Screening Survey of Carbaryl (Sevin™) and 1-naphthol Concentrations in Willapa Bay Sediments

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Screening Survey of Carbaryl (Sevin™) and 1-naphthol Concentrations in Willapa Bay Sediments

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Abstract

Marine sediments were collected from Willapa Bay, Washington during May to September 1998 to assess levels of carbaryl and 1-naphthol prior to and following the annual application of Sevin™ (carbaryl) for the control of burrowing shrimp on oyster beds.

Fifteen sites were sampled prior to the 1998 annual application and seven sites were sampled following the application. Sediments from the pre-spray sites were sampled on one occasion to a depth of 15 cm. Sediments sampled following the 1998 application (post-spray) were sampled to a depth of 6 cm on day-2, -30, and -60.

Significant findings include:

- Carbaryl and 1-naphthol were generally not detected at historically sprayed sites.
- Carbaryl was detected on day-60 at sprayed sites.
- 1-naphthol was generally not detected by day-30.
- Day-2 carbaryl drift occurred in an unsprayed adjacent site at concentrations equivalent to a sprayed site.
- Day-60 carbaryl concentrations in centrifuged pore-water exceeded the National Academy of Sciences and Engineering water quality recommendation for the protection of marine life.

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Summary

The purpose of this study was to gather data on the marine application of Sevin™ (carbaryl). The data will be useful to regulatory agencies in making decisions concerning Sevin's™ use for the control of burrowing shrimp on oyster beds.

Carbaryl, the active ingredient in Sevin™, and 1-naphthol, a toxic breakdown product, were analyzed in sediments from 15 pre-spray and seven post-spray sites in Willapa Bay, Washington during May to September 1998. Day-60 centrifuged pore-water was also analyzed from post-spray sites.

The objectives of this screening survey were to:

- Determine if there are residues of carbaryl or 1-naphthol in the marine sediments at historically sprayed sites and unsprayed adjacent sites.
- Monitor the depletion of these compounds in sediments following applications of Sevin™.
- Measure concentrations of carbaryl in centrifuged pore-water.
- Determine drift potential.

Currently there are no U.S. Environmental Protection Agency (EPA) criteria or state water quality standards for carbaryl. The National Academy of Sciences and Engineering (NAS) (1973) has established a water quality recommendation for carbaryl at 0.06 ppb. This recommendation has been established for the protection of marine life.

Pre-spray is used in this report to describe sites sampled prior to July 1998 and includes a control site at the Nemah Oyster Reserve. The pre-spray sites were selected as historically sprayed areas last treated in 1996 or 1997 and include one adjacent unsprayed site for 1996 and one adjacent unsprayed site for 1997. Adjacent sites were not sprayed in 1995, 1996, or 1997 and were geographically as close as possible to a sprayed bed, preferably abutting one. Sites scheduled to be sampled after the application of Sevin™ (see *Post-spray* below) were also sampled during the pre-spray event.

Post-spray is defined in this report as the sites sampled after the annual July spraying in 1998. Post-spray sites were selected as historically sprayed areas, each with an adjacent unsprayed site, and included the control site at the Nemah Oyster Reserve.

Pre-spray

Fifteen sites were sampled for carbaryl and 1-naphthol. Pre-spray sites included nine historically sprayed beds, five adjacent unsprayed sites, and the Nemah control site. The presence of carbaryl and 1-naphthol were not detected in pre-spray sediments at values above the detection limits which ranged from 21 to 58 ppb.

Post-spray

Carbaryl

Post-spray sites included three historically sprayed sites, three adjacent unsprayed sites and the Nemah control site. Day-2 carbaryl was detected in sediments at four sites at concentrations ranging from 2,000 to 3,400 ppb. Carbaryl was present on day-60 only at treated sites, with concentrations from 86 to 120 ppb.

1-naphthol

The breakdown product of carbaryl, 1-naphthol, was present in the sediment at four sites on day-2 at concentrations ranging between 120 and 170 ppb. 1-naphthol was not found in sediments by day-30. There was one detection at Tokeland (site S7) on day-60 at the detection limit (34 ppb).

Drift

Carbaryl drift was detected at two of three adjacent unsprayed sites. On day-2 one of the adjacent unsprayed sites had carbaryl and 1-naphthol concentrations equivalent to those at the sprayed oyster beds, at 2,000 ppb and 120 ppb respectively.

Centrifuged Pore-water

Carbaryl was not detected on day-60 in the pore-water at the control or adjacent unsprayed sites above the detection limits, which ranged from 0.05 to 0.06 ppb. Carbaryl was detected in day-60 pore-water from all three of the sprayed sites at concentrations ranging from 0.57 to 1.15 ppb. These concentrations exceed the National Academy of Sciences and Engineering (NAS) water quality recommendation of 0.06 ppb. Carbaryl in the pore-water is available to the water column and can, therefore, contribute to background conditions. Weisskopf and Felsot, (1998) found mean background concentrations of carbaryl in Willapa Bay at 0.70 ppb in 1997 (prior to annual application).

This study was valuable in documenting that carbaryl is persistent at levels that can affect the ecosystem for a longer period of time than previously assumed.

Recommendations

1. Improve monitoring of Sevin™ applications to assess compliance with permit conditions and minimize drift to non-target areas.

2. In conjunction with Ecology, oyster growers should develop a monitoring plan to evaluate any adverse long-term impacts on biological resources in Willapa Bay resulting from the use of carbaryl. Components of the plan might include bioaccumulation analyses, sediment toxicity testing, benthic community analyses, and sub-lethal effect studies.

3. Record accurate Differential Global Positioning System coordinates for each spray site to allow matching with the county assessor bed numbers.

4. Monitor water column concentrations of carbaryl over sprayed beds before and after application of carbaryl to determine background concentrations.

5. With assistance from Ecology, oyster growers should develop and implement an integrated pest management (IPM) plan to eliminate, minimize, or mitigate the impacts of toxic chemicals such as carbaryl.

Acknowledgements

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Introduction

Project Background

The insecticide carbaryl (trade name Sevin™) has a long history of use in Willapa Bay and Grays Harbor for control of burrowing shrimp on oyster beds. The Washington State Department of Ecology (Ecology) has been issuing short-term water quality modification permits for the application of carbaryl in marine waters since 1963 under WAC 173-201A-110. This regulation was based on the assumption that certain activities will not interfere with existing water uses or cause long-term and irreparable harm to the marine environment.

Treatment is usually scheduled between July and August when carbaryl is significantly more effective against burrowing shrimp (Creekman and Hurlburt, 1987). This is also the period when impacts on migrating salmon are expected to be the least. Since 1994 carbaryl has been sprayed annually on 600 acres in Willapa Bay and 200 acres in Grays Harbor at the rate of 7.5 lbs/acre. Prior to 1994 the total permitted acreage was 300 acres in Willapa Bay and 100 acres in Grays Harbor. The acreage was increased based on the findings of the Supplemental Environmental Impact Statement (SEIS) (Fisheries and Ecology, 1992).

Washington is the only state that allows the use of carbaryl in marine waters (Fisheries and Ecology, 1992). Both the SEIS (1992) and an earlier 1985 Environmental Impact Statement (EIS) were written to address environmental impacts from the use of carbaryl; however, both reports fall short of looking at long-term impacts of five years or more (Fisheries and Ecology, 1985, 1992). More recently, a study was done to evaluate the feasibility of using an integrated pest management strategy in an attempt to reduce the use of carbaryl. The report from this study by Battelle (1997) also acknowledged a lack of long-term information. Prior to this 1998 study, there were no studies analyzing carbaryl's breakdown product, 1-naphthol, in the sediments of Willapa Bay.

Carbaryl use must comply with provisions of the Washington State Special Local Needs Pesticide Registration No. WA760021, issued by U. S. Environmental Protection Agency (EPA) through the Washington State Department of Agriculture under authority of section 24 (c) *Supplemental Label of the Amended Federal Insecticide, Fungicide, and Rodenticide Act* and with the issuance of a permit by Ecology (Appendix A).

Carbaryl is applied to oyster beds primarily by helicopter. Hand spraying occurs on some beds, since the label prohibits helicopter spraying closer than 200 feet from a channel or slough. Hand spraying is limited to within 50 feet under the same conditions stated above. The permit also prohibits spraying on oysters that are within one year of harvest.

Carbaryl is applied as a wetable powder to the tidelands at low tide. It breaks down into 1-naphthol and is effective as a broad-spectrum pesticide for targeting Arthropoda, which includes Insecta and Crustacea (invertebrates including crab and shrimp). Carbaryl acts as a

neurotoxin affecting the central nervous system of these animals and ultimately results in paralysis and death.

EPA has listed carbaryl as a "low to moderate" toxicant. Evidence suggests that carbaryl may have mutagenic activity (EPA, 1984). Carbaryl is also listed as an endocrine disrupter (EPA, 1997). While carbaryl itself is toxic to crustaceans, 1-naphthol is more toxic to fish, mollusks, and starfish than to crustaceans (Stewart et al., 1967). Carbaryl is currently undergoing a re-registration process under the federal Food Quality and Protection Act.

The objectives of this screening survey were to:

- Determine if there are residues of carbaryl or 1-naphthol in the marine sediments at historically sprayed sites and unsprayed adjacent sites.
- Monitor the depletion of these compounds in sediments following applications of Sevin™.
- Measure concentrations of carbaryl in centrifuged pore-water.
- Determine drift potential.

Data from this study will be useful to regulatory agencies in making decisions concerning the use of carbaryl for the control of burrowing shrimp.

Information gained in the *Eelgrass, Oysters, Burrowing Shrimp, and Carbaryl Workshop* in Astoria, Oregon during January 1998 helped to tailor the scope of this screening survey (Appendix B).

Sampling Design

The purpose of the pre-spray analysis was to determine long-term persistence of carbaryl and 1-naphthol. The purpose of the post-spray time series sampling was to determine the concentration and persistence (depletion rate) of carbaryl in sediment up to 60 days after spraying. Sampling locations for this study are shown in Figures 1 and 2. Positions and descriptions of each station are included in Appendix C (Tables 1 and 2). All sediment samples were analyzed for carbaryl, 1-naphthol, total organic carbon (TOC), and grain size. Centrifuged pore-water samples were analyzed only for carbaryl. Adjacent unsprayed sites were selected for comparison to sprayed sites, in order to determine to what extent drift might be a factor in the dispersal of carbaryl or 1-naphthol.

Survey sites were chosen by dividing Willapa Bay into northern, middle, and southern geographical areas. Core samples were taken at various strata and the depths differed between pre- and post-spray sampling. Muddy sediments were selectively sampled in the pre- and post-spray surveys in an attempt to assess areas more likely to retain carbaryl and 1-naphthol. Sandier environments are not likely to retain these compounds, since there is little or no clay or organic material with which to bond. No samples were collected from the western side of Willapa Bay, because it is sandy. One of the criteria for this 1998 study was to select sites with as fine of sediment as possible. Historical spraying has not been recorded for the area from Long Island and south (Tufts, 1998); therefore, the southern geographical boundary for this 1998 study area is north of Long Island.

Sites varied in size and are sometimes divided into 10-20 acre sections of a larger bed. Beds are often managed and sprayed in alternating years by section. Subsamples were collected from five areas within each site and ranged from approximately 40 ft. to 160 ft. apart, depending on the size of the site. The subsampled areas were selected to provide as full a spatial representation of each site as possible.

During the sampling design of this project, the author noted that the average frequency for spraying has been closer to every three to four years, rather than every six years as reported in the SEIS (Fisheries and Ecology, 1992) which was based on an assessment between 1963-1980 (Tufts, 1998; and Tufts/Wiegardt, 1998).

Pre-spray in this report describes sites sampled prior to July 1998 spraying and includes a control site at the Nemah Oyster Reserve. The selected pre-spray sites (1) were historically sprayed areas, (2) were a mixture of sites – last sprayed in 1996, and 1997, scheduled to be sprayed in 1998, and (3) included some adjacent sites.

One adjacent unsprayed site was selected for 1996, and another one was selected for 1997. Adjacent sites were not sprayed in 1995, 1996 or 1997. These sites were as geographically close as possible, preferably abutting a sprayed bed. Each of the sites to be sprayed in 1998 had an associated adjacent sites. In this survey it became necessary to accept two unsprayed sites that, although adjacent to sprayed sites, were geographically separated by sloughs. It was otherwise impossible to locate adjacent sites that had not been sprayed in 1995, 1996, or 1997.

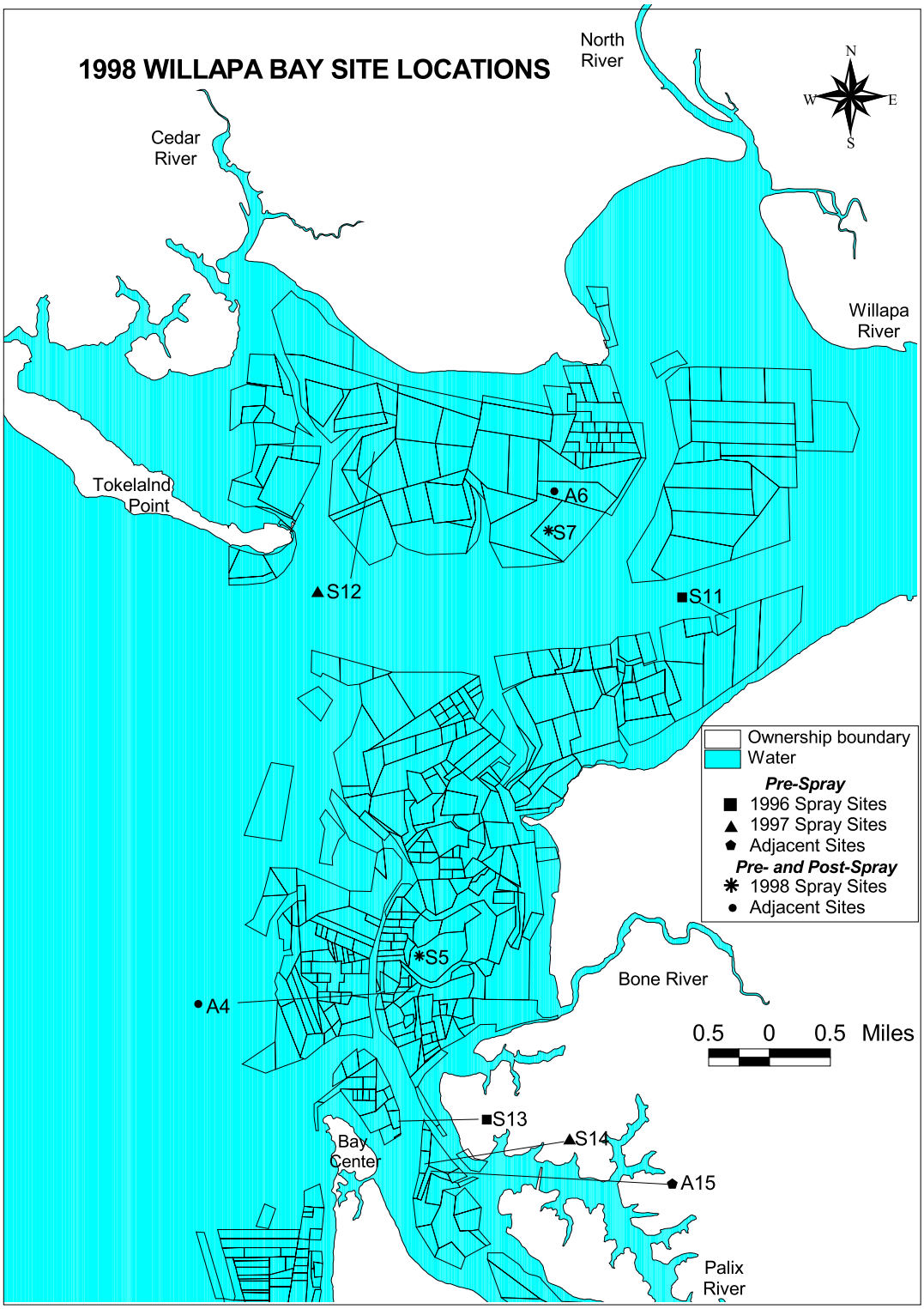

Figure 1. Willapa Bay Site Locations, Tokeland to Bay Center (Willapa Alliance, 1996).

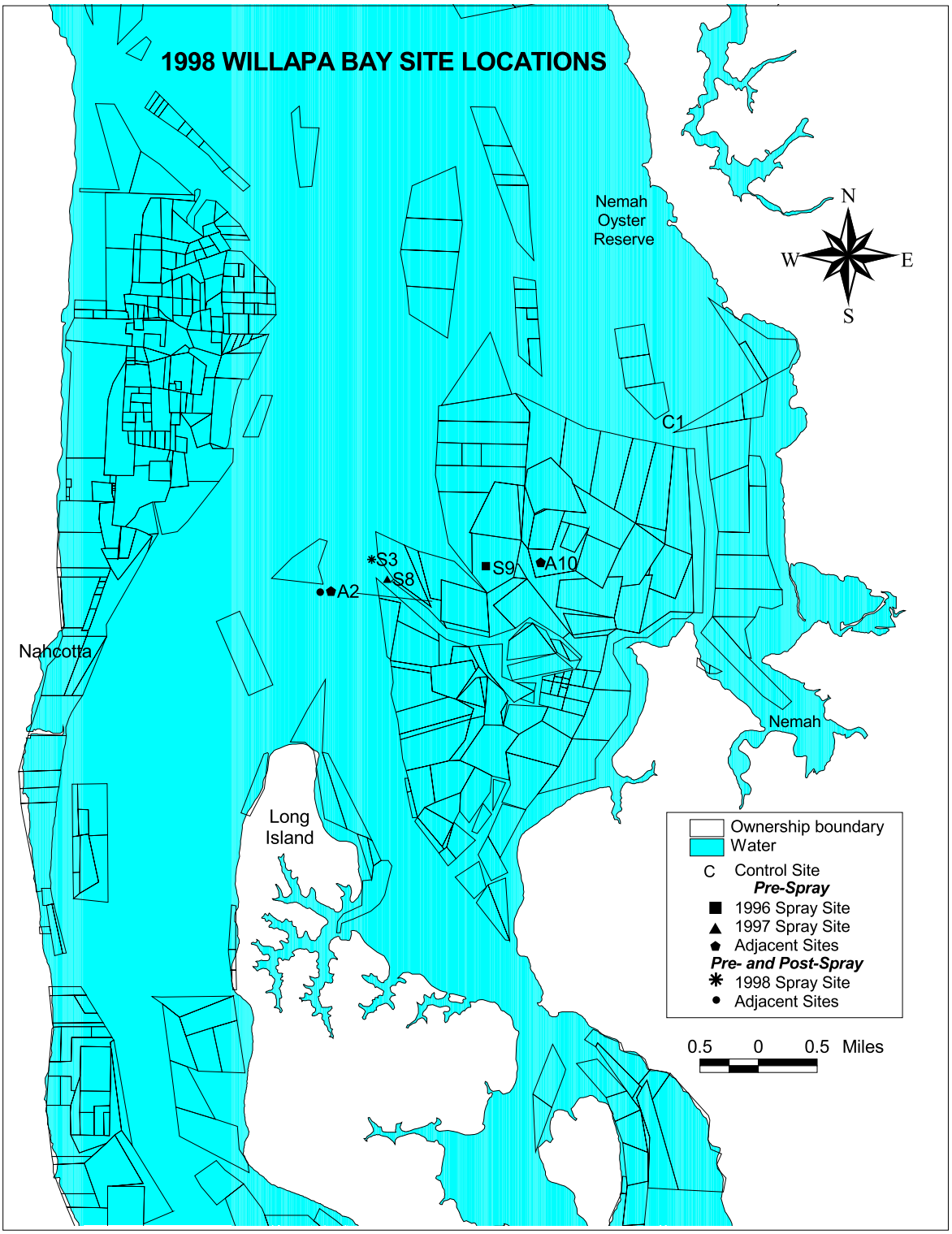

Figure 2. Willapa Bay Site Locations, Nemah to Long Island (Willapa Alliance, 1996).

Pre-spray sampling was scheduled during three low tide events. Each of the 15 sites was sampled once.

Post-spray is defined in this report as sites sampled after the annual July spraying in 1998. Post-spray sites were selected as historically sprayed areas, each with an adjacent unsprayed site, and included the control site at the Nemah Oyster Reserve.

Post-spray samples were collected at three sprayed beds immediately following treatment (spray began July 7, 1998), as well as at an unsprayed site adjacent to each of the sprayed beds. All three of the sprayed beds had received historical applications of carbaryl. Seven sites were sampled including the control site at the Nemah Oyster Reserve. Post-spray monitoring was targeted to occur on day-2, -30 and -60 following application. These time periods were modified by a few days to accommodate tides, weather conditions, and over-lapping spray dates.

Centrifuged pore-water was analyzed to determine whether carbaryl in the pore-water is available to the water column and, therefore, contributes to the background levels that have been detected by Weisskopf and Felsot (1998). The intent also was to determine the partitioning of carbaryl between water and sediment.

Sampling Methods

Puget Sound Estuary Program (PSEP, 1996) protocols do not address the problems associated with the need to collect core samples in environments where fouling of a van Veen grab sampler by oyster shell prohibit use of this tool. The Estuarine Habitat Assessment Protocols (PSEP, 1991) developed by Charles Simenstad are the most applicable, although these protocols were developed for assessment of wildlife and fish habitats and do not address the specific issues of chemistry.

Pre-spray

A decontaminated stainless-steel core-sampling device with an approximately 17 cm diameter was used to collect core samples. The large core diameter acted as a collar while the sediments were dug out. Core samples of the sediment were stratified into the following depths: 0 - 2 cm, 2 - 7.5 cm, and 7.5 - 15 cm. The depth determination was based on the findings of Karinen et al. (1967) where levels of carbaryl were detected down to 15 cm.

The first 0-2 cm samples were collected off the surface of the sediment before the coring device was pushed into the sediment. Large stainless steel spoons were used to scoop out the core sediment. After the 2 cm to 7.5 cm sample was collected, all sediment at the 7.5 cm mark was removed from inside the collar, and a sample from 7.5 to 15 cm was collected. Some beds were so compacted with oyster shell that strata were impenetrable with the large diameter collar. A stainless steel pipe with a 5.3 cm inside diameter and a 7.5 cm depth was used as a back up in these circumstances. It was not always possible to collect sediment at the 7.5 to 15 cm depth, as the smaller-diameter corer at times could not penetrate the substrate to the lower strata. Subsamples were composited for each stratum. Distances between adjacent unsprayed sites and sprayed sites ranged from approximately 60 ft. to 600 ft.

Post-spray

Post-spray sampling deviated from stratified depth sampling, in that only one stratum was collected to a depth of 6 cm, with a decontaminated stainless steel corer with a 5 cm inside diameter. The subsample locations at each site varied between events.

Other Procedures

The sediment was initially placed in 1,000 ml clean glass jars wrapped with aluminum foil. Homogenization was accomplished by hand stirring the sediment until color and grain-size were visually of uniform consistency. After thorough homogenization, the sediment to be analyzed for carbaryl/1-naphthol was placed in ultra-clean amber or aluminum foil covered, glass jars with Teflon-lined lids. Sediments to be analyzed for TOC and grain size were placed in appropriately sized jars. All samples were stored on ice immediately and maintained at a temperature of 4° C.

Decontamination procedures for all stainless steel utensils and corers consisted of:

- Wash in warm water with Liquinox detergent
- Rinse thoroughly with tap water
- Rinse three times with deionized water
- Rinse with acetone

Global Positioning Systems (GPS) readings were taken with a hand-held unit and recorded at the time of sampling for pre- and post-spray sites for the five subsample locations on each site (Appendix C).

At the time of sampling, sediment temperatures were recorded to the nearest 0.1° C at a depth of 6 cm. Temperature readings were made with a hand-held immersion alcohol thermometer.

Analytical Methods

A standard method for analyzing carbaryl and 1-naphthol in marine sediments does not exist. Bob Carrell at the Ecology Manchester Environmental Laboratory (MEL) developed a procedure for this analysis.

Sediment samples for the pore-water samples were centrifuged to remove pore-water and the resultant water was subsequently frozen for later analysis. The water was later thawed at approximately 6°C and extracted.

Analyses were conducted by MEL/EPA Manchester and Rosa Environmental. The analytical methods used are shown in Table 1. Materials and chemistry methods are discussed in Appendix D.

Table 1. Summary of Analytical Methods for Willapa Bay Carbaryl Project 1998

Analysis	Method	Reference	Laboratory
Conventionals			
Total Organic Carbon	$C0_2$ Combustion - EPA Method 415.1 (modified for PSEP)	PSEP, 1996	MEL/EPA, Manchester
Grain Size	Sieve and Pipette	PSEP, 1996	Rosa Environmental
Organics			
Carbaryl, 1-naphthol - Sediment	GC/ITD	Carrell (1998)	MEL/EPA, Manchester
Carbaryl - Pore Water	HPCL Method - 8318	EPA SW-846	MEL/EPA, Manchester
	Centrifugation	EPA, DMMP-TBT Rev. 0, 1998	MEL/EPA, Manchester

GS/ITD – Gas Chromatography with Ion Trap Detection
HPLC – High Performance Liquid Chromatography

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Data Quality

The assessment of quality assurance/quality control (QA/QC) results for carbaryl/ 1-naphthol includes holding times, surrogate recoveries of 4-chloro-1-naphthol, matrix spike/matrix spike duplicate recoveries, and laboratory blanks (Appendix D). Generally quality of the data was good, with the exception of centrifuged sediment and pore-water samples for day-2 and -15 and sediment samples for day-15. MEL staff reviewed the data for QA.

Centrifuged Sediment

Sediment data for day-15 (week 30) carbaryl/1-naphthol were rejected, because reliability was low for the batch based on QA review and QC results. Carbaryl matrix spike/matrix spike duplicate recoveries were 27% and 39%. Surrogate recoveries were 68% and 80%. The 1-naphthol recoveries were inflated artificially high, while carbaryl recoveries were artificially low. The chemist indicated there was an extraction technique problem, possibly due to over-concentration of the extract (Carrell, 1998). Re-extraction results for the MS/MSD had good recoveries. The batch was not re-analyzed.

Sediment

The MS/MSD pair requested for week 32 was not performed. Data were accepted based on recoveries of surrogates for chloro-1-naphthol which were excellent and ranged from 93% to 108%.

Seven sediment samples in the pre-spray monitoring event exceeded holding times; such values tend to be biased low. In these cases, carbaryl and 1-naphthol were not detected, but since the holding time was exceeded the presence of carbaryl or 1-naphthol cannot be ruled out. The day-60 sediment sample at post-spray site S5 also exceeded holding times due to re-extraction needs. Surrogate recoveries were generally within the 50% to 150% acceptable range. Method blanks indicated no contamination, although blank recoveries were generally low and some data had to be qualified. Matrix spikes and matrix spike duplicate recoveries were within acceptable ranges with the exception of one matrix spike the first week of analysis (week 22) with a value of 153%. Precision of the data was good.

Centrifuged Pore-water

Centrifuged samples for day-2 were rejected due to improper centrifugation time (EPA, 1998).

Day-15 centrifuged sediment and pore-water data were rejected due to: 1) improper centrifugation time and 2) the data reliability was low for the batch based on QA review and QC results. The MS/MSD for centrifuged pore-water were 0% and 9%. Pore-water recoveries of surrogates were 5% and 15%. The pore-water sample for the control site was

rejected with 1% surrogate recovery. The chemist indicated that there was an extraction technique problem (see comments under *Centrifuged Sediment*).

Due to the small volume of centrifuged water on day-60, pore-water was analyzed using Method 8318 (as compared to the MEL method used for day-2 and day-15).

There are no recommended holding times for carbaryl in frozen or thawing pore-water. However, once thawed, day-60 samples were extracted within the recommended holding times. Blanks demonstrated no contamination. Surrogate recoveries are considered acceptable by the laboratory and ranged from 38% to 88% with the exception of the sample from site A6 (unsprayed Tokeland site) which had only 21% recovery. Matrix spike recoveries were low, but considered acceptable by the laboratory at 50% and 71%. The surrogate recovery in the matrix spike duplicate sample was 0%. It is suspected that the duplicate may not have been spiked with the surrogate.

Poor recovery of the surrogate (21%) at site A6, along with low matrix spike recoveries, indicate any carbaryl concentration that may have been in the sample would have been biased low. Although the datum indicates it was not found at the detection limit of 0.06 ppb, caution should be exercised in ruling out the possibility that carbaryl was present. The MS/MSD recoveries at 50% and 71% indicate low recovery in general, suggesting all pore-water results are probably biased low for carbaryl concentrations.

Results

Pre-spray

Carbaryl/1-naphthol

The objective of the pre-spray sampling event was to determine whether historically sprayed sites or adjacent unsprayed sites retained carbaryl and/or 1-naphthol at a depth of up to 15 cm (Table 2). All nine of the historically sprayed sites, four of the adjacent unsprayed sites, and the control site did not indicate the presence of carbaryl or 1-naphthol above the detection limits which ranged from 21 to 58 ppb. Sediment at the highest intertidal site, adjacent unsprayed site A15 situated along the Palix River, indicated the presence of carbaryl in the 7.5 to 15 cm stratum. The value was reported as an estimate, because it was close to the detection limit at 29 ppb. This site was adjacent to a sprayed oyster bed, and was unique in that it was in the highest intertidal position of all the sites in this study.

Grain-size and TOC

Grain size in the pre-spray sites ranged from 15% to 79% fines (clay and silt fractions) Table 3 and Appendix E include the laboratory analyses report sheets for grain-size. Total organic carbon (TOC) values were generally low and ranged from 0.33% to 2.39% at 70°C analysis, and from 0.35% to 2.81% at 104°C analysis (Table 3). The Pearson correlation analysis indicates TOC and grain-size are correlated at the pre-spray sites for both 70°C and 104°C, with R^2 values of .78 and .76 respectively.

Post-spray

Sediments

Carbaryl

The mean day-2 concentration of carbaryl for the three sprayed sites was 2,900 ppb, with values ranging from 2,000 to 3,400 ppb (Figure 3). Day-2 carbaryl was detected on the three sprayed beds and on one adjacent site. The mean concentration of carbaryl on day-30 was 200 ppb, with values ranging from 220 to 180 ppb. Day-30 carbaryl concentrations were detected from day-60 sediment at the three sprayed sites and on two of the adjacent sites. Carbaryl was detected on the three sprayed sites, with a mean concentration of 105 ppb and with values ranging from 86 to 120 ppb (Table 4, Appendix E). The exponential regression through day-60 data from the three sprayed sites is strongly correlated, with a R2 value of 0.86. This is consistent with exponential decay.

Table 2. Carbaryl and 1-naphthol Concentrations in Willapa Bay Pre-Spray Sediment

Site Number	Date (1998)	Sample Depth (cm)	Carbaryl in Sediment (µg/Kg)	1-naphthol in Sediment (µg/Kg)
S8	5-26	1-2	37 U	37 U
S8	5-26	2-7.5	30 U	30U
S9	5-27	1-2	43 U	43 U
S9	5-27	2-7.5	28 U	28 U
S9	5-27	7.5-15	28 U	28 U
A10	5-28	1-2	33 U	33 U
A10	5-28	2-7.5	34 U	34 U
A10	5-28	7.5-15	28 U	28 U
C1	5-30	1-2	39 U	39 U
C1	5-30	2-7.5	32 U	32 U
C1	5-30	7.5-15	32 U	32 U
A6	6-9	1-2	42 U,HE	42 U,HE
A6	6-9	2-7.5	29 U	29 U
S11	6-10	1-2	41 U,HE	41 U,HE
S11	6-10	2-7.5	36 U	36 U
S11	6-10	7.5-15	33 U	33 U
S12	6-11	1-2	58 U	58 U
S12	6-11	2-7.5	30 U,HE	30 U,HE
S12	6-11	7.5-15	25 U,HE	25 U,HE
A2	6-12	1-2	52 U	52 U
A2	6-12	2-7.5	32 U	32 U
A2	6-12	7.5-15	28 U,HE	28 U,HE
S7	6-13	1-2	48 U,HE	48 U,HE
S7	6-13	2-7.5	25 U,HE	25 U,HE
S7	6-13	7.5-15	27 UJ,HE	27 UJ,HE
S5	6-23	1-2	37 UJ	37 UJ
S5	6-23	2-7.5	35 UJ	35 UJ
S5	6-23	7.5-15	30 UJ	30 UJ
A4	6-23	1-2	33 UJ	33 UJ
A4	6-23	2-7.5	25 UJ	25 UJ
A4	6-23	7.5-15	21 UJ	21 UJ
S13	6-24	1-2	34 UJ	34 UJ
S13	6-24	2-7.5	29 UJ	29 UJ
S13	6-24	7.5-15	30 UJ	30 UJ
S14	6-24	1-2	25 UJ	25 UJ
S14	6-24	2-7.5	25 UJ	25 UJ
A15	6-24	1-2	31 UJ	31 UJ
A15	6-24	2-7.5	24 UJ	24 UJ
A15	6-24	7.5-15	**29 J**	26 UJ
S3	6-25	1-2	35 UJ	35 UJ
S3	6-25	2-7.5	28 UJ	28 UJ

Site Key: S - Sprayed, A - Adjacent, and C - Control

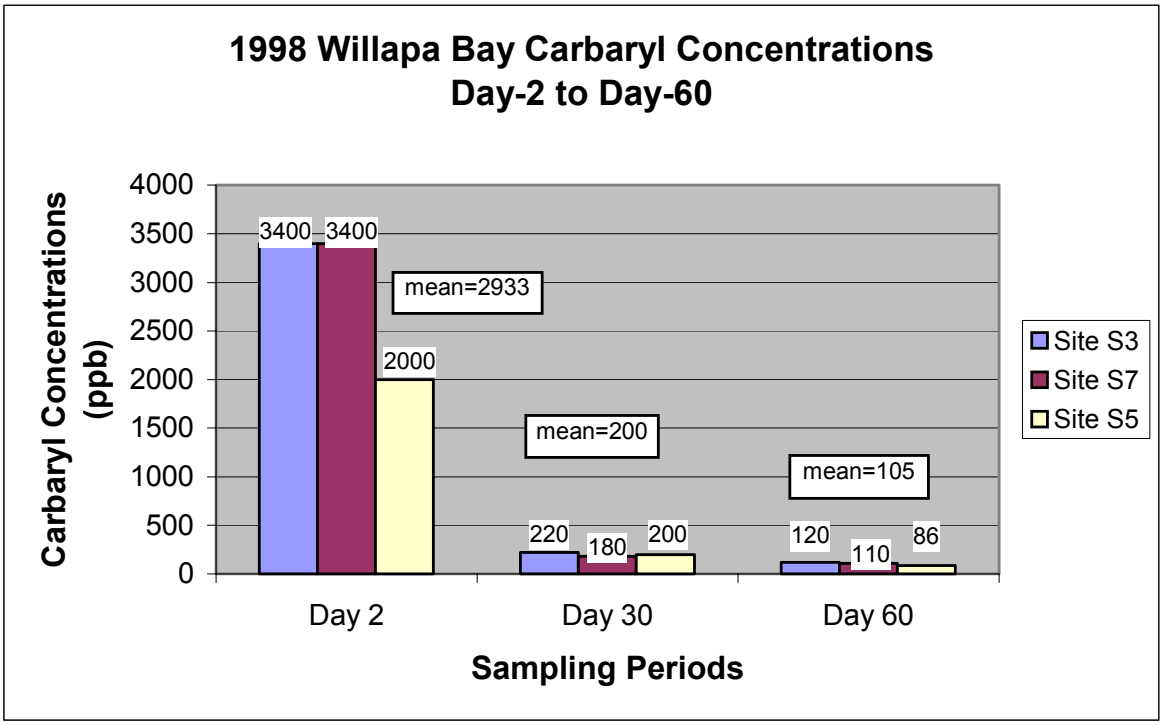
Data Qualifier Codes:
- U - The analyte was not detected at or above the reported result
- UJ - Analyte not detected at or above reported estimated result
- HE - Exceeded holding time
- J - Analyte positively identified. Associated result is an estimate
- **Bold** - Analyte detected

Table 3. Willapa Bay Pre-Spray Fines (silt and clay fractions) and Total Organic Carbon (TOC)

Sites	Depths	Fines	Toc % (70°C)	Toc % (104°C)
S8	1-2cm	38.7	1.22	1.24
S8	2-7.5cm	41.6	1.25	1.26
S9	1-2cm	53.5	1.25	1.26
S9	2-7.5cm	34.5	0.73	0.73
S9	7.5-15cm	20.3	0.49	0.49
A10	1-2cm	47.7	1.07	1.08
A10	2-7.5cm	50.0	1.02	1.04
A10	7.5-15cm	46.1	1.04	1.05
C1	1-2cm	59.7	1.73	1.72
C1	2-7.5cm	63.0	1.56	1.57
C1	7.5-15cm	55.7	1.46	1.48
A6	1-2cm	30.2	1.57	1.74
A6	2-7.5cm	55.3	0.80	0.85
S11	1-2cm	59.0	1.30	1.45
S11	2-7.5cm	61.2	1.46	1.65
S11	7.5-15cm	55.7	1.37	1.53
S12	1-2cm	71.3	2.15	2.47
S12	2-7.5cm	47.0	1.21	1.34
S12	7.5-15cm	37.2	0.99	1.07
A2	1-2cm	79.3	2.39	2.81
A2	2-7.5cm	69.1	1.69	1.84
A2	7.5-15cm	63.3	1.47	1.58
S7	1-2cm	57.0	1.66	1.87
S7	2-7.5cm	41.3	1.05	1.12
S7	7.5-15cm	34.1	1.02	1.08
A4	1-2cm	41.0	0.77	0.80
A4	2-7.5cm	25.6	0.60	0.63
A4	7.5-15cm	19.1	0.40	0.42
A15	1-2cm	22.2	0.64	0.66
A15	2-7.5cm	19.8	0.58	0.60
A15	7.5-15cm	14.8	0.54	0.57
S14	1-2cm	17.5	0.33	0.35
S14	2-7.5cm	17.9	0.48	0.50
S5	1-2cm	58.4	1.60	1.68
S5	2-7.5cm	55.1	1.44	1.52
S5	7.5-15cm	42.8	1.19	1.26
S13	1-2cm	44.9	1.37	1.42
S13	2-7.5cm	52.4	1.54	1.63
S13	7.5-15cm	55.0	1.55	1.60
S3	1-2cm	41.7	1.03	1.10
S3	2-7.5cm	31.3	0.86	0.90

Site Key: S - Sprayed, A - Adjacent, and C - Control

Figure 3. Carbaryl Concentrations at Sprayed Post-Spray Sites.



Each datum consists of five subsamples that were homogenized. The application rate was 7.5 lbs/acre.

1-naphthol

On day-2, 1-naphthol was detected in the sediment at four sites at concentrations that ranged from 120 to 170 ppb (Table 4) and was not detected at or above the detection limit of 23-40 ppb at the other three sites. Chemical analyses indicated that day-30 post-spray sediments contained no 1-naphthol at or above the detection limit, ranging from 22 to 33 ppb (Table 4). Although 1-naphthol was not detected at site S7 on day-30, it was detected on day-60 and was reported at 34 ppb (Appendix E). Once carbaryl degrades to 1-naphthol, the 1-naphthol appears to readily leave the sediment. The detection limit for 1-naphthol in sediment was too high to provide a depletion curve in this study.

Adjacent Sites

Two of the three post-spray adjacent (unsprayed) sites indicated the presence of carbaryl and 1-naphthol after the spray date. Carbaryl and 1-naphthol concentrations were lower at adjacent sites than the associated sprayed beds. On day-2, the A6 Tokeland site, physically bordering the S7 spray site, indicated the presence of carbaryl at 2,000 ppb and 1-naphthol at 120 ppb (Table 4). In the Nemah/Naselle area, site A2 (the adjacent unsprayed site to S3) is located across a slough. Carbaryl was detected at this site on day-30, while it was not detected on day-2 or -60. Interestingly, by day-60 carbaryl was not detected at any of the adjacent unsprayed sites at or above the detection limit that ranged from 27 to 32 ppb.

Table 4. Carbaryl and 1-naphthol Concentrations in Willapa Bay Post-Spray Sediment

Site Number	Date Sampled (1998)	Carbaryl in Sediment (µg/Kg)	1-naphthol in Sediment (µg/Kg)
Day 2			
C1	8-Jul	68 U	34 U
A2	11-Jul	160 U	40 U
S3	11-Jul	**3400**	**130**
A4	10-Jul	93 U	23 U
S5	10-Jul	**2000**	**120**
A6	12-Jul	**2000**	**120**
S7	12-Jul	**3400**	**170**
Day 30			
C1	6-Aug	31 U	31 U
A2	7-Aug	**45**	33 U
S3	7-Aug	**220**	28 U
A4	8-Aug	22 U	22 U
S5	8-Aug	**200**	24 U
A6	9-Aug	**210**	27 U
S7	9-Aug	**180**	29 U
Day 60			
C1	8-Sep	31 U	31 U
A2	7-Sep	32 U	32 U
S3	7-Sep	**120**	28 U
A4	6-Sep	27 U	27 U
S5	6-Sep	**86**	31 U
A6	5-Sep	29 U	29 U
S7	5-Sep	**110**	**34**

Data Qualifier Codes: U – The analyte was not detected at or above the reported result
Site Key: C - Control site, A - Adjacent site, S - Sprayed site **Bold** – Analyte detected

Control Site

Carbaryl and 1-naphthol were not detected in the sediment at or above the detection limits at the control site, C1, located in the Nemah Oyster Reserve. Carbaryl and 1-naphthol detection limits were: day-2, 68 and 34 ppb respectively; day-30, 31 and 31 ppb respectively; and day-60, 31 and 31 ppb respectively (Table 4).

Grain-size and TOC

Fines (clay-silt fractions of the grain size analysis) at post-spray sites ranged from 25% to 73% (Table 5). Appendix E includes data from the laboratory analyses for grain-size. TOC values at post-spray sites were low ranging from 0.58% to 1.92% at 70°C analysis and 0.60% and 2.07% at 104°C analysis (Table 5). A Pearson correlation analysis indicates TOC and grain-size at the post-spray sites are strongly correlated with R^2 values at 70°C, ranging from 0.89 to 0.96. and R^2 values at 104°C ranging from 0.88 to 0.96 (a set of values was analyzed for each post-spray event). No correlation between carbaryl and TOC content was observed.

Table 5. Willapa Bay Post-Spray Fines (silt and clay fractions) and TOC at a Depth of 6 cm

Sites			
Day 2	Fines (%)	TOC % (70°C)	TOC % (104°C)
C1	62.8	1.84	1.99
A2	72.8	1.92	2.07
S3	33.8	0.95	1.01
A4	25.2	0.58	0.64
S5	38.5	0.88	0.95
A6	46.9	1.20	1.29
S7	54.4	1.38	1.48
Day 30			
C1	63.9	1.72	1.98
A2	67.1	1.64	1.82
S3	35.4	0.96	1.05
A4	29.3	0.61	0.67
S5	50.9	1.09	1.20
A6	36.7	1.03	1.12
S7	44.5	1.26	1.41
Day 60			
C1	60.5	1.61	1.63
A2	63.0	1.50	1.50
S3	41.1	1.10	1.09
A4	28.4	0.61	0.60
S5	48.2	1.01	1.01
A6	30.3	0.83	0.83
S7	47.8	1.18	1.15

Site Key: S - Sprayed, A - Adjacent, and C - Control

Pore-water

Carbaryl

Carbaryl concentrations were detected in day-60 pore-water samples from the three sprayed sites. Detected carbaryl concentrations ranged from 0.57 to 1.15 ppb (Table 6).

1-naphthol

1-naphthol was not analyzed in the pore-water.

Table 6. Carbaryl Concentrations in Day-60 Willapa Bay Pore-Water

Site	Carbaryl (µg/L)	Qualifier
C1	0.06	U
A2	0.06	U
S3	**1.15**	
A4	**0.05**	NJ
S5	**0.57**	
A6	0.06	UJ
S7	**0.75**	

Site Key: S - Sprayed, A - Adjacent, and C – Control
Bold - Analyte detected
Data Qualifier Codes
U - The analyte was not detected at or above the reported result
UJ - The analyte was not detected at or above the reported estimated result
NJ - There is evidence that the analyte is present. The associated result is an estimate

Adjacent Sites

Carbaryl was detected at one adjacent site, A4. The concentration was reported as an estimate at .05 ppb, because it was reported at the level of the detection limit. This was the only occasion carbaryl was detected at the A4 site during the entire pre- and post-spray sampling events.

Control Site

Carbaryl was not detected at the control site C1 at or above the detection limit of 0.06 ppb.

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Discussion

Post-spray

Carbaryl Depletion in Sediment

The concentration of carbaryl decreased 15-fold between day-2 and day-30. From day-30 to day-60 the concentration dropped by only a factor of 2. This indicates initial rapid depletion is followed by slower depletion. These findings compare favorably with those of Dumbauld (1994, 1997). The presence of carbaryl on day-60 indicates carbaryl is persisting in the marine environment.

Drift to Adjacent Areas

Due to drift, a larger area is being treated with carbaryl then the allowable acreage. Tidal drift in floodwaters has been documented in several studies, many of which are mentioned in the SEIS (Fisheries and Ecology, 1992). The SEIS discusses one study with measurable levels of carbaryl 1,700 feet from the sprayed tract. Creekman and Hurlburt (1987) detected carbaryl in floodwater 217 yards away from a sprayed area at concentrations of 2,500 ppb on the day of treatment. Wind velocity, depth of water sampled, and current directions (including surface and bottom currents) are variables that can affect concentrations at any given location in the water.

It is clear from site A6 that drift can occur and can contribute substantially to carbaryl and 1-naphthol levels in adjacent non-target areas. There were no other sites proximal to this adjacent unsprayed site which are believed to be responsible for the carbaryl concentrations found, except for that of the abutting sprayed bed. Also, on day-2 the author noted dead animals on the sprayed site as well as its adjacent unsprayed site. It is interesting that site A6 had the same concentration of carbaryl on day-2 as sprayed site S5 in the Palix area.

Comparison of Pore-water Concentrations to Water Quality Recommendations

Currently there are no EPA criteria or state water quality standards for carbaryl. The National Academy of Sciences and Engineering (NAS) (1973) has established a water quality recommendation for carbaryl at 0.06 ppb. This recommendation has been established for the protection of marine life. Carbaryl concentrations in pore-water of all three sprayed sites indicated levels that exceed the NAS water quality recommendation. Low recoveries suggest the concentrations reported are biased low for carbaryl.

Weisskopf found carbaryl in Willapa Bay water column samples prior to the annual application of Sevin™ exceeding the NAS water quality recommendations in 1996 (Weisskopf, 1998) and 1997 (Weisskopf and Felsot, 1998). The water samples ranged from 9.20 ppb in 1996 to a mean of 0.70 ppb in 1997. Illegal spraying in 1996 is one possibility to explain this finding.

It is clear that carbaryl in the pore-water is available to contribute to background levels in the water column at concentrations exceeding the water quality criteria by NAS (1993). According to Erika Hoffman (1998) at EPA, pore-water should not be frozen and should be analyzed the same day collected, if possible. This suggests sediment samples for carbaryl need to be analyzed as soon as possible upon receipt by the laboratory.

1-naphthol

Concentrations of 1-naphthol in the water column may be of concern to juvenile fish, because 1-naphthol is more toxic to fish than is carbaryl (Stewart et al., 1967). Persistence of carbaryl suggests the continual releases of 1-naphthol into the water column, although this was not investigated in this study. According to Lamberton and Claey (1970), 1-naphthol has a half-life in seawater of approximately five days.

Comparison with Historical Data from Willapa Bay

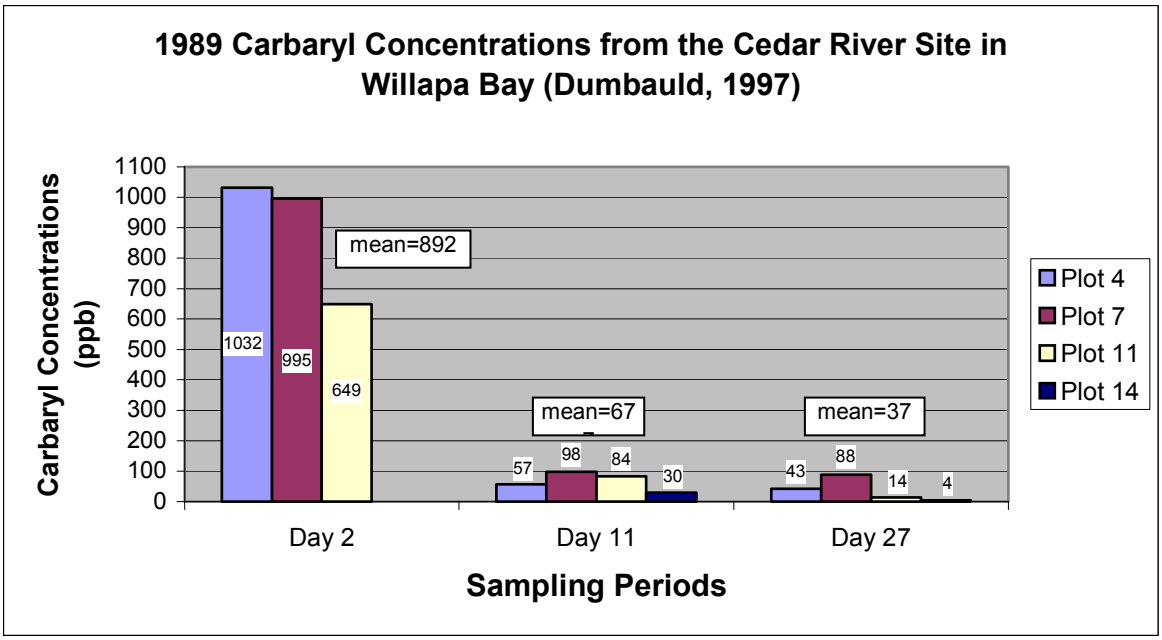
Data for the Cedar River sites in the Dumbauld (1994, 1997) study compare favorably with the findings in this study, in that carbaryl was found to persist in the marine environment. See Table 7 for comparisons between Dumbauld and Ecology studies.

Table 7. Comparison between Dumbauld (1994, 1997) and Ecology (1998) Studies

Study	Analytical Method for Carbaryl	Time	Application Rate	Study Length	Sampling Frequency	# of Sampling Events	Core Depth
Dumbauld (1994, 1997)	Liquid Chromatography (Krause, 1985)	July	5 lbs/acre	27 Days	9-16 Days	3	3 cm
Ecology (1998)	Gas Chromatography - ITD (MEL, 1998)	July - Sept.	7.5 lbs/acre	60 Days	28 - 33 Days	3	6 cm

Day-2 concentrations for carbaryl in the 1998 study were more than three times higher (2,933 ppb) than the mean concentrations in the Dumbauld study (892 ppb) (Figure 4). Carbaryl was applied at a concentration only one-third higher (7.5 lbs/acre) in the 1998 study, so one would not expect the carbaryl concentrations to be more than three times higher. One of several physical factors such as sample depth, weather, grain-size, temperature, and light availability could account for differences between the mean concentrations in these two studies. Analytical methods and percent recoveries may also help to account for the differences.

Figure 4. Carbaryl Concentrations from the Cedar River Site (Dumbauld, 1994, 1997)



Samples 4, 7, 11, and 14 are replicate samples for each sampling period (day-2 has only three replicates). The application rate was 5 lbs/acre.

Problematic in the Dumbauld study is that $t_{1/2}$ for the first-order decay was extrapolated out past the data points to a concentration of 1.0 ppb. The finding in the 1998 study that mean carbaryl concentrations were 105 ppb on day-60 is inconsistent with the finding at the Cedar River that by day-43 there would be only 1.0 ppb.

Perhaps the most representative model would consider the mechanisms involved in depletion and take into account the dramatic change between the rapid initial $t_{1/2}$ and the following slower depletion rate. This could be approached by calculating two depletion half-times – one for the rapid initial depletion and another for the later slow depletion – instead of trying to find a single best-fit equation for the entire depletion period.

The strength of the 1994 report is that the data give a more representative view of the transition period from rapid initial depletion to slow later depletion. The 1998 report may portray a better picture of persistence in muddy environments.

Summary of Toxicity Data on Carbaryl

Five species of phytoplankton utilized by molluskan larvae are intolerant of carbaryl above 100 ppb in water (Butler, 1962). Larvae and juveniles tend to be more sensitive than adults to toxins. A 96-hour EC_{50} (effective concentration producing death or irreversible effects on 50% of test organisms) at 10°C for Dungeness crab (*Cancer magister*) first-stage larvae (zoea) to carbaryl in water was estimated at 10 ppb (Buchanan et al., 1970). A continuous 25-day exposure of Dungeness crab larvae to carbaryl in water resulted in both prevention of molting and death at concentrations as low as 0.1-10.0 ppb (Buchanan et al.,

1970). In this 1998 Willapa Bay survey, the mean concentration of carbaryl in the centrifuged pore-water was 0.82 ppb. These findings are supported by Weisskopf and Felsot (1998). They detected mean water column concentrations of carbaryl at 0.70 ppb (exceeding the 0.06 ppb NAS recommendation) in 1997.

Tagatz et al. (1979) designed a study to determine whether the toxicity of Sevin™ could affect the development of an estuarine community as a whole. Chronic toxicity experiments for 10 weeks in sediment with carbaryl in overlying water indicated that the average number of larval invertebrate non-target species (mollusks, crustaceans other than burrowing shrimp, marine worms, and nemerteans) were significantly reduced when exposed to mean concentrations of carbaryl at 11.1 and 103.0 ppb as compared with 1.1 ppb. Tagatz concluded that at the concentrations of 11.1 and 103.0 ppb, Sevin™ could affect colonizations of annelids, crustaceans, mollusks, and nemerteans.

The findings of Karinen et al. (1967) compared favorably with those of the 1998 study. Karinen et al. found concentrations of carbaryl at 80-200 ppb within the top 6 inches of Yaquina Bay, Oregon sediment 42 days after spraying at an application rate of 10 lbs/acre. In this 1998 study, a mean concentration of 105 ppb was found on day-60 (application rate was 7.51 lbs/acre).

Bioaccumulation found in marine worm tissue after spraying 7.5 lbs/acre of carbaryl averaged 57,000 ppb (Tufts, 1989). These high concentrations of carbaryl may be a result of not depurating the worms prior to analysis. It might follow that these could be the concentrations at which predators such as birds, fish, and other invertebrates are ingesting the carbaryl.

There is little information about concentrations of carbaryl considered to be toxic in marine sediments. There is even less known about the effects of 1-naphthol.

Pozarycki and Weber (1997) noted after a carbaryl spray that sole were present on beds where they had previously been absent, suggesting fish were attracted to sprayed beds abundant with killed prey. Heron, gulls and other birds also congregate to feast on the remains of dead prey items. The direct and indirect effects of this opportunistic foraging on carbaryl-killed prey have not been studied. However, potential mutagenicity and endocrine disruption may contribute population level impacts to species, especially where repeated exposure occurs year after year. Little is understood about the metabolites of carbaryl or 1-naphthol in fish, birds, and invertebrates.

Cancer and grapsoid crabs, shrimp, saddle-back gunnels, sole, staghorn sculpins, nereid worms, and nemerteans were some incidental kills noted by the author on day-2 on the northern sprayed and unsprayed adjacent sites after the spray event. Starfish that had previously been present were absent, and during later events dead clams of various species were also noted.

Recent experimental studies suggest that in the presence of UV B light carbaryl may be up to 10-fold more toxic (Zaga et al., 1997). There is substantial information to suggest the food web, including predator/prey, and competitor relationships are unbalanced due to the

use of carbaryl, although secondary effects are often difficult to substantiate (Hurlburt, 1975).

Thirty-six years ago, when carbaryl was first used in the marine environment, agencies did not understand environmental toxicity, much less carcinogenicity and mutagenicity. EPA has recently placed carbaryl on its list of endocrine disrupters for fin-fish and avian reproduction EPA (1997). Washington State has serious concerns about anthropogenic disturbances that have potential to affect the fate of salmon. At this time while we endeavor to save salmon, carbaryl should come under the same scrutiny as any other substance that causes ecosystem disruption.

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Data Gaps

More sediment and water studies are required to understand the dynamics of carbaryl and its breakdown products. Willapa Bay is a large area; sampling is difficult and analyses are expensive. Carbaryl unquestionably has the capacity to affect the ecosystem by disrupting the food chain; this is a consequence of carbaryl's intended use. Its primary function is to kill burrowing shrimp and oyster drills. This study shows that carbaryl is persistent at levels that can affect the ecosystem for a longer period of time than previously assumed.

Where do we go from here? There are many gaps in the information at hand. There are no long-term studies (five years or more) that specifically address impacts to the benthos. Little is understood about the benthos and it may be difficult to assess the ecosystem impacts after so many years.

This 1998 study and previous studies have had many problems including:

- There are too few sites.
- Sandy sediments, although present in parts of the bay, are not necessarily representative of the marine environments in which carbaryl is expected to be depositing. Analyses of sediments from sandy areas may under-represent toxicity in Willapa Bay. Similarly, analyses using animals located in sandy areas may under-represent toxicity.
- Little is known about
  - ◊ bioaccumulation of carbaryl or 1-naphthol in animals living in muddy areas
  - ◊ effects of 1-naphthol or its breakdown products in the bay
  - ◊ metabolites of carbaryl or 1-naphthol
- Chemists have used analytical methods that have not been compared.
- Taxonomy has been done to various taxonomic levels, sometimes opting to eliminate various phyla.
- Benthos sampling has been done with core sizes too small to capture larger marine worms, nemerteans and bivalves.

Finally, what are the effects of spraying carbaryl on the estuarine ecosystem of Willapa Bay? What are the effects of carbaryl on other resources in the bay including clams, crab, salmon, and other commercial fish?

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