Analyzing Carbaryl in Willapa Bay Water

Quality Assurance Project Plan

by
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Washington State Department of Ecology
Environmental Assessment Program
Watershed Ecology Section

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Background

Since 1963, the pesticide carbaryl (Sevin®) has been applied to oyster beds in Willapa Bay and Grays Harbor to control burrowing shrimp. The Washington State Department of Ecology (Ecology) currently allows treatment of up to 600 acres annually in Willapa Bay at the rate of 7.5 pounds per acre. Up to 200 acres may be similarly treated in Grays Harbor. Spraying takes place during low tides in July and August.

Within the Willapa Bay watershed, carbaryl has also been 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 µg/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).

Carbaryl is also registered for a variety of other uses including gardens, lawns, rangeland, and forest. The extent of its use in the uplands of Willapa Bay is unknown.

A number of studies have shown that off-site transport of carbaryl can occur immediately following treatment to Willapa Bay oyster beds and that there is some persistence in the sediments (Hurlburt, 1986; Creekman and Hurlburt, 1987; Dept. Fisheries and Dept. Ecology, 1992; Tufts, 1989, 1990; Karinen et al, 1967). Results from past investigations in Willapa Bay have been variable due to differences in sampling and analytical methods, water circulation patterns, amount of pesticide applied, area treated, and other reasons. An Ecology study found carbaryl concentrations of 105 µg/Kg in sediment from treated sites 60 days after application and carbaryl was detected in sediment pore water at 0.57 - 1.2 µg/L on day-60 (Stonick, 1999). Dumbauld et al. (1997) reports shorter persistence in the sediments, 40 - 45 days or less, and that the rate of initial decline after application is rapid.

A recent study by Washington State University (WSU), conducted on experimentally treated plots near Oysterville in June 1997, reports there is a carbaryl background of approximately 0.7 µg/L in Willapa Bay water (Weisskopf and Felsot, 1998). This level of carbaryl existed prior to and 28 days after spraying. An unpublished pilot study by WSU, conducted the year before, found similar levels of carbaryl in the water (Felsot, 1999).

The National Academy of Sciences (NAS) has recommended that carbaryl concentrations not exceed 0.06 µg/L in marine waters (NAS, 1973). This value was based on a concentration of 6 µg/L that prevented hatching and molting in Dungeness crabs (Buchanan et al., 1970) and a safety factor of 0.01.

The WSU study is the first on carbaryl in the Willapa Bay water column where low detection limits have been employed (i.e., < 100 µg/L) and where the quality of the data can be adequately assessed; it appears to be very well done. The Ecology Manchester Environmental Laboratory reviewed the WSU method and associated QA/QC and concluded the data were valid (Carrell, 2000).

In light of the WSU findings, the Shoalwater Bay Indian Tribe has requested that the Ecology Environmental Assessment Program (EAP) do additional carbaryl monitoring.

Study Objectives

- Determine if there is a carbaryl background that persists in Willapa Bay water beyond the July/August spray period.
- Analyze carbaryl in other potential sources to Willapa Bay.
- Achieve detection limits for carbaryl sufficiently low for comparison with the NAS 0.06 µg/L recommendation.
- Review the literature on carbaryl's effects to marine organisms and evaluate the appropriateness of the NAS criterion for Willapa Bay.

Sampling Plan

Water sampling will initially be done on two occasions: during June, prior to the 2000 spray season, and in August, one to two weeks after all carbaryl application has stopped. This year, spraying is expected to begin on June 28 and be completed by the end of July, weather permitting (Tufts, 2000). If detectable residues are found, a third round of sampling may be appropriate.

Sampling will be done in four areas, as described below (see Figure 1). No sampling will be targeted at specific spray sites

Oyster Beds

Two types of samples will be collected in the general vicinity of carbaryl-treated oyster beds. First, in an effort to duplicate the findings of Weisskopf and Felsot, water samples will be collected at their experimental site on the Oysterville tideflats on the west shore of Willapa Bay. Three samples will be collected at approximately 1-hour intervals during a rising tide. These will be taken in approximately 1/2-foot of water, moving progressively up the beach with the incoming water. (Weisskopf and Felsot primarily sampled an incoming tide.) A similar set of samples will be collected about four miles to the north in the vicinity of the Stackpole Harbor oyster beds, which, historically, have been among the most heavily treated in Willapa Bay, and four miles to the south at the Washington State Dept. of Fish and Wildlife field station in Nahcotta.

Because results from the above samples could be affected by a localized source of carbaryl, especially for post-spray samples, a second approach will be to collect water samples during ebb from the extensive system of channels (Pine Island, Center Cutoff, and side branches) penetrating

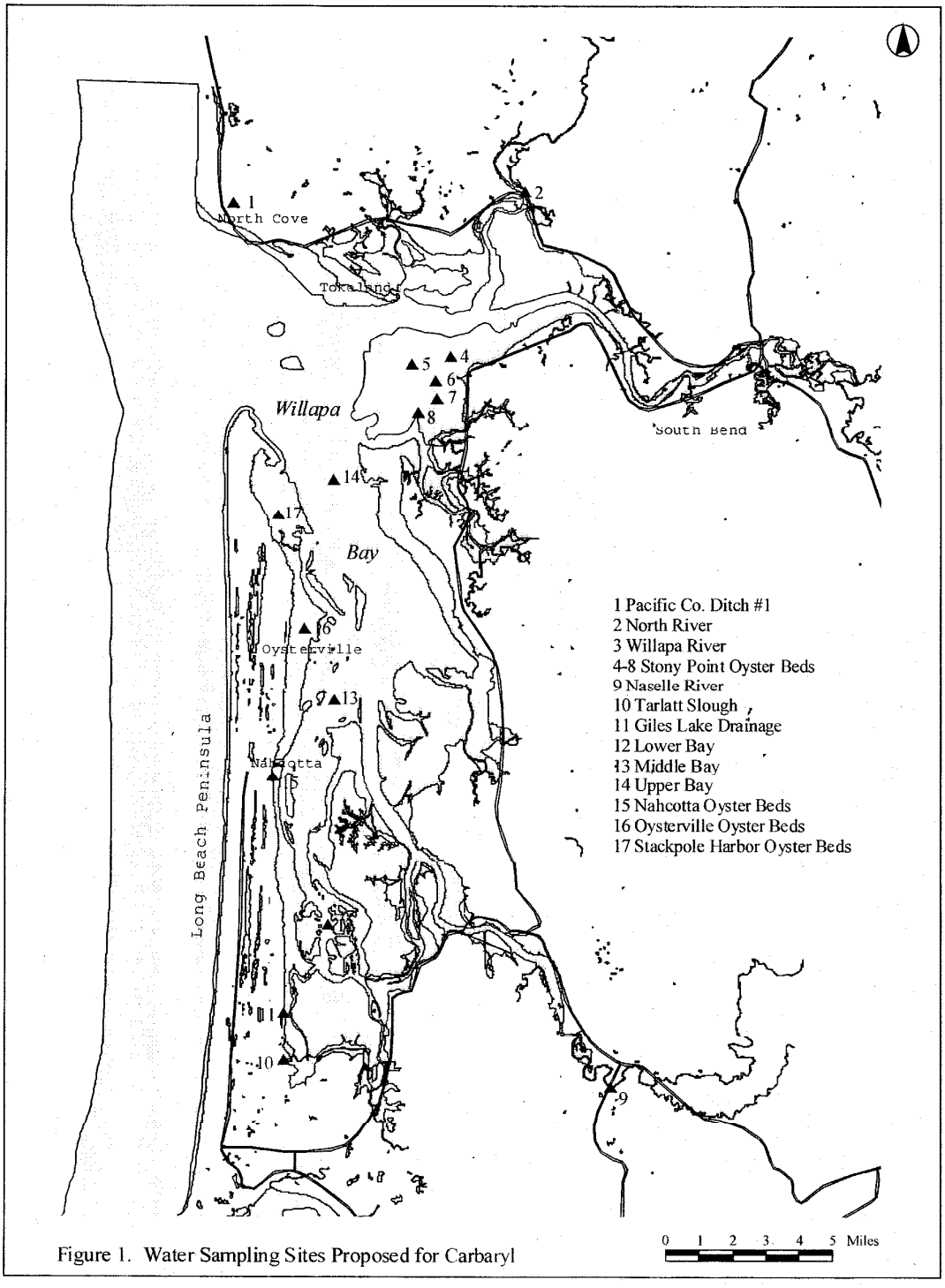

Figure 1. Water Sampling Sites Proposed for Carbaryl

the Stony Point oyster beds on the east side of the bay. The aim here is to collect samples broadly representative of water draining away from oyster beds. These channel features are largely absent on the west side of the bay.

Like Stackpole, the Stony Point beds have also been treated frequently. Carbaryl is generally applied to more acreage in the upper than the lower bay. Five water samples will be taken in the Stony Point area, specific sampling locations to be selected in the field.

Main Bay

Surface and deep water samples will be 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 will also be collected during a falling tide and should be representative of general water quality conditions in the bay, away from areas of carbaryl application.

Cranberry Bog Drainage

Four streams that drain cranberry bogs will be sampled near the point they enter Willapa Bay: PCDD #1 in North Cove, and Tarlatt Slough (two drainages) and the Giles Lake drainage on the Long Beach peninsula. Because the lower parts of these drainages are tidally influenced, the samples will be taken near low tide. PCDD #1 is the only cranberry bog drainage to the north part of Willapa Bay. The Tarlatt and Giles Lake drainages are not the only routes by which cranberry bog drainage enters the lower bay, but are easily the largest (Davis, 2000).

Major Tributaries

Mean daily runoff to Willapa Bay is less than 0.05% of the bay volume (USACE, 1976) so is a minor influence on water quality. Water samples for carbaryl analysis will therefore be limited to the three largest tributaries – the North, Willapa, and Naselle (see Figure 1). 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 SW winds (Dumbauld, 2000).

Tributaries and cranberry bog drainages will be sampled once each for pre- and post spray. Due to the small sample size, these data will be of a screening level nature and may not support strong conclusions about their significance as carbaryl sources to Willapa Bay.

The water samples will be analyzed for carbaryl, total suspended solids (TSS), and salinity. The target reporting limit for carbaryl will be 0.006 µg/L. Field measurements will include temperature and flow (cranberry bog drainage). Flow data for the tributaries will be obtained from USGS. Table 1 shows the number of samples to be collected and the estimated cost of the laboratory analyses.

The Shoalwaters have requested that duplicate samples from the August collection be provided for their analysis. The number and locations of these samples have yet to be determined.

Table 1. Number of Samples and Lab Cost Estimate for Willapa Bay Carbaryl in Water Study

Location or Sample Type	Field samples	Replicate samples	Field + replicate	Sampling periods	Total samples	Cost per sample*	Cost subtotals
Oysterville	3	1	4	2	8	205	1640
Stackpole Harbor	3		3	2	6	205	1230
Nahcotta	3		3	2	6	205	1230
Stony Point	5	1	6	2	12	205	2460
Upper Bay - surface and deep	2		2	2	4	205	820
Middle Bay -surface and deep	2	1	3	2	6	205	1230
Lower Bay - surface and deep	2		2	2	4	205	820
Cranberry Bog Drainage	4	1	5	2	10	205	2050
Tributaries	3		3	2	6	205	1230
Transfer Blank	2		2	2	4	185	740
Pump Blank	1		1	2	2	185	370
Matrix Spikes	2		2	2	4	185	740
						TOTAL LAB COST =	14560

*carbaryl, 1-naphthol (tentative), TSS, and salinity

Literature Review

Studies reporting the toxicity of carbaryl to N.E. Pacific marine organisms will be located and summarized. If sufficient acceptable data exist, EPA methods will be used to derive a marine Criterion Maximum Concentration and a Criterion Continuous Concentration for carbaryl (Stephan et al., 1985). The NAS recommendation for carbaryl will be evaluated in light of this information. The intent of this exercise is to put the results from carbaryl monitoring in perspective, not to translate the data to permit conditions or use limitations.

Schedule

(exact dates to be determined)

June 2000.....First sample collection (pre-spray)
August 2000.....Second sample collection (post-spray)
October 2000.....Laboratory Analyses Completed

December 2000.....Draft Report to SWRO and Other Interested Parties
February 2001.....Final Report
April 2001.....Data Entered into EIM

Project Organization

Project Lead - Art Johnson (360/407-6766)
Supervisor - Dale Norton (360/407-6765)
Watershed Ecology Section Manager - Will Kendra (360/407-6698)
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Shoalwater Bay Indian Tribe - Key McMurry and Gary Burns (360/267-3205)

Data Quality Objectives

Precision and Bias

The objective for total error (random and systematic) will be 40% or less. This allows for a random error of 10% relative standard deviation and 20% bias.

Sources of bias from sampling procedures and sample handling will be minimized by adhering to EAP routine procedures for sampling pesticides in water (Davis et al., 1997).

Representativeness

Because the objective is to determine the presence of persistent, widespread contamination by carbaryl, limited numbers of samples are appropriate. Except for cranberry bog drainages and tributaries, a minimum of six samples will be collected from each area (e.g., Stackpole oyster beds, main channel surface water, etc.) which should be sufficient to detect chronic contamination. Because of small sample size, the cranberry bog drainage and tributary data may not be representative. The data will not be representative of conditions during carbaryl applications.

The total variability in the data (field + laboratory) will be assessed by collecting replicate samples at selected sites, as indicated in Table 1.

Completeness

The amount of useable data obtained will be maximized by careful planning of field work and taking care in sample packaging and handling. An extra sample for carbaryl analysis will be collected at each sampling site and stored at 4 °C, in the event re-analysis is required. The EPA Manchester Laboratory has conducted holding time studies for carbaryl and other carbamate pesticides that show no significant degradation occurs for up to two years in a properly preserved (chloroacetic acid preservative) and stored (4 °C) sample (Reimer, 2000a).

Comparability

Sampling, quality assurance, and analytical methods will be consistent with other pesticide studies done by EAP. The analytical method will yield data that can be compared to the Weisskopf and Felsot study, previously mentioned.

Sampling Methods

Sample containers for carbaryl analysis will be one liter amber glass bottles with Teflon lid liners, cleaned to EPA QA/QC specifications (EPA, 1990) and containing chloroacetic acid buffer as a preservative. The TSS and salinity samples will be collected in polyethylene bottles. All sample containers will be obtained from Manchester Laboratory.

Marine surface water samples will be collected directly into the sample bottles. Deep water samples will be obtained with a peristaltic pump and weighted Teflon tubing. Sampling depth will be approximately 25 feet (depth limit for pumping). The tubing will be pre-cleaned with pesticide-grade acetone. The tubing will be cleaned between stations by pumping one liter of pesticide-grade acetone, then flushing with water from the next deep water site. Cranberry bog drainage and tributaries will be sampled by hand by wading into the stream or from bridges using a weighted 1-gallon glass bottle, pre-cleaned for low-level pesticide analysis.

Each carbaryl sample will be placed in an individual polyethylene bag and all samples will be put on ice immediately on collection. The samples will be transported to Manchester Laboratory within one to two days of collection. Chain-of-custody will be maintained.

Laboratory Methods

All samples will be analyzed by Manchester Laboratory. Carbaryl will be analyzed by High Pressure Liquid Chromatography (HPLC) using a Manchester modification of EPA Method 8318. The target detection limit will be 0.006 µg/L.

TSS and salinity will be analyzed by routine Manchester methods.

To the extent possible, carbaryl samples will be extracted within 7 days and analyzed within 14 days, as specified by EPA. Because the field work may require 4 non-consecutive days, extraction of all samples may not be possible within 7 days. Results of the EPA holding time study show that delaying the extractions will not compromise the carbaryl data.

1-Naphthol, the first breakdown product of carbaryl, can be analyzed by Method 8318 but, in Manchester's experience, results have been variable (Reimer, 2000b). Under optimum conditions it may be possible to quantify 1-naphthol at approximately 0.1 µg/L.

Field Quality Control Procedures

Field QC samples will include transfer blanks, pump blanks, and replicate samples, at the frequency indicated in Table 1.

Transfer blanks will be prepared by opening a new carbaryl sample container in the field, filling it with organic-free water obtained from Manchester, sealing the container, then placing it in a polyethylene bag and on ice. One transfer blank will be prepared while sampling the oyster beds and a second while collecting the main channel samples.

The pump blank will consist of organic-free water pumped through the sampling system and into a carbaryl sample container. The pump blank will be prepared after collecting the three deep water samples, following acetone cleaning and flushing.

Field replicates will consist of two separate sets of samples collected within approximately 5 minutes of each other.

Blanks and replicates will be submitted blind to the laboratory.

Steps to reduce the possibility of cross-contamination between samples will include: 1) the use of new disposable non-talc nitrile gloves for collecting each carbaryl sample, 2) placing each carbaryl sample in a polyethylene bag, and 3) keeping the samples from oyster beds in a separate cooler.

Laboratory Quality Control Procedures

To assess potential interferences from the sample matrix, a carbaryl matrix spike and matrix spike duplicate will be analyzed with each sample set, using a marine sample collected and labeled for that purpose. Surrogate recoveries (4-bromo-3,5-dimethyl-N-methylcarbamate) will be determined on every sample. A method blank will be analyzed with each sample set.

Data Assessment Procedures and Reporting

Manchester's SOP for data reduction, review, and reporting will meet the needs of this project. Each laboratory unit assembles data packages consisting of raw data from the analyses of the samples, copies of the pertinent logbook sheets, QA/QC data, and final reports of data entered into LIMS. These data packages are subjected to a data verification and quality assurance review by another analyst familiar with the procedure. Reviewers use *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*, October, 1999.

A draft report of the study results will be provided to SWRO, the Swinomish Tribe, the Oyster Growers Association, the Washington State Department of Fish & Wildlife, the Washington State Department of Health, and other interested parties by December 2000. The Oyster Growers Association has requested that the final document for this project go through a peer review process prior to being finalized.

The draft report will contain:

- a map of the study area showing sampling sites
- latitude/longitude and other location information for each sampling site
- descriptions of field and laboratory methods
- summary tables of the QA data
- an evaluation of data quality
- summary tables of the results on field samples
- an evaluation of significant findings with respect to exceedances of NAS recommendations, differences within and between sampling areas, and comparisons to previous data
- results of the literature review
- conclusions about the presence or absence of significant contamination
- recommendations for follow-up work if warranted.

A final report will be prepared based on review comments from SWRO, the Shoalwater Tribe, the Oyster Growers Association and their selected peer reviewer(s), sister agencies, other interested parties, and internal comments from EAP. The goal is to have the final report completed in February 2001. The data will be entered into Ecology's Environmental Information Management (EIM) system.

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