.

Table 7. Comparison of Detected Concentrations in Tissue Samples to Puget Sound Data (µg/kg, ppb - wet weight)

	total DDT		total PCBs	
	Mean	Range	Mean	Range
Puget Sound Data				
Shellfish	1.6	0.15 - 11	45	1.0 - 480
Fin Fish	11	<0.1 - 415	138	1.8 - 2,060
Cranberry Bog Drainage Data				
GHCDD-1				
Pacific Oysters	5.1		5	
Softshell Clams	0.8		U[1]	
Sticklebacks	81		U	
PCDD-1				
Dungeness Crabs	3.5		4	

[1] - U = Undetected

Discussion

The drainage ditches appear to be good habitat for fish and invertebrates. It was surprising when no fish or shellfish except sticklebacks could be found in the ditches. This is particularly true for GHCDD-1, which discharges into the Elk River Estuary. There are probably several species that inhabit the Elk River that could easily migrate into the ditch through the estuary (tide gates would not keep them out). At a minimum, sculpins that are present in most small coastal streams should be present. Freshwater mussels (*Margaretacea margaretacea*) are plentiful in some of the irrigation sump ponds within the cranberry bogs, but none were found in the drainage ditches.

There is no direct evidence from this study, but the high concentrations of pesticides seen in water samples and moderate levels in sediments may be preventing other fish and shellfish from colonizing the drainage ditches. Results from laboratory and *in situ* bioassays show that pesticide levels in the ditches are high enough after peak applications to cause acute mortality to indigenous aquatic organisms (Wood, 1997). In addition, several detected concentrations of three insecticides were higher than LC_{50} values for invertebrates representative of ditch microfauna. If pesticides are causing a significant reduction in microfauna populations that are a food source for many fish, then it may not be possible for other fish to colonize the ditches. However, results from a survey of benthic invertebrates indicate low numbers of animals and species diversity in bottom material from the ditches and a reference site (Wood, 1997), suggesting that habitat modifications necessary to maintain drainage ditches may result in low productivity regardless of contamination. More information is needed to determine how the pesticides are affecting ditch fauna.

The highest number of pesticides and the highest concentrations were seen in sticklebacks, which are not consumed by humans. Therefore, the risk to humans from consumption of contaminated tissue taken from the drainage ditches appears to be low. However, dieldrin and the other chlorinated pesticides detected in tissue samples are very long-lived contaminants and may be present in the ditch system for many years. If other fish or shellfish populations ever become established in the ditches, samples should be collected to assess the risk to humans and wildlife.

Softshell clams were collected from beds that are in the discharge of GHCDD-1 as it flows through tide gates into the Elk River estuary. Access to this site is through private land that is restricted by a locked gate, or by boat from South Bay through a narrow and shallow inlet. It is unlikely that shellfish from this site are consumed by humans on a regular basis.

Oysters were collected from a commercial bed that is located at the seaward end of an inlet that receives the discharge from GHCDD-1. The concentrations of total DDT and PCB-1260 in oyster tissue from this site were very low, but may be a concern for subsistence fishermen. The level of total DDT detected was similar to or slightly lower than concentrations found in oyster samples collected from Beardslee Slough and several sites in Willapa Bay from 1965-72 by the USEPA (Butler, 1973) for the National Pesticide Monitoring Program.

Dungeness crabs were collected from Willapa Bay near the discharge to PCDD-1 by a commercial crab fisherman. The level of DDE and PCB-1260 in crab muscle tissue was also very low, and consumption of crabs from this area is probably not a concern for anyone except possibly subsistence fishermen. Concentrations of DDT residues in dungeness crabs from various sites in Puget Sound were similar to or lower than levels in crabs from Willapa Bay. Levels of PCBs in crabs from industrialized sites such as Commencement Bay were higher than Willapa Bay crabs, but PCBs were typically not detected at cleaner sites such as Discovery Bay.

Littleneck clams were used in four studies to assess contamination at various sites in Puget Sound. No pesticides or PCBs were detected in any littleneck samples for these studies, suggesting that this species may not be representative of other shellfish due to its lack of significant organic chemical uptake.

Results from the two studies that summarized shellfish contamination data from Puget Sound are probably the most appropriate values to assess the relative contamination of Willapa Bay/Grays Harbor shellfish. Levels of total DDT in oysters and crabs were higher than the mean value from Puget Sound and near the high end of one reported range. However, all concentrations of total DDT in Puget Sound were low, and the highest level in one study was only 5.6 µg/kg and 11 µg/kg in the other. Levels of PCBs in oysters and crabs were near the low end of the ranges from Puget Sound, and substantially lower than the mean of 45 µg/kg. These comparisons indicate that DDT residues in oysters and crabs sampled for this study are somewhat elevated, but levels of PCBs are low, relative to concentrations in shellfish from Puget Sound.

Compared to concentrations in fin fish, levels of contaminants in shellfish were much lower. Mean concentrations of total DDT and PCBs in fish from Puget Sound were an order of magnitude higher than in shellfish from cranberry bog drainage. The level of total DDT in

sticklebacks was substantially higher than in shellfish from cranberry bog drainage and Puget Sound, and was well above the mean for fin fish from Puget Sound.

None of the detected pesticides exceeded wildlife criteria, suggesting that there should not be any adverse impacts to wildlife that consume tested fish and shellfish. However, wildlife criteria are for individual, not multiple, chemicals. The combination of pesticides detected in sticklebacks may be more damaging to piscivorous wildlife than the individual compounds. Piscivorous wildlife that are regularly consuming sticklebacks from the cranberry bog drainage ditches may be experiencing some related adverse impacts.

Sediment Sampling

Pesticides Detected

Fifteen pesticides and/or breakdown products were detected in sediment samples from seven sites (Table 8). Nine were chlorinated pesticides, three were organophosphorus insecticides, and three were herbicides. The chlorinated compounds or their parent pesticides have been banned for several years; the remaining insecticides and herbicides are currently used on cranberry bogs. DDT and its breakdown products -- DDD, DDE, and DDMU -- were detected most frequently; 4,4'-DDD and 4,4'-DDE were found in all samples. Aldrin and hexachlorobenzene (HCB) were both detected in one sample from each drainage ditch. Pentachloroanisole, a breakdown product of pentachlorophenol, and cis-chlordane were identified in one sample from PCDD-1. Azinphos-methyl and 2,4-D were each detected in only one sample from PCDD-1. Chlorpyrifos, diazinon, and napropamide were found in samples from both ditches. Dichlobenil was detected in all seven samples.

Comparisons to Criteria

Freshwater sediment criteria have not been adopted by Washington State. Provincial Sediment Quality Guidelines (PSQG) developed by the Ontario Ministry of the Environment (Persaud *et al.*, 1993) can be used to compare detected concentrations to values that would be expected to be detrimental to the majority of sediment-dwelling organisms that are chronically exposed. Criteria developed by the New York State Department of Environmental Conservation (NYDEC, 1994) use equilibrium partitioning to identify contaminated sediment that would potentially cause harmful impacts to aquatic ecosystems. Values from both references are organic carbon normalized to reflect the bioavailability of the contaminants (high organic carbon levels indicate low bioavailability).

Of the compounds detected in sediment samples for this study, PSQG are available for all of the chlorinated pesticides except DDMU and pentachloroanisole. Detected concentrations of these compounds were well below severe effects levels. All concentrations of aldrin, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT detected were above the lowest-effect level, which indicates that some sediment-dwelling organisms exposed to these chemicals may be adversely impacted.

Table 8. Pesticides Detected in Sediments Collected from Cranberry Bog Drainage Ditches (µg/kg, ppb - dry weight)

	GHCDD-1				PCDD-1		
	Site 1[1]	Site 2	Site 3[1]	Site 4	Site 1	Site 2	Site 3
% TOC	9.5	6.7	7.5	3.4	11.0	2.7	11.0
% Fines[2]	53	33	30	25	18	10	49
% Solids	13	11	28	41	21	38	9
Chlorinated Insecticides							
4,4'-DDE	[3]100 J	[3]9.7 J	[3]28 J	[3]6.2 J	[3]5.5 J	[3]22 J	[3]150 J
2,4'-DDD	35	4.2 J	13 J	2.9 J		7	44
4,4'-DDD	[3]245 J	[3]20 J	[3]72 J	[3]14 J	[3]10 J	[3]49 J	[3]310 J
4,4'-DDT	[3]6.9 J	[3]4.9 J		[3]4.3 J		[3]6.4 J	[3]13 J
total DDT	387	39	113	27	16	84	517
DDMU	30 J	2.9 J	8.2 J	1.8 J		4.1	41
aldrin	[3]4.3 J						[3]17 J
cis-chlordane							[4]4.1 J
hexachlorobenzene	1.6 J						3.2 J
pentachloroanisole					1.2 J		
Organophosphorus Insecticides							
azinphos-methyl					[4]4.4 NJ		
chlorpyrifos	2.4 NJ				38 J	23 J	38 J
diazinon	[4]7.2 J	[4]3.3 NJ			[4]2.6 NJ		[4]10 NJ
Herbicides							
2,4-D							20 J
dichlobenil	30 J	6.8 J	23 J	13 J	35 J	7.9 J	39 J
napropamide	89 J				35 J		38 J

Shaded values exceed sediment quality criteria

A blank indicates that the target analyte was not detected.

[1] - Values are means of duplicate analyses.

[2] - Percent fines includes all material less than 0.063 mm (silt + clay).

[3] - Exceeds Lowest-Effect Level for Provincial Sediment Quality Guidelines (Persaud *et al.*, 1993)

[4] - Exceeds New York State chronic sediment quality criteria (NYDEC, 1994)

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

NJ = There is evidence that the analyte is present. The numerical value is an estimate.

New York State (NYS) criteria are also available for the chlorinated pesticides aldrin, chlordane, DDT, and hexachlorobenzene, as well as for the organophosphates azinphos-methyl, chlorpyrifos, and diazinon. Of the chlorinated pesticides detected, only chlordane from PCDD-1 Site 3 exceeded chronic criteria. For organophosphorus pesticides, chlorpyrifos did not exceed criteria, but all detected concentrations of azinphos-methyl and diazinon were above chronic criteria.

Comparison of Results to Other Data

Three other studies have been performed to assess pesticide contamination in sediment from PCDD-1. The first study was done in 1978-79 by the U.S. Geological Survey (USGS) (Lum, 1984). One sediment sample was collected from PCDD-1 in April 1978 and one sample was collected in March 1979. Some of the same pesticides were detected as reported here, but concentrations in the USGS samples were lower. Dieldrin and Lindane were detected by USGS, but not in samples for this study. Several compounds were detected in samples for this study, but were not found by the USGS. No pesticides were detected in a sediment sample collected from PCDD-1 and analyzed by Ecology in 1989 (Cubbage, 1989). A third set of samples was collected from two sites in PCDD-1 by the USEPA (1997) in 1995. Moderately high concentrations of DDT and metabolites were found in one sample, but only a low level of DDD was detected in the other. Low levels of dichlobenil were also found in both samples. Organophosphorus pesticides were not detected in samples from any of the three studies.

Some differences between sample sets are probably due to differences in percent fines and organic carbon content of the sediment collected. Higher percent fines and organic carbon content reflect a higher total surface area of the sediment particles, which provides more area for adsorption of organic contaminants. Percent fines and organic carbon content are often correlated with contaminant concentrations. Percent fines and total organic carbon (TOC) for this study were high (Table 8), ranging from 10% to 53% and 2.7% to 11% respectively. Samples with the highest pesticide concentrations had about 50% fines and 10% TOC. For the sample collected by Ecology in 1989, fines were only 1% with 1.3% TOC. Percent fines and TOC were not reported for the USGS samples, but were likely somewhere between values for the above two data sets. These parameters were also not reported by the USEPA, but the samples were described as "hardpan", which is likely to be low in percent fines and TOC.

Freshwater sediments have been collected and analyzed for pesticides from ten sites around the state for the WSPMP (Davis and Johnson, 1994b; Davis and Serdar, 1996b). Most of these sites were selected because they received runoff and irrigation return water from nearby agricultural land, and were likely to be contaminated with pesticides. Sediment collected by the USGS from the Yakima River and many of its tributaries throughout the Yakima Valley for the National Water Quality Assessment Program was also analyzed for pesticides (Rinella *et al.*, 1992). Concentrations of total DDT in WSPMP samples ranged from undetected to 31 µg/kg. In 42 samples analyzed by the USGS, total DDT in eight were above 100 µg/kg, and three were above 500 µg/kg. Three of the sites for this study, Sites 1 and 3 from GHCDD-1 and Site 3 from PCDD-1, have total DDT concentrations similar to the most contaminated sites in the Yakima Valley (the Washington State Department of Health [WSDOH, 1993] has recommended eating fewer bottom fish from the Yakima River due to high levels of total DDT). Aldrin was not

detected in any WSPMP sediment samples, and was found in only three samples analyzed by the USGS, but at much lower levels than were found in two samples for this study. No organophosphorus pesticides were detected in WSPMP samples, and were not analyzed for by the USGS. Based on these comparisons, sediment in GHCDD-1 and PCDD-1 contain some of the highest concentrations of total DDT, aldrin, and organophosphorus insecticides in the state.

Discussion

Sediment sampling sites for this study were carefully chosen to represent fine organic material that is washed into the ditches from cranberry bogs. As discussed above, organic contaminants tend to accumulate in fine organic sediments to higher concentrations than in coarse or inorganic sediments, such as sand. Bottom materials in the ditches are primarily composed of medium to fine sand, but there are a few sites in each ditch where fine organic material accumulates. This organic material is representative of worst-case sediment contamination within the ditches, and was the kind of material that was collected for this study.

Organic debris is also used by many organisms at the bottom of the food chain as a food source. As the organic material is consumed, associated contaminants are accumulated by the organisms and passed up the food chain. Therefore, samples of fine organic sediment are also representative of contaminants that find their way into the food chain, and ultimately into fish and shellfish consumed by humans and wildlife at the top of the food chain.

As a result of careful site selection, samples for this study are probably more representative than samples from past studies. Due to analytical difficulties, accuracy of specific values are questionable, but actual concentrations were probably below PSQG levels that would result in severe adverse effects to sediment-dwelling organisms. Concentrations of total DDT and aldrin in samples from GHCDD-1 Site 1 and PCDD-1 Site 3 are some of the highest in the state, and may be high enough to result in adverse effects for some organisms. In addition, two highly toxic organophosphorus insecticides -- chlorpyrifos and diazinon -- were found in samples from these two sites, and finding either of these compounds in sediment is unusual. Diazinon exceeded NYS sediment criteria in both samples. Chlordane was above the NYS criterion in the sample from PCDD-1 Site 3. These results indicate that sediment-dwelling organisms at GHCDD-1 Site 1 and PCDD-1 Site 3 are probably experiencing some adverse effects from pesticide contamination.

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Appendices

Appendix A

Sampling Site Positions

	Latitude			Longitude			State Plane	
	deg	min	sec	deg	min	sec	X	Y
Water Sampling Sites								
GHCDD-1	46	48	58 N	124	05	25 W	1,101,412	561,171
PCDD-1	46	44	27 N	124	04	21 W	1,104,615	533,544
Tissue Sampling Sites								
GHCDD-1								
Pacific Oysters	46	51	23 N	124	03	31 W	1,110,000	575,500
Softshell Clams	46	50	27 N	124	04	16 W	1,106,614	569,960
PCDD-1								
Razor and Piddock Clams	46	43	36 N	124	03	15 W	1,108,974	528,176
Dungeness Crabs	46	43	41 N	124	03	33 W	1,107,745	528,738
Sediment Sampling Sites								
GHCDD-1								
Site 1	46	48	21 N	124	05	29 W	1,100,963	557,440
Site 2	46	49	20 N	124	05	23 W	1,101,652	563,391
Site 3	46	50	22 N	124	04	36 W	1,105,202	569,517
Site 4	46	50	25 N	124	04	30 W	1,105,632	569,802
PCDD-1								
Site 1	46	45	20 N	124	04	35 W	1,103,885	538,952
Site 2	46	44	27 N	124	04	21 W	1,104,615	533,544
Site 3	46	44	13 N	124	04	07 W	1,105,525	532,084

Sticklebacks were collected over a reach of one to two miles in each ditch, sites in Figure 1 represent the general area of collection.

Appendix B-1. Target Pesticides List for Water Analyses

Organophosphorus Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
acephate	0.30	fensulfothion	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	0.050	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
dimethoate	0.060	phosphamidan	0.18
dioxathion	0.12	propetamphos	0.15
disulfoton	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	tetrachlorvinphos	0.15
fenitrothion	0.055		

Chlorinated Herbicides

2,4-D	0.042	bromoxynil	0.042
2,4-DB	0.050	DCPA (Dacthal)	0.033
2,4,5-T	0.033	dicamba	0.042
2,4,5-TB	0.038	dichlorprop	0.046
2,4,5-TP (Silvex)	0.033	diclofop-methyl	0.063
2,3,4,5-tetrachlorophenol	0.023	dinoseb	0.063
2,3,4,6-tetrachlorophenol	0.023	ioxynil	0.042
2,4,5-trichlorophenol	0.025	MCPA	0.083
2,4,6-trichlorophenol	0.025	MCPP	0.083
3,5-dichlorobenzoic acid	0.042	pentachlorophenol	0.021
4-nitrophenol	0.073	picloram	0.042
acifluorfen	0.17	trichlopyr	0.035
bentazon	0.063		

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

Appendix B-1 (cont.). Target Pesticides List for Water Analyses

Chlorinated Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
4,4'-DDT	0.035	cis-nonachlor	0.035
4,4'-DDE	0.035	trans-nonachlor	0.035
4,4'-DDD	0.035	oxychlordane	0.035
2,4'-DDT	0.035	dicofol (kelthane)	0.17
2,4'-DDE	0.035	dieldrin	0.035
2,4'-DDD	0.035	endosulfan I	0.035
DDMU	0.035	endosulfan II	0.035
aldrin	0.035	endosulfan sulfate	0.035
alpha-BHC	0.035	endrin	0.035
beta-BHC	0.035	endrin aldehyde	0.035
delta-BHC	0.035	endrin ketone	0.035
gamma-BHC (Lindane)	0.035	heptachlor	0.035
captan	0.14	heptachlor epoxide	0.035
captafol	0.21	methoxychlor	0.035
cis-chlordane	0.035	mirex	0.035
trans-chlordane	0.035	pentachloroanisole	0.035
alpha-chlordene	0.043	toxaphene	0.85
gamma-chlordene	0.035		

Pyrethroid Pesticides

fenvalerate	0.14	phenothrin	0.14
cis-permethrin	0.14	resmethrin	0.14

Sulfur-Containing Pesticides

propargite	0.28

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

Appendix B-1 (cont.). Target Pesticides List for Water Analyses

Nitrogen-Containing Pesticides

Analyte	Quantitation Limit[1] (µg/L, ppb)	Analyte	Quantitation Limit (µg/L, ppb)
alachlor	0.26	metolachlor	0.28
ametryn	0.071	metribuzin	0.071
atraton	0.21	MGK-264	0.50
atrazine	0.071	molinate	0.14
benefin	0.11	napropamide	0.21
bromacil	0.28	norflurazon	0.14
butachlor	0.25	oxyfluorfen	0.28
butylate	0.14	pebulate	0.14
carboxin	0.78	pendimethalin	0.11
chlorothalonil	0.17	profluralin	0.17
chlorpropham	0.28	prometon	0.071
cyanazine	0.11	prometryn	0.071
cycloate	0.14	pronamide	0.28
diallate	0.27	propachlor	0.17
dichlobenil	0.16	propazine	0.071
diphenamid	0.21	simazine	0.072
diuron	0.48	tebuthiuron	0.11
eptam	0.14	terbacil	0.21
ethalfluralin	0.11	terbutryn	0.071
fenarimol	0.21	triadimefon	0.18
fluridone	0.43	triallate	0.18
hexazinone	0.11	trifluralin	0.11
metalaxyl	0.48	vernolate	0.14

Carbamates

1-naphthol	NAF[2]	carbofuran	0.28
3-hydroxycarbofuran	NAF	methiocarb	NAF
aldicarb	NAF	methomyl	NAF
aldicarb sulfone	NAF	oxamyl	NAF
aldicarb sulfoxide	NAF	propoxur	NAF
carbaryl	0.28		

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

[2] - NAF = Not Analyzed For

Appendix B-2. Target Pesticides List for Tissue Analyses

Analyte	Quantitation Limit[1] (µg/kg, ppb wet)	Analyte	Quantitation Limit (µg/kg, ppb wet)
2,4'-DDD	3.6	endosulfan I	5
4,4'-DDD	3.6	endosulfan II	3.6
2,4'-DDE	3.6	endosulfan sulfate	3.6
4,4'-DDE	3.6	endrin	3.6
4,4'-DDMU	3.6	endrin aldehyde	3.6
2,4'-DDT	3.6	endrin ketone	3.6
4,4'-DDT	3.6	ethion	14
aldrin	3.6	heptachlor	3.6
alpha-BHC	3.6	heptachlor epoxide	3.6
beta-BHC	3.6	hexachlorobenzene	1.8
delta-BHC	3.6	methoxychlor	3.6
gamma-BHC (Lindane)	3.6	mirex	3.6
cis-chlordane	3.6	oxadiazon	3.6
trans-chlordane	3.6	ethyl-parathion	7.1
oxychlordane	3.6	methyl-parathion	7.1
cis-nonachlor	3.6	pentachloroanisole	1.8
trans-nonachlor	3.6	tetradifon	14
alpha-chlordene	3.6	toxaphene	110
gamma-chlordene	3.6	trifluralin	3.6
chlorpyrifos	7.1	PCB-1232	36
DCPA (Dacthal)	3.6	PCB-1242	36
diazinon	36	PCB-1248	36
dichlorobenzophenone	14	PCB-1254	36
dicofol (Kelthane)	14	PCB-1260	36
dieldrin	3.6		

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

Appendix B-3. Target Pesticides List for Sediment Analyses

Chlorinated Pesticides

Analyte	Quantitation Limit[1] (µg/kg, ppb dry)	Analyte	Quantitation Limit (µg/kg, ppb dry)
4,4'-DDT	17	dieldrin	17
4,4'-DDE	17	endrin	17
4,4'-DDD	17	endrin aldehyde	17
2,4'-DDT	17	endrin ketone	17
2,4'-DDE	17	endosulfan I	17
2,4'-DDD	17	endosulfan II	17
DDMU	17	endosulfan sulfate	17
aldrin	17	heptachlor	17
alpha-BHC	17	heptachlor epoxide	17
beta-BHC	17	hexachlorobenzene (HCB)	3.0
delta-BHC	17	mirex	17
gamma-BHC (Lindane)	17	pentachloroanisole	3.0
cis-chlordane	17	tetradifon	25
trans-chlordane	17	toxaphene	180
alpha-chlordene	17	PCB-1221	62
gamma-chlordene	17	PCB-1232	124
cis-nonachlor	17	PCB-1242	62
trans-nonachlor	17	PCB-1248	62
oxychlordane	17	PCB-1254	62
dicofol (kelthane)	75	PCB-1260	62

Pyrethroid Pesticides

fenvalerate	100	phenothrin	510
cis-permethrin	510	resmethrin	510

Sulfur-Containing Pesticides

Propargite	62

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

Appendix B-3 (cont.). Target Pesticides List for Sediment Analyses

Organophosphorus Pesticides

Analyte	Quantitation Limit[1] (µg/kg, ppb dry)	Analyte	Quantitation Limit (µg/kg, ppb dry)
azinphos-ethyl	41	ethoprop	21
azinphos-methyl	47	fenitrothion	18
carbophenothion	26	fenthion	18
chlorpyrifos	21	fonofos	16
chlorpyrifos-methyl	21	malathion	21
coumaphos	31	merphos	31
DEF	36	parathion	21
demeton-O	18	phorate	18
demeton-S	18	propetamphos	52
diazinon	21	ronnel	18
dichlorvos	21	sulfotepp	16
dioxathion	44	sulprofos	18
disulfoton	16	temephos	230
EPN	26	tetrachlorvinphos	52
ethion	18		

Chlorinated Herbicides

2,4-D	110	bromoxynil	110
2,4-DB	130	DCPA (Dacthal)	87
2,4,5-T	87	dicamba	110
2,4,5-TB	98	dichlorprop	120
2,4,5-TP	87	diclofop-methyl	160
2,3,4,5-tetrachlorophenol	60	ioxynil	110
2,3,4,6-tetrachlorophenol	60	MCPA	220
2,4,5-trichlorophenol	65	MCPP	220
2,4,6-trichlorophenol	65	pentachlorophenol	54
3,5-dichlorobenzoic acid	110	picloram	110
4-nitrophenol	190	trichlopyr	92
bentazon	160		

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

Appendix B-3 (cont.). Target Pesticides List for Sediment Analyses

Nitrogen-Containing Pesticides

Analyte	Quantitation Limit[1] (µg/kg, ppb dry)	Analyte	Quantitation Limit (µg/kg, ppb dry)
alachlor	93	metolachlor	100
ametryn	26	metribuzin	26
atrazine	26	molinate	52
benfluralin	39	napropamide	78
bromacil	100	oxyfluorfen	100
butachlor	91	pebulate	52
butylate	52	profluralin	62
carboxin	280	prometryn	26
chlorpropham	100	pronamide	100
cyanazine	39	propachlor	62
cycloate	52	propazine	26
diallate	98	simazine	26
dichlobenil	60	terbacil	78
diphenamid	78	terbutryn	26
eptam	52	triadimefon	67
ethalfluralin	39	triallate	67
fenarimol	78	trifluralin	39
hexazinone	39	vernolate	52

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

Appendix B-4. Distribution of Compounds Eluted from Florisil Columns for Tissue Analyses

Fraction 1 (0%)	Fraction 2 (6%)	Fraction 3 (15%)	Fraction 4 (50%)
alpha BHC*	alpha BHC*	DCPA (Dacthal)	endosulfan II
aldrin	beta BHC	diazinon	endosulfan sulfate
alpha chlordene	gamma BHC	dichlorobenzophenone	endrin aldehyde
gamma chlordene	delta BHC	dieldrin	endrin ketone
2,4'-DDE	cis-chlordane	endosulfan I	
4,4'-DDE	trans-chlordane	endrin	
4,4'-DDMU*	chlorpyrifos	oxadiazon	
2,4'-DDT	2,4'-DDD	ethyl parathion	
4,4'-DDT*	4,4'-DDD	methyl parathion	
heptachlor	4,4'-DDMU*	tetradifon	
hexachlorobenzene	4,4'-DDT*		
mirex	dicofol (kelthane)		
trans-nonachlor	ethion		
PCB-1232	heptachlor epoxide		
PCB-1242	methoxychlor		
PCB-1248	cis-nonachlor		
PCB-1254	oxychlordane		
PCB-1260	pentachloroanisole		
	toxaphene		
	trifluralin		

* - Found in both 0% and 6% fractions

Appendix C

Sample Collection and Processing Procedures

Water Samples

Water sampling procedures essentially followed those described in the Illinois EPA (1987) field methods manual. Depths in the ditches at the water sampling sites were typically less than two feet, which allowed the use of a hand held bottle to collect water samples. Use of a hand held bottle minimizes sample handling and the chance of contamination during sample collection. The sample jar was filled at three points (quarter point transect) across each ditch. The contents of the sample jar was hand split into the sample containers, filling each container one-third full from each quarter point. A new sample jar was used for each sample. Sample containers included one-gallon glass jars for pesticide analyses, one-liter polyethylene bottles for TSS, and 60 ml polyethylene bottles for TOC. TOC samples were preserved with sulfuric acid. All samples were transported to the laboratory on ice. Samples from each site were transported in ice chests separately from other sites to minimize the chance of cross contamination. All ice chests were sealed with chain-of-custody seals.

All sample jars and containers for pesticide analysis were precleaned by Eagle-Picher Environmental Services in Miami, Oklahoma using the following procedure:

- wash in laboratory grade detergent,
- rinse three times with distilled water,
- rinse with 1:1 nitric acid,
- rinse three times with organic free water,
- oven dry for one hour,
- rinse with hexane, and
- oven dry again for one hour.

Lids were fitted with teflon liners.

Temperature was measured with a long-line thermometer, pH with an Orion Model 250 temperature compensating pH meter, conductivity with a Beckman Model RB-5, and flow with a Swoffer Model 2100 TSR.

Tissue Samples

Twenty-five oysters were collected by hand at low tide. Size selection was biased toward larger specimens to assess worst-case contamination; larger and thus older oysters would have more time to accumulate contaminants. Twenty-five razor clams, 35 softshell clams, and 40 piddock

clams were collected with shovels. Only specimens with intact shells were used for analysis. All sizes of razor clams collected were included for analysis, but only the largest individuals of softshell and piddock clams were collected and analyzed. Each sample was wrapped in aluminum foil with the dull side in contact with the specimens, placed in polyethylene bags, and transported to the laboratory on ice. These shellfish were kept alive, stored on ice in a walk-in refrigerator until they could be processed, which was less than seven days for all samples.

Sticklebacks were collected with a backpack electroshocker. These fish were not plentiful and collection of an adequate number for analysis required shocking of at least a one mile reach of each ditch. In GHCDD-1, 199 sticklebacks were collected, and 93 individuals were collected from PCDD-1. Each sample was wrapped in aluminum foil, placed in polyethylene bags, transported to the laboratory on ice, and frozen until they could be processed.

Twelve dungeness crabs were collected with crab pots by Doug Davis, a commercial fisherman out of Tokeland, Washington. Only males larger than the legal size limit were collected. The crabs were placed on ice for transportation to the laboratory, and then wrapped in aluminum foil and frozen until they could be processed. All containers used to store tissue samples prior to processing were sealed with chain-of-custody seals.

Shell length and weight of soft parts was recorded for each oyster and clam individual. The length and weight of individual sticklebacks was not recorded, only the total weight. The carapace width and total weight was recorded for each crab, and then 20 to 30 grams of meat was collected from each individual by removing the legs and taking the meat from the body cavity at the leg holes. Tissue from individuals for each sample was combined, passed through a meat grinding attachment for a Kitchen-Aid food mixer three times, and mixed by hand to ensure thorough homogenization. The homogenized tissue was split into two precleaned 8 ounce jars and frozen. One jar was archived and the other was submitted for analysis. All jars used for tissue and sediment samples were precleaned by Eagle-Picher Environmental Services using the same procedure as for water sample jars.

Sediment Samples

All sediment samples except one were collected with a stainless steel $0.05m^2$ Petite Ponar grab sampler. The sample from PCDD-1 Site 1 could not be collected with the grab sampler. Accumulated fine material that was found earlier in the year was no longer present. Rather than locating another site, different material was used for the sample. Chunks of peat that lined the bottom of the ditch at this site were removed, and the top 2-3 mm was scraped off as a sample. Peat is almost completely composed of organic material and should accumulate pesticides similar to depositional material. In addition, a peat sample may be representative of pesticide concentrations within the cranberry bogs.

For samples collected with the grab, overlying water was removed by siphoning with a short piece of tubing, being careful not to disturb the surface of the sediment. The top 2cm of sediment was removed with a stainless steel spatula or spoon and placed in a stainless steel bowl. At least five

grabs were collected for each sediment composite, or more to obtain enough to fill two 8 ounce jars and two 4 ounce jars. The composite sample was homogenized to a uniform color and consistency prior to filling the jars. Sediment samples were placed on ice during transportation to the laboratory and then frozen. As with tissue samples, one jar was archived and the other submitted for analysis. Tissue and sediment samples were transported to the laboratory for analysis in ice chests sealed with chain-of-custody seals.

Decontamination Procedures

All field sampling equipment that came into contact with the sediment samples, and the tissue processing equipment was cleaned using the following procedure:

- washed with laboratory grade detergent,
- rinsed with tap water,
- rinsed with deionized water,
- rinsed with pesticide grade acetone, and
- allowed to air dry.

To ensure that the Petite Ponar grab sampler was free of contaminants from previous use, the initial cleaning included a final rinse with hexane in addition to the above procedure. Field equipment and tissue processing equipment was decontaminated between each sample.

Appendix D

Analytical Methods

Water Analyses

Target compounds for water analyses were grouped into two extractions at Manchester Laboratory. Chlorinated, organophosphorus, nitrogen-containing, sulfur-containing, and pyrethroid pesticides, and carbaryl and carbofuran were extracted simultaneously from one sample, and chlorinated herbicides required another extraction. Both these extractions were performed using Manchester Laboratory SOP 73011, version 1.0. Extracts were analyzed using Draft EPA Method 8085 (formerly modified EPA Method 1618 and Method 8150). Briefly, samples were extracted with methylene chloride, and analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of detected pesticides was performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD).

Total organic carbon was measured following EPA Method 415.1, and EPA Method 160.2 was used to determine the concentration of total suspended solids in water samples.

Tissue Analyses

Tissue samples were analyzed using a method developed by the California Department of Fish and Game (CDFG, 1990). Using this method, the sample is extracted (Manchester Laboratory SOPs 7300722, version 1.0 and 730073, version 1.0), and then cleaned up by eluting the sample through a Florisil column (Manchester Laboratory SOP 730018, version 1.0) in four fractions with petroleum ether and increasing portions of ethyl ether (0%, 6%, 15%, and 50%). The four fractions were analyzed following modified EPA Method 8080, using Gas Chromatography with Electron Capture Detectors (GC/ECD). The distribution of compounds in the four Florisil fractions is listed in Appendix C.

A gravimetric analysis (Manchester Laboratory SOP 730009, version 1.0) was performed on a small portion of each tissue sample for percent lipid content.

Sediment Analyses

Sediment samples were extracted (Manchester Laboratory SOP 730012, version 1.0) and analyzed using Draft EPA Method 8085, which is the same method as used for water analyses, or EPA Method 8081. Target compounds were grouped into three extractions.

Organophosphorus, nitrogen-containing, sulfur-containing, and pyrethroid pesticides were extracted simultaneously, and chlorinated pesticides and chlorinated herbicides were each extracted separately. Chlorinated pesticides were analyzed following EPA Method 8081, which uses GC/ECD. All other target compounds were analyzed with Method 8085, using GC/AED. The sampling plan called for using Method 8085 to analyze all pesticides for sediments, but a separate method was used for chlorinated pesticides to improve detection limits. Confirmations of detected pesticides were performed by dual dissimilar column retention comparison and/or GC/ITD.

Total organic carbon samples were analyzed by Sound Analytical Services, Inc., Tacoma, Washington, using the method as outlined in the Puget Sound Protocols (Puget Sound Estuary Program, 1986). Samples were analyzed for grain size by Soil Technology, Inc., Bainbridge Island, Washington, using ASTM D-422 modified.

Appendix E

Quality Assurance/Quality Control

Water Sampling

All water samples from one site were duplicated (split) on alternating weeks, starting the week of May 20, as an estimate of sampling and analytical precision. For the intensive sampling events, one duplicate sample was collected for analysis of the complete WSPMP target list, and one duplicate was collected for analysis of organophosphorus pesticides only. Conventional parameters were also duplicated.

Split samples were also collected for interlaboratory comparisons. Each of the weekly samples and three of the five intensive sample sets were split and sent to the Washington State Department of Agriculture (WSDA) Chemical and Hop Laboratory in Yakima to provide secondary confirmations of detected organophosphorus insecticides. Separate duplicate and matrix spike samples were analyzed by the WSDA Laboratory to assess their performance.

Matrix spike and matrix spike duplicate samples were collected to evaluate potential interferences and as an estimate of analytical accuracy and precision. Matrix spike and spike duplicates required two additional containers of water to be collected for each pesticide analysis. Matrix spike samples were collected in May and July on the first day of intensive sampling events. WSPMP samples were collected at the GHCDD-1 and PCDD-1 sites in mid-June and in the second week of August, which included matrix spike and duplicate samples that were used to assess data for this project. This results in a total of four matrix spike and matrix spike duplicate sample sets for cranberry bog drainage pesticide data.

A transfer/bottle blank was prepared for the intensive sampling event in July to ensure that decontamination procedures are satisfactory. Duplicate field spikes of organophosphorus pesticides into organic-free water were also prepared for the intensive sampling event in July to evaluate laboratory performance (accuracy and precision) and to assess possible analyte degradation between sample collection and analysis. Field spike and transfer/bottle blank samples were also prepared and sent to the WSDA Laboratory in July.

Accuracy and precision criteria have not been established for the methods used for pesticide analysis. Accuracy and precision for organophosphorus pesticides analyses performed for the WSPMP have typically been excellent (Davis and Johnson, 1994b; Davis, 1996). Matrix spike recoveries have ranged from 69% to 110%, with an average of 89%, and an average relative percent difference (RPD) between spike duplicates of 11. Results from field spikes analyzed for the WSPMP in 1993 were also good; recoveries averaged 71% and the average RPD between duplicate samples was 16 for the organophosphorus pesticides. Quality control results for other

pesticide analyses have been variable, but are generally similar to the organophosphorus pesticides analysis.

Based on historical results from the WSPMP and a desire to obtain exceptionally high quality organophosphorus insecticides data for this study, matrix spike recoveries for the organophosphorus pesticides analysis were regarded as questionable when between 40 and 60%. Data associated with spike recoveries between 40 and 60% were qualified as estimates ("J" qualifier). Associated data were rejected ("Rej" qualifier) for matrix spike recoveries below 40%. Affected data were qualified as estimates when RPDs between duplicate organophosphorus pesticides analyses fell between 25 and 75. Data associated with duplicate RPDs above 75 were rejected.

Quality control requirements for pesticide analyses other than organophosphates were not as rigorous. Data were qualified as estimates when spike recoveries were between 20 and 40%, and RPDs were between 50 and 100. Data were rejected when spike recoveries were below 20% and RPDs were above 100.

Tissue and Sediment Sampling

One tissue and one sediment sample were analyzed in duplicate (field split) as an estimate of sampling and analytical precision. The GHCDD-1 Site 1 sediment sample and the oyster tissue sample was field split and analyzed in duplicate. A laboratory duplicate analysis was performed on the sediment sample from GHCDD-1 Site 3. TOC, grain size, and lipid analyses were also duplicated.

Matrix spike and matrix spike duplicate analyses were performed on the sediment sample collected from PCDD-1 Site 3, and the razor clam tissue sample. These analyses provide information to evaluate potential interferences and an estimate of analytical accuracy and precision.

Accuracy and precision criteria have not been established for the methods used for pesticide analysis. Accuracy and precision of tissue and sediment analyses performed for the WSPMP have typically been excellent (Davis and Johnson, 1994a; Davis *et al.*, 1995; Davis and Serdar, 1996b). Matrix spike recoveries for tissue analyses have ranged from 25% to 150%, with an average of 85%, and an average RPD between spike duplicates of 8. The range for sediment analyses was 20% to 143%, with an average of 90% and an average RPD of 15. Results from fish tissue quality control check material analyzed for the WSPMP have also been good; recoveries have averaged 120%, with a range of 54% to 231%.

Data are qualified as estimates when matrix spike recoveries are below 40% or above 150%, or when the RPDs of duplicate analyses (analytical or field duplicates) are greater than 20. Data are rejected when spike recoveries are below 10 % or when RPDs of duplicate analyses are greater than 100.

Appendix F

Data Review

Water Samples

Analytical Comments

No significant analytical problems were encountered for any of the water samples. However, there was a minor problem with continuing calibration. Drift from the initial calibration for many of the target compounds was greater than the criteria of 20%. Quantitation limits were not affected, but associated results were qualified as estimates ("J" qualifier). Several detections of azinphos-methyl, chlorpyrifos, and diazinon were affected.

Detection of some target compounds was not confirmed. Results for these compounds were qualified as tentitive identifications ("NJ" qualifier). Results for several pesticides were affected, including some detections of azinphos-methyl, chlorpyrifos, malathion, and methamidophos.

Some compounds were judged to be responding below normal on the instruments. Results for these compounds were qualified "J" if detected and "UJ" if non-detected.

Complete copies of the data validation reports for water analyses are included as Appendix G.

QA/QC Samples

No accuracy or precision criteria have been established for Method 8085, but analysis of duplicate field samples, matrix spikes, and field spikes provide estimates of accuracy and precision. Results are shown in Appendices F-1, 2, and 3 (duplicates), F-4, 5, 6, and 7 (matrix spikes), and F-8 (field spikes). In general, spike recoveries near 100% indicate good accuracy, and low relative percent difference (RPD) between duplicate analyses indicates high precision. Specific QA/QC limits set for this project are listed in the previous section (Quality Assurance/Quality Control).

Matrix spike recoveries for samples analyzed by Manchester Laboratory were generally excellent. Recoveries for all organophosphorus pesticides were above even the highest limit of 60%. Fourteen other pesticides had recoveries below the limits; five were below minimum limits and associated data were rejected. Of the 14, only one, carbaryl, was detected in any of the samples. Carbaryl was not detected in the June sample that was associated with the low spike recovery, but was found in samples collected in May and July. Spike recoveries for carbaryl in May were near 90%; carbaryl was not included in the July matrix spikes. Other than carbaryl, none of the 14 pesticides with recoveries below QA/QC limits were chemicals that are typically used on cranberries.

Some problems were encountered by the WSDA Laboratory while running matrix spike samples on June 5 and 7. The laboratory explained the low recoveries on these dates as a result of spiking

clean tap water. Better results were obtained on May 31 and later dates by using "dirty" water (prepared by adding uncontaminated dirt to tap water). Based on this explanation, associated data were not rejected, but were qualified as estimates.

Results from duplicate analyses were generally acceptable from both laboratories. The RPD between duplicate samples for several pesticides, including some organophosphates, exceeded QA/QC limits. However, most results that were substantially different between duplicate analyses were very low concentrations detected below the quantitation limits, and were already qualified as estimates. The only exceptions to this were the organophosphorus pesticides detected in PCDD-1 on August 13. Detected concentrations for the three compounds were above quantitation limits, but RPDs between duplicate samples were slightly above the limit of 25%, and associated data were qualified as estimates. No RPDs were high enough to require rejection of associated data.

RPDs between matrix spike and matrix spike duplicate samples were also calculated. The only results that affected pesticide detections were the parathion recoveries in May. The RPD between these values exceeded the QA/QC limit, and all parathion detections in May were qualified as estimates. The RPD between parathion recoveries in August was much lower, but parathion was detected only in samples collected in May.

Most of the field spike results from both laboratories were excellent. Only the azinphos-methyl results from Manchester Laboratory were poor. Recoveries for this pesticide were only 15 and 32%, and the RPD between recoveries was high at 72. Recoveries for other compounds in the spike samples for both laboratories were between 92 and 120%, and the RPDs ranged from 0 to 15. The problem with azinphos-methyl analyzed by Manchester Laboratory cannot be explained. The same spike kit was used for the samples sent to the WSDA Laboratory, and their recoveries were excellent. Matrix spike recoveries and duplicate analysis results for azinphos-methyl by Manchester Laboratory were generally good. Most azinphos-methyl detections were already qualified as estimates for other reasons.

No target analytes were detected in transfer/bottle blanks analyzed by either laboratory, indicating that decontamination procedures were satisfactory. In addition, no analytes were detected in any laboratory blanks, indicating that the analytical systems were free of contamination.

Interlaboratory Comparisons

Comparison of data between laboratories is presented in Appendix F-9. No limits were set for comparison of results between laboratories, but a RPD of 40 between results would indicate a difference of 50%. Values that are 100% different (one is double the other) would have a RPD of 67. Differences of an order of magnitude or more would result in RPDs greater than 164. RPDs of 40 or less would indicate good similarity of results between laboratories. Results with RPDs from 40 to 67 are still reasonably similar, but RPDs above 67 suggest that the results are substantially different.

RPDs for only seven comparisons were above 67; most were below 40. None of the seven were for chlorpyrifos results, two were for diazinon, and five for azinphos-methyl results. Azinphos-

methyl results for July 15, 17, 19, and 23 all had high RPDs. This might be expected if the detected concentrations were below the quantitation limits, but most were at or above the limits. Although the concentrations were substantially different, there is agreement that the levels of azinphos-methyl were high on those dates.

Acephate Results

Acephate is an organophosphorus pesticide that is typically used on cranberries in May, and was also used on a trial basis under a Section 24(c) Special Local Needs label modification in July of 1996 to control blackheaded fireworms. On this basis, acephate was originally requested to be included as an organophosphorus target pesticide, but assessment of this compound by the laboratory indicated that spike recoveries were near zero, and new method development would be required to achieve acceptable results. The laboratory did not have time to complete this work prior to the start of this study, so acephate was dropped from the target list. However, acephate was detected in several samples analyzed using the method for organophosphorus pesticides. These results were quantified, but earlier poor recoveries suggest that reported levels probably substantially under estimate the true sample concentrations. Acephate was not included in matrix spikes prepared and analyzed for this study.

Tissue Samples

Analytical Comments

No substantial analytical problems were encountered for the tissue analyses. Endrin aldehyde was not included as a target due to the lack of recovery after the Florisil cleanup. Dicofol (Kelthane) was included in the matrix spike, but this compound breaks down to dichlorobenzophenone during analysis. Both were monitored, but recoveries for each were not calculated. Neither was detected in any of the tissue samples; quantitation limits were qualified as estimates. Trifluralin was not included in the matrix spike, but was monitored for; quantitation limits were also qualified as estimates.

QA/QC Samples

Matrix spike recoveries for most tissue target analytes were above QA/QC limits. The only detected pesticide with spike recoveries below the limits was hexachlorobenzene, which was found in the stickleback sample at a low concentration that was already qualified as a tentative detection ("NJ" qualifier). Other compounds with low spike recoveries were heptachlor and methyl parathion.

Duplicate analysis results were available for only three compounds detected in oyster tissue. The RPD between values of 4,4'-DDE was slightly above the QA/QC limit, resulting in all 4,4'-DDE detections in tissue samples being qualified as estimates. RPDs between matrix spike recoveries for five of the tissue target analytes also exceeded QA/QC limits, but none of the affected compounds were detected in samples.

No analytes were detected in laboratory blanks.

Sediment Samples

Analytical Comments

Unusually high proportions of the sediment samples were composed of water (70 to 90%), which resulted in higher detection limits for some compounds, poor spike recoveries for several target analytes, and unacceptable recoveries for others. The laboratory determined that a different analytical method was necessary for chlorinated pesticides to achieve acceptable detection limits for these compounds. The following compounds were deleted from the target analyte list as a result of unacceptable matrix spike recoveries:

Nitrogen-Containing Pesticides			
atraton	chlorothalonil	diuron	fluridone
MGK 264	metalaxyl	norflurazon	prometon
pendimethalin	tebuthiuron		
Organophosphorus Pesticides			
dimethoate	fenamiphos	fensulfothion	imidan
mevinphos	methyl paraoxon	methyl parathion	phosphamidan
Chlorinated Pesticides			
captafol	captan	methoxychlor	
Chlorinated Herbicides			
acifluorfen	dinoseb		

Results for the following target analytes were qualified as estimates ("J" qualifier) by the laboratory due to low matrix spike recoveries:

Nitrogen-Containing Pesticides		
benfluralin	carboxin	ethalfluralin
oxyfluorfen	profluralin	trifluralin
Organophosphorus Pesticides		
EPN	fenitrothion	parathion
Chlorinated Herbicides		
4-nitrophenol		

Dicofol (Kelthane) was recovered in the matrix spikes as its breakdown product, dichlorobenzophenone, but the recoveries were not quantitated. Results for dicofol were "J" qualified on this basis.

QA/QC Samples

Results from 22 additional target pesticides were qualified as estimates as a result of matrix spike recoveries below QA/QC limits set for this study. Among the numerous target analytes affected by poor spike recoveries, only three compounds -- 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT -- were detected in sediment samples. However, results for these three compounds constitute the majority of detections. In addition to poor spike recoveries, RPDs between recoveries and results

from duplicate analyses were above QA/QC limits. Due to the importance of these results, none were rejected, but all were qualified as estimates, and should be viewed with an extra note of caution. These results appear to be highly variable, and accuracy and precision are poor, but there is little doubt that these contaminants are present at some of the sites in substantial concentrations.

Numerous RPDs between spike recoveries and duplicate analyses exceeded QA/QC limits. Eight of these -- aldrin, cis-chlordane, DDMU, azinphos-methyl, chlorpyrifos, diazinon, 2,4-D, and dichlobenil -- were detected in sediment samples, and results were qualified as estimates. Of these eight, all but two -- aldrin and DDMU -- had RPDs below 30, which is only slightly above the limit of 20. Many of these results were already qualified as estimates by the laboratory because they were detected below quantitation limits.

No analytes were detected in laboratory blanks.

Representativeness, Completeness, and Comparability

Sampling procedures employed for this study were designed to result in water samples that were representative of cumulative contamination from all cranberry bog drainage associated with GHCDD-1 and PCDD-1. Sampling for PCDD-1 was done at low tide because ditch water backs up from the tide gates to the sampling site during high tide. Tissue samples from sticklebacks were representative of contamination in the average adult population. Razor clam and dungeness crab samples were representative of tissue that would be consumed from typical public collection techniques (average legal size). Oyster, softshell clam, and piddock clam samples were biased by selecting larger individuals, which represents a worst-case contamination sample. Sediment samples were collected at depositional sites where fine organic material had accumulated, which were representative of organic material that washes out from the cranberry bogs, and were representative of worst-case sediment contamination within the ditches.

No samples were lost during transport, sample processing, or sample analysis, resulting in 100% completeness. Due to analytical difficulties, some sediment target analytes were dropped, and poor QA/QC results for several compounds required rejection of associated data, resulting in the loss of some information.

Quality of water and tissue data from this study is high, and these data can be compared, with appropriate qualification, to pesticide data from other studies obtained using similar collection and analytical techniques. Specific concentrations of contaminants obtained from sediment analyses for this project are probably not reliable and extra caution should be used if these data are compared to results from other studies.

Appendix F-1. Duplicate Analysis Results for Water Samples (µg/L, ppb)
Samples Analyzed by the Manchester Environmental Laboratory

GHCDD-1				PCDD-1			
	Sample 1	Sample 2	RPD[1]		Sample 1	Sample 2	RPD[1]
13-May				24-May			
acephate	0.11	0.16	**37**	acephate	0.022	0.014	**44**
chlorpyrifos	0.0057	0.0041	**33**	azinphos-methyl	0.22	0.22	0
diazinon	4.4	4.3	2	chlorpyrifos	0.044	0.039	12
methamidophos	0.065	0.072	10	diazinon	0.94	0.86	9
				methamidophos	0.0038	0.003	24
20-May							
acephate	0.0095	0.016	**51**	18-Jun			
azinphos-methyl	0.2	0.22	10	azinphos-methyl	0.028	0.02	**33**
carbaryl	0.024	0.035	37	chlorpyrifos	0.022	0.019	15
carbofuran	0.13	0.1	26				
chlorpyrifos	0.006	0.005	18	15-Jul			
diazinon	0.31	0.33	6	azinphos-methyl	0.0071	0.0055	**25**
dichlorprop	0.066	0.077	15	carbaryl	0.052	0.032	48
methamidophos	0.019	0.018	5	carbofuran	0.01	1.7 U[2]	
napropamide	0.45	0.5	11	chlorpyrifos	3.5	3.8	8
norflurazon	0.44	0.43	2	diazinon	0.0071	0.0087	20
parathion	0.11	0.09	20	MCPP	0.017	0.011	43
simazine	0.004	0.007	**55**	napropamide	0.06	0.024	**86**
terbacil	0.031	0.049	45	norflurazon	0.058	0.05	15
2,4-D	0.26	0.3	14	sulfotep	0.018	0.02	11
4,4'-DDD	0.0078	0.0081	4	2,4-D	0.04	0.038	5
				3,5-dichlorobenzoic acid	0.013	0.0067	**64**
4-Jun				4,4'-DDD	0.029	0.024	19
azinphos-methyl	0.015	0.13 U					
diazinon	5.34	5.5	3	30-Jul			
				azinphos-methyl	0.02	0.021	5
1-Jul				chlorpyrifos	0.39	0.37	5
diazinon	0.11	0.12	9	diazinon	0.35	0.32	9

[1] - RPD = Relative Percent Difference (difference/mean x 100)

[2] - U = Undetected at or above the reported value

Values in bold exceed QA/QC criteria; affected data are qualified as estimates ("J" qualifier)

Appendix F-1 (cont.). Duplicate Analysis Results for Water Samples (µg/L, ppb)
Samples Analyzed by the Manchester Environmental Laboratory

GHCDD-1

	Sample 1	Sample 2	RPD[1]
19-Jul			
acephate	0.013	0.011	17
azinphos-methyl	0.76	0.69	10
chlorpyrifos	0.0044	0.0061	**32**
diazinon	1.8	1.6	12
methamidophos	0.13	0.12	8
12-Aug			
azinphos-methyl	0.012	0.02	**50**
chlorpyrifos	0.004	0.002	**67**
diazinon	2.2	2.3	4

PCDD-1

	Sample 1	Sample 2	RPD[1]
13-Aug			
azinphos-methyl	0.16	0.23	**36**
chlorpyrifos	0.098	0.13	**28**
diazinon	0.048	0.064	**29**
dichlobenil	0.3	0.37	21
dichlorprop	0.016	0.018	12
MCPP	0.015	0.018	18
napropamide	0.062	0.09	37
norflurazon	0.17	0.23	30
2,4-D	0.084	0.1	17
3,5-dichlorobenzoic acid	0.041 U[2]	0.028	
4,4'-DDD	0.008	0.015	**61**
15-Aug			
azinphos-methyl	0.052	0.05	4
chlorpyrifos	0.077	0.079	3
diazinon	0.052	0.05	4

Swamp Creek[3]

	Sample 1	Sample 2	RPD[1]
11-Jun			
dichlobenil	0.03	0.036	18
MCPP	0.032	0.028	13
prometon	0.031	0.035	12
simazine	0.04	0.043	7
trichlopyr	0.086	0.083	4
2,4-D	0.03	0.027	11

[1] - RPD = Relative Percent Difference (difference/mean x 100)

[2] - U = Undetected at or above the reported value

[3] - Samples for Swamp Creek were analyzed as a group with those from GHCDD-1 and PCDD-1 for the WSPMP

Swamp Creek is in King County and was a site sampled for the 1996 WSPMP

Values in bold exceed QA/QC criteria; affected data are qualified as estimates ("J" qualifier)

Appendix F-2. Duplicate Analysis Results for Water Samples (µg/L, ppb)
Samples Analyzed by the WSDA Laboratory

GHCDD-1				PCDD-1			
	Sample 1	Sample 2	RPD[1]		Sample 1	Sample 2	RPD[1]
20-May				22-May			
acephate	0.12	0.156	**26**	acephate	0.627	0.676	8
azinphos-methyl	0.14	0.16	13	azinphos-methyl	0.497	0.518	4
diazinon	0.26	0.3	14	chlorpyrifos	0.078	0.085	9
				diazinon	0.474	0.55	15
28-May							
acephate	0.137	0.141	3	11-Jun			
diazinon	0.45	0.451	0	chlorpyrifos	0.01	0.02	**67**
				diazinon	0.021	0.031	**38**
24-Jun							
diazinon	0.046	0.045	2	5-Aug			
				azinphos-methyl	0.391	0.341	14
9-Jul				chlorpyrifos	0.113	0.106	6
diazinon	0.02	0.023	14	diazinon	1.68	1.76	5
17-Jul				20-Aug			
azinphos-methyl	1.33	1.28	4	chlorpyrifos	0.045	0.041	9
diazinon	0.295	0.292	1	diazinon	0.047	0.047	0
14-Aug							
diazinon	0.963	0.906	6				

Values in bold exceed QA/QC criteria; affected data are qualified as estimates ("J" qualifier)

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-3. Duplicate Analysis Results for Tissue and Sediment Samples (µg/kg, ppb)

Tissue (Oysters)

	Sample 1	Sample 2	RPD[1]
4,4'-DDE	2.8	3.5	**22**
4,4'-DDD	1.8	1.9	5
PCB-1260	5	5	0

Sediment

GHCDD-1 Site 1 (Field Duplicate)

	Sample 1	Sample 2	RPD[1]
4,4'-DDE	110	90	20
2,4'-DDD	37	33	11
4,4'-DDD	250	240	4
4,4'-DDT	19 U[2]	6.9	
DDMU	37	22	**51**
aldrin	4.1	4.5	9
chlorpyrifos	2.6	2.1	**21**
diazinon	6.2	8.2	**28**
dichlobenil	33	27	20
hexachlorobenzene	1.4	1.7	19
napropamide	88	90	2

GHCDD-1 Site 3 (Lab Duplicate)

	Sample 1	Sample 2	RPD[1]
4,4'-DDE	23	33	**36**
2,4'-DDD	10	15	**40**
4,4'-DDD	59	85	**36**
DDMU	7.2	9.2	**24**
dichlobenil	22	24	9

Values in bold exceed QA/QC criteria; affected data are qualified as estimates ("J" qualifier)

[1] - RPD = Relative Percent Difference (difference/mean x 100)

[2] - U = Undetected at or above the reported value

Appendix F-4. Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

May 20

	MS	MSD	RPD[1]
2,3,4,5-tetrachlorophenol	95	112	16
2,3,4,6-tetrachlorophenol	82	99	19
2,4,5-T	75	90	18
2,4,5-TB	74	89	18
2,4,5-trichlorophenol	112	140	22
2,4,6-tribromophenol	118	130	10
2,4,6-trichlorophenol	80	99	21
2,4-D	86	111	25
2,4-DB	89	98	10
3,5-dichlorobenzoic acid	77	93	19
4,4'-DDE	78	91	15
4,4'-DDT	108	127	16
4-nitrophenol	44	44	0
acifluorfen	58	76	27
alachlor	92	80	14
aldrin	**28**	**32**	13
alpha-BHC	99	92	7
atrazine	83	76	9
azinphos-methyl	150	140	7
bentazon	68	69	1
beta-BHC	173	161	7
bromacil	73	70	4
bromoxynil	73	87	18
carbaryl	92	89	3
carbofuran	89	81	9
coumaphos	125	115	8
DCPA	**38**	44	15
delta-BHC	107	99	8
diazinon	160	150	6
dichlorprop	87	106	20
diclofop-methyl	67	79	16
dieldrin	91	84	8

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

May 20 (cont.)

	MS	MSD	RPD[1]
dinoseb	80	86	7
diphenamid	78	78	0
endosulfan I	97	97	0
endosulfan II	99	90	10
endosulfan sulfate	97	89	9
endrin	107	103	4
endrin aldehyde	90	77	16
endrin ketone	107	84	24
ethalfluralin	145	138	5
ethoprop	121	122	1
fensulfothion	164	153	7
fenthion	110	106	4
fluridone	**39**	**32**	20
gamma-chlordane	91	90	1
heptachlor	44	**37**	17
heptachlor epoxide	100	90	11
imidan	122	111	9
ioxynil	68	79	15
lindane	127	118	7
MCPA	77	89	14
MCPP	86	103	18
metholachlor	90	80	12
methoxychlor	124	104	18
metribuzin	79	72	9
napropamide	83	77	8
norflurazon	56	51	9
oxyfluorfen	67	66	2
parathion	161	100	**47**
parathion-methyl	123	121	2
pendimethalin	99	86	14
pentachlorophenol	107	124	15
phorate	103	102	1

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

May 20 (cont.)

	MS	MSD	RPD[1]
prometryne	53	48	10
pronamide	82	71	14
ramrod	82	78	5
ronnel	104	103	1
silvex	76	93	20
simazine	80	77	4
sulprofos	101	105	4
tebuthiuron	82	76	8
terbacil	88	90	2
trichlopyr	74	86	15
trifluralin	84	75	11

June 11

2,4'-DDD	77	79	3
2,4'-DDE	72	71	1
2,4'-DDT	82	81	1
3-hydroxycarbofuran	75	51	38
alachlor	89	80	11
aldicarb	50	**30**	50
aldicarb sufone	92	67	31
aldicarb sulfoxide	73	50	37
atrazine	101	94	7
azinphos-ethyl	127	123	3
bromacil	85	81	5
captafol	92	86	7
captan	84	81	4
carbaryl	50	**33**	41
carbofuran	70	47	39
carbophenothion	126	129	2
chlorpyrifos	123	122	1

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

June 11 (cont.)

	MS	MSD	RPD[1]
demeton-o	101	96	5
demeton-s	103	99	4
dichlobenil	85	77	10
diphenamid	94	90	4
disulfoton	138	136	1
EPN	112	123	9
ethalfluralin	87	78	11
ethion	124	123	1
fenitrothion	124	120	3
fluridone	105	97	8
fonofos	117	117	0
kelthane	92	89	3
malathion	130	131	1
merphos	117	120	3
methiocarb	**13**	**9**	36
methomyl	74	50	39
metolachlor	76	71	7
metribuzin	95	88	8
mirex	79	79	0
napropamide	90	87	3
norflurazon	100	95	5
oxamyl	73	48	41
oxyfluorfen	82	90	9
pendimethalin	75	72	4
prometryn	115	97	17
pronamide	89	85	5
propachlor	80	72	11
propoxur	67	45	39
simazine	144	132	9
sulfotepp	110	108	2
tebuthiuron	67	68	1
terbacil	81	77	5
trans-nonachlor	75	76	1
trifluralin	86	80	7

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

July 15

	MS	MSD	RPD[1]
2,3,4,5-tetrachlorophenol	186	172	8
2,3,4,6-tetrachlorophenol	152	128	17
2,4'-DDD	94	81	15
2,4'-DDE	110	91	19
2,4'-DDT	91	90	1
2,4,5-T	84	77	9
2,4,5-TB	116	100	15
2,4,5-trichlorophenol	245	198	21
2,4,6-tribromophenol	111	97	13
2,4,6-trichlorophenol	154	126	20
2,4-D	83	72	14
2,4-DB	98	90	9
3,5-dichlorobenzoic acid	76	63	19
4-nitrophenol	90	70	25
acifluorfen	73	83	13
ametryn	86	56	42
azinphos-ethyl	100	95	5
benfluralin	94	80	16
bentazon	99	83	18
bromoxynil	133	111	18
butylate	89	86	3
captafol	140	98	35
captan	120	88	31
carbophenothion	100	98	2
chlorpropham	110	95	15
chlorpyrifos	100	95	5
chlorpyrifos-methyl	100	94	6
cyanazine	110	89	21
cycloate	95	94	1
daconil	110	93	17
DCPA	40	**36**	11
DEF	100	100	0

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

July 15 (cont.)

	MS	MSD	RPD[1]
demeton-s	72	64	12
dicamba	69	62	11
dichlorprop	104	97	7
diclofop-methyl	85	77	10
dinoseb	**38**	59	43
disulfoton	78	87	11
EPN	98	87	12
eptam	90	90	0
ethion	88	85	3
fenitrothion	110	98	12
fonophos	93	88	6
hexazinone	**31**	120	**118**
ioxynil	88	77	13
kelthane	**0**	**0**	
malathion	110	104	6
MCPA	123	104	17
MCPP	125	109	14
merphos	**0**	**0**	
mirex	98	76	25
molinate	92	88	4
pebulate	90	89	1
pentachlorophenol	141	119	17
picloram	**23**	**18**	24
profluralin	98	84	15
prometon	110	67	49
propargite	100	94	6
propazine	110	87	23
silvex	94	86	9
sulfotep	93	91	2
terbutryn	83	49	**52**
trans-nonachlor	92	80	14
trichlopyr	99	90	10
vernolate	89	83	7

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

August 13

	MS	MSD	RPD[1]
2,3,4,5-tetrachlorophenol	120	119	1
2,3,4,6-tetrachlorophenol	108	122	12
2,4,5-T	107	101	6
2,4,5-TB	110	98	12
2,4,5-TP	124	118	5
2,4,5-trichlorophenol	128	142	10
2,4,6-trichlorophenol	88	118	29
2,4-D	110	107	3
2,4-DB	116	110	5
3,5-dichlorobenzoic acid	92	107	15
3-hydroxycarbofuran	95	82	15
4,4'-DDD	76	83	9
4,4'-DDE	66	75	13
4,4'-DDT	75	81	8
4-nitrophenol	42	**26**	47
acifluorfen	59	**37**	46
aldicarb	61	52	16
aldicarb sulfone	115	104	10
aldicarb sulfoxide	104	89	16
aldrin	**16**	**19**	17
alpha-BHC	84	85	1
ametryn	74	70	6
azinphos-methyl	89	101	13
benfluralin	78	80	3
bentazon	93	112	19
beta-BHC	81	87	7
bromoxynil	112	115	3
butylate	83	84	1
carbaryl	84	88	5
carbofuran	97	86	12
chlorothalonil	97	94	3
chlorpropham	80	82	2

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

August 13 (cont.)

	MS	MSD	RPD[1]
coumaphos	89	101	13
cyanazine	68	75	10
cycloate	80	82	2
DCPA	55	51	8
delta-BHC	89	95	7
dicamba	92	83	10
dichlofop-methyl	99	95	4
dichlorprop	133	120	10
dieldrin	75	77	3
dimethoate	69	81	16
dinoseb	**37**	**16**	79
endosulfan I	79	85	7
endosulfan II	77	88	13
endosulfan sulfate	80	84	5
endrin	77	81	5
endrin aldehyde	76	84	10
endrin ketone	77	89	14
eptam	74	71	4
ethoprop	86	89	3
fensulfothion	85	100	16
fenthion	93	99	6
gamma-BHC	85	91	7
heptachlor	**26**	**29**	11
heptachlor epoxide	83	80	4
hexazinone	81	94	15
imidan	87	99	13
ioxynil	119	106	12
MCPA	103	97	6
MCPP	110	110	0
methiocarb	**38**	61	46
methomyl	104	96	8
methoxychlor	80	92	14

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-4 (cont.). Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the Manchester Environmental Laboratory

August 13 (cont.)

	MS	MSD	RPD[1]
molinate	78	83	6
oxamyl	97	82	17
parathion	93	104	11
parathion-methyl	85	95	11
pebulate	76	79	4
pentachlorophenol	128	127	1
phorate	94	98	4
picloram	**18**	**19**	5
profluralin	73	82	12
prometon	78	86	10
propazine	91	94	3
propoxur	82	81	1
ronnel	90	101	12
sulprofos	92	99	7
terbutryn	49	62	23
trans-chlordane	59	65	10
trichlopyr	130	119	9
vernolate	79	86	8

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-5. Matrix Spike Recoveries for Water Samples (%)
Samples Analyzed by the WSDA Laboratory

	Date	MS	MSD	RPD[1]
azinphos-methyl	31-May	108	73	**39**
	5-Jun	**14**	**6**	**80**
	7-Jun	**9**	**6**	**40**
	27-Jun	168	130	**26**
	15-Jul	138	171	21
	12-Aug	97	106	9
	27-Aug	131	127	3
chlorpyrifos	31-May	93	77	19
	5-Jun	**23**	**13**	**56**
	7-Jun	**19**	**15**	24
	27-Jun	117	81	**36**
	15-Jul	89	93	4
	12-Aug	99	105	6
	27-Aug	100	95	5
diazinon	31-May	101	75	**30**
	5-Jun	**52**	**50**	4
	7-Jun	**52**	**49**	6
	27-Jun	116	87	**29**
	15-Jul	101	117	15
	12-Aug	105	112	6
	27-Aug	103	104	1

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-6. Matrix Spike Recoveries for Tissue Samples (%)

	MS	MSD	RPD[1]
2,4'-DDD	87	87	0
2,4'-DDE	78	74	5
2,4'-DDT	79	75	5
4,4'-DDD	83	84	1
4,4'-DDE	73	64	13
4,4'-DDT	76	81	6
aldrin	73	59	**21**
alpha-BHC	69	66	4
alpha-chlordene	77	60	**25**
beta-BHC	83	84	1
chlorpyrifos	124	147	17
cis-chlordane	76	73	4
cis-nonachlor	84	83	1
DCPA	108	97	11
DDMU	82	79	4
delta-BHC	96	92	4
diazinon	113	109	4
dieldrin	75	68	10
endosulfan I	82	73	12
endosulfan II	99	95	4
endosulfan sulfate	96	95	1
endrin	77	75	3
endrin ketone	88	106	19
ethion	66	70	6
gamma-BHC	77	76	1
gamma-chlordene	62	75	19
heptachlor	49	16	**102**
heptachlor epoxide	79	77	3
hexachlorobenzene	**33**	**27**	20
methoxychlor	95	85	11
mirex	99	97	2
oxychlordane	75	72	4
parathion	130	121	7
parathion-methyl	61	**33**	**60**
pentachloroanisole	45	43	5
tetradifon	70	56	**22**
trans-chlordane	81	79	3
trans-nonachlor	83	77	8

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-7. Matrix Spike Recoveries for Sediment Samples (%)

	MS	MSD	RPD[1]
2,3,4,5-tetrachlorophenol	99	98	1
2,3,4,6-tetrachlorophenol	84	88	5
2,4'-DDD	121	118	3
2,4'-DDE	107	103	4
2,4'-DDT	114	110	4
2,4,5-T	79	75	5
2,4,5-TB	75	75	0
2,4,5-TP	79	83	5
2,4,5-trichlorophenol	101	100	1
2,4,6-trichlorophenol	99	87	13
2,4-D	80	63	**24**
2,4-DB	84	76	10
3,5-dichlorobenzoic acid	84	88	5
4,4'-DDD	**35**	71	**68**
4,4'-DDE	**30**	108	**113**
4,4'-DDT	**8**	**24**	**100**
4-nitrophenol	**23**	**16**	**36**
alachlor	72	58	**22**
aldrin	84	53	**45**
alpha-BHC	48	**10**	**131**
alpha-chlordene	85	62	**31**
ametryn	40	**39**	3
atrazine	51	**37**	**32**
azinphos-ethyl	70	58	19
azinphos-methyl	64	50	**25**
benfluralin	**5**	**0**	**200**
bentazon	80	73	9
beta-BHC	75	59	**24**
bromacil	52	41	**24**
bromoxynil	50	**12**	**123**
butachlor	48	55	14
butifos	81	87	7
butylate	76	66	14
carbophenothion	70	55	**24**

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-7. Matrix Spike Recoveries for Sediment Samples (%)

	MS	MSD	RPD[1]
carboxin	**15**	**18**	18
chlorpropham	88	75	16
chlorpyrifos	84	68	**21**
chlorpyrifos-methyl	72	61	17
cis-chlordane	81	63	**25**
cis-nonachlor	178	57	**103**
coumaphos	60	51	16
cyanazine	66	76	14
cycloate	79	68	15
DCPA	113	102	10
DDMU	105	89	16
delta-BHC	59	52	13
demeton-o	40	**26**	**42**
demeton-s	**38**	40	5
di-allate	58	75	**26**
diazinon	77	60	**25**
dicamba	129	127	2
dichlobenil	77	59	**26**
dichlorprop	91	84	8
dichlorvos	**32**	46	**36**
diclofop-methyl	44	50	13
dieldrin	95	70	**30**
dioxathion	65	76	16
diphenamid	**34**	**29**	16
disulfoton	62	58	7
endosulfan I	68	**38**	**57**
endosulfan II	69	48	**36**
endosulfan sulfate	99	41	**83**
endrin	70	54	**26**
endrin aldehyde	43	**28**	**42**
endrin ketone	59	42	**34**
EPN	**18**	**12**	**40**
eptam	78	73	7
ethalfluralin	**2**	**0**	**200**

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-7. Matrix Spike Recoveries for Sediment Samples (%)

	MS	MSD	RPD[1]
ethion	66	51	**26**
ethoprop	65	52	**22**
fenarimol	65	83	**24**
fenitrothion	**16**	**9**	**56**
fenthion	64	52	**21**
fonofos	72	56	**25**
gamma-BHC	51	81	**45**
gamma-chlordene	85	70	19
heptachlor	69	55	**23**
heptachlor epoxide	78	59	**28**
ioxynil	106	**39**	**92**
malathion	44	45	2
MCPA	110	92	18
MCPP	85	77	10
merphos	**31**	**24**	**25**
metolachlor	68	53	**25**
metribuzin	42	**34**	**21**
mirex	99	95	4
molinate	74	62	18
napropamide	65	60	8
oxychlordane	83	67	**21**
oxyfluorfen	**6**	**3**	**67**
parathion	**21**	**18**	15
pebulate	79	71	11
pentachlorophenol	73	79	8
phorate	68	51	**29**
picloram	**22**	**17**	**26**
profluralin	**9**	**5**	**57**
prometryn	40	**34**	16
pronamide	88	65	**30**
propachlor	48	**37**	**26**
propazine	**39**	**32**	20
propetamphos	75	84	11
ronnel	72	51	**34**

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-7. Matrix Spike Recoveries for Sediment Samples (%)

	MS	MSD	RPD[1]
simazine	44	**30**	**38**
sulfotepp	74	61	19
sulprofos	71	53	**29**
temephos	63	82	**26**
terbacil	66	59	11
terbutryn	45	**33**	**31**
tetrachlorvinphos	65	75	14
trans-chlordane	75	61	**21**
trans-nonachlor	97	95	2
trifluralin	**2**	**0**	**200**
triadimefon	**36**	45	**22**
trichlopyr	84	83	1
vernolate	73	68	7

Values in bold exceed QA/QC criteria

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-8. Field Spike Results

	Detected Concentrations		Expected Values	Percent Recovery		
	Sample 1	Sample 2		Sample 1	Sample 2	RPD[1]
Samples Analyzed by the Manchester Environmental Laboratory						
azinphos-methyl	0.015	0.032	0.1	15	32	72
chlorpyrifos	0.1	0.11	0.1	100	110	10
diazinon	0.11	0.12	0.1	110	120	9
malathion	0.095	0.11	0.1	95	110	15
Samples Analyzed by the WSDA Laboratory						
azinphos-methyl	0.113	0.101	0.1	113	101	11
chlorpyrifos	0.097	0.092	0.1	97	92	5
diazinon	0.106	0.106	0.1	106	106	0

[1] - RPD = Relative Percent Difference (difference/mean x 100)

Appendix F-9. Interlaboratory Comparison of Results from Split Samples (µg/L, ppb)

Azinphos-Methyl

	GHCDD-1			PCDD-1		
Date	MEL[1]	WSDA[2]	RPD[3]	MEL	WSDA	RPD
20-May	0.21	0.15	33	0.74	0.62	18
22-May	0.18	0.17	6	0.56	0.508	10
24-May	0.049	0.05	2	0.22	0.195	12
28-May	0.025	0.05	67	0.14	0.129	8
4-Jun	0.013	0.05 U[4]		0.04	0.053	28
11-Jun	0.15 U	0.06 U		0.019	0.05 U	
18-Jun	0.12 U	0.05 U		0.024	0.05 U	
24-Jun	0.14 U	0.05 U		0.013	0.05 U	
9-Jul	0.13 U	0.05 U		0.012	0.05 U	
15-Jul	0.12	0.036	108	0.006	0.06	164
17-Jul	0.66	1.31	66	0.018	0.05 U	
19-Jul	0.73	1.53	71	0.13	0.303	80
23-Jul	0.11	0.18	48	0.10	0.205	69
30-Jul	0.069	0.067	3	0.021	0.05 U	
6-Aug	0.094	0.106	12	0.38	0.366	4
12-Aug	0.016	0.05 U		0.18	0.252	33
14-Aug	0.010	0.05 U		0.096	0.088	9
20-Aug	0.12 U	0.05 U		0.015	0.05 U	

[1] - Manchester Environmental Laboratory, Manchester, Washington.

[2] - Washington State Department of Agriculture Chemical and Hop Laboratory, Yakima, Washington.

[3] - RPD = Relative Percent Difference (difference/mean x 100)

[4] - U = Undetected at or above the reported value

Appendix F-9 (cont.). Interlaboratory Comparison of Results from Split Samples (µg/L, ppb)

Chlorpyrifos

	GHCDD-1			PCDD-1		
Date	MEL[1]	WSDA[2]	RPD[3]	MEL	WSDA	RPD
20-May	0.006	0.01 U[4]		0.13	0.12	8
22-May	0.037 U	0.012		0.055	0.082	39
24-May	0.012	0.023	63	0.042	0.061	37
28-May	0.065 U	0.010		0.018	0.028	43
4-Jun	0.058 U	0.01 U		0.013	0.021	47
11-Jun	0.066 U	0.01 U		0.013	0.02	42
18-Jun	0.055 U	0.01 U		0.021	0.025	17
24-Jun	0.061 U	0.01 U		0.009	0.01 U	
9-Jul	0.056 U	0.01 U		0.003	0.01 U	
15-Jul	0.058 U	0.05 U		3.7	5.1	32
17-Jul	0.058 U	0.01 U		1.3	2.03	44
19-Jul	0.005	0.01 U		1.3	1.1	17
23-Jul	0.054 U	0.01 U		0.54	0.582	7
30-Jul	0.016	0.021	27	0.38	0.344	10
6-Aug	0.009	0.01 U		0.14	0.110	24
12-Aug	0.003	0.01 U		0.064	0.063	2
14-Aug	0.058 U	0.01 U		0.069	0.053	26
20-Aug	0.055 U	0.01 U		0.054	0.043	23

[1] - Manchester Environmental Laboratory, Manchester, Washington.

[2] - Washington State Department of Agriculture Chemical and Hop Laboratory, Yakima, Washington.

[3] - RPD = Relative Percent Difference (difference/mean x 100)

[4] - U = Undetected at or above the reported value

Appendix F-9 (cont.). Interlaboratory Comparison of Results from Split Samples (µg/L, ppb)

Diazinon

	GHCDD-1			PCDD-1		
Date	MEL[1]	WSDA[2]	RPD[3]	MEL	WSDA	RPD
20-May	0.32	0.28	13	0.057	0.063	10
22-May	0.51	0.59	15	0.56	0.51	9
24-May	0.077	0.108	34	0.90	0.991	10
28-May	0.40	0.45	12	0.25	0.241	4
4-Jun	5.42	5.2	4	0.22	0.293	28
11-Jun	0.45	0.361	22	0.027	0.026	4
18-Jun	0.07	0.059	17	0.065 U[4]	0.01 U	
24-Jun	0.056	0.046	20	0.022	0.014	44
9-Jul	0.026	0.02	26	0.01	0.02	67
15-Jul	0.70	0.107	147	0.008	0.012	40
17-Jul	0.28	0.294	5	0.01	0.022	75
19-Jul	1.7	1.99	16	0.39	0.342	13
23-Jul	0.35	0.403	14	0.075	0.077	3
30-Jul	0.053	0.055	4	0.34	0.309	10
6-Aug	0.055	0.056	2	1.7	1.72	1
12-Aug	2.3	2.60	12	0.046	0.048	4
14-Aug	1.1	0.935	16	0.069	0.045	42
20-Aug	0.41	0.319	25	0.048	0.047	2

[1] - Manchester Environmental Laboratory, Manchester, Washington.

[2] - Washington State Department of Agriculture Chemical and Hop Laboratory, Yakima, Washington.

[3] - RPD = Relative Percent Difference (difference/mean x 100)

[4] - U = Undetected at or above the reported value

Appendix G

Data Validation Reports for Water Analyses

Sample Number	Sampling Date
96204640	May 13
96204641	
96204642	
96214640	May 20
96214641	
96214642	
96214644	May 21
96214645	
96214646	May 22
96214647	
96214648	May 23
96214649	
96214650	May 24
96214651	
96214652	
96224640	May 28
96224641	
96234655	June 4
96234656	
96234657	
96248025	June 11
96248026	
96254658	June 18
96254659	
96254660	
96264661	June 24
96264662	
96274670	July 1
96274671	
96274672	
96284670	July 9
96284671	
96294360	July 18
96294361	
96294362	
96294363	July 19
96294364	
96294365	
96294366	
96294670	July 15
96294671	
96294672	
96294673	
96294674	
96294675	
96294676	
96294677	July 16
96294678	
96294679	
96294680	July 17
96294681	
96294682	
96304670	July 23
96304671	
96304672	
96314670	July 30
96314671	
96314672	
96324685	August 6
96324686	
96334685	August 12
96334686	
96334687	
96338056	August 13
96338057	
96338058	
96334688	August 14
96334689	
96334690	
96334691	August 15
96334692	
96334693	
96344685	August 20
96344686	

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 6, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96204640, 96204641, and 96204642

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for these samples is TEC-669A and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check:

The samples were analyzed only for the organo-phosphorous pesticides. A degradation check for DDT and endrin was, therefore, not necessary.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. The instrumental response for the target compounds was judged acceptable.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed near the end of the analytical sequence as continuing calibration checks.

The % Drift (%D) from the initial calibration for the target compounds met the criteria of $\leq$20% except for merphos II, dimethoate, and fensulfothion. The instrumental response or signal-to-noise for these compounds, even where %Ds indicated a decrease in sensitivity, was still acceptable for detection. Therefore, the reported quantitation limits were judged to be acceptable. There were no detected sample results for these compounds.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates: Acceptable

The surrogate recoveries for samples and blanks met the CLP criteria of 30-150% recovery. The recoveries were judged acceptable.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

An MS/MSD analysis was not performed using a sample from this set.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for chlorpyrifos and diazoxon. Detected results for these compounds were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The detected acephate results are considered minimum quantities and were qualified J. The method's or laboratory's performance for the analysis of this compound is known to be poor.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

DATA QUALIFIERS

U	-	The analyte was not detected at or above the reported result.
J	-	The analyte was positively identified. The associated numerical result is an estimate.
EXP	-	The result is equal to the number before EXP times 10 to the power of the number after EXP. As an example 3EXP6 equals 3×10^6.
REJ	-	The data are unusable for all purposes.
N	-	There is evidence the analyte is present in this sample.
NJ	-	There is evidence that the analyte is present. The associated numerical result is an estimate.
UJ	-	The analyte was not detected at or above the reported estimated result. The associated numerical value is an estimate of the quantitation limit of the analyte in this sample.
NAF	-	Not analyzed for.
NAR	-	No analytical result.
*	-	The analyte was present in the sample. (Visual aid to locate detected compounds on the report sheet.)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 5, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Herbicides Results for the Grayland Cranberry Bog Project Samples 96214640, 96214641, and 96214642

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the herbicides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using a modified SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of herbicides. This report covers the samples listed above.

The project code for this sample is TEC-669A and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. Compound independent calibration standards (CICs) were also analyzed to evaluate the RFs over a range of elemental amounts. Percent relative standard deviations (%RSDs) of the RFs from the CICs were ≤10%.

III. Continuing Calibration: Acceptable

The standards used for the initial calibration were also reanalyzed at the end of the analytical sequence as continuing calibration checks. The % Drift (%D) from the initial calibration for the target compounds met the criteria of ≤20%. The %RSD for the CIC RFs were <10%.

IV. Blanks:

Blanks were prepared with each extraction batch, however, surrogates were not spiked. The target compounds were not detected in the blanks. Since the surrogate recoveries were acceptable for the samples (see below), the lack of surrogates in the blanks was judged insignificant as the recoveries would likely have been acceptable.

V. Surrogates:

The surrogate recoveries for samples and matrix spikes were within 50-150%. Surrogates were not spiked into the blanks, however, based on the sample results the recoveries would likely have been acceptable if spiked. No qualifiers were applied based on surrogates.

VI. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

Sample 96214640 was used for the MS/MSD analyses. The applied criteria for recoveries were 50-150%. The following recoveries did not meet the applied criteria:

Compound	% Recovery (MS/MSD)
4-nitrophenol	44/44
DCPA	38/44
picloram	13/15

The compounds above were not detected in sample 96214640. The reported results for these compounds were qualified UJ for this sample due to the low recoveries above.

The recoveries for picloram were judged representative of the method's or laboratory's ability to analyze for this compound

for all samples. This compound was not detected in the samples and the results were qualified UJ.

VII. Compound Identification: Acceptable

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis.

VIII. Compound Quantitation: Acceptable

Calculations were based on the initial calibration CIC. Detected results below the quantitation limits were qualified J.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 4, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96214640, 96214641, 96214642, 96214644, 96214645, 96214646, 96214647, 96214648, 96214649, 96214650, 96214651, 96214652, 96224640, 96224641, 96234655, 96234656, and 96234657

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for this sample is TEC-669A and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check: Acceptable

Degradation of DDT and endrin as measured from the calibration standards' analyses were <20%. Resolution of the target compounds were judged acceptable.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. Compound independent calibration standards (CICs) were also analyzed to evaluate the RFs over a range of elemental amounts. Percent relative standard deviations (%RSDs) of the RFs from the CICs were ≤10%.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed near the end of the analytical sequence as continuing calibration checks except for the chlorinated pesticides standards. This was not judged to be significant since only samples 96214640, 96214641, and 96214642 were analyzed for the chlorinated pesticides and these analyses occurred just after the initial calibration.

The % Drift (%D) from the initial calibration for the target compounds met the criteria of ≤20% except for demeton-O, sulfotepp, demeton-S, disulfoton, fenitrothion, malathion, chlorpyrifos, ethion, carbophenothion, EPN, azinphos ethyl, dimethoate, fensulfothion, dioxathion, abate, fenvalerate-II, hexazinone, and diuron. The instrumental response or signal-to-noise for these compounds, even where %Ds indicated a decrease in sensitivity, was still acceptable for detection. Therefore, the reported quantitation limits were judged to be acceptable. Associated detected sample results for these compounds were qualified J.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates: Acceptable

The surrogate recoveries for samples, blanks, and matrix spikes met the CLP criteria of 30-150% recovery. The recoveries were judged acceptable.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

Sample 96214640 was used for the MS/MSD analyses. The applied criteria for recoveries were 50-150%. Recoveries were not measurable for dichlobenil, diazinon, parathion, napropamide, norflurazon, azinphos methyl, and carbofuran due to the spike level being too low relative to the native amounts. The following recoveries did not meet the applied criteria:

Compound	% Recovery (MS/MSD)
beta-BHC	173/161
aldrin	28.4/31.6
fensulfothion	164/153
fluridone	39.1/31.6
heptachlor	43.6/36.6
parathion	161/
prometryne	/48.4
acephate	0.6/0.5

Parathion and acephate were detected in sample 96214640. These results were previously qualified J due to detection below the quantitation limits. The other compounds above were not detected in this sample. The reported results for aldrin, fluridone, heptachlor, and prometryne were qualified UJ for this sample due to the low recoveries above. No qualifiers were applied based on the recoveries for beta-BHC and fensulfothion since these results do not indicate a problem with detection.

The recoveries for acephate were judged representative of the method's or laboratory's ability to analyze for this compound for all samples. All detected results for this compound were qualified J. No quantitation limit can be provided for non-detected results.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for methamidophos. Detected results for this compound were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The detected acephate results are considered minimum quantities.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

August 26, 1996

Subject: WSPMP waters, weeks 24 & 25
Walla Walla waters, week 25

Samples: 96248020-26, 96258000-01 & 96258080,82,84,86,88,90,92

Officer(s): Dale Davis (for WSPMP)
Art Johnson (for Walla Walla)

By: Norman Olson
Bob Carrell
Organics Analysis Unit

PESTICIDE & HERBICIDE ANALYSIS

ANALYTICAL METHODS: (Draft EPA Method 8085; formerly modified 1618 & 1658) Separate water samples, one each for the neutrals and Acids, were extracted following Manchester Laboratory's standard operating procedure for the extraction of pesticides and herbicides. The samples for neutrals (NPest, ClPest, OPPest, SPest & Pyrethriods) analyses were extracted with methylene chloride and solvent exchanged to iso-octane. The samples for acid herbicide analysis were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and methylated. The extracts were separately analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of detected pesticides and herbicides was performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of heteroatoms to empirical formulas.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection level (MDL). If a target analyte is detected and confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier. This procedure also applies to the method blanks.

NITROGEN-CONTAINING PESTICIDE ANALYSIS

BLANKS: No nitrogen-containing target compounds were detected in the laboratory blanks. Hence, the blanks demonstrate the system was free from this type of contamination.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: 1,3-Dimethyl-2-nitrobenzene recoveries were acceptable, ranging from 73% to 105%.

MATRIX SPIKING: Recoveries of spiked analytes were acceptable ranging from 67% to 144%. The range of recoveries for all spiked targets other then Simazine was 67% to 115%. The higher recoveries for Simazine are most likely due to interference because it was not detected in the sample associated with the matrix spiking.

COMMENTS: The data is useable as qualified.

ORGANOPHOSPHOROUS PESTICIDE ANALYSIS

BLANKS: No organophosphorous target compounds were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: Triphenylphosphate recoveries were acceptable, ranging from 94% to 130%.

MATRIX SPIKING: Recoveries of spiked analytes were acceptable ranging from 96% to 138%.

COMMENTS: The data is useable as qualified

ORGANOCHLORINE PESTICIDE ANALYSIS

BLANKS: No organochlorine target compounds were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: Decachlorobiphenyl recoveries were acceptable, ranging from 65% to 106%.

MATRIX SPIKING: Recoveries of spiked analytes were acceptable ranging from 71% to 92%. The recoveries for Kelthane were calculated from its breakdown product, 4,4'-dichlorobenzophenone.

COMMENTS: The data is useable as qualified.

SULFUR-CONTAINING AND PYRETHROID PESTICIDE ANALYSIS

BLANKS: None of these types of target analytes were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: There no designated surrogate compounds for these groups of targets. Recovery efficiencies of surrogates from other neutral pesticide groups should also apply to this group.

MATRIX SPIKING: No matrix spiking was performed for these groups of targets during this run.

COMMENTS: The data is useable as qualified.

ACID HERBICIDE ANALYSIS

BLANKS: No acid herbicide target compounds were detected in the laboratory blanks

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: 2,4,6-Tribromophenol recoveries were acceptable, ranging from 67% to 137%.

Manchester Environmental Laboratory

7411 Beach Dr E
Port Orchard Washington 98366
August 5, 1996

Project: **WSPMP and Walla Walla 16, 17, 24, 25**

Samples: 96168060 through 168066, 178067, 178068, 178096 through 178096
248020 through 248026, 258000, 258001, 258080 through 258086, 258088

By: Karin Feddersen KF

These samples were analyzed by EPA Method 531.1, modified, for Carbamates.

Holding Times:

This method states that the analytes are stable in water for twenty-eight days prior to analysis. The samples were extracted within twenty-eight days from collection. The extracts were then stored in methanol. Although there has been no holding time established for this method between extraction and analysis, it has been observed that the analytes of interest are extremely stable when stored in methanol even for several months.

Method Blanks:

No analytes of interest were detected in either method blank.

Initial Calibration:

Standard responses were acceptable for all target analytes. The calibration coefficient was at least 0.995 for all target analytes with several exceptions, which did not affect the results.

Surrogates:

BDMC was added as a surrogate to each sample. No QC limits have yet been established for this modified method. All surrogate recoveries for these samples, the matrix spikes, and the associated method blanks are between 50 and 150% with several exceptions. Low surrogate recovery may indicate low bias of analyte concentration.

Since sensitivity is unaffected by surrogate recoveries above 150%, analytes which were not detected do not require qualification. No analytes of interest were detected in any of the samples. Therefore, all sample and blank results with BDMC recoveries below 50% have been qualified "UJ".

Matrix Spikes (MS/MSD):

Samples 96168061 and 96248023 were also analyzed as MS/MSD. Typical recoveries range from 40% to 100%.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 6, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96254658, 96254659, 96254660, 96264661, and 96264662

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for these samples is TEC-669A and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check:

The samples were analyzed only for the organo-phosphorous pesticides. A degradation check for DDT and endrin was, therefore, not necessary.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. The instrumental response for each compound was judged to be acceptable. A compound independent calibration standard (CIC) was also analyzed to evaluate the RFs over a range of elemental amounts. The percent relative standard deviation (%RSD) of the RFs for the phosphorous channel was 12% which was judged acceptable.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed near the end of the analytical sequence as continuing calibration checks. The % Drift (%D) from the initial calibration for most of the target compounds did not meet the criteria of $\leq$20% except for abate, diazinon, phorate, dimethoate, ronnel, fenthion, sulprofos, and imidan. The instrumental response or signal-to-noise for the compounds with %Ds >20, even where the %Ds indicated a decrease in sensitivity, was still acceptable for detection. Therefore, the reported quantitation limits were judged to be acceptable while the associated detected results were qualified J.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates:

The surrogate recoveries for samples 96254658, 96254659, 96264661, and blank BW6173 were slightly above the applied criteria of 30-150%. All other samples and blank resulted with recoveries just <150%. This suggests that the spiked amount of the surrogate may have been higher than planned. Therefore, no qualifiers were applied based on the high surrogate recoveries.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

An MS/MSD analysis was not performed using a sample from this set.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for azinphos-methyl for samples 96254660 and 96264662. The detected results for this compound and samples were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The method's or laboratory's performance for the analysis of acephate is known to be poor. Therefore, non-detected results for this compound were not reported. Acephate was not detected in these samples.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 7, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96274670, 96274671, 96274672, 96284670, and 96284671

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for these samples is TEC-669C and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check:

The samples were analyzed only for the organo-phosphorous pesticides. A degradation check for DDT and endrin was, therefore, not necessary.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. The instrumental response for each compound was judged to be acceptable. A compound independent calibration standard (CIC) was also analyzed to evaluate the RFs over a range of elemental amounts. The percent relative standard deviation (%RSD) of the RFs for the phosphorous channel was 16% which was judged acceptable.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed after sample analyses as continuing calibration checks except for one of the three pesticides standard mixes. This third standard mix analysis resulted in no data as the detector discharge tube broke. A reanalysis was not performed.

The % Drift (%D) from the initial calibration for the target compounds met the criteria of $\leq$20% except for fenthion, fensulfothion, and parathion. The instrumental response or signal-to-noise for these compounds was still acceptable for detection, therefore, the reported quantitation limits were judged to be acceptable. These compounds were not detected in the samples. No qualifiers were applied based on the lack of continuing calibration check results for the pesticides associated with the third standard mix. It is likely that this standard would have performed as well as the other two.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates: Acceptable

The surrogate recoveries for samples and blanks met the applied criteria of 30-150% recovery. No qualifiers were applied based on the surrogates.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

An MS/MSD analysis was not performed using a sample from this set.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for azinphos-methyl for samples 96274672 and 96284671. The detected results for this compound and samples were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The method's or laboratory's performance for the analysis of acephate is known to be poor. Therefore, non-detected results for this compound were not reported. Acephate was not detected in these samples.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 10, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96294360, 96294361, 96294362, 96294363, 96294364, 96294365, 96294366, 96294670, 96294671, 96294672, 96294673, 96294674, 96294675, 96294676, 96294677, 96294678, 96294679, 96294680, 96294681, 96294682, 96304670, 96304671, and 96304672

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for these samples is TEC-669C and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check: Acceptable

Degradation of DDT and endrin as measured from the calibration standards' analyses were <20%. Resolution of the target compounds were judged acceptable.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. Compound independent calibration standards (CICs) were also analyzed to evaluate the RFs over a range of elemental amounts. Percent relative standard deviations (%RSDs) of the RFs from the CICs were ≤10% for the elements nitrogen and chlorine, ≤20% for phosphorous which was judged acceptable.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed near the end of the analytical sequences as continuing calibration checks.

The % Drift (%D) from the initial calibration for the target compounds met the criteria of ≤20% except for tebuthiuron, hexazinone, cis-permethrin, fenvalerate II, butachlor, kelthane, sulfotepp, methyl chlorpyrifos, fenithrothion, malathion E50, azinphos ethyl, imidan, dimethoate, and abate. The instrumental response or signal-to-noise for these compounds, even where %Ds indicated a decrease in sensitivity, was still acceptable for detection except for compounds noted in the Compound Quantitation section. Associated detected sample results for these compounds were qualified J.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates: Acceptable

The surrogate recoveries for samples, blanks, and matrix spikes met the applied criteria of 30-150% recovery. No qualifiers were applied based on the surrogates.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

Sample 96294670 was used for the MS/MSD analyses. The applied criteria for recoveries were 50-150%. The following recoveries did not meet the applied criteria:

Compound	% Recovery (MS/MSD)
hexazinone	31/
kelthane	0/0
merphos	0/0

The compounds above were not detected in sample 96294670. The reported result for hexazinone was qualified UJ for this sample. The reported results for kethane and merphos were qualified REJ for this sample due to the <10 recoveries above.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for the following:

Sample	Compound
96294364	acephate
96294365	malathion E50
96294680	malathion E50
	methamidophos
96304670	2,6-dichlorobenzamide
	2,6-dichlorobenzonitrile (dichlobenil)
	carbofuran
	napropamide
	norflurazon
96304671	methamidophos
	2,6-dichlorobenzamide
	N,N-diethyl-3-methylbenzamide (DEET)
	2,6-dichlorobenzonitrile (dichlobenil)
	carbaryl
	daconil
	napropamide
	norflurazon

Detected results for these compounds were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The detected acephate results are considered minimum quantities and were qualified J. The method's or laboratory's performance for the analysis of this compound is known to be poor, therefore, non-detected results were not reported. Detected results for azinphos-methyl were qualified J due to the lack of agreement between the calculated values using the CIC and the compound's RF.

The following compounds were judged to be responding below normal on the instruments:

Compound
abate
demeton-O
demeton-S
merphos
methamidophos
propetamphos
dimethoate
dioxathion
diuron
fenithrothion
fluridone
hexazinone
kelthane
methyl paraoxon
resmethrin

All sample results for the above compounds were qualified J if detected and UJ if non-detected.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 10, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Herbicides Results for the Grayland Cranberry Bog Project Samples 96294670, 96294671, 96294672, and 96294676

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the herbicides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using a modified SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of herbicides. This report covers the samples listed above.

The project code for this sample is TEC-669C and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. Initial Calibration:

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. Compound independent calibration standards (CICs) were also analyzed to evaluate the RFs over a range of elemental amounts. Percent relative standard deviations (%RSDs) of the RFs from the CICs were ≤10%.

The instrumental response for dinoseb was much lower than expected. This compound was not detected in the samples. The reported sample results for this compound were qualified UJ.

III. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed at the end of the analytical sequence as continuing calibration checks. The % Drift (%D) from the initial calibration for the target compounds met the criteria of ≤20% except for picloram. The response from the continuing calibration check indicated an increase in sensitivity for this compound, therefore, no qualifiers were applied toward non-detected results based on the %D. Picloram was not detected in the samples.

IV. Blanks: Acceptable

Blanks were prepared with the extraction batch. The target compounds were not detected in the blanks.

V. Surrogates: Acceptable

The surrogate recoveries for samples, blanks, and matrix spikes were within 50-150%. No qualifiers were applied based on surrogates.

VI. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

Sample 96294670 was used for the MS/MSD analyses. The applied criteria for recoveries were 50-150%. The following recoveries did not meet the applied criteria:

Compound	% Recovery (MS/MSD)
2,4,5-trichlorophenol	245/198
2,4,6-trichlorophenol	154/
DCPA	40/36
dinoseb	38/
2,3,4,5-tetrachlorophenol	186/172
2,3,4,6-tetrachlorophenol	152/
picloram	23/18

The compounds above were not detected in sample 96294670. The reported results for DCPA, dinoseb, and picloram were qualified UJ for this sample due to the low recoveries above. No qualifiers were applied based on the high recoveries above since these results do not indicate a problem with detection.

The recoveries for picloram were judged representative of the method's or laboratory's ability to analyze for this compound for all samples. This compound was not detected in the samples and the results were qualified UJ.

VII. Compound Identification: Acceptable

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for the following:

Sample	Compound
96294671	3,5-dichlorobenzoic acid
	MCPP
96294672	3,5-dichlorobenzoic acid
96294676	3,5-dichlorobenzoic acid
	dicamba

The results for these compounds and samples were qualified NJ.

VIII. Compound Quantitation: Acceptable

Calculations were based on the initial calibration CIC or compound RF from the initial calibration. Detected results below the quantitation limits were qualified J.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10 LABORATORY
7411 Beach Dr. East
Port Orchard, Washington 98366

February 11, 1997

MEMORANDUM

SUBJECT: Data Validation Report of Pesticides Results for the Grayland Cranberry Bog Project Samples 96314670, 96314671, 96314672, 96324685, 96324686, 96334685, 96334686, 96334687, 96334688, 96334689, 96334690, 96334691, 96334692, 96334693, 96344685, and 96344686

FROM: Gerald H. Dodo, Chemist
USEPA

TO: Dale Davis, Project Officer
WDOE

CC: Karl Arne
USEPA

The following is a data validation report of the pesticides' analyses results for water samples collected for the Grayland Cranberry Bog project. The analyses were performed at the USEPA Region 10 Laboratory using SW846 Method 8085 (draft) which utilizes a GC/AED for the screening of pesticides. This report covers the samples listed above.

The project code for these samples is TEC-669C and the account number is 9697B10PBFK.

Data qualifications

The following comments refer to laboratory performance meeting the Quality Control specifications outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

I. Holding Times: Acceptable

The holding time for the extraction of water samples is seven days from the date of sampling. The holding time for extracts is 40 days. All samples were extracted and analyzed within these criteria.

II. System Performance Check:

The samples were analyzed only for the organo-phosphorous pesticides. A degradation check for DDT and endrin was, therefore, not necessary.

III. Initial Calibration: Acceptable

Response factors (RFs) for calculations were determined from single level calibration standards at the quantitation limit. The instrumental response for each compound was judged to be acceptable. A compound independent calibration standard (CIC) was also analyzed to evaluate the RFs over a range of elemental amounts. The percent relative standard deviation (%RSD) of the RFs for the phosphorous channel was <10% which was judged acceptable.

IV. Continuing Calibration:

The standards used for the initial calibration were also reanalyzed after sample analyses as continuing calibration checks. The % Drift (%D) from the initial calibration for all the target compounds did not meet the criteria of ≤20%. The response for each compound indicated an increase in sensitivity, therefore, non-detected results were not qualified. All detected results for the target compounds were qualified J.

V. Blanks: Acceptable

Blanks were prepared with each extraction batch. The target compounds were not detected in the blanks.

VI. Surrogates: Acceptable

The surrogate recoveries for samples and blanks met the applied criteria of 30-150% recovery. No qualifiers were applied based on the surrogates.

VII. Matrix Spike/Matrix Spike Duplicate (MS/MSD):

An MS/MSD analysis was not performed using a sample from this set.

VIII. Compound Identification:

Detected compounds were confirmed by elemental ratios and/or GC/ITD analysis except for the following:

Sample	Compound
96334685	azinphos-methyl
	chlorpyrifos
96334686	azinphos-methyl
96344693	azinphos-methyl

The detected results for these compounds and samples were qualified NJ.

IX. Compound Quantitation:

Calculations were based on the initial calibration. Detected results below the quantitation limits were qualified J. The method's or laboratory's performance for the analysis of acephate is known to be poor. Therefore, non-detected results for this compound were not reported. Acephate was not detected in these samples.

The following compounds were judged to be responding below normal on the instrument:

Compound
abate
demeton-O
demeton-S
methamidophos
phosphamidan

All sample results for the above compounds were qualified J if detected and UJ if non-detected.

Overall Assessment for the Case

The usefulness of the data is based on the criteria outlined in SW846 Method 8085 (draft) and the USEPA Laboratory Data Validation Functional Guidelines for Evaluating Organics Analyses, 12/94.

All requirements for data qualifiers from the preceding sections were accumulated. Each sample data summary sheet and each compound was checked for positive or negative results. From this the overall need for data qualifiers for each analysis was determined. In cases where more than one of the preceding sections required data qualifiers, the most restrictive qualifier has been added to the data.

The usefulness of qualified data should be treated according to the severity of the qualifier. Should questions arise regarding the qualification of data and its relation to the usefulness, the reader is encouraged to contact the Region 10 laboratory.

Manchester Environmental Laboratory

7411 Beach Dr E, Port Orchard Washington 98366

CASE NARRATIVE

October 24, 1996

Subject: WSPMP waters, weeks 32 & 33

Samples: 96328050,51, & 96338052-58

Officer(s): Dale Davis (for WSPMP)

By: Norman Olson
Bob Carrell
Organics Analysis Unit

PESTICIDE & HERBICIDE ANALYSIS

ANALYTICAL METHODS: (Draft EPA Method 8085; formerly modified 1618 & 1658) Separate water samples, one each for the neutrals and Acids, were extracted following Manchester Laboratory's standard operating procedure for the extraction of pesticides and herbicides. The samples for neutrals (NPest, ClPest, OPPest, SPest & Pyrethriods) analyses were extracted with methylene chloride and solvent exchanged to iso-octane. The samples for acid herbicide analysis were hydrolyzed at pH > 12, extracted with methylene chloride at pH < 2, solvent exchanged and methylated. The extracts were separately analyzed by capillary Gas Chromatography and Atomic Emission Detection (GC/AED). Confirmation of detected pesticides and herbicides was performed by Gas Chromatography and Ion-Trap mass spectrometry (GC/ITD) or comparisons of elemental ratios of heteroatoms to empirical formulas.

All analytes have a respective practical quantitation limit (PQL) that is higher than the corresponding method detection level (MDL). If a target analyte is detected and confirmed at a concentration below its PQL, the reported concentration is qualified as an estimate, ' J' qualifier. This procedure also applies to the method blanks.

NITROGEN-CONTAINING PESTICIDE ANALYSIS

BLANKS: No nitrogen-containing target compounds were detected in the laboratory blanks. Hence, the blanks demonstrate the system was free from this type of contamination.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: 1,3-Dimethyl-2-nitrobenzene recoveries were acceptable, ranging from 71% to 106%.

MATRIX SPIKING: Recoveries and precision of spiked analytes were acceptable with recoveries ranging from 70% to 97% and RPD's not more than 25%, except Terbutryn with lower recoveries of 49% and 62%. Terbutryn's recoveries, although lower, are still in the acceptable range.

COMMENTS: Sample 96338055 contains a relatively large concentration of Nitrogen-containing compounds that interfered with the detection of Hexazinone. The practical quantitation limit for Hexazinoe in this sample has been sustantially raised as a result. The interfering compounds appear to be "Long Chain Amides".

Data is useable as qualified.

ORGANOPHOSPHOROUS PESTICIDE ANALYSIS

BLANKS: No organophosphorous target compounds were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: Triphenylphosphate recoveries were acceptable, ranging from 88% to 139%.

MATRIX SPIKING: Recoveries and precision of spiked analytes were acceptable with recoveries ranging from 69% to 104% and RPD's not more than 16%. Recoveries for Diazinon were not obtained due to interference from the relatively large concentration of native Diazinon present in the sample.

COMMENTS: The data is useable as qualified

ORGANOCHLORINE PESTICIDE ANALYSIS

BLANKS: No organochlorine target compounds were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: Decachlorobiphenyl recoveries were acceptable ranging from 53% to 124%, except for one of the matrix spike samples (LMX1) with a recovery of 44%.

MATRIX SPIKING: Recoveries and precision of spiked analytes were acceptable with recoveries ranging from 59% to 95% and RPD's not more than 15%, except Aldrin and Heptachlor with recoveries of 16 & 19% and 26 & 29% respectively. All results for these two analytes are 'UJ' qualified.

COMMENTS: The data is useable as qualified.

SULFUR-CONTAINING AND PYRETHROID PESTICIDE ANALYSIS

BLANKS: None of these types of target analytes were detected in the laboratory blanks.

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: There no designated surrogate compounds for these groups of targets. Recovery efficiencies of surrogates from other neutral pesticide groups should also apply to this group.

MATRIX SPIKING: Recoveries for the S-Pest, Propargite, were acceptable at 82 & 89%.

COMMENTS: The data is useable as qualified.

ACID HERBICIDE ANALYSIS

BLANKS: No acid herbicide target compounds were detected in the laboratory blanks

HOLDING TIMES: All samples were extracted within seven days of sampling.

SURROGATES: 2,4,6-Tribromophenol recoveries were acceptable, ranging from 37% to 134%.

MATRIX SPIKING: Recoveries of spiked analytes were acceptable ranging from 26% to 142% with RPD's not more than 47%, except Picloram and Dinoseb, @18% & 19% and 16% & 37% respectively.

Dinoseb and Picloram are qualified 'UJ' throughout due to the poor precision these analytes have historically shown.

COMMENTS: The data is useable as qualified.

DATA QUALIFIER CODES:

U	-	The analyte was not detected at or above the reported value.
J	-	The analyte was positively identified. The associated numerical value is an estimate.
UJ	-	The analyte was not detected at or above the reported estimated result.
REJ	-	The data are unusable for all purposes.
NAF	-	Not analyzed for.
N	-	For organic analytes there is evidence the analyte is present in this sample.
NJ	-	There is evidence that the analyte is present. The associated numerical result is an estimate.
E	-	This qualifier is used when the concentration of the associated value exceeds the known calibration range.

Manchester Environmental Laboratory

7411 Beach Dr E
Port Orchard Washington 98366
October 8, 1996

Project: **WSPMP 32 & 33**

Samples: 96328050, 96328051, and 96338052 through 96338058

By: Karin Feddersen KF

These samples were analyzed by EPA Method 531.1, modified, for Carbamates.

Holding Times:

This method states that the analytes are stable in water for twenty-eight days prior to analysis. The samples were extracted within twenty-eight days of the date of collection. The extracts were then stored in methanol. Although there has been no holding time established for this method between extraction and analysis, it has been observed that the analytes of interest are extremely stable when stored in methanol even for several months.

Method Blanks:

No analytes of interest were detected in either method blank.

Initial Calibration:

Standard responses were acceptable for all target analytes. The calibration coefficient was at least 0.995 for all target analytes.

Surrogates:

BDMC was added as a surrogate to each sample. No QC limits have yet been established for this modified method. Most surrogate recoveries are below 50 %. However, the matrix spike recoveries were acceptable, indicating that if analytes had been present in the samples, they would have been detected. No qualification of the data was warranted.

Matrix Spikes (LMX1/LMX2):

Aliquots of sample 96338058 were spiked and analyzed as LMX1 and LMX2.

1-Napthol was not added as a spike compound.

Methiocarb recovery was low (38%) in LMX1 only. Methiocarb was detected in the final low standard analyzed, and would thus most likely be detectable if present in the samples. Therefore, the quantitation limit does not need to be raised for this analyte.