WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

Carbaryl Concentrations in Willapa Bay and Recommendations for Water Quality Guidelines

March 2001

Publication No. 01-03-005
printed on recycled paper

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ECOLOGY

Carbaryl Concentrations in Willapa Bay and Recommendations for Water Quality Guidelines

by
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March 2001

Waterbody No. WA-24-0020

Publication No. 01-03-005
printed on recycled paper

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Abstract

The insecticide carbaryl (Sevin®) was analyzed in water samples collected before and after its annual application to control burrowing shrimp on oyster beds in Willapa Bay. This was done to follow-up on 1996-97 data that appeared to show long-term persistence at about 0.7 ug/L. Results showed no evidence of a carbaryl background in the Willapa Bay water column.

Based on an analysis of toxicity data, the following guidelines were recommended for evaluating the significance of carbaryl residues in Willapa Bay water: 0.06 ug/L as a probable safe level for marine organisms; 0.1 - 0.7 ug/L as a potential effects threshold; and 3.0 ug/L as being equivalent to an EPA acute water quality criterion. Data are presented that show carbaryl concentrations were at or below 0.1 ug/L after the end of the July 5-31, 2000 spray period, but that concentrations were in the potential effects threshold range at locations several miles from oyster beds soon after large areas were treated. Comparable low-level data are not available to show what the concentrations are closer to treated beds during or within a few days of applications.

Summary

The carbamate insecticide carbaryl (Sevin®) is applied to Willapa Bay oyster beds during low tides in July and August for control of burrowing shrimp. The Washington State Department of Ecology (Ecology) currently issues permits (short-term water quality variance) for annual treatment of up to 600 acres in Willapa Bay at the rate of eight pounds per acre. Up to 200 acres may be similarly treated in Grays Harbor.

During the summer of 2000, Ecology measured carbaryl concentrations in water samples collected before and after the Willapa Bay applications. This was done to follow-up on evidence of long-term persistence at about 0.7 ug/L (parts per billion) reported in a 1996-97 experimental study by Washington State University.

Ecology's samples were analyzed at a quantitation limit of 0.004 ug/L, orders of magnitude lower than historical monitoring data. Samples were collected in the intertidal zone along the Long Beach peninsula, deeper channels adjacent to the Stony Point oyster beds, out in the main bay, and in selected tributaries and cranberry bog drainages. Results showed no evidence of a carbaryl background in the Willapa Bay water column. Carbaryl was undetected in all but one of 23 pre-spray samples from the bay. The sample in question had an estimated concentration of 0.002 ug/L. Tributaries and cranberry bog drainages were not significant carbaryl sources.

Based on an analysis of toxicity data for 35 marine species, the following guidelines were recommended for evaluating the significance of carbaryl residues in Willapa Bay water: 0.06 ug/L as a probable safe level for marine organisms; 0.1 – 0.7 ug/L as a potential effects threshold; and 3.0 ug/L as being equivalent to an EPA acute water quality criterion.

One to four days after the end of the July 5-31 spray period, carbaryl was detectable in 83% of Willapa Bay samples analyzed (19 out of 23), but all concentrations were at or below 0.1 ug/L, the lower end of the effects threshold. Data collected as part of a separate effort by the Shoalwater Bay Indian Tribe, after a four-day period of heavy carbaryl applications to the Stony Point area (350 acres treated on July 14-17), showed that carbaryl concentrations were in the potential effects threshold range at locations several miles away from treated oyster beds. However, concentrations never approached the recommended 3.0 ug/L acute criterion. Comparable low-level data are not available to show what carbaryl concentrations occur closer to treated beds during or within a few days of applications.

Recommendations

If further water quality monitoring is to be done for carbaryl in Willapa Bay, it should focus on the period during or immediately after applications. Detection limits should be at or below 0.1 ug/L to give useful data. There is a need for better data on the 1-naphthol breakdown product.

The water quality guidelines for carbaryl recommended in the present report could be used to estimate the duration of toxic conditions following spraying and to help guide permitting decisions in the future. Laboratory toxicity tests with potentially sensitive Willapa Bay organisms would be useful for verifying or refining these guidelines, since data are currently limited to only a few sensitive species. Test organisms to consider include the amphipod *Corophium* spp., an important crustacean prey item for juvenile salmon and other fish, and, given their apparent sensitivity, a sea urchin or other echinoderm. The tests should be conducted on the early life stages.

Acknowledgements

The assistance on this project provided by Brett Dumbauld, Washington State Department of Fish and Wildlife (WDFW), and oyster grower Dennis Tufts is very much appreciated. Field work was conducted with the help of Dale Norton, John Summers, Janet Boyd, and Kerry Carroll, Washington State Department of Ecology. The samples were analyzed by EPA and Ecology staff at Manchester Environmental Laboratory. Special thanks are due the carbaryl analyst, Steve Reimer, of EPA.

The author is grateful to the Shoalwater Bay Tribe's Director of Environmental Programs, Gary Burns, and the Shoalwater Bay Environmental Laboratory Manager, Ron Boquist, for giving permission to use their data. Key McMurray, formerly with the Tribe and now with WDFW, provided useful information for planning this project.

The quality assurance project plan was reviewed by Ecology's Cliff Kirchmer, who made valuable suggestions for improvements. Ecology librarians Jean Hariot and Phyllis Shafer spent many hours locating papers for the literature search. This report benefited from review by Dale Norton, Janet Boyd, and Mark Bentley. Formatting was done by Joan LeTourneau.

Introduction

Carbaryl*, a carbamate insecticide with the trade name Sevin®, has been applied to control burrowing ghost shrimp (*Neotrypaea californiensis*) and mud shrimp (*Upogebia pugettensis*) in Willapa Bay oyster beds since 1963. The Washington State Department of Ecology (Ecology) currently allows treatment of up to 600 acres annually at the rate of eight pounds per acre. Up to 200 acres may be similarly treated in Grays Harbor. Spraying takes place during low tides in July and August.

Willapa Bay and Grays Harbor are the only U.S. marine waters where the use of carbaryl or other insecticides is permitted. Because of the scope of the applications, direct toxicity to non-target organisms including Dungeness crab, uncertainty about indirect effects on species such as salmon, and perceived human health concerns, this has been a controversial issue. Control of burrowing shrimp is necessary to keep the substrate firm enough to support commercial oyster production where shrimp are abundant (Dumbauld et al., 1997), and growers maintain that without carbaryl large areas of Willapa Bay would no longer be viable for oyster culture, severely damaging the industry. They also point to the habitat value of oyster shell for crab and other animals as a mitigating factor off-setting short-term harm by long-term habitat improvement (Doty et al., 1990; Feldman et al., 2000). The Willapa Bay & Grays Harbor Oyster Growers Association has been working to find alternatives to carbaryl, so far without success (DeWitt et al., 1997).

The regulatory history of carbaryl's use in Willapa Bay and Grays Harbor is described in Tufts (1990). The Washington State Department of Fish & Wildlife (WDFW) formerly supervised and regulated the control and treatment of burrowing shrimp on oyster lands. In September 1992, Ecology took over as lead agency. Ecology has been issuing short-term water quality variances for spray projects, thereby certifying no interference with existing water uses or long-term and irreparable harm to the environment. WDFW continues to serve in an advisory role.

WDFW has done extensive carbaryl monitoring in Willapa Bay (e.g., Hurlburt, 1986; Creekman and Hurlburt, 1987; Washington State Dept. Fisheries and Dept. Ecology, 1992; and Tufts, 1989, 1990). Results have shown there can be off-site transport from sprayed oyster beds immediately following treatment, but that persistence in water is short. Results from past monitoring efforts have been variable due to differences in sampling designs, analytical methods, water circulation patterns, amount of pesticide applied, and area treated.

Longer-term persistence has been observed in the sediments. An Ecology study found an average carbaryl concentration of 105 ug/Kg (parts per billion) in sediment from treated sites 60 days after application, and carbaryl was detected in sediment pore water at 0.57-1.2 ug/L (parts per billion) on day-60 (Stonick, 1999). Dumbauld et al. (1997) reported shorter persistence in the sediments, 40-45 days or less, and that the rate of initial decline after application is rapid.

*1-naphthyl methylcarbamate, CAS No. 63-25-2

During the summer of 2000, the Ecology Environmental Assessment Program analyzed carbaryl concentrations in Willapa Bay water before and after the application period. The impetus for this work was two-fold: First, while toxicity to sensitive marine species can occur at concentrations of 10 ug/L or less, the methods for carbaryl analysis used by WDFW have had a lower detection limit of approximately 100 ug/L. Second, results from a small-scale field experiment conducted by Washington State University (WSU) in 1997 appeared to show a persistent carbaryl background of about 0.7 ug/L in Willapa Bay water. The National Academy of Sciences has recommended that carbaryl concentrations not exceed 0.06 ug/L in marine waters (NAS, 1973).

In the WSU study (Weisskopf and Felsot, 1998), carbaryl and imidacloprid were applied to small plots at Oysterville, on the west side of Willapa Bay. Imidacloprid was being tested as a possible alternative to carbaryl. Carbaryl concentrations were 0.704 ug/L prior to application and averaged 0.634 ug/L 28 days after application. The study was conducted in June 1997 prior to the commercial applications of carbaryl. The authors concluded that due to a background water concentration of "approximately 0.7 ppb…hazard to aquatic organisms from carbaryl applications cannot be ruled out." A similar background level of carbaryl had been measured by these investigators in 1996 during a pilot study for this project (Felsot, 1999).

The objectives of the Ecology sampling program were to:

- Determine if there is a carbaryl background that persists in Willapa Bay water outside the July-August spray period.

- Analyze carbaryl in other potential sources to Willapa Bay.

- Achieve quantitation limits for carbaryl sufficiently low to evaluate the potential for causing toxicity to sensitive marine organisms.

- Review the literature on carbaryl's effects on marine organisms and evaluate appropriate water quality guidelines for carbaryl in Willapa Bay.

Sampling Plan

The year 2000 carbaryl applications to Willapa Bay oyster beds began on July 5 and ended on July 31 (Figure 1). Six hundred acres were treated with approximately 4,800 pounds of carbaryl (active ingredient). The bulk of the applications were done by helicopter in the Stony Point/ Bay Center area on July 14-17, where 350 acres were treated (Tufts and Sheldon, 2000).

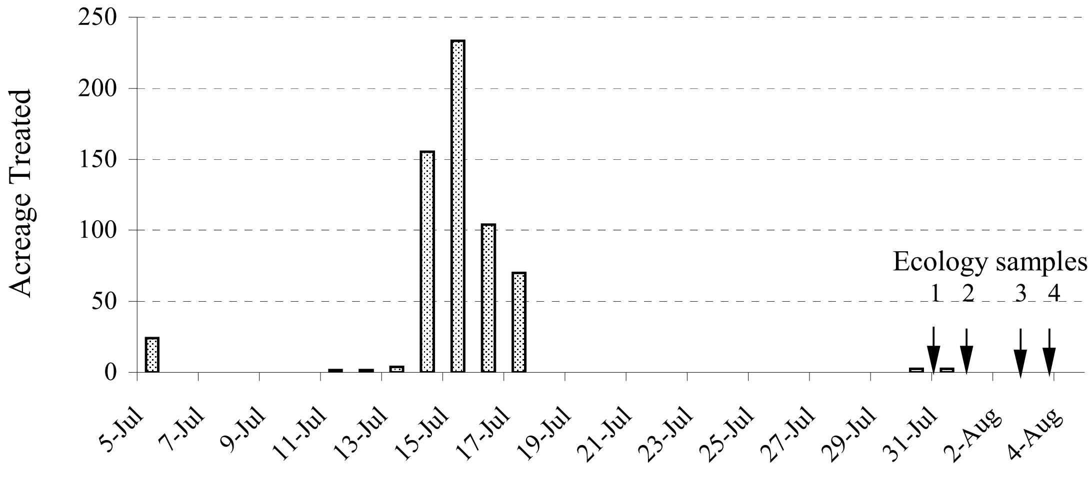


Figure 1. Timing of Carbaryl Applications in Willapa Bay and Ecology Post-Spray Water Samples, July 2000 [1=tributaries, 2=intertidal, 3=Stony Pt., 4=main bay]

Ecology collected pre-spray water samples on June 6-9 and post-spray water samples on July 31-August 4. Sampling was done in the four areas described below. Figure 2 shows where samples were collected and their general relationship to treated beds. Sampling sites were not located over beds scheduled for treatment, but rather were intended to be representative of general water quality conditions in a particular area. Appendix A has descriptions of each sampling site.

1. Oyster Beds

Two types of samples were collected in the general vicinity of treated oyster beds. First, in an effort to duplicate the findings of Weisskopf and Felsot (1998), water samples were collected near their experimental site on the Oysterville tideflats. Three samples were collected at approximately 1-hour intervals during a rising tide, before and after the carbaryl application period. Samples were taken in approximately 1/2-foot of water, moving progressively up the beach with the incoming tide. (Weisskopf and Felsot primarily sampled on flood tide.) A similar set of samples was collected about five miles to the north in the Stackpole Harbor area which historically has been heavily treated with carbaryl, and two miles to the south at the WDFW field station in Nahcotta.

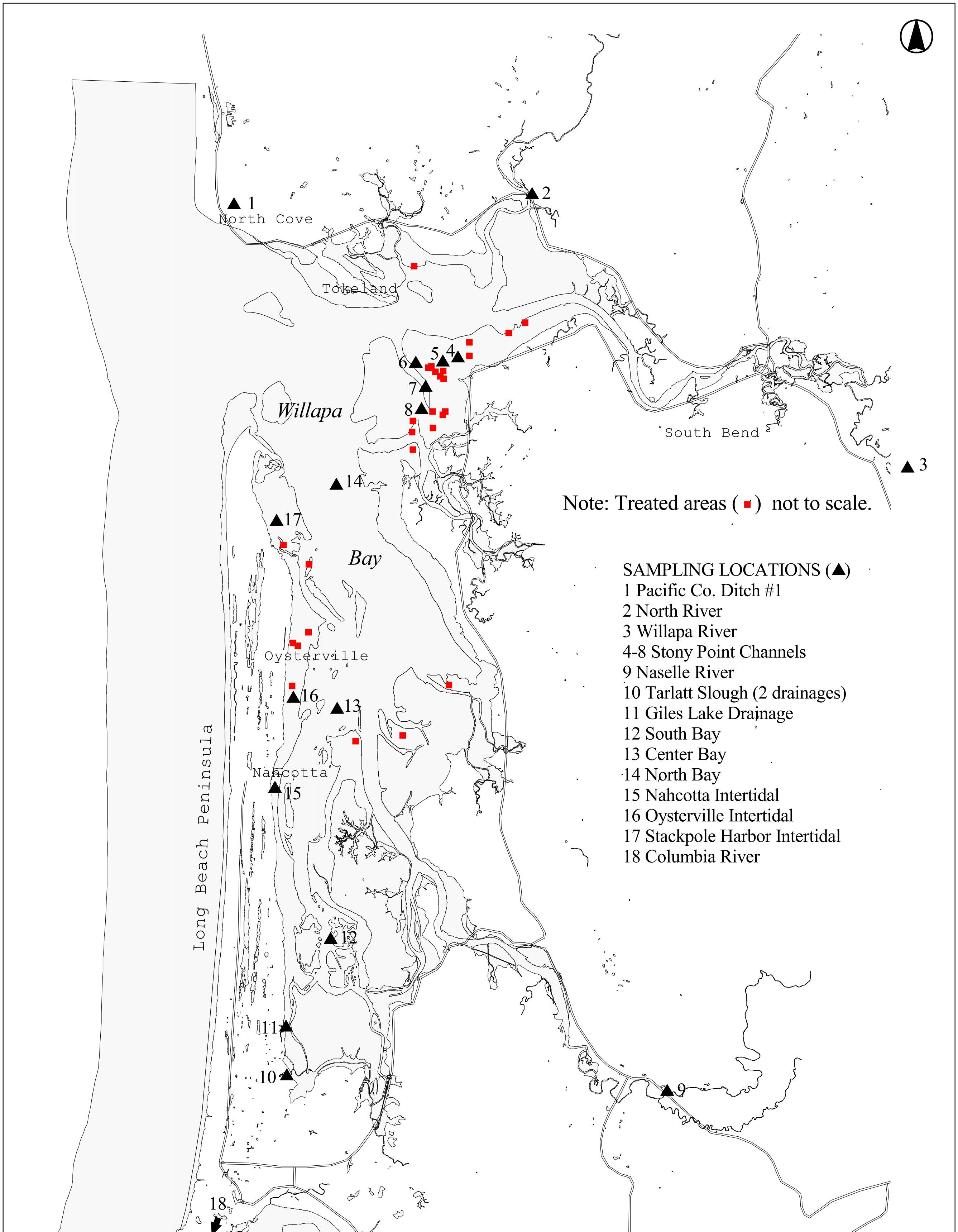


Figure 2. Ecology's Water Sampling Sites for Carbaryl and Approximate Location of Oyster Beds Treated during July 2000.

Because of concern that the above samples could be affected by a nearby carbaryl application, a second approach to sampling in oyster bed areas was to collect water from the system of channels (Pine Island, Bay Center Cutoff, Russell) that penetrate the Stony Point oyster beds on the northeast side of Willapa Bay. As noted above, the Stony Point area was heavily treated in the summer of 2000. The samples were collected during ebb tide in an effort to obtain data broadly representative of carbaryl concentrations in water draining away from oyster beds. Surface water was sampled from five sites in the Stony Point area, before and after carbaryl applications. Water depths ranged from 7 to 13 feet.

2. Main Bay

Surface and subsurface (~25 feet) water samples were collected from three sites in the main channel of Willapa Bay: upper bay between Goose Point and Leadbetter Point, middle bay between Oysterville and Nahcotta, and lower bay off the southern part of Long Island (Smokey Hollow). These samples were also taken during a falling tide and were intended to represent general water quality conditions in the bay, away from areas of carbaryl application. Pre- and post-spray samples were collected. Water depths ranged from 47 to 55 feet.

3. Cranberry Bog Drainage

Within the Willapa Bay watershed, carbaryl is also used on cranberry bogs in the North Cove area and on the Long Beach peninsula. It has been detected at concentrations of 0.029-0.042 ug/L in water samples from Pacific County Drainage Ditch (PCDD) #1, which drains the North Cove bogs to the mouth of Willapa Bay (Davis et al., 1997). Although carbaryl is currently registered for cranberries, its use has been declining in recent years (Davis, 2000).

Four streams that drain cranberry bogs were sampled where they enter Willapa Bay: PCDD #1 in North Cove, and Tarlatt Slough (two drainages, north and south) and the Giles Lake drainage at the south end of the Long Beach peninsula. Because the lower parts of these drainages are tidally influenced, the samples were taken near low water. PCDD #1 is the only cranberry bog drainage to the north part of Willapa Bay. The Tarlatt Slough and Giles Lake drainages are not the only routes by which cranberry bog drainage may enter the lower bay, but are easily the largest (Davis, 2000). The cranberry bog drainages were sampled once each for pre- and post-spray.

4. Major Tributaries

Mean daily runoff to Willapa Bay is less than 0.05% of the bay volume (USACE, 1976) so tributaries are a minor influence on water quality. Water samples for carbaryl analysis were therefore limited to the three largest tributaries: the North, Willapa, and Naselle rivers. Samples were also collected at the mouth of the Columbia River. The Columbia River plume can dominate surface water quality in the bay, but this occurs primarily during the winter and early spring, October-April (USACE, 1976). Plume water is sometimes present in the summer during periods of sustained storms with southwest winds (Newton, 2000). The rivers were sampled near low tide, once each for pre- and post-spray.

All the above-mentioned samples were analyzed for carbaryl, total suspended solids (TSS), and salinity. Data were also obtained on 1-naphthol, a toxic breakdown product of carbaryl, but the analysis was not optimized for this compound. Field measurements included temperature and flow (cranberry bog drainage). Flow data for the tributaries was obtained from the U.S. Geological Survey. Table 1 shows the number of samples collected and analyzed.

Table 1. Number and Type of Water Samples Collected

Location or Sample Type	Field Samples	Replicate Samples	Field + Replicate	Sampling Periods	Total Samples
Stackpole Harbor intertidal	3		3	2	6
Oysterville intertidal	3	1	4	2	8
Nahcotta intertidal	3		3	2	6
Stony Point channels	5	1	6	2	12
North Bay	2		2	2	4
Center Bay	2	1	3	2	6
South Bay	2		2	2	4
Cranberry Bog drainage	4	1*	4	2	9
Tributaries	4		4	2	8
Transfer blank	2		2	2	4
Pump blank	1		1	2	2
Matrix spikes	2		2	2	4
				Total Samples =	73

*pre-spray only

Sampling Methods

Sample containers for carbaryl analysis were one-liter amber glass bottles with Teflon lid liners, cleaned to EPA QA/QC specifications (EPA, 1990), and containing ChlorAc, a commercial product, as preservative (2.5 M in a chloroacetic acid and acetic acid mixture adjusted to pH 3 with potassium hydroxide). The TSS and salinity samples were collected in polyethylene bottles. All sample containers, with preservative added, were obtained from the Ecology Manchester Environmental Laboratory. Flows were gaged with a Swoeffer meter and top-setting rod.

Surface water samples were collected directly into the sample bottles. Subsurface samples from the main bay were obtained with a peristaltic pump and weighted polyethylene tubing. Sampling depth was approximately 25 feet (depth limit for peristaltic pump). The tubing was pre-cleaned with pesticide-grade acetone. Between sampling sites, the tubing was cleaned by pumping one liter of pesticide-grade acetone, then flushing with water from the next deep water site.

Each carbaryl sample was put in a bubble-wrap envelope and then placed in a polyethylene bag. All samples were put on ice immediately after collection. The samples were transported to Manchester Laboratory within one to two days of collection. Chain-of-custody was maintained.

Chemical Analysis

All samples were analyzed by Manchester Laboratory. Carbaryl was analyzed by High Pressure Liquid Chromatography (HPLC) using a Manchester modification of EPA Method 8318. The method was modified to lower the quantitation limit by increasing the volume extracted to one liter and reducing the final extract volume to one mL. TSS and salinity were analyzed by EPA Method 160.2 and Standard Methods 2520, respectively.

Data Quality

Holding Time

The EPA recommended holding time for carbamate pesticides is 7 days to extraction and 14 days to analysis. The post-spray samples for carbaryl and 1-naphthol were extracted within 4-7 days of collection and analyzed 1 day after extraction.

The pre-spray samples were extracted within 11-15 days of collection and analyzed 18-20 days after extraction. The EPA Manchester Laboratory has conducted a holding time study for carbamates that shows carbaryl and 1-naphthol are stable for months in a properly preserved sample (Reimer, 2000).

Extracts for two of the post-spray samples from the Stony Point area (site #4 sample 31-8423 and site #5 sample 31-8424) were inadvertently combined at the laboratory before being analyzed. Duplicates of these samples had been collected and saved at 4^{o}C. The saved samples were extracted within 45 days of collection and analyzed 3 days after extraction. The average of the results for these two samples was 0.041 ug/L, in close agreement to the earlier result of 0.045 ug/L for the combined extracts.

Method Blanks

Five method blanks each were analyzed with the pre- and the post-spray sample sets. No carbaryl was detected in any method blank at or above 0.004 ug/L. 1-Naphthol was not detected in the post-spray method blanks at or above approximately 0.01 ug/L. No 1-naphthol was reported as being present in the pre-spray method blanks, but a quantitation limit had not been established.

Surrogate Recoveries

To provide an estimate of accuracy for the analytical procedure, each sample was spiked with 4-bromo-3,5-dimethylphenyl-N-methylcarbamate (BDMC), a carbaryl surrogate compound. The surrogate was added prior to extraction at 0.050 ug/L. Surrogate recoveries averaged 95 ± 24% (pre-spray) and 93 ± 12% (post-spray), well within EPA Contract Laboratory Program (CLP) acceptance limits of 50 - 150%. Two pre-spray samples had surrogate recoveries outside control limits: 40% in sample 23-8205 (Stony Point) and 176% in sample 23-8189 (Stackpole Harbor). Carbaryl was not detected in either of these samples. No post-spray recoveries were outside control limits.

Matrix Spikes

Matrix spikes were analyzed to evaluate the potential for bias due to interference from the sample matrix (Table 2). For the pre- and post-spray sample sets, a surface water sample from

Table 2. Recovery of Matrix Spikes and Matrix Spike Duplicates

Sample No.	Sample Type/Location	Date (2000)	Analyte	Spike	Spike Duplicate	RPD*
238207	Surface water, north part of main bay	6-Jun	carbaryl	75%	92%	20%
318425	"	4-Aug	carbaryl	95%	108%	13%
			1-naphthol	7%	8%	13%

*Relative Percent Difference (range as percent of duplicate mean)

the north part of Willapa Bay was spiked with carbaryl at 0.050 ug/L. Carbaryl recoveries were 75% and 92% in the pre-spray sample and 98% and 108% in the post-spray sample, showing no significant bias. CLP acceptance limits are 50 - 150%.

1-Napthol was not a target compound for the present study. In light of its detection in some pre-spray samples, matrix spikes for 1-naphthol (0.050 ug/L) were analyzed with the post-spray sample set. Although precision was good, recoveries were poor, 7% and 8%. As a result, all the 1-naphthol data in the present report are qualified as estimates and probably underestimate the true values by a substantial amount.

Field Blanks

Four bottle (transfer) blanks and two pump blanks were analyzed to detect contamination arising from the sample containers, preservative, sampling procedures, or sample handling. The field blanks were submitted blind to the laboratory.

Transfer blanks were prepared by opening a new carbaryl sample bottle in the field, filling it with organic-free water obtained from Manchester Laboratory, then sealing the bottle and handling it as a sample. The transfer blanks were prepared while collecting the intertidal samples at Oysterville and the mid-channel samples out in Willapa Bay.

Pump blanks consisted of organic-free water pumped through the sampling system and into a carbaryl sample container. The pump blank was prepared out in the mid-channel of Willapa Bay after collecting the three subsurface water samples and following acetone cleaning and flushing of the pump system.

The field blank results are shown in Table 3. Five of the six blanks analyzed had no carbaryl detected, and none of the blanks had 1-naphthol detected.

Table 3. Field Blanks

Location	Date (2000)	Time	Sample No. (23-)	Carbaryl (ug/L)	1-Naphthol (ug/L)
Oysterville, Intertidal					
Bottle blank	8-Jun	1850	8198	0.004 U	nd*
Bottle blank	1-Aug	1350	8415	0.004 U	0.01 UJ
Main Bay, North Part					
Pump blank	6-Jun	1230	8214	0.004 U	nd
Bottle blank	6-Jun	1230	8215	0.004 U	nd
Pump blank	4-Aug	1130	8427	0.004 U	0.01 UJ
Bottle blank	4-Aug	1140	8428	**0.002** J	0.01 UJ

Note: Detections highlighted in **BOLD**
*nd = not detected; quantitation limit for 1-naphthol not determined in pre-spray samples
U = not detected at or above reported value
J = estimated value

One of the main bay transfer blanks for the post-spray samples appeared to contain a trace amount of carbaryl, estimated at 0.002 ug/L. One of the post-spray field samples (sample 31-8414, Oysterville) was also reported to contain carbaryl at 0.002 ug/L (estimated). All other carbaryl detections in post-spray samples were at or above 0.003 ug/L. While it is suspected this blank result was due to mislabeling while collecting the main bay samples – only one of the main bay samples had no carbaryl detected and the blank in question had the same four small peaks ranging from carbofuran's retention time to just after 1-naphthol as in the main bay samples – there is no concrete information to confirm this.

Replicate Samples

Replicate sampling was done to obtain estimates of the combined effects of field, sampling, and analytical variability. The replicates were separate samples collected a few minutes apart and submitted blind to the laboratory. The results for most replicates were identical (Table 4).

Table 4. Results on Replicate Samples (ug/L)

Location	Date (2000)	Sample No. (23-)	Carbaryl Rep. #1	Carbaryl Rep. #2	Carbaryl RPD*	1-Naphthol Rep. #1	1-Naphthol Rep. #2	1-Naphthol RPD
Oysterville, Intertidal								
Sample #2	8-Jun	8195/96	0.004 U	0.004 U	**0%**	nd**	nd	**0%**
Sample #1	1-Aug	8411/12	0.004 U	0.004 U	**0%**	**0.059** J	**0.038** J	**43%**
Channels off Stony Point								
Pine Island Channel, north	9-Jun	8203/04	0.004 U	0.004 U	**0%**	nd	nd	**0%**
Pine Island Channel, south	3-Aug	8420/21	**0.096**	**0.084**	**13%**	**0.039** J	**0.039** J	**0%**
Main Bay								
Center - surface	6-Jun	8209/10	0.004 U	0.004 U	**0%**	nd	nd	**0%**
Center - surface	4-Aug	8429/30	**0.003** J	**0.003** J	**0%**	0.01 UJ	0.01 UJ	**0%**
Cranberry Bog Drainage								
Pacific Co. Drainage Ditch #1	7-Jun	8180/81	**0.016**	**0.016**	**0%**	nd	nd	**0%**

Note: Detections highlighted in **BOLD**
*Relative Percent Difference (range as percent of duplicate mean)
**not detected; quantitation limit for 1-naphthol not determined
U = not detected at or above reported value
J = estimated value

Quantitation Limit vs. Detection Limit

The quantitation limit is the level at which a chemical can be accurately measured without qualification as an estimated quantity. In the analysis done for the present study the quantitation limit was 0.004 ug/L. The detection limit is the level at which a small amount of a chemical can be "seen" by an analysis, based on the variability of either the blank response or that of a low-level standard. In some of the samples analyzed for the present study, carbaryl was detected at concentrations below 0.004 ug/L. These results are qualified as estimates to indicate there is more uncertainty associated with these values than with values at or above 0.004 ug/L.

Results and Discussion

Pre-spray Samples

The results on the pre-spray water samples collected June 6-9 are summarized in Table 5.

Carbaryl was detected in only one of the 23 pre-spray samples taken within Willapa Bay. That sample, from the subsurface of the north part of the main bay, had a trace of carbaryl at 0.002 ug/L (estimated). The only other pre-spray detection of carbaryl was in cranberry bog drainage from Pacific County Drainage Ditch #1 (PCDD #1) near Tokeland, where 0.016 ug/L was detected in each of two replicate samples. The quantitation limit for carbaryl in the other pre-spray samples analyzed was 0.004 ug/L.

For 1-naphthol the only detections during pre-spray were in the intertidal samples at Stackpole Harbor, Oysterville, and Nahcotta. Among the samples collected, these were the most closely associated with oyster beds. The concentrations reported for 1-naphthol were 0.048 - 0.098 ug/L, but are likely substantial underestimates as previously discussed.

Post-spray Samples

Table 6 has the results on post-spray water samples collected July 31 – August 4.

Carbaryl was detected in 19 of the 23 post-spray samples (83%) collected within Willapa Bay. None of these samples were collected above treated oyster beds. Concentrations ranged from 0.002 ug/L (estimated) to 0.112 ug/L. The highest concentrations, averaging 0.070 ug/L, were found in the Stony Point area, followed by the intertidal samples, with the main bay samples being lowest. Figure 3 shows the Stony Point sampling sites in relation to treated oyster beds (based on Tufts and Sheldon, 2000). The concentrations in the Stony Point samples appeared to decrease with distance from treated beds. Similarly, samples from the north part of the main bay also had higher carbaryl concentrations than those collected to the south, further from areas where most of the applications occurred.

As in the pre-spray sampling, carbaryl was also detectable in cranberry bog drainage. PCDD #1 had an estimated 0.003 ug/L, much lower than the 0.016 ug/L detected in the pre-spray sample, and the Tarlatt Slough south ditch had 0.027 ug/L. Carbaryl was also detected in the North River post-spray sample at 0.018 ug/L, the only detection in a major tributary. There was some salinity associated with this sample, so it is possible that Willapa Bay rather than the watershed was the source. Either way, the flows in the cranberry bog drainages and North River were not sufficient to affect carbaryl concentrations in the bay. (Flow data are in Appendix B.)

1-Naphthol was detected in the intertidal and Stony Point post-spray samples. Concentrations were similar to those seen in the intertidal pre-spray samples, but, again, the accuracy of these results is uncertain.

Table 5. Results from Ecology's **Pre-Spray** Sampling in Willapa Bay and Tributaries

Location	Site No.	Date (2000)	Time	Sample No. (23-)	Temp. (^oC)	Salinity (0/00)	TSS (mg/L)	Carbaryl (ug/L)	1-Naphthol (ug/L)
Long Beach Peninsula - Intertidal									
Stackpole Harbor, sample #1	17	8-Jun	1645	8188	20.5	24.5	21	0.004 U	**0.070** J
" " sample #2	"	8-Jun	1715	8189	20.6	24.0	11	0.004 U	**0.070** J
" " sample #3	"	8-Jun	1805	8190	20.6	23.5	12	0.004 U	*
Oysterville, sample #1	15	8-Jun	1615	8194	24.5	20.0	8	0.004 U	**0.098** J
" sample #2	"	8-Jun	1730	8195	23.2	20.5	3	0.004 U	*
" sample #2 (replicate)	"	8-Jun	1735	8196	- -	- -	- -	0.004 U	*
" sample #3	"	8-Jun	1830	8197	22.1	17.0	6	0.004 U	*
Nahcotta, sample #1	16	8-Jun	1445	8191	19.6	22.0	15	0.004 U	**0.048** J
" sample #2	"	8-Jun	1500	8192	20.3	22.5	21	0.004 U	*
" sample #3	"	8-Jun	1845	8193	20.6	22.0	6	0.004 U	*
Bottle blank	- -	8-Jun	1850	8198	- -	- -	- -	0.004 U	*
Channels off Stony Point									
Bay Center Cutoff Channel	8	9-Jun	1253	8201	15.3	23.0	22	0.004 U	*
Pine Island Channel, south	7	9-Jun	1309	8202	16.0	23.0	19	0.004 U	*
Pine Island Channel, north	"	9-Jun	1319	8203	- -	23.0	13	0.004 U	*
Pine Island Channel, north (rep.)	6	9-Jun	1325	8204	- -	24.0	- -	0.004 U	*
Russell Channel, west	4	9-Jun	1341	8205	- -	22.5	14	0.004 U	*
Russell Channel, east	5	9-Jun	1352	8206	- -	22.0	16	0.004 U	*
Main Bay									
North - surface	14	6-Jun	1100	8207	15.5	24.0	12	0.004 U	*
North - subsurface	"	6-Jun	1115	8208	15.3	24.0	15	**0.002** J	*

Table 5. **Pre-Spray** Results (continued)

Location	Site No.	Date (2000)	Time	Sample No. (23-)	Temp. (^{o}C)	Salinity (0/00)	TSS (mg/L)	Carbaryl (ug/L)	1-Naphthol (ug/L)
Main Bay (continued)									
Center - surface	13	6-Jun	1001	8209	16.3	21.5	11	0.004 U	*
Center - surface (replicate)	"	6-Jun	1003	8210	- -	- -	- -	0.004 U	*
Center - subsurface	"	6-Jun	1030	8211	16.3	21.5	18	0.004 U	*
South - surface	12	6-Jun	1210	8212	16.6	20.0	15	0.004 U	*
South - subsurface	"	6-Jun	1220	8213	16.6	20.0	15	0.004 U	*
Pump blank	- -	6-Jun	1230	8214	- -	- -	- -	0.004 U	*
Bottle blank	- -	6-Jun	1230	8215	- -	- -	- -	0.004 U	*
Cranberry Bog Drainage									
Pacific Co. Drainage Ditch #1	1	7-Jun	1055	8180	12.5	<2.0	6	**0.016**	*
" " " " " (rep.)	"	7-Jun	1058	8181	- -	<2.0	- -	**0.016**	*
Tarlatt Slough - south ditch	10	7-Jun	1215	8182	15.0	<2.0	9	0.004 U	*
Tarlatt Slough - north ditch	10	7-Jun	1330	8183	14.8	<2.0	7	0.004 U	*
Giles Lake drainage	11	7-Jun	1355	8184	14.0	<2.0	6	0.004 U	*
Tributaries									
North River	2	7-Jun	1100	8187	15.5	5.0	48	0.004 U	*
Willapa River	3	7-Jun	0855	8186	13.0	<2.0	3	0.004 U	*
Naselle River	9	8-Jun	2010	8185	12.0	<2.0	<1	0.004 U	*
Columbia River									
Inside North Jetty	18	7-Jun	1225	8216	15.2	9.0	16	0.004 U	*

Note: Detections highlighted in **BOLD**
*not detected; quantitation limit for 1-naphthol not determined
U = not detected at or above reported value
J = estimated value

Table 6. Results from Ecology's **Post-Spray** Sampling in Willapa Bay and Tributaries

Location	Site No.	Date (2000)	Time	Sample No. (31-)	Temp. (^{o}C)	Salinity (0/00)	TSS (mg/L)	Carbaryl (ug/L)	1-Naphthol (ug/L)
Long Beach Peninsula - Intertidal									
Stackpole Harbor, sample #1	17	1-Aug	1332	8408	21.5	25.0	10	**0.019**	**0.024** J
" " sample #2	"	1-Aug	1403	8409	22.0	27.0	8	**0.044**	**0.012** J
" " sample #3	"	1-Aug	1433	8410	22.0	25.5	12	**0.016**	0.01 UJ
Oysterville, sample #1	15	1-Aug	1305	8411	24.3	19.5	7	0.004 U	**0.059** J
" sample #1 (replicate)	"	1-Aug	1307	8412	--	--	--	0.004 U	**0.038** J
" sample #2	"	1-Aug	1342	8413	22.2	28.0	5	0.004 U	0.01 UJ
" sample #3	"	1-Aug	1428	8414	23.7	25.5	15	**0.002** J	0.01 UJ
Nahcotta, sample #1	16	1-Aug	1250	8416	22.6	28.0	12	**0.004**	**0.027** J
" sample #2	"	1-Aug	1320	8417	23.9	24.0	8	**0.004**	**0.029** J
" sample #3	"	1-Aug	1405	8418	23.7	26.0	9	**0.008**	0.01 UJ
Bottle blank	- -	1-Aug	1350	8415	--	--	--	0.004 U	0.01 UJ
Channels off Stony Point									
Bay Center Cutoff Channel	8	3-Aug	0845	8419	17.8	27.5	54	**0.112**	**0.045** J
Pine Island Channel, south	7	3-Aug	0855	8420	17.9	27.5	22	**0.096**	**0.039** J
Pine Island Channel, south (rep.)	6	3-Aug	0858	8421	--	--	--	**0.084**	**0.039** J
Pine Island Channel, north	"	3-Aug	0905	8422	17.8	27.5	15	**0.067**	0.01 UJ
Russell Channel, west	4	3-Aug	0915	8423	16.8	28.0	76	**0.051**	NAF
Russell Channel, east	5	3-Aug	0930	8424	17.8	28.0	14	**0.031**	NAF
Main Bay									
North - surface	14	4-Aug	1200	8425	18.2	28.0	7	**0.010**	0.01 UJ
North - subsurface	"	4-Aug	1140	8426	17.3	28.0	9	**0.009**	0.01 UJ

Table 6. **Post-Spray** Results (continued)

Location	Site No.	Date (2000)	Time	Sample No. (31-)	Temp. (^oC)	Salinity (0/00)	TSS (mg/L)	Carbaryl (ug/L)	1-Naphthol (ug/L)
Main Bay (continued)									
Center - surface	13	4-Aug	1115	8429	19.4	26.5	7	**0.003** J	0.01 UJ
Center - surface (replicate)	"	4-Aug	1116	8430	--	--	--	**0.003** J	0.01 UJ
Center - subsurface	"	4-Aug	1105	8431	19.5	27.0	10	**0.003** J	0.01 UJ
South - surface	12	4-Aug	1035	8432	19.6	27.0	10	0.004 U	0.01 UJ
South - subsurface	"	4-Aug	1030	8433	19.8	26.4	24	**0.003** J	0.01 UJ
Pump blank	- -	4-Aug	1130	8427	--	--	--	0.004 U	0.01 UJ
Bottle blank	- -	4-Aug	1140	8428	--	--	--	**0.002** J	0.01 UJ
Cranberry Bog Drainage									
Pacific Co. Drainage Ditch #1	1	31-Jul	0930	8400	15.4	<2	4	**0.003** J	0.01 UJ
Tarlatt Slough - south ditch	10	31-Jul	1155	8404	19.5	<2	29	**0.027**	0.01 UJ
Tarlatt Slough - north ditch	10	31-Jul	1115	8405	18.6	<2	2	0.004 U	0.01 UJ
Giles Lake drainage	11	31-Jul	1050	8406	14.0	<2	5	0.004 U	0.01 UJ
Tributaries									
North River	2	31-Jul	0855	8401	20.2	7.5	15	**0.018**	0.01 UJ
Willapa River	3	31-Jul	1340	8403	21.5	<2	2	0.004 U	0.01 UJ
Naselle River	9	31-Jul	1115	8402	19.0	<2	1	0.004 U	0.01 UJ
Columbia River									
Inside North Jetty	18	1-Aug	0950	8407	17.7	2.5	28	0.004 U	0.01 UJ

Note: Detections highlighted in **BOLD**
U = not detected at or above reported value
J = estimated value

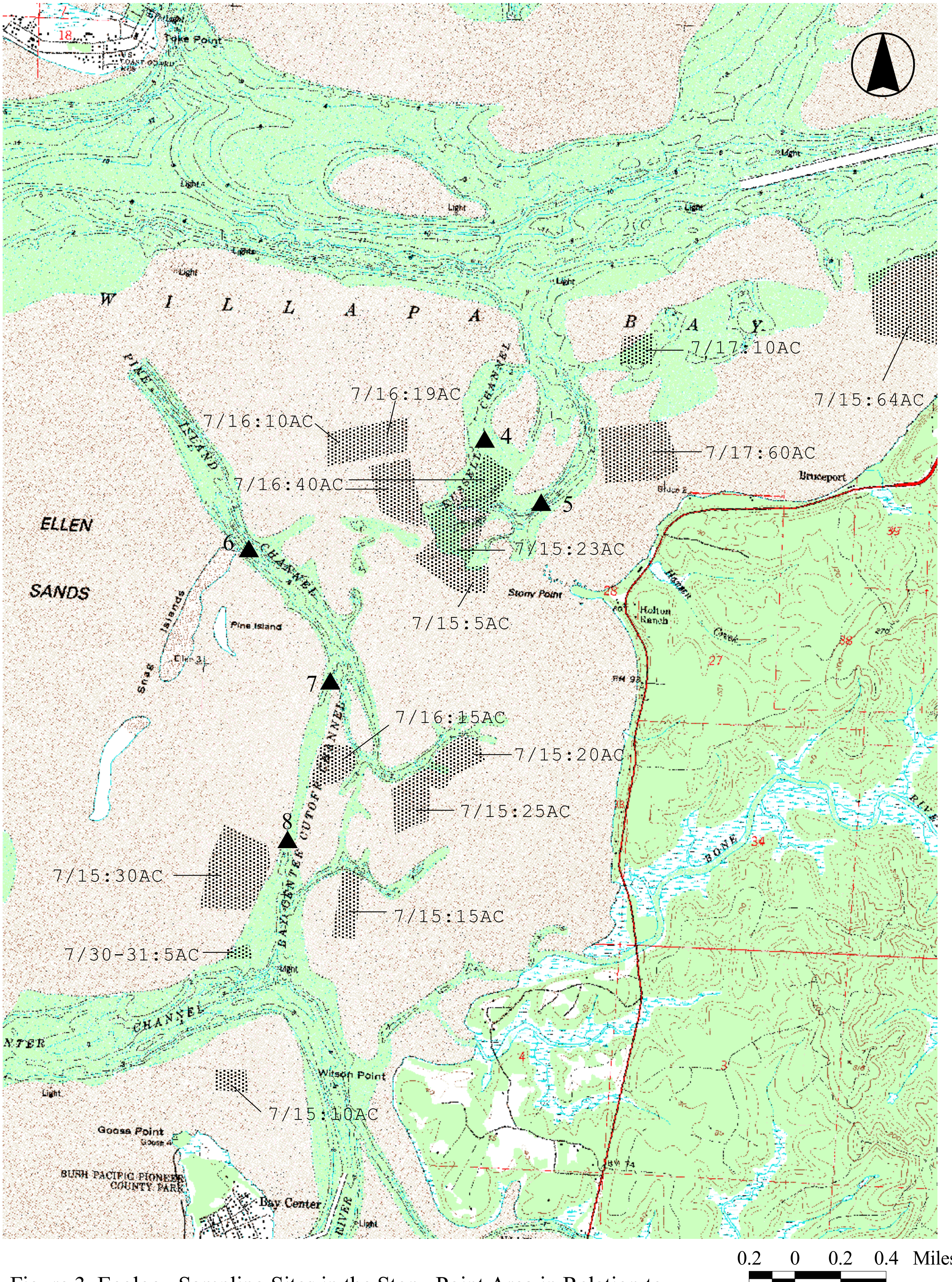


Figure 3. Ecology Sampling Sites in the Stony Point Area in Relation to Treated Oyster Beds [location and size depicted for treated beds are approximate]

Table 7. Summary of Carbaryl Data from Ecology's **Post-Spray** Samples July 31-August 4, 2000 [ug/L]

Location	N =	Detection Frequency	Mean	Median	Maximum	Minimum
Channels off Stony Point	6	100%	**0.070**	**0.076**	**0.112**	**0.031**
Long Beach Peninsula - Intertidal	10	70%	**0.011***	**0.004**	**0.044**	**0.002** J
Main Bay	7	86%	**0.005***	**0.003** J	**0.010**	0.004 U
Cranberry Bog Drainage	4	50%	**0.008***	0.004 U	**0.027**	0.004 U
Tributaries and Columbia River	4	25%	0.004 U	0.004 U	**0.018**	0.004 U

Note: Detections highlighted in **BOLD**
*1/2 the quantitation limit used for non-detects
U = not detected at or above reported value
J = estimated value

Other Data

The Shoalwater Bay Tribe conducted a monitoring program for pesticides in Willapa Bay during the summer of 2000. Carbaryl was among the target compounds. The monitoring included samples collected July 17-18, at the end of the peak carbaryl application period of July 14-17, and on August 15-16, about two weeks after the last carbaryl application on July 31.

The locations of the Tribe's samples are shown in Figure 4. Sampling points were clustered along the north shore of Willapa Bay, but included some sites in the Bay Center area and along the Long Beach peninsula. Cranberry bog drainage and major tributaries were also sampled. The Willapa Bay samples were taken at the end of the ebb by wading out onto the tide flats and collecting the samples by hand. Supporting quality assurance information is in Appendix C.

The carbaryl data obtained through the Tribe's monitoring program are in Table 8. Carbaryl was detected in 14 out of 16 samples (88%) collected within Willapa Bay at the end of the peak spray period. Concentrations ranged from 0.03 to 0.66 ug/L. Average concentrations were 0.30 ug/L along the north shore of Willapa Bay and 0.41 ug/L in the Bay Center area. Lower levels were

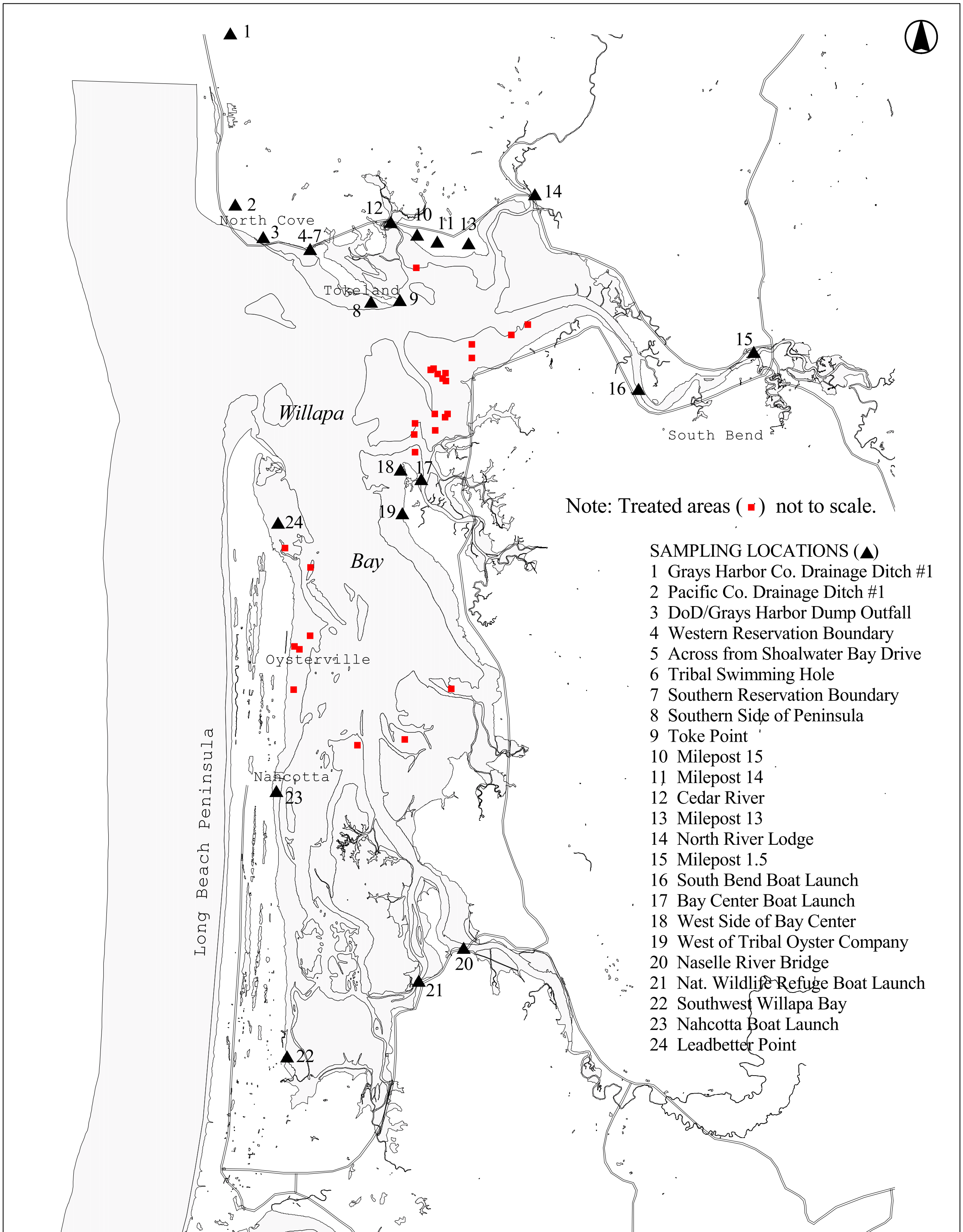


Figure 4. Shoalwater Bay Tribe's Water Sampling Sites and Approximate Location of Oyster Beds Treated during July 2000.

Table 8. Shoalwater Bay Tribe Data on Carbaryl Concentrations in Willapa Bay and Tributaries (ug/L)

Location	Site No.	July 17-18, 2000 Date	July 17-18, 2000 Concentration	August 15-16, 2000 Concentration
Long Beach Peninsula				
Leadbetter Point	24	17-Jul	**0.54**	0.012 U
Nahcotta boat launch	23	17-Jul	**0.14**	0.012 U
Southwest Willapa Bay	22	17-Jul	0.012 U	0.012 U
Long Island				
Wildlife Refuge boat launch	21	17-Jul	**0.030**	0.012 U
Bay Center				
Bay Center boat launch	17	17-Jul	**0.30**	0.012 U
West side of Bay Center	18	17-Jul	**0.59**	**(trace)** 0.012 U
West of Tribal Oyster Co.	19	17-Jul	**0.34**	0.012 U
Willapa Bay, North Shore				
D.O.D./Grays Harbor Dump outfall	3	18-Jul	0.012 U	0.012 U
West reservation boundary	4	18-Jul	**0.12**	0.012 U
Opposite Shoalwater Bay Drive	5	18-Jul	**0.16**	0.012 U
Tribal swimming hole	6	18-Jul	**0.17**	0.012 U
South reservation boundary	7	18-Jul	**0.14**	0.012 U
South side Toke Point	8	18-Jul	**0.44**	0.012 U
Toke Point	9	18-Jul	**0.66**	0.012 U
Milepost 15	10	18-Jul	**0.48**	0.012 U
Milepost 14	11	18-Jul	**0.43**	0.012 U
Cedar River outfall	12	18-Jul	**0.17**	0.012 U
Milepost 13	13	18-Jul	**0.58**	0.012 U
Cranberry Bog Drainage				
Pacific Co. Drainage Ditch #1	2	18-Jul	0.012 U	**0.057** U
Tributaries				
North River @ lodge	14	18-Jul	**0.099**	0.012 U
Willapa River @ milepost 1.5	15	17-Jul	0.012 U	0.012 U
Willapa River @ South Bend	16	17-Jul	**0.066**	0.012 U
Naselle River @ Hwy. 101	20	17-Jul	0.012 U	0.012 U

Note: Detections highlighted in **BOLD**
U = not detected at or above reported value

generally found along the Long Beach peninsula and inside Long Island. These concentrations are an order of magnitude higher than Ecology measured following the end of the carbaryl application period.

The Tribe's Long Beach peninsula, Long Island, and Bay Center samples were collected on the morning of July 17 after three days of heavy carbaryl application by helicopter (Figure 1). The Willapa Bay north shore samples were collected July 18, one day after the fourth and final helicopter spraying. The north shore sampling sites were two to four miles from the area of concentrated spraying off Stony Point. Two days earlier on July 16, there had been one application in the north shore area, a 20-acre bed about ½ mile northeast of Toke Point (Figure 4).

Carbaryl was detected at the mouth of the North River at 0.099 ug/L and in the Willapa River at South Bend at 0.066 ug/L. These detections are most likely a result of the spraying in Willapa Bay.

Except for cranberry bog drainage and a possible trace detection in a Bay Center sample, no carbaryl was detected in the Tribe's August 15-16 samples. The quantitation limit was 0.012 ug/L. Further sampling conducted by the Tribe in September also showed no carbaryl detectable.

Table 9. Summary of Carbaryl Data from Shoalwater Bay Tribe, July17-18, 2000 Samples [ug/L]

Location	N =	Detection Frequency	Mean	Median	Maximum	Minimum
Bay Center	3	100%	**0.41**	**0.34**	**0.59**	**0.30**
Willapa Bay, North Shore*	11	91%	**0.34**	**0.30**	**0.66**	0.012U
Long Beach Peninsula	3	66%	**0.23****	**0.14**	**0.54**	0.012U
Long Island	1	100%	**0.03**	- -	- -	- -
Cranberry Bog Drainage	1	0%	0.012 U	- -	- -	- -
Tributaries	4	50%	**0.044****	**0.039**	**0.099**	0.012U

Note: Detections highlighted in **BOLD**
*excluding outfall sample
**1/2 the quantitation limit used for non-detects
U = not detected at or above reported value

Water Quality Guidelines

Neither Washington State nor EPA has surface water quality standards or criteria for carbaryl. The only authoritative guideline for carbaryl in the marine environment comes from the National Academy of Sciences (NAS). As previously mentioned, NAS (1973) recommended that marine life "should be protected" where the maximum carbaryl concentration does not exceed 0.06 ug/L. The value 0.06 ug/L was determined by taking the lowest EC-50* for Dungeness crab and multiplying by an application (safety) factor of 0.01. In that study (Buchanan et al., 1970), crab larvae (zoea) were exposed to carbaryl in three separate experiments, and the 24-hour EC-50s for prevention of molting were 6, 20, and 30 ug/L.

A literature search was conducted to locate data on carbaryl's toxicity to marine organisms. The objectives were to determine: 1) if the NAS carbaryl recommendation is an appropriate safe level for Willapa Bay, and 2) what would be reasonably protective guidelines for short-term exposure to carbaryl. The search focused on obtaining data that could be used to calculate EPA numerical water quality criteria. The data requirements and methods for deriving EPA criteria are described in Stephan et al. (1985).

Results of the literature search are summarized in Table 10. Among the animal groups that have been tested, carbaryl has been shown to be much more toxic to crustaceans and echinoderms than to fish, molluscs, or polychaetes. Similar information was not collected on 1-naphthol, but studies have shown it is more toxic than carbaryl to fish and molluscs – by about a factor of 2 – but less toxic to crustaceans (Stewart et al., 1967).

Only limited toxicity data were available for potentially sensitive Willapa Bay species, making it impossible to derive site-specific water quality criteria for carbaryl that would be protective. For example, of the hundreds of N.E. Pacific species of crustaceans, only three have been tested in addition to burrowing shrimp, one of which, the shore crab, is relatively insensitive, at least as an adult. For a number of other N.E. Pacific invertebrate phyla, no data are available. Therefore, the acute guideline derived below draws on data for all U.S. species tested, based on the conservative assumption that the distribution of sensitivities among local species would be comparable. This is the approach used in the Washington State surface water quality standards for toxic substances (WAC 173-201A-040), which are adopted directly from the EPA national water quality criteria.

Acute Guideline

EPA methods for deriving numerical water quality criteria for protection of aquatic organisms and their uses were applied to the data in Table 10. In the EPA procedure, an acute criterion (Criterion Maximum Concentration or CMC) and a chronic criterion (Criterion Continuous Concentration or CCC) are calculated. Not enough data were located to derive a CCC. Because carbaryl is not strongly bioaccumulated (WHO, 1994) and has lower toxicity to plants than animals, EPA criteria based on tissue residues or plant toxicity are not useful. Carbaryl is also

*Concentration affecting 50% of the organisms tested

Table 10. Summary of Data on Carbaryl's Toxicity to Marine Organisms (bold values use in criteria calculation)

Common Name	Species Name	Life Stage	Effect	Test Duration (hours)	Endpoint	Concentration (ug/L)	Remarks	Reference
FISH								
Shiner perch	*Cymatogaster aggregata*	juvenile	mortality	24	LC-50	**3,900**		Stewart et al., 1967
English sole	*Parophyrs vetulus*	juvenile	mortality	24	LC-50	**4,100**		Stewart et al., 1967
Threespine stickleback	*Gasterosteus aculeatus*	juvenile	mortality	24	LC-50	6,700		Stewart et al., 1967
Threespine stickleback	*Gasterosteus aculeatus*	adult	mortality	96	LC-50	**3,990**		Katz, 1961
Coho salmon	*Oncorhynchus kisutch*	fingerling	mortality	96	LC-50	**1,300**	freshwater test	Post & Schroeder, 1971
Coho salmon	*Oncorhynchus kisutch*	juvenile	mortality	96	LC-50	**764**	freshwater test	Macek & McAllister, 1970
Coho salmon	*Oncorhynchus kisutch*	fingerling	mortality	96	LC-50	**4,340**	freshwater test	Johnson & Finley, 1980
Coho salmon	*Oncorhynchus kisutch*	fingerling	mortality	96	LC-50	**997**	freshwater test	Katz, 1961
Chinook salmon	*Oncorhynchus tshawytscha*	fingerling	mortality	96	LC-50	**2,400**	freshwater test	Johnson & Finley, 1981
Cutthroat trout	*Oncorhynchus clarki*	fingerling	mortality	96	LC-50	**1,834**	freshwater test	Post & Schroeder, 1971
Cutthroat trout	*Oncorhynchus clarki*	fingerling	mortality	96	LC-50	**7,100**	freshwater test	Johnson & Finley, 1980
Striped bass	*Morone saxatilis*	?	mortality	96	LC-50	**1,000**	California	Korn & Earnest, 1974
Striped bass	*Morone saxatilis*	juvenile	mortality	96	LC-50	>1,000	California	Schoettger, 1970
Striped bass	*Morone saxatilis*	juvenile	mortality	96	LC-50	**2,300**	Florida	Palawski et al., 1985
White mullet	*Mugil curema*	juvenile	mortality	48	LC-50	**2,500**	Florida	Butler, 1963
Goby	*Chasmichthys dolichognatus*	?	mortality	48	LC-50	1500	Japan	Hirose & Kitsukawa, 1976
Green fish	*Girella punctata*	?	mortality	48	LC-50	900	Japan	Hirose & Kitsukawa, 1976
Yellowtail	*Seriola quinqueradiata*	?	mortality	24	LC-50	3,500	Japan	Hirose & Kitsukawa, 1976
Tigerfish	*Therapon jarbua*	?	mortality	96	LC-50	2,200	Indian Ocean	Lingaraja & Venugopalan, 1978
MOLLUSCS								
Bay mussel	*Mytilus edulis*	larvae	abnormal develop.	48	EC-50	**2,300**		Stewart et al., 1967
Bay mussel	*Mytilus edulis*	embryo	abnormal develop.	48	EC-50	**1,500**		Liu & Lee, 1975
Bay mussel	*Mytilus edulis*	adult	mortality	96	LC-50	22,700		Liu & Lee, 1975
Pacific oyster	*Crassostrea gigas*	larvae	abnormal develop.	48	EC-50	**2,200**		Stewart et al., 1967
American oyster	*Crassostrea virginica*	eggs	abnormal develop.	48	EC-50	**3,000**		Davis & Hidu, 1969

Table 10. Carbaryl Toxicity (cont'd)

Common Name	Species Name	Life Stage	Effect	Test Duration (hours)	Endpoint	Concentration (ug/L)	Remarks	Reference
MOLLUSCS (cont'd)								
Cockle clam	*Clinocardium nuttali*	adult	mortality	24	LC-50	7,300		Stewart et al., 1967
Cockle clam	*Clinocardium nuttali*	adult	mortality	96	LC-50	**3,850**		Butler et al., 1968
Bent-nosed clam	*Macoma nasuta*	adult	mortality	96	LC-50	**17,000**		Armstrong & Milleman, 1974
Bent-nosed clam	*Macoma nasuta*	adult	mortality	48	LC-50	27,500		Armstrong & Milleman, 1974
Hard clam	*Mercenaria mercenaria*	eggs	abnormal develop.	48	EC-50	**3,820**	New England	Davis & Hidu, 1969
Mactrid clam	*Rangia cuneata*	adult	mortality	96	LC-50	125,000	Gulf of Mexico	Chaiyarach et al., 1975
POLYCHEATES								
Lugworm	*Arenicola marina*	adult	mortality	48	LC-50	**7,200**		Conti, 1987
ECHINODERMS								
Sea urchin	*Pseudochinus magellanicus*	embryo	abnormal develop.	12	EC-50	6	S.E. Atlantic	Hernandez et al., 1990
Sea urchin	*Pseudochinus magellanicus*	embryo	abnormal develop.	36	EC-50	11	S.E. Atlantic	Hernandez et al., 1990
Sea urchin	*Pseudochinus magellanicus*	larvae	abnormal develop.	48	EC-50	157	S.E. Atlantic	Hernandez et al., 1990
Sea urchin	*Pseudochinus magellanicus*	larvae	abnormal develop.	98	EC-50	92	S.E. Atlantic	Hernandez et al., 1990
CRUSTACEANS								
Dungeness crab	*Cancer magister*	larvae	prevented molting	24	EC-50	**6**	experiment #1	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	larvae	prevented molting	24	EC-50	**20**	experiment #2	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	larvae	prevented molting	24	EC-50	**30**	experiment #3	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	larvae	mortality	96	LC-50	**10**	10°C	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	larvae	mortality	48	LC-50	**5**	17°C	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	juvenile	paralysis/mortality	96	LC-50	250		Buchanan et al., 1970
Dungeness crab	*Cancer magister*	adult	mortality	96	LC-50	180	18°C	Buchanan et al., 1970
Dungeness crab	*Cancer magister*	adult	mortality	96	LC-50	260	11°C	Buchanan et al., 1970

Table 10. Carbaryl Toxicity (cont'd)

Common Name	Species Name	Life Stage	Effect	Test Duration (hours)	Endpoint	Concentration (ug/L)	Remarks	Reference
CRUSTACEANS (cont'd)								
Dungeness crab	*Cancer magister*	juvenile	equilib./paral./mort.	24	EC-50	600	males	Stewart et al., 1967
Dungeness crab	*Cancer magister*	juvenile	equilib./paral./mort.	24	EC-50	630	females	Stewart et al., 1967
Mud shrimp	*Upogebia pugettensis*	adult	mortality	48	LC-50	**90**	16^oC	Stewart et al., 1967
Mud shrimp	*Upogebia pugettensis*	adult	mortality	48	LC-50	**40**	20^oC	Stewart et al., 1967
Ghost shimp	*Neotrypaea californiensis*	larvae	mortality	48	LC-50	**80**	17^oC	Stewart et al., 1967
Ghost shimp	*Neotrypaea californiensis*	larvae	mortality	48	LC-50	**30**	20^oC	Stewart et al., 1967
Ghost shimp	*Neotrypaea californiensis*	adult	mortality	24	EC-50	**130**	20^oC	Stewart et al., 1967
Ghost shrimp	*Neotrypaea californiensis*	adult	equilibrium	24	EC-50	**82**		Estes & Pritchard, 1988
Shore crab	*Hemigraspus oregonensis*	adult	equilib./paral./mort.	24	EC-50	710	males	Stewart et al., 1967
Shore crab	*Hemigraspus oregonensis*	adult	equilib./paral./mort.	24	EC-50	**270**	females	Stewart et al., 1967
Shrimp	*Crangon septemspinosa*	adult	mortality	53	LC-50	**20**		McLeese et al., 1979
Prawn	*Metapenaeus monoceros*	adult	mortality	96	LC-50	25	Indian Ocean	Reddy & Rao, 1992
Blue crab	*Callinectes sapidus*	juvenile	equilibrium/mortality	48	EC-50	**550**	Florida	Butler, 1963
Brown shrimp	*Penaeus aztecus*	adult	equilibrium/mortality	48	EC-50	**2.5**	Florida	Butler, 1963
Sand shrimp	*Metapenaeus monoceros*	adult	mortality	96	LC-50	25	Indian Ocean	Jayaprada & Rao, 1991
Korean shrimp	*Paleomon macrodactylus*	?	mortality	96	LC-50	**7**	California	Schoettger, 1970
Edible crab	*Scylla serrata*	juvenile	mortality	96	LC-50	466	Indian Ocean	Rao & Kannupandi, 1990
Fiddler crab	*Uca lactea*	?	mortality	24	LC-50	1,450	Indian Ocean	Rao & Kannupandi, 1984
Red-jointed fiddler crab	*Uca minax*	larvae	mortality	25	LC-50	**100**	New England	Capaldo, 1987
Opposum shrimp	*Mysidopsis bahia*	juvenile	mortality	96	LC-50	>7.7	Florida	Nimmo et al., 1981
Opposum shrimp	*Mysidopsis bahia*	?	mortality	96	LC-50	**9.3**	Florida	EPA, 1995

EC-50 = concentration causing mortality or loss of equilibrium or paralysis to 50 percent of organisms tested
LC-50 = concentration causing mortality to 50 percent of organisms tested

practically non-toxic to birds (Mount and Oehme, 1981), so ingestion of contaminated organisms following spraying should not be a significant concern.

Acute toxicity tests were located for 35 marine species (12 fish, 7 molluscs, 1 polychaete, 1 echinoderm, and 14 crustaceans). Values that were deemed appropriate for calculating a marine carbaryl criterion are highlighted in the table. Reasons for excluding certain data were that: 1) the test was for an insensitive life stage, 2) the test was short duration (e.g., 24 vs. 96 hours), or 3) a non-U.S. species was tested.

The CMC is derived by calculating a Genus Mean Acute Value (GMAV) from the acceptable EC-50s and LC-50s, and ranking the GMAVs from high to low (Table 11). Geometric means are used. The criterion calculation then goes as follows:

$S^2 = \Sigma\ ((\ln \text{GMAV})^2) - ((\Sigma(\ln \text{GMAV}))^2/4)\ /\ \Sigma(P) - ((\Sigma(P^{1/2}))^2/4)$
$L = (\Sigma\ (\ln \text{GMAV}) - S(\Sigma(P^{1/2})))\ /\ 4$
$A = S(0.05^{1/2}) + L$
$FAV = e^A$
$CMC = FAV / 2$

Where:
P = cumulative probability for each GMAV (Genus Mean Acute Value)
P = R / (N+1)
R = sum of ranks of GMAVs
N = number of GMAV values
FAV = final acute value

Using the values in Table 11:
$S^2 = 0.0977$
L = 1.710
A = 1.780
FAV = 5.929
CMC = 3.0 ug/L

EPA water quality criteria are intended to protect 95% of a diverse genera. Because a concentration that would harm 50% of a sensitive important species would not be considered protective of that species, the FAV is divided by 2 to “result in a concentration that will not severely adversely affect too many of the organisms” (Stephan et al., 1985).

Although the CMC calculation is relatively insensitive to which high GMAVs are used (fish, for example), it is sensitive to the lower GMAVs. If, for example, only N.E. Pacific genera were included in the calculation, thereby excluding three of the four lowest GMAVs in Table 11, the CMC would be 13 ug/L, obviously too high given the sensitivity of Dungeness crab. Not including a single low GMAV, however, has a relatively minor effect on the end result. For example, with the lowest GMAV in Table 11 not included, 2.5 ug/L for a shrimp, the CMC goes from 3.0 to 4.1 ug/L.

Table 11. National Values Used to Calculate an EPA Criterion Maximum Concentration (CMC) for Carbaryl (ug/L)

Common Name	Species Name	Genus Mean Acute Value	Remarks
Mactrid clam	*Rangia cuneata*	**125,000**	Gulf of Mexico
Bent-nosed clam	*Macoma nasuta*	**17,000**	
Lugworm	*Arenicola marina*	**7,200**	
English sole	*Parophyrs vetulus*	**4,100**	
Threespine stickleback	*Gasterosteus aculeatus*	**3,990**	
Shiner perch	*Cymatogaster aggregata*	**3,900**	
Cockle clam	*Clinocardium nuttali*	**3,850**	
Hard clam	*Mercenaria mercenaria*	**3,820**	New England
Oyster	*Crassostrea sp.*	**2,569**	
White mullet	*Mugil curema*	**2,500**	Florida
Salmon, trout	*Oncorhynchus sp.*	**2,014**	freshwater tests
Bay mussel	*Mytilus edulis*	**1,857**	
Striped bass	*Morone saxatilis*	**1,517**	California/Florida
Blue crab	*Callinectes sapidus*	**550**	Florida
Shore crab	*Hemigraspus oregonensis*	**270**	
Red-jointed fiddler crab	*Uca minax*	**100**	New England
Ghost shrimp	*Neotrypaea californiensis*	**71**	
Mud shrimp	*Upogebia pugettensis*	**65**	
Shrimp	*Crangon septemspinosa*	**20**	
Opossum shrimp	*Mysidopsis bahia*	**9.3**	Florida
Dungeness crab	*Cancer magister*	**8.7**	
Korean shrimp	*Paleomon macrodactylus*	**7.0**	California
Brown shrimp	*Penaeus aztecus*	**2.5**	Florida

EPA criteria are expressed in terms of duration and frequency of the allowed exceedances. Using the CMC calculated for carbaryl, the acute criterion would be stated as follows:

"The procedures described in *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* indicate that, except possibly where a locally important species is very sensitive, saltwater aquatic organisms and their uses should not be affected unacceptably if the one-hour average concentration of carbaryl does not exceed 3.0 ug/L more than once every three years on the average."

“Safe” Concentrations

When chronic toxicity data are lacking, safety factors are sometimes used to extrapolate from acute toxicity data to environmentally safe concentrations. This was the NAS approach in recommending 0.06 ug/L as a protective concentration for carbaryl, based on a safety factor of .01 applied to the 6 ug/L EC-50 for Dungeness crab.

Judging from the available toxicity data (Table 10), 6 ug/L appears to be a good basis for setting a safe level of carbaryl exposure to marine organisms. Three other species of marine crustaceans have 48- or 96-hour LC-50s around this level, 2.5 - 9 ug/L. A 13-day LC-50 of 7.0 ug/L has been determined for a prawn (Table 12). In the only test conducted on an echinoderm, development of sea urchin embryos was adversely affected at EC-50s of 6 - 11 ug/L.

NAS proposed a range of safety factors from 0.01 to 0.1 depending on the toxicity, persistence, and cumulative effects of the chemical in question. For its recommendations on toxic chemicals in the marine environment, NAS applied the 0.01 safety factor across the board to more than 75 different insecticides and other chemicals, some of which (e.g., dieldrin, DDT, and dursban) are more toxic and persistent than carbaryl, others of which are less toxic and persistent. Large safety factors decrease the probability of underestimating risk, but it should be recognized that safe concentrations are a biological concept and are not the equivalent of a measured no-effect level.

The use of safety factors in environmental risk assessment has been critically reviewed by Chapman et al. (1998). Because of the uncertainty inherent in the use of safety factors and the importance of being neither under protective nor over protective (i.e., denying people the benefits of using a particular substance), Chapman et al. recommended using point estimates of the threshold for adverse effects and that “a policy decision be made about a desired margin of safety in the resulting cleanup concentration or environmental guidelines.”

The lowest concentrations of carbaryl that have been shown to result in an adverse effect or illicit some level of biological response in marine organisms are listed in Table 12. In the laboratory, effects such as delayed molting of crab larvae and reduced cholinesterase activity* in shrimp have occurred down to 0.1 ug/L.

Based on their review of studies with a variety of chemicals, Chapman et al. concluded that the potential threshold effects range is somewhere between >0.1 EC-50 to <EC-50. They note that in Europe, Canada, and the United States a factor of 0.1 has been considered a reliable and appropriate value to apply to acute and chronic tests to estimate the threshold for sublethal effects in the environment. Therefore, based on Chapman’s recommendations and judging from the data in Table 12, the effects threshold for carbaryl appears to be in the region of 0.1 - 0.7 ug/L for marine organisms.

British Columbia recently established an interim marine guideline for carbaryl of 0.32 ug/L for protection of aquatic life (CCME, 1999). This guideline is in good agreement with the carbaryl effects threshold of 0.1 - 0.7 ug/L proposed here. B.C. has a freshwater carbaryl guideline of 0.20 ug/L.

* Inhibition of nerve transmission, a reversible effect.

Table 12. Lowest Carbaryl Concentrations Adversely Affecting Marine Organisms

Common Name Species Name Life Stage	Effect Test Duration Endpoint	Concentration (ug/L)	References
Prawn *Paleomon serratus* adult	mortality 13 days LC-50	7	Bocquene & Galgani, 1991
Sea urchin *Pseudochinus magellanicus* embryo	abnormal development 12 hours EC-50 (lowest)	6	Hernandez et al., 1990
Dungeness crab *Cancer magister* larvae	prevented molting 24 hours EC-50 (lowest)	6	Buchanan et al., 1970
Opposum shrimp *Mysidopsis bahia* ?	mortality 96 hours LC-50 (lowest)	5.7	EPA, 1995
Dungeness crab *Cancer magister* larvae	mortality 48 hours (@ 17°C) LC-50	5	Buchanan et al., 1970
Dungeness crab *Cancer magister* larvae	mortality 25 days greater morality than control	3.2	Buchanan et al., 1970
Brown shrimp *Penaeus aztecus* adult	equilibrium/mortality 48 hours EC-50	2.5	Butler, 1963
Dungeness crab *Cancer magister* larvae	molting 25 days molting delayed	0.1	Buchanan et al., 1970
Prawn *Paleomon serratus* adult	cholinesterase activity 29 days reduced cholinesterase activity	0.1	Bocquene & Galgani, 1991

Recommended Water Quality Guidelines

Table 13 summarizes the water quality guidelines recommended for carbaryl, to protect marine organisms in Willapa Bay.

Table 13. Water Quality Guidelines Recommended for Carbaryl in Willapa Bay (ug/L)

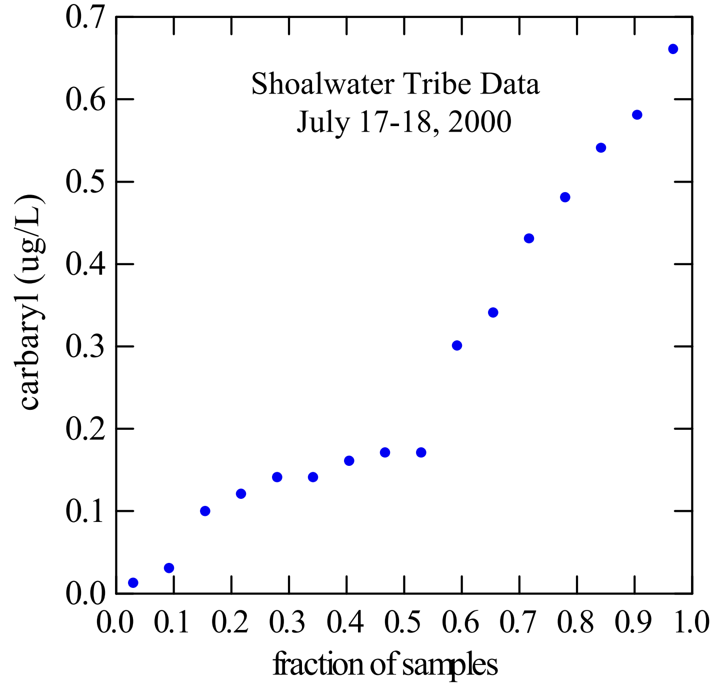
Guideline	Concentration	Approach/Rationale
Probable Safe Concentration	0.06	NAS Recommendation
Potential Effects Threshold	0.1 - 0.7	Lowest Effects Concentrations x 0.1
Acute Criterion	3.0	Equivalent to EPA Criterion Maximum Concentration

Hazard Assessment

Results of the sampling conducted by Ecology during the summer of 2000 showed no evidence of long-term persistence of carbaryl in Willapa Bay water, as had been indicated by the WSU study of Weisskopf and Felsot (1998). This finding is consistent with experimental data on the fate of carbaryl in seawater (Armbrust and Crosby, 1991). Under the July 2000 application scenario, carbaryl concentrations were at or below 0.1 ug/L 17 days after the peak applications of July 14-17 and may have reached this level sooner. Ecology's pre-spray samples did show some evidence of long-term persistence of the 1-naphthol breakdown product, but since the actual levels are uncertain, the significance of this finding is unknown.

From a technical standpoint the WSU study was unusually well done, so errors arising from sampling or analysis are unlikely. The Washington State Department of Agriculture has suggested that illegal spraying could have caused elevated carbaryl levels at this site in 1996-97 (Merkel, 2000). The Willapa Bay & Grays Harbor Oyster Growers Association take an active role in discouraging the illegal use of carbaryl.

The July 17-18 data collected by the Shoalwater Bay Tribe and the post-spray data collected by Ecology are compared in Figure 5. The results for cranberry bog drainage and tributaries were excluded, except for samples at the mouth of the North River. The few non-detects were plotted at half the quantitation limit.



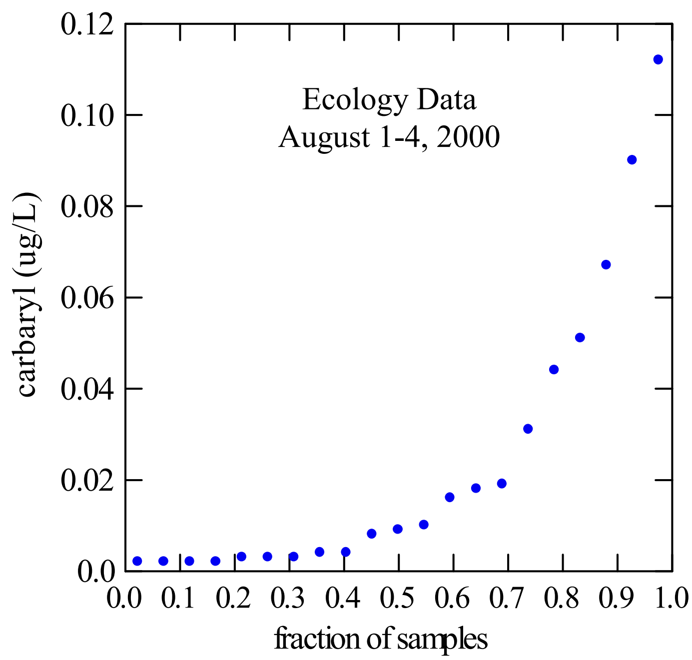


Figure 5. Carbaryl Concentrations in Willapa Bay Immediately Following the Peak Application Period and After the Spray Season

All but two of the July 17-18 samples (88%) were in the potential effects threshold range of 0.1 – 0.7 ug/L, but none approached the 3.0 ug/L acute criterion. At the end of the spray season, 14% of the August 1-4 samples were marginally above the NAS recommended safe level of 0.06 ug/L, but all were at or below 0.1 ug/L. The Tribe's data show that large carbaryl applications can affect water quality in areas distant from spray sites, and that the concentrations have the potential to reach effects thresholds. On the other hand, Ecology's data clearly demonstrate that no widespread adverse effects from carbaryl would be expected in Willapa Bay soon after the end of the application period. Comparable low-level data are not available to show what carbaryl concentrations occur closer to treated beds during or within a few days of applications.

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Appendices

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Appendix A. Location of Ecology's Willapa Bay Sampling Sites, June 6-9 and July 31-Aug 4, 2000

Site Name	Description	Latitude*	Longitude
Long Beach Peninsula			
Stackpole Harbor	north end Leadbetter Point State Park	46^o 36.51'	124^o 02.54'
Oysterville	signpost 31720	46^o 31.90'	124^o 01.55'
Nahcotta	Dept. Fish & Wildlife field station	46^o 29.74'	124^o 01.79'
Channels off Stony Point			
Bay Center Cutoff Channel	near south end of channel	46^o 39.33'	123^o 56.72'
Pine Island Channel, south	south end of channel, near dolphin	46^o 39.98'	123^o 56.72'
Pine Island Channel, north	off north end of Snag Islands	46^o 40.41'	123^o 57.41'
Russell Channel, west	west side	46^o 40.98'	123^o 56.12'
Russell Channel, east	east side	46^o 40.40'	123^o 55.92'
Main Bay			
North	1.9 miles west of Bay Center	46^o 38.01'	124^o 00.34'
Center	1.6 miles northeast of Nahcotta boat basin	46^o 31.28'	124^o 00.14'
South	off Smokey Hollow	46^o 26.00'	123^o 59.61'
Cranberry Bog Drainage			
Pacific Co. Drainage Ditch #1	Larkin Road	46^o 44.44'	124^o 04.32'
Tarlatt Slough - south ditch	east end of 95th Street	46^o 22.18'	124^o 01.11'
Tarlatt Slough - north ditch	east end of 95th Street	46^o 22.25'	124^o 01.10'
Giles Lake drainage	east end of Cranberry Road	46^o 23.76'	124^o 01.47'
Tributaries			
North River	Highway 105	46^o 45.10'	123^o 53.34'
Willapa River	Camp One Road bridge	46^o 38.99'	123^o 39.20'
Naselle River	Highway 4 bridge	46^o 22.12'	123^o 46.85'
Columbia River	North Jetty	46^o 16.77'	124^o 3.63'

*NAD 83

Appendix B. Flow Data for Ecology Water Samples in Willapa Bay and Tributaries

Location	Date (2000)	Flow (cfs)
Pacific Co. Drainage Ditch #1	7-Jun	9.4
	31-Jul	4.6
Tarlatt Slough - south ditch	7-Jun	5 est.
	31-Jul	5 est.
Tarlatt Slough - north ditch	7-Jun	3.8
	31-Jul	no data
Giles Lake drainage	7-Jun	0.3
	31-Jul	no flow
North River	7-Jun	*
	31-Jul	*
Willapa River @ Willapa	7-Jun	199
	31-Jul	52
Naselle River @ Naselle	8-Jun	133
	31-Jul	47

*Flow data not available due to missing gage. Historical flows in the North River have averaged 278 csf in June, 110 cfs in July, and 60 cfs in August (USGS data).

Appendix C. Quality Assurance Information for Willapa Bay Carbaryl Samples Collected July 17-18 and August 15-16, 2000 by the Shoalwater Bay Indian Tribe

Water samples were collected in 1-liter amber glass bottles, placed on ice immediately after collection, and transported to Pacific Agricultural Laboratory in Portland, Oregon. Chain of custody was maintained. The samples were analyzed by EPA Method 632. High carbaryl concentrations were confirmed using diode array spectral matching.

Holding Time

The samples were extracted within 48 hours and analyzed within 7 days.

Method Blanks

Two method blanks were analyzed with each sample set. No carbaryl was detected at or below 0.012 ug/L.

Matrix Spikes

Two pairs of matrix spike/spike duplicates were analyzed with each sample set. The results, shown below, were within EPA CLP acceptance limits of 50 – 150%.

Sample Set	Spike	Spike Duplicate	RPD*
July 17-18	82%	77%	6%
	63%	80%	23%
August 15-16	75%	70%	7%
	115%	125%	8%

*Relative Percent Difference (range as percent of duplicate mean)

Surrogates

Not analyzed.

Field Blanks

A bottle blank analyzed for the tribe's monitoring program on 1/19/01 had no carbaryl detectable at or below 0.010 ug/L.

Interlaboratory Comparison

Two water samples collected by Ecology in the Stony Point area on 8/3/00 and stored at 4^oC were analyzed by Pacific Agricultural Laboratory on 1/19/01 using EPA Method 632. Replicates of these samples (separately collected) had been analyzed by Ecology on 8/9/00. The results obtained by the two laboratories were in good agreement.

Sample No.	Pacific Analytical Result	Ecology Result	RPD*
31-8419	0.13	0.11	17%
31-8422	0.091	0.067	30%

*Relative Percent Difference (range as percent of duplicate mean)