PNNL-13990



Operated by Battelle for the U.S. Department of Energy

Year 5 Post-Remediation Biomonitoring of Pesticides and Other Contaminants in Marine Waters Near the United Heckathorn Superfund Site, Richmond, California

N.P. Kohn R.K. Kropp

Battelle Marine Sciences Laboratory Sequim, Washington

August 2002

Prepared for the U.S. Environmental Protection Agency Region 9 under a Related Services Agreement with the U.S. Department of Energy under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory Richland, Washington



#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty**, **express or implied**, **or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

# PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC06-76RL01830

#### Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062; ph: (865) 576-8401 fax: (865) 576-5728 email: reports@adonis.osti.gov Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161 ph: (800) 553-6847 fax: (703) 605-6900 email: orders@ntis.fedworld.gov online ordering: http://www.ntis.gov/ordering.htm

This document was printed on recycled paper. (8/00)

PNNL-13990

# YEAR 5 POST-REMEDIATION BIOMONITORING OF PESTICIDES AND OTHER CONTAMINANTS IN MARINE WATERS NEAR THE UNITED HECKATHORN SUPERFUND SITE, RICHMOND, CALIFORNIA

N.P. Kohn R.K. Kropp

Battelle Marine Sciences Laboratory Sequim, Washington

August 2002

Prepared for the U.S. Environmental Protection Agency Region 9 under a Related Services Agreement with the U.S. Department of Energy under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory Richland, Washington

### SUMMARY

Marine sediment remediation at the United Heckathorn Superfund Site in Richmond, California, was completed in April 1997. The Record of Decision included a requirement that five years of postremediation monitoring be conducted in the waterways near the site. The present monitoring year, 2001-2002, is the fifth and possibly final year of post-remediation monitoring. In March 2002, water and mussel tissues were collected from the four stations in and near Lauritzen Channel that have been routinely monitored since 1997-98. A fifth station in Parr Canal was sampled in Year 5 to document postremediation water and tissue concentrations there. Dieldrin and dichlorodiphenyl trichloroethane (DDT) were analyzed in water samples and in tissue samples from resident (i.e., naturally occurring) mussels. Year 5 concentrations of dieldrin and total DDT in water and total DDT in tissue were compared with those from Years 1 through 4 of post-remediation monitoring (Antrim and Kohn 2000a,b<sup>1</sup>; Kohn and Kropp 2000, 2001), and with preremediation data from the California State Mussel Watch Program (Rasmussen 1995) and the Ecological Risk Assessment for the United Heckathorn Superfund Site (Lee et al., 1994). Year 5 water samples and mussel tissues were also analyzed for polychlorinated biphenyls (PCBs), which were detected in sediment samples during Year 2 monitoring and were added to the water and mussel tissue analyses in 1999. Contaminants of concern in Year 5 water samples were analyzed in both bulk (total) phase and dissolved phase, as were total suspended solids, to evaluate the contribution of particulates to the total contaminant concentration.

Mean chlorinated pesticide concentrations in some Year 5 water samples were the lowest post-remediation levels yet, but still did not meet remediation goals. DDT and dieldrin were detected in Year 5, albeit at very low levels, in Richmond Inner Harbor Channel (Station 303.1), where pesticides were not detected in Year 4. Mean total DDT concentrations in the total fraction of water samples collected at the other stations, including Santa Fe Channel and Parr Canal, ranged from 1.7 ng/L to 18.4 ng/L, exceeding the remediation goal of 0.59 ng/L. Mean dieldrin concentrations in the total fraction of water samples ranged from 0.16 ng/L at Richmond Inner Harbor Channel to 2.08 ng/L at Lauritzen Channel/End. Total DDT in water from Lauritzen Channel/End was 87% lower in Year 5 than in Year 4; dieldrin was 76% lower in Year 5 than in Year 4. PCB Aroclor 1254 concentrations were below the method detection limit for all replicates collected from all five stations.

<sup>1</sup> Reports for Years 1 and 2 of post-remediation monitoring were revised and republished in July 2000, after discovery of a reporting unit error in the original documents published in 1998 and 1999. Revised documents were distributed to all names on the original distribution list; they are also available on the web by searching for "Heckathorn" at http://www.pnl.gov/main/publications.

Mussel tissue analyses indicated that the bioavailability of total DDT in Year 5 was substantially lower than preremediation levels and relative to previous years throughout the study area. Total DDT concentrations in mussel tissues measured in Year 5 were 59% to 84% lower than Year 4 values at all stations. Total DDT (wet weight) concentrations were an order of magnitude lower than preremediation levels at all stations for which preremediation data were collected. Dieldrin concentrations measured in Year 5 were equal to or lower than Year 4 values at all stations. Year 5 dieldrin concentrations were also an order of magnitude lower than preremediation levels at those stations for which preremediation levels were determined. Mean chlorinated pesticide concentrations measured in Year 5 were highest in tissues from Lauritzen Channel/End (310 µg/kg total DDT and 17.0 µg/kg dieldrin wet weight), whereas the lowest mean total DDT (9 µg/kg wet weight) occurred in tissues collected from Richmond Inner Harbor Channel. Richmond Inner Harbor and Santa Fe Channel tissues had similarly low dieldrin levels  $(0.7 \,\mu\text{g/kg} \text{ and } 0.6 \,\mu\text{g/kg} \text{ wet weight, respectively})$ . The Aroclor 1254 concentration measured in tissue collected in Year 5 was 10% higher than in Year 4 at the Lauritzen Channel/Mouth station (303.2), but was 28% to 58% lower than Year 4 values in the Lauritzen Channel/End, Richmond Inner Harbor Channel, and Santa Fe Channel stations. Aroclor 1254 concentration in mussel tissue collected in Year 5 was highest at Lauritzen Channel/End (113 µg/kg wet weight) and lowest at Richmond Inner Harbor Channel (38.2 µg/kg wet weight).

The passive samplers showed the same gradient of concentrations as the tissue and water samples with the highest total DDT and dieldrin concentrations occurring at Lauritzen Channel/End, decreasing with distance from Lauritzen Channel/Mouth to Santa Fe Channel/End, and with the lowest concentrations at the Richmond Inner Harbor Channel station. Passive sampler concentrations were surprisingly comparable with the dry weight mussel tissue concentrations from the same stations. Comparability with field tissue concentrations is a promising advance in environmental monitoring, but more research is needed in this area to demonstrate a repeatable relationship between field measurements to biological endpoints.

Results from the fifth post-remediation monitoring survey indicated that chlorinated pesticides appear to be less bioavailable throughout the study area than in previous years, although without prior monitoring we are unable to determine whether pesticide bioavailability in Parr Canal has changed since remediation. The five years of post-remediation monitoring completed thus far fulfill the minimum requirement of the ROD. Biomonitoring using mussel tissues has provided documentation of changes in the long-term bioavailability of pesticides from the Lauritzen Channel sediment that cannot be assessed through water sample analyses alone. Future monitoring may be appropriate pending the results of ongoing sediment and outfall investigations.

# CONTENTS

SUMMARY	iii
1.0 Introduction	1
2.0 Methods	5
2.1 Sample Collection	7
2.2 Sample Analysis	8
3.0 Results and Discussion	11
3.1 Mussel Size and Condition	11
3.2 Water	12
3.3 Tissues	21
3.4 Passive Water Samplers	26
4.0 Conclusions	29
5.0 References	30

Appendix A: Field Sampling Report

Appendix B: Analytical Results for Water and Tissue Samples

Appendix C: Mussel Shell Length and Weight Data

# **TABLES**

<u>Table 2.1</u> .	Sampling Stations for Year 5 Post-remediation Monitoring (2001-2002) of the United Heckathorn Site	7
<u>Table 3.1</u> .	Summary of Length and Weight Data from Mussels Collected for Tissue Samples in March 2002 for Year 5 Post-remediation Monitoring of the United Heckathorn Superfund Site	.12
<u>Table 3.2</u> .	Concentrations of DDT, Dieldrin, and Total Suspended Solids (TSS) in the Total Fraction of Water Samples Collected in March 2002 for Post-remediation Monitoring of the United Heckathorn Superfund Site	.14
<u>Table 3.3</u> .	Concentrations of DDT and Dieldrin in the Dissolved Fraction of Water Samples Collected in March 2002 for Post-remediation Monitoring of the United Heckathorn Superfund Site	.15
<u>Table 3.4</u> .	Comparison of Year 4 and Year 5 Dissolved Pesticide Concentrations	.16
<u>Table 3.5</u> .	Comparison of Post-Remediation Concentration of Total DDT and Dieldrin in Total Fraction of Water Samples with Preremediation Levels and Remedial Goal Concentrations	.17
<u>Table 3.6</u> .	Concentrations of DDT, Dieldrin, and PCB Aroclor 1254 in Tissue Samples Collected in March 2002 for Post-Remediation Monitoring of the United Heckathorn Site	.22
<u>Table 3.7</u> .	Comparison of Pre- and Post-Remediation Tissue Concentrations of Total DDT, Dieldrin, and PCB (µg/kg wet weight)	.23
<u>Table 3.8</u> .	Comparison of Pre- and Post-remediation Lipid-Normalized Total DDT, Dieldrin, and PCBs in Tissues (µg/kg lipid)	.24
Table 3.9.	Concentrations of DDT, Dieldrin, and PCB Aroclor 1254 in Passive Water Samplers, Year 5 (2002) Post-Remediation Monitoring of the United Heckathorn Site	.27

# **FIGURES**

Figure 1.1.	Location of the United Heckathorn Superfund Site, Richmond, California
Figure 2.1.	Sampling stations for Year 5 of long-term post-remediation monitoring of the United Heckathorn Site.
Figure 3.1.	Comparison of preremediation (Ecological Risk Assessment) and post-remediation total DDT concentrations in water samples (total fraction) collected at the United Heckathorn Site. The open triangle for Station 303.3 sampled in 2000 is the mean value of only two replicates
Figure 3.2.	Comparison of preremediation (Ecological Risk Assessment) and post-remediation dieldrin concentrations in water samples (total fraction) collected at the United Heckathorn Site. The open triangle for station 303.3 sampled in 2000 is the mean value of only two replicates.
Figure 3.3.	Comparison of total and dissolved total DDT in water, March 2002
Figure 3.4.	Comparison of total and dissolved total dieldrin in water, March 2002
Figure 3.5.	Comparison of preremediation (Ecological Risk Assessment) and post-remediation total DDT concentrations in mussel tissue samples collected at the United Heckathorn Site
Figure 3.6.	Comparison of preremediation (Ecological Risk Assessment) and post-remediation dieldrin25

## **1.0 INTRODUCTION**

The United Heckathorn Site is located in Richmond Harbor, on the east side of San Francisco Bay in Contra Costa County, California (Figure 1.1). The site is an active marine shipping terminal operated by the Levin Richmond Terminal Corporation. The U.S. Environmental Protection Agency (EPA) listed the site on its National Priorities List of Federal Superfund sites because of chemical contamination of upland and marine sediments and because the site had the highest levels of dichlorodiphenyl trichloroethane (DDT) contamination measured during the California State Mussel Watch program (Rasmussen 1995). A remedial investigation of adjacent marine areas revealed widespread contamination of sediment by pesticides, particularly DDT and dieldrin (White et al., 1994). Significant pesticide contamination was limited to the soft, geologically recent deposits known as "younger bay mud." Pesticide concentrations were highest in Lauritzen Channel and decreased with increasing distance from the former United Heckathorn Site, clearly indicating that Heckathorn was the source of contamination. An ecological risk assessment at the Heckathorn Site (Lee et al., 1994) reported data collected in 1991 and 1992 for contaminant concentrations in marine water, organisms, and sediment. This assessment revealed that DDT and dieldrin originating from the United Heckathorn Site had been actively transported to offsite areas via surface waters.

Major components of the final remediation actions at the Heckathorn Site outlined in the Record of Decision (ROD 1996) are

- dredging of all younger bay mud from Lauritzen Channel and Parr Canal, with offsite disposal of the dredged material
- placement of clean sand after dredging
- construction of a cap around the former Heckathorn facility to prevent erosion
- enactment of a deed restriction limiting use of the property at the former Heckathorn facility location to nonresidential uses
- marine monitoring to verify the effectiveness of the remediation.

Remediation levels protective of the environment and human health were established to provide benchmarks for determining the effectiveness of the remediation actions. The Feasibility Study (Lincoff et al., 1994) and the ROD reviewed federal and state environmental laws that contained Applicable or Relevant and Appropriate Requirements (ARARs) for the remediation actions. EPA marine chronic and human health water quality criteria were identified as ARARs for surface water. Human health standards



Figure 1.1. Location of the United Heckathorn Superfund Site, Richmond, California.

based on consumption of contaminated fish were used to establish remediation goals because they are lower than marine chronic criteria. No chemical-specific ARARs were identified as remediation goals for marine sediment or tissues at the site.

Sediment remediation by dredging, dewatering, and offsite disposal took place between July 1996 and March 1997. Extensive core sampling was conducted to verify that the younger bay (contaminated) mud was removed and that only older bay (less contaminated) mud remained. EPA collected post-remediation samples of the remaining older bay mud, and analyses determined the average concentration of DDT to be 263  $\mu$ g/kg dry weight (Lincoff 1997), below the remediation goal of 590  $\mu$ g/kg DDT dry weight specified in the ROD. In April 1997, 9100 cubic yards of clean sand were placed in Lauritzen Channel to improve the older bay mud surface for colonization by benthic invertebrates. The volume of sand was equivalent to an average depth of 1 ft over the dredged area, although the exact layer thickness undoubtedly varied because of the uneven, sloping channel bottom. Since remediation and sand placement in 1997, Lauritzen Channel has been returned to industrial use by Levin Richmond Terminals and Manson Construction, resulting in frequent vessel traffic throughout the channel.

The purpose of the marine monitoring study is to document the expected reduction in flux of contaminants from the United Heckathorn Superfund Site following EPA response actions. The measurement endpoints for this long-term monitoring are mussel and surface water chemical concentrations. The remediation levels for waters set forth in the ROD are 0.59 ng/L for total DDT (the sum of the 4,4'- and 2,4'-isomers of DDT, DDD, and DDE) and 0.14 ng/L for dieldrin.

Year 1 of post-remediation biomonitoring was conducted 6 months after remediation (Antrim and Kohn 2000a). Year 1 biomonitoring showed that pesticide concentrations in the tissues of mussels exposed at the site were higher than those observed before remediation. Year 2 monitoring, conducted about 18 months after remediation, showed tissue levels that were much reduced from Year 1 and that only exceeded preremediation levels at Richmond Inner Harbor Channel (Antrim and Kohn 2000b). During both years, the concentrations were higher at Lauritzen Channel stations than at the Richmond Inner Harbor Channel or Santa Fe Channel stations. Year 3 monitoring results were very similar to Year 2, with water concentrations still exceeding the cleanup goal and mussel tissue concentrations similar to those of Year 2. The lack of a decrease in DDT concentration in the biomonitoring organisms suggested that DDT was still present and bioavailable in Lauritzen Channel, especially near its head.

Sediment samples collected from Lauritzen Channel in late 1998 and summer of 1999 and analyzed for pesticides showed that soft surface sediments still had total DDT concentrations in the part-per-million range (Kohn and Gilmore 2001). That DDT was still bioavailable to organisms was confirmed by Year 4

(2001) post-remediation biomonitoring results, which showed a slight *increase* in mussel tissue concentrations compared with those of Year 3. Even though Year 4 tissue concentrations were below pre-remediation levels, it was clear that Lauritzen Channel sediment is still contaminated and that DDT bioavailability to marine organisms is not decreasing with time post-remediation.

This report focuses on the Year 5 (2002) post-remediation biomonitoring results. Year 5 biomonitoring repeated the water and resident mussel tissue sampling and analyses of the previous years, but added a station in the Parr Canal to determine effectiveness of the remedy there. In Year 5, only resident mussels were sampled (as in Years 3 and 4), and Year 5 water samples were analyzed for both total and dissolved pesticides and total suspended solids (as in Year 4). Year 5 results are compared with water and tissue pesticide data from two preremediation studies (Lee et al., 1994; Rasmussen 1995) and the Years 1, 2, 3, and 4 monitoring studies (Antrim and Kohn 2000a, 2000b; Kohn and Kropp 2000, 2001). All Heckathorn post-remediation monitoring reports to date, as well as the 1999 Sediment Investigation (Kohn and Gilmore 2001) are available on the web at <a href="http://www.pnl.gov/main/publications.">http://www.pnl.gov/main/publications.</a>

### 2.0 METHODS

Detailed methods for the collection, processing, and analysis of tissue and water samples in Year 5 were outlined in the Field Sampling and Analysis Plan for Long-Term Post-Remediation Monitoring at the Heckathorn Site (Battelle 1997). All procedures for sampling, sample custody, field and lab documentation, other aspects of documentation, quality assurance, and sample analysis were consistent with the more general procedures described in the Quality Assurance Project Plan (QAPP) for Remediation Investigation and Feasibility Study of Marine Sediments at the United Heckathorn Superfund Site (Battelle 1992). Updates to the existing plan were provided in Addendum 1 to the QAPP (Battelle 2002) to cover the following modifications for Year 5:

- Collection of water and resident mussel tissue samples from Parr Canal,
- Analysis of total suspended solids and dissolved contaminants in water samples,
- Deployment of polyethylene passive water samplers at the four routine monitoring locations, and
- Analysis of pesticides and PCBs in the passive water samplers (concurrently with mussel tissue).

A brief review of methods is provided here. All samples were collected by EPA and analyzed at Battelle Marine Sciences Laboratory (MSL).

Four of the post-remediation monitoring stations selected are those stations in the project area that were sampled during the State Mussel Watch Program; the Parr Canal station, named 303.6, was added in Year 5 (Figure 2.1). Three of the stations also approximate locations sampled during the Ecological Risk Assessment (Lee et al., 1994). The Lauritzen Channel/End Station (Mussel Watch Station 303.3) corresponds to the Ecological Risk Assessment-Lauritzen Channel Station; the Santa Fe Channel Station (Mussel Watch Station 303.4) corresponds to the Ecological Risk Assessment-Santa Fe Channel Station. The Richmond Inner Harbor Channel Station (Mussel Watch Station 303.4) corresponds to the Ecological Risk Assessment-Santa Fe Channel Station. The Richmond Inner Harbor Channel Station (Mussel Watch Station 303.1) is approximately 1200 ft inshore from the Ecological Risk Assessment-Richmond Inner Harbor station, which was at navigational nun buoy (No. 16). The Ecological Risk Assessment had no sampling station near the entrance to Lauritzen Channel (Mussel Watch Station 303.2, Lauritzen Channel/Mouth). Parr Canal had not been monitored at all prior to Year 5. The sand layer placed in Parr Canal in April 1997 was found to be intact in July 1999 (Kohn and Gilmore 2001); the biomonitoring data will determine remedy effectiveness at 5 years post-remediation. A more detailed description of sampling stations for the Year 5 biomonitoring is provided in Table 2.1 and in the Field Sampling Summary and Field Sampling Report memorandum (Appendix A).



Figure 2.1. Sampling stations for Year 5 of long-term post-remediation monitoring of the United Heckathorn Site.

Station Number	Station Name	Sample Types Collected	Location	Remarks
303.1	Richmond Inner Harbor Channel	Water, mussel tissue, passive sampler	37°54' 32.869" N 122°21' 33.523" W	On western most wooden dolphin, near abandoned Ford automotive plant, southeast of public fishing pier.
303.2	Lauritzen Channel/ Mouth (South)	Water, mussel tissue, passive sampler	37°55' 12.561" N 122°22' 01.326" W	On east side of canal, on pilings beneath the Levin Dock near the northern end of a large fender structure. Collected extra water for quality control (matrix spike and matrix spike duplicate).
303.3	Lauritzen Channel/ End (North)	Water, mussel tissue, passive sampler	37°55' 22.699" N 122°22' 00.094" W	On east side of canal, southern end of small wooden pier that extends out into the channel.
303.4	Santa Fe Channel/End	Water, mussel tissue, passive sampler	37°55' 21.235" N 122°22' 17.684" W	At northwest corner of floating boat shed, east of small boat fuel dock
303.6	Parr Canal	Water, mussel tissue	37°55' 11.817" N 122°21' 45.996" W	

 Table 2.1.
 Sampling Stations for Year 5 Post-remediation Monitoring (2001-2002) of the United Heckathorn Site

# 2.1 SAMPLE COLLECTION

Approximately 45 resident blue mussels (*Mytilus edulis*) were collected from each of the five stations on March 5, 2002 (Figure 2.1). Resident mussels can be one of several subspecies or hybrids in the *M. edulis* complex that cannot easily be distinguished by the shells alone (Harbo 1997). The coordinates presented in Table 2.1 for each station were determined using a Global Positioning System (GPS) with differential correction.

Mussels were collected near the surface of the water, at about 1 ft above mean lower low water (MLLW) at all stations except Santa Fe Channel/End (Station 303.4), where mussels were collected near the surface from a floating dock. Thus, mussels at the Santa Fe Channel/End station were collected at a fixed depth relative to the water surface. Mussels were cleaned gently in the field to remove external growth and packaged whole in ashed foil and plastic bags. Mussels were frozen at -20°C, shipped to the analytical laboratory in coolers, and held at -20°C until they were prepared for analysis. To prepare tissue samples, mussels were partially thawed, the valve or shell length was measured, and byssal threads were cut from the tissue. Sand and mud on the soft tissue were rinsed off with deionized water and soft tissues were transferred to a sample jar. Each composite tissue sample consisted of from 40 to 50 mussels. The

total wet weight of each tissue sample was recorded. Tissue samples were refrozen and stored at -20°C until extracted.

On March 5, 2002, surface water samples were collected approximately 1 ft (0.3 m) below the water surface. To collect a sample, a 1-gal amber glass bottle was submerged, the cap was removed underwater to allow water in, and the cap replaced before the bottle was lifted from the water. At each station, three 3.8-L (1 gal) water samples were collected for analysis. Additional water samples were collected for quality control (QC) analyses (i.e., matrix spike, matrix spike duplicate [MS/MSD]) (Table 2.1). Water samples were chilled to and held at 4°C until extracted.

Polyethylene passive water samplers deployed at the four traditional monitoring stations on February 5, 2002. The passive samplers consist of a strip of solvent-cleaned polyethylene secured to a wire loop and either attached to a fixed object (i.e., piling) or to a weight with a float to keep the sampler at the appropriate height in the water column. The passive samplers were left in place for four weeks and retrieved at the same time the water and tissue samples were collected. Passive samplers were placed in precleaned glass jars with Teflon-lined lids and frozen until extracted.

#### 2.2 SAMPLE ANALYSIS

Chemical analyses followed methods described in the QAPP (Battelle 1992), including the updates in Addendum 1 to the QAPP (2002). The water samples collected on March 5, 2002, were split upon receipt for total suspended solids, total pesticide, and dissolved pesticide analysis. To create the water sample for dissolved pesticide analysis, an aliquot of the bulk water sample was filtered through a 0.45-µm glass fiber filter. Bulk and filtered water samples (for total and dissolved pesticides) were extracted on March 8 through March 18, 2002, and analyzed for chlorinated pesticides and polychlorinated biphenyl (PCB) aroclors March 21 through March 27, 2002, within acceptable holding times. Sample-specific detection limits (Appendix B) were calculated using the sample volume and achieved detection limits for water samples determined in a previous study at MSL. Total suspended solids were analyzed in bulk water samples according to Standard Method 2540-D, Solids (APHA 1998) on March 28, 2002.

The mussel tissue samples collected on March 5, 2002, were extracted on April 8, 2002, and analyzed for chlorinated pesticides and PCB aroclors on April 11-14, 2002. Although the target sample holding times to extraction was exceeded by two weeks, tissue samples were stored frozen prior to extraction and are not expected to have suffered any loss of sample integrity. Tissue samples were also analyzed for percentage of lipids. Sample-specific detection limits (Appendix B) were calculated using the sample weight and achieved detection limits for tissue samples determined in a previous study at MSL. Total

DDT was calculated as the sum of detected concentrations for six DDT compounds (2,4-DDE, 4,4-DDE, 2,4-DDD, 4,4-DDD, 2,4-DDT, and 4,4-DDT), following the methods used in the California State Mussel Watch Program (Rasmussen 1995) and in the Ecological Risk Assessment of Marine Sediments at the United Heckathorn Superfund Site (Lee et al. 1994). Undetected analytes were not included in the total DDT calculation.

Polyethylene passive water samplers deployed at the four traditional monitoring stations for four weeks were retrieved on March 5, 2002. These samples were stored frozen until extraction (April 8, 2002) and analysis (April 11-14, 2002). Because the samples were frozen until extracted, no loss of analyte or sample integrity is expected even though extraction occurred outside of the 7-d target holding time. Pesticide analysis methods for the passive samplers were the same as those used for tissue samples.

### **3.0 RESULTS AND DISCUSSION**

This section presents the results of physical measurements to assess the size and condition of the resident mussels, and the results of chemical analyses of the water and mussel tissue samples. All extractions and analyses were conducted within the target holding times specified in the QAPP. Complete chemistry data tables, including associated QC data, are provided in Appendix B. In the following discussion, the Year 5 water data are compared with preremediation data from the Ecological Risk Assessment (Lee et al., 1994), post-remediation data from the previous four monitoring years (Antrim and Kohn 2000a, 2000b; Kohn and Kropp 2000, 2001), and the remediation goals for the site. The Year 5 tissue data are compared with preremediations from the California State Mussel Watch Program (Rasmussen 1995) and the Ecological Risk Assessment (Lee et al., 1994), and with post-remediation data from the previous four monitoring years.

# 3.1 MUSSEL SIZE AND CONDITION

Raw data for shell-length measurements and mean wet weight per mussel are provided in Appendix C. Only resident mussels were collected and analyzed in Year 5. Mussels collected for tissue samples ranged from 4.69 cm to 8.05 cm in shell length (Table 3.1). Shell lengths of 59 mussels (26.7% of the total) were larger than the preferred size range of 4.0 cm to 6.5 cm, which is a combination of the preference ranges cited by Rasmussen (1995) and Lee et al. (1994). The oversized mussels were collected from Santa Fe Channel/End, Lauritzen Channel/Mouth, and Richmond Inner Harbor Channel. 96% of the mussels from Lauritzen Channel/End and Parr Canal were within the target size range. Mussel wet weights were also much higher than in previous years, because the mass increases as a function of the shell length increase cubed. The mussels were collected at least a month later than in previous years, which could explain some of the increased size. The differences in the mean shell length among stations were all less than 1 cm (Table 3.1). The grand mean shell length (all stations) was 6.17 cm (standard deviation 0.17) in Year 5, about 0.8 cm longer than the mean shell length of resident mussels analyzed in previous monitoring years (5.61 cm, 5.28 cm, 5.34, and 5.32 cm in Years 1, 2, 3, and 4, respectively). The station mean wet weight per mussel, which was calculated as the total wet weight of the station tissue sample divided by the number of individuals per sample, ranged from 10.1 g to 14.8 g (Table 3 1). The overall mean wet weight per mussel (calculated as the mean of the station means) was 12.9 g (standard deviation 2.5), approximately twice the weight of mussels collected in previous years.

	Station							
-	303.1	303.2	303.3	303.4				
	Richmond Inner Harbor Channel	Lauritzen Channel/Mouth	Lauritzen Channel/End	Santa Fe Channel/End	Parr Cana			
Shell Length (cm)								
n	40	41	50	40	50			
min	4.75	4.69	4.93	4.88	4.78			
max	7.14	7.37	6.55	8.05	6.66			
mean	6.18	6.39	5.75	6.72	5.82			
standard deviation	0.73	0.63	0.43	0.85	0.48			
n outside range <sup>(a)</sup>	15	16	1	24	3			
grand mean <sup>(b)</sup>	6.17							
standard deviation	0.17							
<u> Tissue Wet Weight (g)</u>								
sample weight	589.3	607.4	507.9	585.1	506.8			
mean wt/mussel	14.7	14.8	10.2	14.6	10.1			
grand mean	12.9							
standard deviation	2.5							
Lipid Content (% dry weig	<u>ght)</u>							
	8.65	7.44	8.57	7.31	8.58			
grand mean	8.11							
standard deviation	0.673							

 Table 3.1.
 Summary of Length and Weight Data from Mussels Collected for Tissue Samples in March

 2002 for Year 5 Post-remediation Monitoring of the United Heckathorn Superfund Site

(a) All individuals outside preferred size range of 4.0-6.5 cm were longer than 6.5 cm.

(b) Mean of all stations combined.

Lipid content of resident mussels ranged from 7.3% to 8.7% dry weight (Table 3.1; grand mean of 8.1%; standard deviation of 0.67%). Tissue lipid content is not a definitive indicator of organism health, because lipid content in bivalves can vary significantly depending on the availability of food and the bivalve's reproductive cycle. However, because nonpolar organic contaminants tend to accumulate in fatty tissues, normalizing contaminant data to tissue lipid content permits more equitable comparisons among samples to be made.

# 3.2 WATER

The triplicate water samples that were collected at each site provide a snapshot of water-column concentrations of DDT compounds and dieldrin at a specific location. Such samples provide no information about the temporal variability or vertical stratification of these contaminants in the water

column, information that would be useful in the interpretation of the biomonitoring results. The inability to evaluate temporal or spatial variability of water chemistry should be considered when these data are compared with the results of earlier studies. The differences between two such sampling events do not necessarily verify trends, nor are individual samples necessarily representative of typical conditions.

In Years 1 through 3, only total pesticides were measured in bulk water samples, and results were highly variable. Suspended particulates in the water column were considered to contribute to the variability in pesticide concentrations between replicate samples; hence, the modification to the program starting in Year 4 to evaluate suspended particulates and associated pesticides. In Year 5 as in Year 4, a larger volume of water was collected from each monitoring station to evaluate dissolved pesticides and total suspended solids, as well as total pesticides. Total pesticide and total suspended solids concentrations in water samples are provided in Table 3.2; dissolved pesticide concentrations in water samples are provided in Table 3.3.

Complete water chemistry and QC data are provided in Appendix B. In the method blank for the total fraction, all analytes were below the method detection limit (MDL). In the method blank for the dissolved fraction, 4,4'-DDD was detected just at the detection limit of 0.09 ng/L. Associated dissolved sample concentrations that were less than five times the blank concentration are flagged with a "B" in Table 3.3. Recoveries of spiked surrogate compounds (PCB 103 and PCB 198) in Year 5 water samples ranged from 40.2% to 138%, with only one PCB 198 surrogate recovery outside the target range (40% to 120%) (Appendix B). Blank spike recoveries of dieldrin, 4,4'-DDT, and Aroclor 1254 were all within the target range (40% to 120%). MS/MSD recoveries for dieldrin, 4,4'-DDT, and Aroclor 1254 were also all within the target range (40% to 120%) in both the total and dissolved fraction MS/MSD samples. The low relative percent difference (RPD) between duplicate matrix spikes (0% to 12%) and duplicate blank spikes (4.4% to 6.9%) indicate good precision between replicate laboratory measurements.

Average total DDT concentrations in bulk water samples ranged from 0.72 ng/L at Richmond Inner Harbor Channel Station 303.1, to 18.4 ng/L at Lauritzen Channel/End Station 303.3 (Table 3.2). Results were fairly consistent between replicates except at Station 303.3, where all three replicates differed considerably, ranging from about 5.5 ng/L to 36.7 ng/L. However, both the concentrations and degree of variability at Station 303.3 were much lower than the previous monitoring year (2001) when total DDT ranged from 40 ng/L to 294 mg/L in the replicates. It is typical of all monitoring years that the highest and most variable concentrations are observed at Station 303.3, Lauritzen Channel/End.

						C	oncentration (	ng/L)				
Station	Location	TSS (mg/L)	Dieldrin	2,4'-DDE	4,4'-DDE	2,4'-DDD	4,4'-DDD	2,4'-DDT	4,4'-DDT	Total DDT	Aroclor 1	1254
303.1A		1.0U <sup>(a)</sup>	0.03 U	0.06 U	0.06	0.13	0.26	0.03 U	0.04 U	0.45	17.9	U
303.1B	Richmond Inner	1.0U	0.05 0	0.00 U	0.07	0.18	0.36	0.05 U 0.04 U	0.01 U	0.61		U
303.1C	Harbor Channel	1.0U	0.03 U	0.06 U	0.16	0.21	0.56	0.03 U	0.05 U	0.93		U
	Mean <sup>(b)</sup>	ND <sup>(c)</sup>	0.16	ND	0.10	0.17	0.39	ND	ND	0.66	ND	
	standard deviation	(1)	NA	NA	0.06	0.04	0.15	NA	NA	0.24	NA	
303.2A	T	1.0U	0.42	0.07 U	0.13	0.07 U	0.78	0.24	0.67	1.82	19.9	U
303.2B	Lauritzen Channel/Mouth	NA	0.37	0.09	0.21	0.06 U	0.77	0.22	0.47	1.76	16.6	U
303.2C	Chamies Would	NA	0.50	0.09 U	0.19	0.10 U	0.83	0.04 U	0.49	1.51	25.9	U
	Mean <sup>(b)</sup>	ND	0.43	0.09	0.18	ND	0.79	0.23	0.54	1.70	ND	
	standard deviation	NA	0.07	NA	0.04	NA	0.03	0.01	0.11	0.16	NA	
303.3A	Lauritzen Channel/	1. <b>0</b> U	1.50	0.06 U	0.31	0.85	1.23	0.73	2.37	5.49	19.2	U
303.3B	End	1.0U	1.72	0.06 U	0.53	0.86	1.50	0.94	9.28	13.11	18.5	U
303.3C	Lind	1.0U	3.01	0.06 U	0.79	1.89	2.70	2.50	28.8	36.68	17.3	U
	Mean <sup>(b)</sup>	ND	2.08	ND	0.54	1.20	1.81	1.39	13.5	18.4	ND	
	standard deviation	NA	0.82	NA	0.24	0.60	0.78	0.97	13.7	16.3	NA	
	Santa Fe Channel/											
303.4A	End <sup>(e)</sup>	1.0U	0.20	0.06 U	0.14 B	0.07 U	0.36	0.03 U	0.10	0.60	18.3	U
303.6A		1.0U	0.99	0.06 U	0.36	0.29	0.93	0.25	0.89	2.72	17.2	U
303.6B	Parr Canal	1.0U	0.98	0.06 U	0.32	0.29	0.90	0.24	0.84	2.59	18.1	U
303.6C		1.0U	0.96	0.06 U	0.31	0.27	0.80	0.22	0.81	2.41		U
	Mean <sup>(b)</sup>	ND	0.98	ND	0.33	0.28	0.88	0.24	0.85	2.57	ND	
	standard deviation	NA	0.02	NA	0.03	0.01	0.07	0.02	0.04	0.16	NA	

Table 3.2. Concentrations of DDT, Dieldrin, and Total Suspended Solids (TSS) in the Total Fraction of Water Samples Collected in March 2002 for Post-remediation Monitoring of the United Heckathorn Superfund Site

(a) U Undetected above given concentration.(b) Mean calculated using only detected values.

(c) ND None detected.

(d) NA Not applicable.

(e) Sample containers for two of the three replicate water samples collected from 303.4 Santa Fe Channel End were broken during shipping.

					(	Concentration	(ng/L)			
Station	Location	Dieldrin	2,4'-DDE	4,4'-DDE	2,4'-DDD	4,4'-DDD	2,4'-DDT	4,4' <b>-</b> DDT	Total DDT	Aroclor 125
303.1A 303.1B	Richmond Inner Harbor Channel	0.15 0.04U	$0.08{ m U}^{(a)}$ $0.08{ m U}$	0.09B <sup>(b)</sup> 0.11B	0.09U 0.08U	0.05U 0.05U	0.04U 0.04U	0.06U 0.05U	0.09 B 0.11 B	23.4 U 22.6 U
303.1C		0.04U	0.08U	0.05U	0.09U	0.05U	0.04U	0.06U	ND	23.9 U
	Mean <sup>(c)</sup>	0.15	ND <sup>(d)</sup>	0.10B	ND	ND	ND	ND	0.10 B	ND
	standard deviation	NA <sup>(e)</sup>	NA	0.01	NA	NA	NA	NA	0.10	NA
303.2A		0.46	0.08U	0.05U	0.09U	0.74	0.04U	0.42	1.16	23.6 U
303.2B	Lauritzen Channel/Mouth	0.26	0.10U	0.09B	0.11U	0.56	0.05U	0.27	0.92	29.1 U
303.2C		0.30	0.08U	0.05U	0.09U	0.64	0.04U	0.27	0.91	23.4 U
	Mean <sup>(c)</sup>	0.34	ND	0.09B	ND	0.65	ND	0.32	1.00	ND
	standard deviation	0.11	NA	NA	NA	0.09	NA	0.09	0.14	NA
303.3A		1.50	0.09U	0.05U	0.81	1.12	0.63	1.10	3.66	26.3 U
303.3B	Lauritzen Channel/ End	1.34	0.08U	0.20B	0.81	1.06	0.51	1.26	3.84	23.3 U
303.3C		2.60	0.12	0.33B	1.32	1.55	0.91	1.80	6.03	23.6 U
	Mean <sup>(c)</sup>	1.81	0.12	0.27B	0.98	1.24	0.68	1.39	4.51	ND
	standard deviation	0.69	NA	0.09	0.29	0.27	0.21	0.37	1.32	NA
303.4A	Santa Fe Channel/ End <sup>(f)</sup>	0.22	0.08U	0.09B	0.09U	0.35	0.04U	0.06U	0.44	24.2 U
303.6A		0.91	0.08U	0.14B	0.27	0.05U	0.04U	0.67	1.08	23.0 U
303.6B	Parr Canal	0.90	0.08U	0.21B	0.23	0.71	0.04U	0.53	1.68	24.2 U
303.6C		0.90	0.08U	0.23B	0.22	0.70	0.04U	0.57	1.72	22.6 U
	Mean <sup>(c)</sup>	0.90	ND	0.19B	0.24	0.71	ND	0.59	1.49	ND
	standard deviation	0.01	NA	0.05	0.03	0.01	NA	0.07	0.36	NA

Table 3.3. Concentrations of DDT and Dieldrin in the Dissolved Fraction of Water Samples Collected in March 2002 for Post-remediation Monitoring of the United Heckathorn Superfund Site

(a) U Undetected above given concentration.

(b) B Analyte detected in associated blank; sample concentration is <5X amount in blank. When any detected constituent is flagged B, the total DDT concentration was also flagged B.

(c) Mean calculated using only detected values.

(d) ND None detected.

(e) NA Not applicable.

(f) Sample containers for two of the three replicate water samples collected from 303.4 Santa Fe Channel End were broken during shipping.

Total suspended solids were not detected above 1 mg/L in any of the Year 5 water samples, so pesticide variability cannot easily be attributed to differences in suspended material concentrations. It is possible, however, that the pesticides could be associated with suspended material <1 mg/L, or organic material in dissolved or colloidal form.

Dissolved pesticide concentrations in water are shown in Table 3.3. Dissolved concentrations of DDT averaged 4.5 ng/L at Station 303.3 (Lauritzen Channel/End), or on average 24% of the total DDT at that station, indicating that a greater percentage of DDT could be associated with the small (<1 mg/L) particulate fraction. Dissolved DDT was lower (average 1 ng/L) at 303.2 (Lauritzen Channel/Mouth) and at the Parr Canal (average 1.5 ng/L), and less than 0.5 ng/L at 303.4 (Santa Fe Channel End) and 303.1 (Richmond Inner Harbor Channel). Dissolved DDT and dieldrin concentrations in Year 5 were approximately 50% of the Year 4 (2001) concentrations at most stations (Table 3.4).

As in previous years, Lauritzen Channel/End (Station 303.3) had the highest mean concentration of total DDT in 2002 (Table 3.5; Figure 3.1). Figure 3.1 shows water concentrations for all years at all stations, with Year 3 (2000) data for Station 303.3 plotted with and without the anomalous replicate which had much higher concentrations of DDT than the other two (Kohn and Kropp 2000). Total DDT concentrations in the total fraction of water samples collected from Lauritzen Channel in 2002 were lower than those measured in 2001 and 2000, except at Richmond Inner Harbor Channel (Figure 3.1). DDT was not detected in Richmond Harbor Channel in 2001 (Year 4), but it was detected in 2002 at a lower concentration than in 2000.

		Total DI	Dieldrin (ng/L)		
Station	Location	Year 4 (2001)	Year 5 (2002)	Year 4 (2001)	Year 5 (2002)
303.1	Richmond Inner Harbor Channel	0.33	0.10 B	0.34	0.15
303.2	Lauritzen Channel/ Mouth	2.57	1.00	0.46	0.34
303.3	Lauritzen Channel/ End	10.4	4.51	4.23	1.81
303.4	Santa Fe Channel/ End	2.21	0.44	0.47	0.22
303.6	Parr Canal	NS	1.49	NS	0.90

Table 3.4. Comparison of Year 4 and Year 5 Dissolved Pesticide Concentrations

(a) B Total DDT concentration is flagged B when a constituent is 4,4'-DDE was detected in associated blank at <5X amount in blank. When any detected constituent is flagged B, the

		Water Concentration (ng/L)							
Water		Remediation		1998	1999	2000	2001	2002	
Sample ID	D Location	Goal	Preremediation <sup>(a)</sup>	Postremediation	Postremediation	Postremediation	Postremediation	Postremediation	
Total DD1	<u> </u>								
303.1	Richmond Inner Harbor Channel	0.59	1	0.65	14.4	2.56	ND <sup>(b)</sup>	0.66	
303.2	Lauritzen Channel/Mouth	0.59	no sample	42.6	4.61	27.9	2.88	1.70	
303.3	Lauritzen Channel/End	0.59	50	103	62.3	83.7 (w/o rep b) 1773 (all reps)	142	18.4	
303.4	Santa Fe Channel/ End	0.59	8.6	11	19.2	3.70	2.51	0.60 (1 rep only)	
303.6	Parr Canal	0.59	not sampled	not sampled	not sampled	not sampled	not sampled	2.57	
Dieldrin									
303.1	Richmond Inner Harbor Channel	0.14	<1	0.65	0.62	1.57	ND	0.16	
303.2	Lauritzen Channel/Mouth	0.14	no sample	8.18	0.48	8.96	0.46	0.43	
303.3	Lauritzen Channel/End	0.14	18	18.1	12.5	83 (w/o rep b) 625 (all reps)	8.49	2.08	
303.4	Santa Fe Channel/ End	0.14	1.8	2.47	0.37	2.11	0.46	0.20 (1 rep)	
303.6	Parr Canal	0.14	not sampled	not sampled	not sampled	not sampled	not sampled	0.98	

Table 3.5. Comparison of Post-Remediation Concentration of Total DDT and Dieldrin in Total Fraction of Water Samples with Pren	remediation
Levels and Remedial Goal Concentrations	

(a) Preremediation water concentration is the average of samples collected in October 1991 and February 1992 for the Ecological Risk Assessment (Lee et al. (b) ND None detected.



<u>Figure 3.1</u>. Comparison of preremediation (Ecological Risk Assessment) and post-remediation total DDT concentrations in water samples (total fraction) collected at the United Heckathorn Site. The open triangle for Station 303.3 sampled in 2000 is the mean value of only two replicates.

The total DDT concentrations measured in Richmond Inner Harbor and Santa Fe Channel were just slightly higher than the remediation goal of 0.59 ng/L. Lauritzen Channel Mouth and Parr Canal total DDT concentrations in water were 3 to 4.5 times the remedial goal, whereas at Lauritzen Channel End, total DDT in water was 31 times the remedial goal. Although the bulk water samples show that the water quality goal is not yet being met, the concentrations are significantly lower than those measured in previous monitoring years.

Concentrations of dieldrin were below the MDL in two of three replicates of the total fraction of water samples collected at Richmond Inner Harbor Channel (Station 303.1) in Year 5. Dieldrin concentrations among replicate samples collected at the remaining four stations ranged from 0.16 ng/L to 3.0 ng/L (Table 3.2). Mean detected concentrations of dissolved dieldrin ranged from 0.15 ng/L to 1.81 ng/L (Table 3.3). Concentrations of dieldrin at all stations except Richmond Inner Harbor Channel were lower in 2002 than in 2001 (Figure 3.2, Table 3.5); at Richmond Inner Harbor Channel, dieldrin was undetected in all replicates in 2001, but detected at 0.16 ng/L in one replicate in 2002.



<u>Figure 3.2</u>. Comparison of preremediation (Ecological Risk Assessment) and post-remediation dieldrin concentrations in water samples (total fraction) collected at the United Heckathorn Site. The open triangle for station 303.3 sampled in 2000 is the mean value of only two replicates.

Water concentrations of total DDT were above remediation goals in all water samples and at all stations except Santa Fe Channel (Table 3.4, Figures 3.1 and 3.2). Water concentrations of dieldrin were above remediation goals at all stations, although dieldrin concentrations at Santa Fe Channel (0.20 ng/L) and Richmond Inner Harbor Channel (0.16 ng/L) were very close to the remediation goal of 0.14 ng/L. The most elevated contaminant concentrations were still found in water samples collected from Lauritzen Channel/End, where contaminated sediment remains and may be periodically resuspended by vessel traffic. However, water concentrations of DDT in Lauritzen Channel/End were much lower in 2002 than in previous monitoring years. Concentrations of both total and dissolved PCB Aroclor 1254 in water samples collected from all stations in 2002 were below the MDL. Aroclor 1254 was also undetected at all stations in 2001, but had been detected in both Lauritzen Channel stations in 2000.

An attempt to address replicate variability and suspended sediment influence was made by analyzing total suspended solids and dissolved and total pesticides and PCBs in water samples. At most stations, there was little difference between concentrations of analytes found in the total and dissolved fractions of the water samples (Tables 3.2 and 3.3). However, there were substantial differences in analyte concentrations in the two fractions at Lauritzen Channel/End: concentrations of total DDT and dieldrin in the dissolved fraction were much lower and much less variable than they were in the total fraction (Figures 3.3 and 3.4).



Figure 3.3. Comparison of total and dissolved total DDT in water, March 2002



Figure 3.4. Comparison of total and dissolved total dieldrin in water, March 2002

## **3.3 TISSUES**

Tissue samples from biomonitoring organisms provide a time-integrated indication of contaminant concentrations in the water column and are not as susceptible to small-scale temporal or spatial variability in contaminant concentrations as are water samples. For tissue analyses, all QC requirements, except the precision of the MS/MSD analysis for 4,4'-DDT (71% relative percent difference), were met. Both the MS and MSD spike recoveries were acceptable. The post-remediation tissue data are summarized in Table 3.6 and compared with preremediation data in Tables 3.7 (wet-weight basis) and Table 3.8 (lipid-normalized basis). Evaluation of wet-weight data is appropriate for ecological risk assessment because wet-weight data represent concentrations of contaminants available to consumers of the tissues. Lipid-normalization removes differences attributable to tissue moisture and lipid content, allowing a better assessment of bioavailability between years and stations (Figures 3.5 and 3.6).

As in previous years, Year 5 post-remediation levels of total DDT were highest at the Lauritzen Channel/End (Station 303.3) and decreased with distance from Station 303.3. Total DDT concentrations (wet weight) in resident mussels were 310  $\mu$ g/kg at Lauritzen Channel/End and 139  $\mu$ g/kg at Lauritzen Channel/Mouth (Station 303.2). At Santa Fe Channel/End (Station 303.4), total DDT levels were 24  $\mu$ g/kg. The lowest concentrations were found at Richmond Inner Harbor Channel (Station 303.1), where total DDT in tissues was 9.3  $\mu$ g/kg. Mussels from Parr Canal, which had not been monitored previously, had 40  $\mu$ g/kg total DDT in tissue. The trend for dieldrin in mussel tissues was similar, with the highest levels occurring at Lauritzen Channel/End (17  $\mu$ g/kg) and the lowest levels found at Richmond Inner Harbor Channel (0.68  $\mu$ g/kg). Dieldrin in Parr Canal mussels was 1.2  $\mu$ g/kg wet weight, approximately twice the levels in Santa Fe or Richmond Harbor Channels, but half the level of Lauritzen Channel/Mouth. Parr Canal mussel tissue DDT and dieldrin concentrations are higher than those in Santa Fe or Richmond Inner Harbor Channels.

Tissue burdens of total DDT from Year 5 of post-remediation biomonitoring decreased from Year 4 postremediation levels at all stations, and were the lowest measured since 1997 when remediation was completed (Table 3.7, Table 3.8, Figure 3.5). Present tissue DDT concentrations at all stations are at least an order of magnitude lower than preremediation and 6-month post-remediation tissue DDT concentrations. On a wet weight basis, tissue burdens of dieldrin were also lower in Year 5 than in Year 4, and, like DDT, an order of magnitude lower than both preremediation and 6-month postremediation tissue dieldrin concentrations (Table 3.7). Annual tissue analyses have shown very similar patterns of DDT and dieldrin fluctuation over the years of post-remediation monitoring (Figures 3.5 and 3.6).

	Sample ID and Concentration (µg/kg)									
	303.1		303.2	303.2		3.3	303.4	303.	6	
	Richmone	d Inner	Lauritz	zen	Laur	itzen	Santa Fe	Parr		
Analyte	Harbor C	nannel	Channel/I	Mouth	Chann	el/End	Channel/End	Canal		
2,4'-DDE	0.12	U	0.66		3.22	D10 <sup>(b)</sup>	0.21	0.13	U <sup>(a)</sup>	
4,4'-DDE	4.67		28.8		45.9	D10	6.27	10.8		
2,4'-DDD	1.41		13.0		43.5	D10	2.20	3.48		
4,4'-DDD	0.17	U	30.4		86.8	D10	6.31	12.1		
2,4'-DDT	0.24	U	25.0		48.9	D10	2.79	3.82		
4,4'-DDT	3.13		41.5	D5 <sup>(c)</sup>	82.1	D10	5.79	9.47		
Total DDT <sup>(d)</sup> (wet wt)	9.21		139.4		310.4		23.6	39.7		
Dieldrin (wet wt)	0.68		2.93		17.0		0.62	1.16		
Percent Dry Wt	8.79		8.20		9.80		7.39	7.93		
Total DDT (dry wt)	105		1700		3168		319	500		
Dieldrin (dry wt)	7.7		35.7		173		8.4	14.6		
Lipids (% dry wt)	8.65		7.44		8.57		7.31	8.58		
Total DDT (ppb <sup>(e)</sup> lipid)	1211		22846		36955		4365	5834		
Dieldrin (ppb lipid)	89.5		480		2024		115	171		
Aroclor 1254 (wet wt)	38.2		101	D5	113		42.0	55.7		
Aroclor 1254 (dry wt)	435		1232		1153		568	702		
Aroclor 1254 (ppb lipid)	5026		16557		13452		7778	8191		

<u>Table 3.6</u> .	Concentrations of DDT, Dieldrin, and PCB Aroclor 1254 in Tissue Samples Collected in
	March 2002 for Post-Remediation Monitoring of the United Heckathorn Site

(a) U Not detected at or above given concentration.

(b) D10 10X dilution required to quantify analytes.

(c) D5 5x dilution required to quantify analytes.

(d) Total DDT is sum of detected 2,4- and 4,4- DDD, DDE, and DDT.

(e) Parts per billion, lipid-normalized (µg contaminant/kg lipid).

		Preremediation			Post-Remediation					
Station Number	Station Name	State Mussel Watch <sup>(a)</sup> Transplant	Ecological Risk Assessment <sup>(b)</sup> Resident	1998 (Year 1) Resident	1999 (Year 2) Resident	2000 (Year 3) Resident	2001 (Year 4) Resident	2002 (Year 5) Resident		
Total DD7										
303.1	Richmond Inner Harbor Channel	47.0 <sup>(c)</sup>	40	127	30	52	25	9.3		
303.2	Lauritzen Channel/Mouth	$629^{(d)}$ 5074 <sup>(d)</sup>		1222	176	310	340	139		
303.3	Lauritzen Channel/End	1369 <sup>(c)</sup>	2,900	4504	606	522	1,136	310		
303.4	Santa Fe Channel/End	369 <sup>(c)</sup>	350	256	76	75	150	24		
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	40		
<u>Dieldrin</u>										
303.1	Richmond Inner Harbor Channel	7.7 <sup>(c)</sup>	4.0	5.4	1.9	5.4	0.7	0.7		
303.2	Lauritzen Channel/Mouth	$87^{(d)}$ $602^{(d)}$		40.3	6.5	28	6.3	2.9		
303.3	Lauritzen Channel/End	100 <sup>(c)</sup>	97	184	28	43	32.1	17.0		
303.4	Santa Fe Channel/End	33 <sup>(c)</sup>	19	8.2	2.8	6.4	3.3	0.6		
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	1.2		
Total PCB	<u>3s</u>									
303.1	Richmond Inner Harbor Channel	176 <sup>(c)</sup>	not measured	not measured	51	150	53	38		
303.2	Lauritzen Channel/Mouth	120 <sup>(d)</sup> 196 <sup>(d)</sup>	not measured	not measured	75	187	92	101		
303.3	Lauritzen Channel/End	137 <sup>(c)</sup>	not measured	not measured	124	169	158	113		
303.4	Santa Fe Channel/End	138 <sup>(c)</sup>	not measured	not measured	67	123	99	42.0		
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	56		

Table 3.7. Comparison of Pre- and Post-Remediation Tissue Concentrations of Total DDT, Dieldrin, and PCB (µg/kg wet weight)

(a) Most recent data available from State Mussel Watch program, transplanted California mussels (Rasmussen 1995).

(b) Average concentration in resident mussel tissue from samples collected in October 1991 and February 1992 (Lee et al., 1994).

(c) State Mussel Watch program sample from March 1991 (Rasmussen 1995).

(d) State Mussel Watch program sample from January 1988 (Rasmussen 1995).

23

		Prerem	nediation		Ро	st-Remediation	1	
	_	State Mussel	Ecological Risk	1998	1999	2000	2001	2002
Station		Watch <sup>(a)</sup>	Assessment <sup>(b)</sup>	(Year 1)	(Year 2)	(Year 3)	(Year 4)	(Year 5)
Number	Station Name	Transplant	Resident	Resident	Resident	Resident	Resident	Resident
Total DD7	<u> </u>							
303.1	Richmond Inner Harbor Channel	9,215 <sup>(c)</sup>	3,275	12,338	4,672	4,423	3,623	1,228
303.2	Lauritzen Channel/Mouth	78,481 <sup>(d)</sup>	not sampled	134,633	24,855	31,281	54,337	22,846
303.3	Lauritzen Channel/End	583,819 <sup>(d)</sup> 380,361 <sup>(c)</sup>	250,411	427,423	94,061	80,657	130,360	36,955
303.4	Santa Fe Channel/End	47,283 <sup>(c)</sup>	21,919	45,695	8,193	9,182	21,885	4,365
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	5,834
Dieldrin								
303.1	Richmond Inner Harbor Channel	1,507 <sup>(c)</sup>	322	525	293	457	103	89
303.2	Lauritzen Channel/Mouth	10,861 <sup>(d)</sup>	not sampled	4439	919	2,791	1,001	480
303.3	Lauritzen Channel/End	69,272 <sup>(d)</sup> 27,778 <sup>(c)</sup>	8,590	17463	4,410	6,598	3,685	2,024
303.4	Santa Fe Channel/End	$4,167^{(c)}$	1,126	1462	300	779	486	115
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	171
<u>Total PCB</u>	<u>Bs</u>							
303.1	Richmond Inner Harbor Channel	34,440	not measured	not measured	8,020	12,752	7,726	5,026
303.2	Lauritzen Channel/Mouth	14,981	not measured	not measured	10,599	18,842	14,673	16,557
303.3	Lauritzen Channel/End	30,305	not measured	not measured	19,255	26,112	18,136	13,452
303.4	Santa Fe Channel/End	17,667	not measured	not measured	7,302	15,028	14,546	7,778
303.6	Parr Canal	not sampled	not sampled	not sampled	not sampled	not sampled	not sampled	8191
		-	-	1	-	-	-	

Table 3.8. Comparison of Pre- and Post-remediation Lipid-Normalized Total DDT, Dieldrin, and PCBs in Tissues (µg/kg lipid)

(a) Most recent data available from State Mussel Watch program, transplanted California mussels (Rasmussen 1995).

(b) Average concentration in resident mussel tissue from samples collected in October 1991 and February 1992 (Lee et al., 1994).

(c) State Mussel Watch program sample from March 1991 (Rasmussen 1995).

(d) State Mussel Watch program sample from January 1988 (Rasmussen 1995).

24



Figure 3.5. Comparison of preremediation (Ecological Risk Assessment) and post-remediation total DDT concentrations in mussel tissue samples collected at the United Heckathorn Site.



<u>Figure 3.6</u>. Comparison of preremediation (Ecological Risk Assessment) and post-remediation dieldrin concentrations in mussel tissue samples collected at the United Heckathorn Site.

As in previous monitoring years, Aroclor 1254 was the only PCB detected in mussels collected from postremediation monitoring stations in 2002. Wet-weight PCB concentrations were highest in Lauritzen Channel/End (113  $\mu$ g/kg), and lowest at Richmond Harbor Inner Channel (38  $\mu$ g /kg) (Table 3.5). Year 5 tissue PCB concentrations at Lauritzen Channel/Mouth were about the same as they were in Year 4, whereas those from Lauritzen Channel/End were 28% lower than those in Year 4. PCB concentrations in mussels from Santa Fe and Richmond Inner Harbor Channels were 58% and 28% lower than those in Year 4, respectively. As with DDT and dieldrin, Parr Canal mussel PCB concentrations were closest to the Santa Fe Channel concentrations. PCBs in Year 5 resident mussels were below 1988 or 1991 (Mussel Watch) preremediation levels for transplanted mussels (9% to 70%; average 44% lower, wet weight basis).

# 3.4 PASSIVE WATER SAMPLERS

In 2002, polyethylene passive water samplers were deployed for one month at the four historical postremediation monitoring stations, to explore the relationship between biotic and abiotic indicators of pesticide bioavailability. Passive samplers are designed to sample only the dissolved fraction of pesticides in water, in contrast to mussels that filter bulk water that includes small particles and dissolved organic matter. If passive sampler and tissue data can be related, passive samplers have several advantages. For example, passive samplers can be deployed inexpensively relative to transplanting live organisms, they can be deployed in specific locations or heights in the water column, and they can be used in locations where biota do not occur. In addition, passive samplers are not subject to metabolic changes or physiological variability.

Passive sampler data are expressed as µg pesticide per kg of polyethylene material; results of pesticide analyses of the passive samplers at the monitoring stations are provided in Table 3.9. The passive samplers showed the same gradient of concentrations as the tissue and water samples with the highest total DDT and dieldrin concentrations occurring at Lauritzen Channel/End, decreasing with distance from Lauritzen Channel/Mouth to Santa Fe Channel/End, and with the lowest concentrations at the Richmond Inner Harbor Channel station. Passive sampler concentrations were surprisingly comparable with the dry weight tissue concentrations from the same stations-- within 35% of each other (Table 3.9)--despite differences in exposure duration, uptake rates, and unknown equilibrium state. While passive samplers have demonstrated their utility in accumulating contaminants occurring at sub-detection level in water and in source identification studies (Litten et al. 1993; Peterson et al. 1995), this comparability with field tissue data shows that passive samplers show promise in the area of contaminant measurements that can be related to a biological effect.

-	on (µg/kg polyethyle	ene)			
<u> </u>	303.1	303.2	303.3	303.4	
	Richmond Inner	Lauritzen	Lauritzen	Santa Fe	
Analyte	Harbor Channel	Channel Mouth	Channel End	Channel End	
2,4'-DDE	1.98	7.46	35.9	4.95	
4,4'-DDE	13.4	256	454	50.7	
2,4'-DDD	14.1	194	730	47.1	
4,4'-DDD	35.9	558	1380	115	
2,4'-DDT	5.61	188	685	27.4	
4,4'-DDT	12.0	501	1220	57.8	
Total <sup>(a)</sup> DDT in Passive					
Water Sampler	83.0	1704	4505	303	
Total DDT in Tissue					
(µg/g dry weight)	111	1700	3168	319	
Dissolved DDT in Water					
(ng/L)	0.10	1.0	4.5	0.44	
Dieldrin in Passive					
Water Sampler	9.31	97.3	478	23.9	
Dieldrin in Tissue					
(µg/g dry weight)	7.7	35.7	173	8.4	
Dissolved Dieldrin in					
Water (ng/L)	0.15	0.34	1.81	0.22	
Aroclor 1254 in Passive					
Water Sampler	122	1160	1520	182	

Table 3.9. Concentrations of DDT, Dieldrin, and PCB Aroclor 1254 in Passive Water Samplers, Year 5(2002) Post-Remediation Monitoring of the United Heckathorn Site

### 4.0 CONCLUSIONS

Results from the fifth post-remediation monitoring survey indicate that chlorinated pesticides appear to be less bioavailable throughout the study area than in previous years, although without prior monitoring we are unable to determine whether pesticide bioavailability in Parr Canal has changed since remediation. Water samples collected in March 2002 indicate that the total DDT and dieldrin concentrations in water throughout the study area, including Lauritzen Channel, were lower than preremediation levels. Year 5 water samples were generally lower in DDT and dieldrin than in previous monitoring years; however, water concentrations of DDT and dieldrin in Lauritzen Channel, Santa Fe Channel, and Parr Canal still exceed the remediation goals. Thus, remediation goals for total DDT and dieldrin in water have not yet been fully achieved for the study site.

Year 5 biomonitoring data show that total DDT and dieldrin appear to be substantially less bioavailable to resident mussels in Lauritzen, Santa Fe, and Richmond Harbor Channels than in previous years. Total DDT concentrations in mussels from all stations in Year 5 were 77% to 93% lower than the preremediation concentrations—generally a full order of magnitude lower. Dieldrin concentrations were 82% to 97% lower than preremediation concentrations, also a full order of magnitude lower. Total DDT concentrations in mussels from all stations were 59% to 84% lower in 2002 than in 2001, when some stations had exhibited increased bioavailability relative to the previous monitoring year. Dieldrin was also lower at all stations in 2002 relative to 2001. PCBs were lower in 2002 than in 2001 at all stations except Lauritzen Channel/Mouth, where PCBs were slightly (10%) higher in 2002 than in 2001.

The five years of post-remediation monitoring completed thus far fulfill the minimum requirement of the ROD. Biomonitoring using mussel tissues has provided documentation of changes in the long-term bioavailability of pesticides from the Lauritzen Channel sediment that cannot be assessed through water sample analyses alone. The experimental deployment of passive samplers showed promise for monitoring applications, but in the case of Heckathorn, resident mussels have proven most valuable for tracking long term bioavailability. Future monitoring may be appropriate pending the results of ongoing sediment and outfall investigations.

## **5.0 REFERENCES**

Antrim, L.D., and N.P. Kohn. 2000a. *Post-remediation Biomonitoring of Pesticides in Marine Waters Near the United Heckathorn Site, Richmond, California.* PNNL-11911, Rev. 1. Prepared for the U.S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.

Antrim, L.D., and N.P. Kohn. 2000b. *Post-remediation Biomonitoring of Pesticides and Other Contaminants in Marine Waters and Sediment Near the United Heckathorn Site, Richmond, California.* PNNL-13059, Rev 1. Prepared for the U.S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.

APHA (American Public Health Association). 1998. *Standard Methods for the Examination of Water and Wastewater*. APHA, Washington, D.C.

Battelle. 1992. *Quality Assurance Project Plan for Remediation Investigation and Feasibility Study of Marine Sediments at the United Heckathorn Superfund Site*. QA Plan EES-80, Rev. 0. Battelle Marine Sciences Laboratory, Sequim, Washington.

Battelle. 1997. *Field Sampling and Analysis Plan for Long-Term Post-remediation Monitoring at the United Heckathorn Superfund Site*. April 22, 1997. Prepared for U.S. Environmental Protection Agency, Region 9, San Francisco, California. Battelle Marine Sciences Laboratory, Sequim, Washington.

Battelle. 2002. Addendum 1 to the Quality Assurance Project Plan for Remediation Investigation and Feasibility Study of Marine Sediments at the United Heckathorn Superfund Site (QA Plan EES-80, Rev. 0). Battelle Marine Sciences Laboratory, Sequim, Washington.

Harbo, R.M. 1997. *Shells and Shellfish of the Pacific Northwest: A Field Guide*. Harbour Publishing, Nadeira Park, B.C., Canada.

Kohn, N. P., and T. J. Gilmore. 2000. *Field Investigation to Determine the Extent of Sediment Recontamination at the United Heckathorn Superfund Site, Richmond, California.* PNNL-13730. Prepared for the U.S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.

Kohn, N. P., and R. K. Kropp. 2000. Year 3 Post-Remediation Monitoring of Pesticides and Other Contaminants in Marine Waters Near the United Heckathorn Superfund Site, Richmond, California. PNNL-13286. Prepared for the U.S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.

Kohn, N. P., and R. K. Kropp. 2001. Year 4 Post-Remediation Monitoring of Pesticides and Other Contaminants in Marine Waters Near the United Heckathorn Superfund Site, Richmond, California. PNNL-13632. Prepared for the U.S. Environmental Protection Agency by Battelle Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.
Lee II, H., A. Lincoff, B.L. Boese, F.A. Cole, S.P. Ferraro, J.O. Lamberson, R.J. Ozretich, R.C. Randall, K.R. Rukavina, D.W. Schults, K.A. Sercu, D.T. Specht, R.C. Swartz, and D.R. Young. 1994. *Ecological Risk Assessment of the Marine Sediments at the United Heckathorn Superfund Site*. U. S. EPA, ERL-N: N269. Final Report to Region IX; Pacific Ecosystems Branch, ERL-N, U.S. Environmental Protection Agency, Newport, Oregon.

Lincoff, A. 1997. Results of Post-remedial Sediment Sampling at the United Heckathorn Superfund Site Richmond California. Memorandum to D. Vesperman dated April 1, 1997. U.S. Environmental Protection Agency Region 9 Laboratory, Richmond, California.

Lincoff, A.H., G.P. Costan, M.S. Montgomery, and P.J. White. 1994. *Feasibility Study for the United Heckathorn Superfund Site Richmond, California*. PNL-9991/UC-600. Prepared for the U.S. Environmental Protection Agency. Pacific Northwest Laboratory, Richland, Washington.

Litten, S., B. Mead, and J. Hassett. 1993. *Application of passive samplers (PISCES) to locating a source of PCBs on the Black River, New York.* Environ. Toxicol. Chem. 12(4): 639-647.

Petersen, S.M., S. C. Apte, G. E. Batley, and G. Coade. 1995. *Passive sampler for chlorinated pesticides in estuarine waters*. Chem. Spec. Bioavail. 7(3): 83-88.

Rasmussen, D. 1995. *State Mussel Watch Program 1987-1993 Data Report*. Report 94-1WQ. State Water Resources Control Board, California Environmental Protection Agency.

ROD (Record of Decision). 1996. United Heckathorn Superfund Site, Richmond, California. EPA ID# CAD981436363. U. S. Environmental Protection Agency, Region IX, San Francisco, California.

White, P.J., N.P. Kohn, W.W. Gardiner, and J.Q. Word. 1994. *The Remediation Investigation of Marine Sediment at the United Heckathorn Superfund Site*. PNL-9383. Prepared for the U.S. Environmental Protection Agency by Battelle/Marine Sciences Laboratory, Sequim Washington; published by Pacific Northwest Laboratory, Richland, Washington.

# APPENDIX A

## FIELD SUMMARY REPORT

Field Sampling Summary for Mussels, Surface Water, Sediments and Passive Samplers at the United Heckathorn Site in Richmond, California, conducted 2/6 - 3/5/2002.

> Andrew Lincoff EPA Region 9 Laboratory PMD-2 April 10, 2002

## **INTRODUCTION**

This sampling event involved the deployment of passive samplers and sediment traps in outfalls at the United Heckathorn Superfund Site and at other locations in Richmond Harbor in Richmond, California. The samplers were subsequently collected along with mussels and surface water samples. Deployment was performed on February 6, 2002 by Andrew Lincoff and Peter Husby of the EPA Region 9 Laboratory, and Carmen White, United Heckathorn RPM. Samples were collected on March 5, 2002 by Peter Husby, Carmen White and Patrick Borthwick, of the EPA Region 9 Laboratory. Sampling was performed in accordance with Battelle's "United Heckathorn Post-Remediation Field Monitoring Plan" (FSP), dated February 5, 1997, and "Sampling and Analysis Plan for the Investigation of Contaminant Source and Contaminant Movement in the Lauritzen Channel, United Heckathorn Site, Richmond, California" (SAP), drafted January 11, 2002.

## **OBJECTIVE**

EPA conducted this field sampling as part of the oversight of a final Remedial Action under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) at the United Heckathorn Site in Richmond, California. The sampling effort involved collecting physical environmental samples to analyze for the presence of hazardous substances.

The United Heckathorn Site was used to formulate pesticides from approximately 1947 to 1966. Soils at the Site and sediments in Richmond Harbor were contaminated with various chlorinated pesticides, primarily DDT, as a result of these pesticide formulation activities. The final remedy contained in EPA's October, 1994 Record of Decision addressed remaining hazardous substances, primarily in the marine environment. The major marine components of the selected remedy included:

- Dredging of all soft bay mud from the Lauritzen Channel and Parr Canal, with offsite disposal of dredged material.
- Marine monitoring to verify the effectiveness of the remedy.

The first component of the remedy selected in the ROD called for dredging all "young bay mud" from those channels in Richmond Harbor which contained average DDT concentrations greater than 590 ppb (dry wt.). The dredging was completed in April, 1997. The short-term monitoring, performed according to EPA's September 5, 1996 FSP, consisted of sediment chemistry monitoring to ensure that the average sediment concentration after dredging was below the cleanup level selected in the ROD. This monitoring was completed shortly prior to the placement of the sand cap in April, 1997. Subsequent monitoring has found some remaining contamination of surface sediment.

Long-term monitoring is addressed by Battelle's February 5, 1997 FSP. The purpose of the long-term monitoring is to demonstrate the effectiveness of the remedy. Prior to the remediation, mussels in the Lauritzen Channel contained the highest levels of DDT and dieldrin in the State, and surface water exceeded EPA's Ambient Water Quality Criteria for DDT by a factor of 50. Lower but still elevated levels were found in mussels and surface water in the Santa Fe Channel. It was concluded in EPA's Remedial Investigation that these elevated levels were the result of continuous flux from contaminated sediments. Approximately 98% of the mass of DDT in sediments in Richmond Harbor was removed by the remedial dredging. The long-term monitoring will demonstrate whether this action has succeeded in reducing the levels of DDT in mussels and surface waters.

Battelle's FSP included monitoring using both transplanted California mussels and resident Bay mussels. The first round of the long-term sampling occurred in January, 1998. This is the fifth annual round of sampling. The seasonal timing was chosen to match the protocol used by the California State Mussel Watch Program, in order to permit comparison with the State's results over the past 15 years. In the first two rounds, both transplanted and resident mussels are analyzed to determine any difference. Based on the results of the first two rounds and discussions with California State Mussel Watch Program personnel, only resident mussels were collected in subsequent rounds. Mussels and water samples collected on March 6, 2002 were shipped to Battelle for analysis.

Battelle's SAP contains additional monitoring of sediments, sediment traps in outfalls, and passive samplers in an attempt to determine contaminant sources. The sediment traps and passive samplers were deployed on February 6 and collected on March 6, 2002. The passive samplers were shipped to Battelle for analysis. Sediment samples collected on February 6 were returned to the EPA Region 9 Laboratory for analysis. Additional sediment samples and the sediment traps were collected by the Battelle field team during the week of March 11, 2002.

## FIELD NOTES AND OBSERVATIONS

1. Sediment traps manufactured by Battelle were deployed at two outfalls in the Lauritzen Channel on February 6, 2002. The GPS locations of the sediment traps are listed in Table 1. The first sediment trap (ST-1) was deployed in the large storm drain outfall at the head of the channel as shown in Photo 1. Clear water was flowing from the storm drain. The flow was approximately 1 inch deep. The end of the storm drain was not square so most of the flow poured out below the trap although there was a small continuous flow through the trap. The second sediment trap (ST-2) was placed in an 8-inch pipe on the eastern shore of the Lauritzen Channel as shown in Photo 2. Again the pipe was not square so the small flow of about 100 drops per minute did not go through the trap. An attempt was made to place another sediment trap on a 5  $\frac{1}{2}$  inch pipe hear ST-2, but none of the trap mounts were small enough. The 5  $\frac{1}{2}$  inch pipe had no flow and contained no sediment.

2. Eight passive polyethylene samplers were placed in the Lauritzen, Santa Fe and Richmond Inner Harbor Channels on February 6, 2002. Two were placed in the two outfalls with sediment traps (ST-1 and ST-2). PS-1 was placed 128 inches up the storm drain and PS-2 was placed approximately one foot up the pipe. PS-3 was hung from the remnants of a small pier on the eastern shore of the northern Lauritzen, shown in Photo 3. PS-4 was hung from a ladder beneath the Manson pier on the western shore of the Lauritzen, shown in Photo 4. The locations of PS-5, PS-6, PS-7 and PS-8 are approximately the same as the routine mussel sampling stations 303.3 (northern Lauritzen), 303.2 (Lauritzen mouth), 303.4 (Santa Fe), and 303.1 (Richmond Inner Harbor Channel mouth). No photos are available for PS-5 and PS-6. PS-7 is shown in Photo 5 and PS-8 in Photo 6. The GPS locations of the passive samplers are also listed in Table 1.

3. Additional pipes which were not sampled are shown in Photos 8 and 9. The GPS location for the 'L'-shaped pipe in Photo 7 is 37° 55' 25.207" N, 122° 21' 59.031" W. The 'L'-shaped pipe had a gate valve which appeared to be closed. The pipe in Photo 8 was under the Levin pier at station 20. No accurate GPS reading could be taken for this pipe because of its location under the pier. An approximate GPS location is the same as listed in Table 1 for sediment sample S-5, discussed below. Two outfalls that were identified on a City of Richmond drainage map as discharging to Lauritzen Channel (15 and 21 inch diameter) were planned for passive sampler and sediment sampling, but the two pipes were not found at low tide.

4. Sediment samples were collected from the storm drain (S-1) and 8 inch pipe (S-2) shown in Photos 1 and 2. Two sediment samples were collected from the Lauritzen Channel embankment near the small floating dock next to the Levin pier. These samples were taken from a distinct light sediment layer (S-3) overlying a darker layer (S-4) shown in Photo 9. An additional sediment sample (S-5) was collected from a light-colored soil layer near the base of the pipe under the Levin pier at station 20, shown in Photo 8. The soil was about 5 feet above the water level. The GPS location for this sample is approximate because it was under the pier. The location coordinates given for this sample are from the closest point outside the pier where GPS satellites

could be received. The sediment samples were promptly submitted on 2/6/02 to the Region 9 Lab for analysis of pesticides and PCBs.

5. The passive samplers, seawater samples, and resident bay mussels were collected on March 5, 2002, with the exception of PS-2 which was retrieved on March 14 by Battelle. The seawater and mussel samples were given the routine Mussel Watch station numbers 303.1 to 303.4 used in the previous annual collections. An additional station was established in the Parr Canal and given station number 303.6. Three gallons of seawater were collected from approximately one foot below the surface at each location. An additional two gallons were collected at station 303.2 for lab QC. Forty-five mussels were collected at each station. The mussels were all collected near the surface, which at the collection time was approximately at 1 ft above Mean Lower Low Water (MLLW) except for station 303.4 where the mussels were collected near the surface from a floating dock. The samples were promptly delivered to the Region 9 Lab and the seawaters and passive samplers were placed in a 4 C cold room. The mussels were cleaned of gross debris in the laboratory's clean filtered seawater, wrapped in ashed foil, placed in zip-loc bags, and stored in a -20° C freezer. The passive samplers, seawaters and mussels were packaged and shipped on March 7, 2002 by Fed Ex to Battelle for analysis of pesticides and PCBs.

	GPS Coordin	ates (NAD 83) <sup>(a)</sup>	
Sample ID	Lat	Long	Remarks
ST-1, PS-1, S-1	37° 55' 28.589" N	122° 21' 59.477" W	sed. trap, passive sampler, sediment
ST-2, PS-2, S-2	37° 55' 25.556" N	122° 21' 59.441" W	sed. trap, passive sampler, sediment
PS-3	37° 55' 25.760" N	122° 21' 59.551" W	passive sampler
PS-4	37° 55' 21.523" N	122º 22' 02.221" W	passive sampler
PS-5, 303.3	37° 55' 28.589" N	122° 21' 59.477" W	passive sampler, seawater, mussels
PS-6, 303.2	37° 55' 22.699" N	122° 22' 00.094" W	passive sampler, seawater, mussels
PS-7, 303.4	37° 55' 21.235" N	122° 22' 17.684" W	passive sampler, seawater, mussels
PS-8, 303.1	37° 54' 32.869" N	122° 21' 33.523" W	passive sampler, seawater, mussels
303.6	37° 55' 11.817" N	122° 21' 45.996" W	seawater, mussels
S-3, S-4	37° 55' 28.589" N	122° 21' 59.477" W	sediment
S-5	37° 55' 18.717" N	122° 22' 00.899" W	sediment

## Table 1. Sample Locations

(a) Location coordinates were determined using GPS with differential correction.



Photo 1 - Sediment Trap 1 (ST-1) and Passive Sampler 1 (PS-1) installation. 2/6/02.



Photo 2 - Sediment Trap 2 (ST-2) and Passive Sampler 2 (PS-2) installation. 2/6/02.



Photo 3 - Passive Sampler 3 (PS-3) installation, northern Lauritzen Channel. 2/6/02.



Photo 4 - Passive Sampler 4 (PS-4) installation, beneath Manson dock. 2/6/02.



Photo 5 - Passive Sampler 7 (PS-7) installation, Santa Fe Channel. 2/6/02.



Photo 6 - Passive Sampler 8 (PS-8) installation, Richmond Inner Harbor Channel. 2/6/02.



Photo 7 - 'L'-shaped pipe with gate valve. 2/6/02.



Photo 8 - Pipe under Levin dock near sediment sample S-5. 2/6/02.

# APPENDIX B

# ANALYTICAL RESULTS FROM WATER AND TISSUE SAMPLES

### WATER QA/QC SUMMARY

PROJECT:	Heckathorn Biomonitoring Year 5
PARAMETER:	Pesticides, PCBs
LABORATORY:	Battelle/Marine Sciences Laboratory, Sequim, Washington
MATRIX:	Water, total and dissolved

**SAMPLE CUSTODY:** Five water samples (triplicate containers of each) were received on 3/8/02 in multiple coolers. Cooler temperatures ranged from 2.8°C to 6.2°C. All containers were received in good condition with the exception of sample 303.4 (1780-4): 2 of the 3 bottles for that sample arrived broken. One additional water sample was received in good condition on 3/13/02. The cooler temperature upon arrival was 5.8°C. Samples were assigned a Battelle Central File (CF) identification number (1780) and were entered into Battelle's log-in system.

#### QA/QC DATA QUALITY OBJECTIVES:

					Detect	on Limits
Analyte	Extraction <u>Method</u>	Analytical <u>Method</u>	Range of Recovery	Relative Precision	Target (ng/L)	Achieved (ng/L)
2,4'-DDE	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.15
Dieldrin	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.08
4,4'-DDE	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.09
2,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.16
4,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.09
2,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0.07
4,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	5	0,10
PCB Aroclor 1242	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	50	43.5
PCB Aroclor 1248	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	50	43.5
PCB Aroclor 1254	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	50	43.5
PCB Aroclor 1260	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	50	43.5

#### **METHOD:**

On arrival at the laboratory, approximately ½ of each of the water samples (except 1780-11, Outfall) were centrifuged. The supernatant liquid was analyzed as the dissolved fraction. The uncentrifuged water was analyzed as the total fraction.

Water samples for analysis of chlorinated pesticides and PCBs were processed according to Battelle SOP MSL-O-010, *Extraction and Clean-Up of Water for Surrogate Internal Standard Method*. Water samples were extracted with methylene chloride. Interferences were removed by aluminum/silicon column chromatography. Sample extracts were then transferred to cyclohexane and analyzed by capillary-column (DB-1701) gas chromatography with electron-capture detection (GC/ECD) according to SOP MSL-O-004, *Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection*, which is based on EPA Method 8081.

HOLDING TIMES: All extractions and analyses were conducted within target holding times: 14 days to extraction, and 40 days to analysis after extraction. Samples were collected on 3/5/02, received on 3/8/02, and held at 4°C. Samples were extracted from 3/8/02 to 3/18/02 and analyzed from 3/21/00 to 3/27/02. The sample that arrived separately on 3/13/02 was extracted on 3/18/02 and analyzed in the same batch as the initial samples.

# WATER QA/QC SUMMARY

DETECTION LIMITS:	Detection limits were determined by a previously conducted MDL study where replicates were analyzed and the standard deviation was multiplied by the Student's-t value for the number of replicates. Sample detection limits are calculated using the achieved detection limit and the sample volume.
METHOD BLANKS:	One method blank was analyzed with the set of samples. None of the analytes of interest were detected in Blank 1; 4,4'-DDE was detected in Blank 2 (associated with dissolved samples) at a concentration less than 5 times its MDL. Dissolved samples with 4,4'-DDE detected at concentrations less than 5 times their blank values were flagged with a "B".
BLANK SPIKES:	Two pairs of blank samples (reagents only, carried through all sample preparation processes) were spiked with 33.3 ng/L Dieldrin and 4,4'- DDT, and 333 ng/L Aroclor 1254. Blank spike recoveries of the three spiked analytes of interest ranged from 65% to 105%, and were within the target range of 40%-120%.
MATRIX SPIKES AND MATRIX SPIKE DUPLICATES:	Two pairs of matrix spike samples (MS A and MS B) were prepared and analyzed using additional portions of sample 303.2. Three analytes of interest, dieldrin, 4,4'-DDT, and Aroclor 1254, were spiked into the samples at concentrations of 13.9 ng/L dieldrin and 4,4'-DDT, and 139 ng/L Aroclor 1254 in the first MS A/MS B pair, and 18.9 ng/L dieldrin and 4,4'-DDT, and 189 ng/L Aroclor 1254 in the second MS A/ MS B pair. Matrix spike recoveries ranged from 66% to 115%, and were within the target range of 40%-120%.
	Replicate precision of the MS A/MS B analyses, expressed as the RPD between the MS A and MS B pairs, was within the QC criteria of $\pm 30\%$ for dieldrin (0% and 12%); 4,4'-DDT (2% in both pairs); and Aroclor 1254 (1% in both pairs).
REPLICATES:	Two portions of sample 1780-2 (303.2) were analyzed in duplicate for the analytes of interest. Precision of duplicate analysis is determined by calculating the relative percent difference (RPD) of replicate results. In the first pair of duplicates, RPDs of all detected analytes of interest ranged from 13% to 25%, and were all within the QC limits of $\pm$ 30%. In the second pair of duplicates, RPDs of all detected analytes of interest ranged from 32% to 54%, exceeding the QC limits of $\pm$ 30%; however, the concentrations of these analytes in the sample were less than 10 times their respective MDLs.
SURROGATE RECOVERIES:	Chlorinated compounds PCBs 103 and 198 were added to each sample during the preparation step as surrogates to assess the efficiency of the extraction procedure. Recoveries of surrogate PCB 198 exceeded the target range of 40%-120% in three samples: 138% in 1780-1b (300.1); 139% in 1780-11 (Outfall); and 132% in Blank 2 Spike B. The data were flagged and no other corrective action was taken. Surrogate recoveries among all other analyses ranged from 40.2% to 118% and were within the target range.

BATTELLE MARINE SCIENCES 1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643	LABORATORY				Pe	ED HECKATHOR esticides in Water ples Received 3/8/	N	Print Date: 08/22/2002
LOCATION:	<b>Richmond Chann</b>	el. Total			<b>Richmond Chanr</b>	nel. Dissolved		
MSL Code	1780-1a	1780-1b	1780-1c		1780-1a	1780-1b	1780-1c	and the second se
STATION NO	300.1	300.1	300.1	TOTAL	300.1	300.1	300.1	DISSOLVED
	Total	Total	Total	RSD	Dissolved	Dissolved	Dissolved	RSD
Matrix	Water	Water	Water		Water	Water	Water	19 - Mar 19 - 20 - 20 - 20 - 20 - 20 - 20 - 20 - 2
Extraction Date	03/08/2002	03/08/2002	03/08/2002		03/09/2002	03/09/2002	03/09/2002	
Dilution	1x	1x	1x		1x	1x	1x	
Analytical Batch	1	1	1		1	1	1	
Unit	ng/L	ng/L	ng/L		ng/L	ng/L	ng/L	
2,4'-DDE	0.06 U	0.07 U	0.06 U	NA	0.08 U	0.08 U	0.08 U	NA
Dieldrin	0.03 U	0.16	0.03 U	NA	0.15	0.04 U	0.04 U	NA
4,4'-DDE	0.06	0.07	0.16	57%	0.09 B	0.11 B	0.05 U	NA
2,4'-DDD	0.13	0.18	0.21	23%	0.09 U	0.08 U	0.09 U	NA
4,4'-DDD	0.26	0.36	0.56	39%	0.05 U	0.05 U	0.05 U	NA
2,4'-DDT	0.03 U	0.04 U	0.03 U	NA	0.04 U	0.04 U	0.04 U	NA
4,4'-DDT	0.04 U	0.05 U	0.05 U	NA	0.06 U	0.05 U	0.06 U	NA
AROCLORS								
1242	17.9 U	21.7 U	19.0 U		23.4 U	22.6 U	23.9 U	
1248	17.9 U	21.7 U	19.0 U		23.4 U	22.6 U	23.9 U	
1254	17.9 U	21.7 U	19.0 U		23.4 U	22.6 U	23.9 U	
1260	17.9 U	21.7 U	19.0 U		23.4 U	22.6 U	23.9 U	
SURROGATE RECOVERIES (%)								
PCB103	85.1	89.7	84.2		71.9	113	90.7	
PCB198	102	100	99.4		83.8	138 #	105	
								1.000
TOTAL SUSPENDED SOLIDS (n TSS	ng/L) 1.0 U	1.0 U	1.0 U					
TSS Duplicate	1.0 0	1.0 0	1.0 0					
RPD								
U Not detected at or above DI B Concentration is less than 5 # Outside QAQC limits (SIS 44 NQ Not quantifiable	x blank value	D)						

:

÷

B.3

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643					Pe	ED HECKATHOI sticides in Water les Received 3/8		
LOCATION:	Lauritzen - South	n, Total			Lauritzen - Sout	h, Dissolved		
MSL Code	1780-2a	1780-2b	1780-2c		1780-2a	1780-2b	1780-2c	
STATION NO	303.2	303.2	303.2	TOTAL	303.2	303.2	303.2	DISSOLVED
	Total	Total	Total	RSD	Dissolved	Dissolved	Dissolved	RSD
Matrix	Water	Water	Water		Water	Water	Water	
Extraction Date	03/08/2002	03/08/2002	03/08/2002		03/11/2002	03/09/2002	03/11/2002	
Dilution	1x	1x	1x		• 1x	1x	1x	
Analytical Batch	1	1 . L	· 1		1	1	1	
Unit	ng/L	ng/L	ng/L		ng/L	ng/L	ng/L	
2.4'-DDE	0.07 U	0.09	0.09 U		0.08 U	0.10 U	0.08 U	NA
Dieldrin	0.42	0.37	0.50	15%	0.46	0.26	0.30	31%
4,4'-DDE	0.13	0.21	0.19	24%	0.05 U	0.09 B	0.05 U	NA
2,4'-DDD	0.07 U	0.06 U	0.10 U	NA	0.09 U	0.11 U	0.09 U	NA
4,4'-DDD	0.78	0.77	0.83	4%	0.74	0.56	0.64	14%
2,4'-DDT	0.24	0.22	0.04 U	- NA	0.04 U	0.05 U	0.04 U	NA
4,4'-DDT	0.67	0.47	0.49	20%	0.42	0.27	0.27	27%
AROCLORS								
1242	19.9 U	16.6 U	25.9 U		23.6 U	29.1 U	23.4 U	
1248	19.9 U	16.6 U	25.9 U	100	23.6 U	29.1 U	23.4 U	
1254	19.9 U	16.6 U	25.9 U		23.6 U	29.1 U	23.4 U	
1260	19.9 U	16.6 U	25.9 U		23.6 U	29.1 U	23.4 U	
SURROGATE RECOVERIES (%)								
PCB103	82.1	84.3	80.0		87.7	89.5	79.3	
PCB198	99.7	. 99.5	104		104	115	97.5	
TOTAL SUSPENDED SOLIDS (mg								
TSS	1.0 U							
TSS Duplicate RPD		ţ						
U Not detected at or above DL s B Concentration is less than 5x # Outside QAQC limits (SIS 40-	blank value	6D)						

B.4

Þ

Print Date: 08/22/2002

360/681-3643					Samp	sticides in Water les Received 3/8		
LOCATION:	Lauritzen - North			**************************************	Lauritzen - North			1000
MSL Code	1780-3a	1780-3b	1780-3c		1780-3a	1780-3b	1780-3c	
STATION NO	303.3	303.3	303.3	TOTAL	303.3	303.3	303.3	DISSOLVED
·····	Total	Total	Total	RSD	Dissolved	Dissolved	Dissolved	RSD
Matrix	Water	Water	Water		Water	Water	Water	
Extraction Date	03/08/2002	03/09/2002	03/09/2002		03/11/2002	03/11/2002	03/11/2002	
Dilution	1x ·	1x	1x		1x	1x	1x.	
Analytical Batch	· · · · · · · · · · · · · · · · · · ·	1	1		1	1	- 1	
Unit	ng/L	ng/L	ng/L		ng/L	ng/L	ng/L	Constraint and the second
2,4'-DDE	0.06 U	0.06 U	0.06 U	- NA	0.09 U	0.08 U	0.12	N/
Dieldrin	1.50	1.72	3.01	39%	1.50	1.34	2.60	38%
4,4'-DDE	0.31	0.53	0.79	44%	0.05 U	0.20 B	0.33 B	N/
2,4'-DDD	0.85	0.86	1.89	50%	0.81	0.81	1.32	30%
4,4'-DDD	1.23	1.50	2.70	43%	1.12	1.06	1.55	21%
2,4'-DDT	0.73	0.94	2.50	70%	0.63	0.51	0.91	30%
4,4'-DDT	2.37	9.28	28.8	102%	1.10	1.26	1.80	26%
AROCLORS								
1242	19.2 U	18.5 U	17.3 U		26.3 U	23.3 U	23.6 U	
1248	19.2 U	18.5 U	17.3 U		26.3 U	23.3 U	23.6 U	
1254	19.2 U	18.5 U	17.3 U		26.3 U	23.3 U	23.6 U	
1260	19.2 U	18.5 U	17.3 U		26.3 U	23.3 U	23.6 U	
SURROGATE RECOVERIES (%)								
PCB103	87.5	79.2	85.6		40.2	41.7	43.4	
PCB198	108	90.0	103		49.6	46.7	53.8	
TOTAL SUSPENDED SOLIDS (m	ad )							
TSS	1.0 U	1.0 U	1.0 U					
TSS Duplicate	1.0 U	1.0 0						1.11
RPD	NA							
U Not detected at or above DL	chown							

WATER Results, Year 5

Page 3

Print Date: 08/22/2002

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

UNITED HECKATHORN Pesticides in Water Samples Received 3/8/02

LOCATION:	Santa Fe Channel, Total and Disso	bived
MSL Code	1780-4	1780-4
STATION NO	303.4	303.4
	Total	Dissolved
Matrix	Water	Water
Extraction Date	03/09/2002	03/12/2002
Dilution	1x	1x
Analytical Batch	1	1
Unit	ng/L	ng/L
2,4'-DDE	0.06 U	0.08 U
Dieldrin	0.20	0.22
4,4'-DDE	0.14 B	0.09 B
2,4'-DDD	0.07 U	0.0 <del>9</del> U
4,4'-DDD	0.36	0.35
2,4'-DDT	0.03 U	0.04 U
4,4'-DDT	0.10	0.06 U
AROCLORS		
1242	18.3 U	24.2 U
1248	18.3 U	24.2 U
1254	18.3 U	24.2 U
1260	18.3 U	24.2 U
SURROGATE RECOVERIES (%)		
PCB103	86.7	42.1
PCB198	107	48.7
TOTAL SUSPENDED SOLIDS (m	10/L)	
TSS	1.0 U	- 
TSS Duplicate		
RPD	·	

U Not detected at or above DL shown

B Concentration is less than 5x blank value

# Outside QAQC limits (SIS 40-120%R; RPD <30%D)

NQ Not quantifiable

BATTELLE MARINE SCIEI 1529 West Sequim Bay Roa Sequim, WA 98382-9099 360/681-3643	ad				Pe Samp	ED HECKATHOR esticides in Water eles Received 3/8/		Print Date: (	08/22/2002
LOCATION:	Parr Canal, Tota			<u>A.</u>	Parr Canal, Dise			and the second second	
MSL Code	1780-5a	1780-5b	1780-5c		1780-5a	1780-5b	1780-5c		
STATION NO	303.5	303.5	303.5	TOTAL	303.5 Disastand	303.5 Disastand	303.5 Discubus d	DISSOLVED	
Matrix	Total Water	Total Water	Total Water	RSD	Dissolved Water	Dissolved Water	Dissolved Water	RSD	
Extraction Date	03/09/2002	03/09/2002	03/09/2002		03/12/2002	03/12/2002	03/12/2002		
Dilution	1x	1x	1x		1x	1x	1x	1.2	
Analytical Batch	1	. 1	1	200 A	. 1	1	1	200 C 100	
Unit	ng/L	ng/L	ng/L		ng/L	ng/L	ng/L		· .
2,4'-DDE	0.06 U	0.06 U	0.06 U		0.08 U	0.08 U	0.08 U	NA	
Dieldrin	0.99	0.98	0.96	2%	0.91	0.90	0.90	1%	
4,4'-DDE	0.36	0.32 0.29	0.31 0.27	8%	0.14 B 0.27	0.21 B 0.23	0.23 B 0.22	24% 11%	
2,4'-DDD 4,4'-DDD	0.29	0.90	0.27		0.27 0.05 U	0.23	0.22	70%	
2,4'-DDT	0.53	0.24	0.80	6%	0.03 U 0.04 U	0.04 U	0.04 U	64 S NA	
4,4'-DDT	0.89	0.84	0.81	5%	0.67	0.53	0.57	12%	
4,4-001	0.00	0.04	0.01		0.07	0.00	0.07		
AROCLORS								1000	
1242	17.2 U	18.1 U	16.5 U		23.0 U	24.2 U	22.6 U		
1248	17.2 U	18.1 U	16.5 U		23.0 U	24.2 U	22.6 U		
1254	17.2 U	18.1 U	16.5 U		23.0 U	24.2 U	22.6 U		
1260	17.2 U	18.1 U	16.5 U		23.0 U	24.2 U	22.6 U		
SURROGATE RECOVERIE									
PCB103	86.5	82.2	83.1		40.6	40.4	40.5		
PCB198	103	98.7	96.6		45.5	46.6	45.4		
TOTAL SUSPENDED SOLI									
TSS	1.0 U	1.0 U	1.0 U						
TSS Duplicate	1.0 0	1.0 0	1.0 0					Cul.	
RPD								1.044	
U Not detected at or abo B Concentration is less t # Outside QAQC limits (S NQ Not quantifiable		%D)							

**B**.7

WATER Results, Year 5

.

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

#### UNITED HECKATHORN Pesticides in Water

Samples Received 3/8/02

		BSA			BSB				BSA			BSB		
MSL Code	Blank 1	Blank 1 Spike A	Spike	Percent	Blank 1 Spike B	Spike	Percent	Blank2	Blank 2 Spike A	Spike	Percent	Blank 2 Spike B	Spike	Percent
STATION NO	Total	Spike A	Amount	Recovery	Shike P	Amount	Recovery	Dissolved	Spike A	Amount	Recovery	Shike P	Amount	Recovery
Matrix	Water	Water	Amount	newvery	Water	Anount	newvery	Water	Water	Anount	nettively	Water	Amount	neuvery
Extraction Date	03/08/02	03/08/02			03/08/02			03/09/02	03/09/02			03/09/02		
Dilution	1x	1x			1x			1x	1x			1x		
Analytical Batch	1	1	-		1			- 1	1			1		
Unit	ng/L	ng/L_	ng/L	%	ng/L	ng/L	%	ng/L	ng/L	ng/L	%	ng/L	ng/L	%
2,4'-DDE	0.15 U	0.15 U	NS	NA -	0.15 U	NS	NA	0.15 U	1.69	NS	NA	0.15 U	NS	NA
Dieldrin	0.08 U	25.7	33.3	77%	27.0	33.3	81%	0.08 U	23.1	33.3	69%	21.8	33.3	65%
4,4'-DDE	0.09 U	0.09 U	NS	NA	0.09 U	NS	NA	0.09	0.09 U	NS	NA	0.09 U	NS	NA
2,4'-DDD	0.16 U	0.16 U	NS	NA	0.16 U	NS	NA	0.16 U	17.8	NS	NA	0.16 U	NS	NA
4,4'-DDD	0.09 U	0.09 U	NS .	NA	0.09 U	NS	NA	0.09 U	0.09 U	NS	NA	0.09 U	NS	NA
2,4'-DDT	0.07 U	0.07 U	NS	NA	0.07 U	NS	NA	0.07 U	0.07 U	NS	NA	0.07 U	NS	NA
4,4'-DDT	0.10 U	32.8	33.3	98%	35.0	33.3	105%	0.10 U	32.7	33.3	98%	31.0	33.3	93%
AROCLORS														
1242	43.5 U							43.5 U						
1248	43.5 U							43.5 U						
1254	43.5 U	328	333	98%	346	333	104%	43.5 U	309	333	93%	297	333	89%
1260	43.5 U							43.5 U						
SURROGATE REC	COVERIES (%)													
PCB103	84.4	92.6			93.8			91.2	103			107		
PCB198	109	107			110			104	118			132 #		

TOTAL SUSPENDED SOLIDS (mg/L) TSS 1.0 U

U Not detected at or above DL shown

B Concentration is less than 5x blank value

# Outside QAQC limits (SIS 40-120%R; RPD <30%D)

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

**B**.9

#### UNITED HECKATHORN Pesticides in Water

Samples Received 3/8/02

	Lauritzen - South	MSA			MSB				Lauritzen - South	MSA			MSB			
MSL Code	1780-2a	1780-2 <sup>(a)</sup>	Spike	Percent	1780-2 <sup>(a)</sup>	Spike	Percent		1780-2a	1780-2 <sup>(b)</sup>	Spike	Percent	1780-2 <sup>(b)</sup>	Spike	Percent	
STATION NO	303.2	303.2			303.2				303.2	303.2			303.2			
	Total		Amount	Recovery	Spike B	Amount	Recovery	RPD	Dissolved	Spike A	Amount	Recovery	Spike B	Amount F	lecovery	RPD
Matrix	Water	Water			Water				Water	Water			Water			
Extraction Date	03/08/02	03/08/02			03/08/02				03/11/02	03/11/02			03/11/02			
Dilution	1x	1x			1x				1x	1x			1x			
Analytical Batch	h 1	1			1				1	1			1			
Unit	ng/L.	ng/L	ng/L	%	ng/L_	ng/L	%	%	ng/L	ng/L	ng/L	%	ng/L	ng/L.	%	%
2.4'-DDE	0.07 U	0.79	NS	NA	0.06 U	NS	NA		0.08 U	1.05	NS	NA	1.14	NS	NA	
Dieldrin	0.42	10.2	13.9	70%	10.1	13.7	71%	0%	0.46	12.9	18.9	66%	15.4	20.2	74%	12%
4,4'-DDE	0.13	0.69	NS	NA	0.70	NS	NA		0.05 U	0.93	NS	NA	0.05 U	NS	NA	
2,4'-DDD	0.07 U	7.77	NS	NA	7.91	NS	NA		0.09 U	0.09 U	NS	NA	11.5	NS	NA	
4,4'-DDD	0.78	0.04 U	NS	NA	0.04 U	NS	NA		0.74	0.05 U	NS	NA	0.05 U	NS	NA	
2,4'-DDT	0.24	0.03 U	NS	NA	0.03 U	NS	NA		0.04 U	0.04 U	NS	NA	0.04 U	NS	NA	
4,4'-DDT	0.67	14.9	13.9	102%	15.0	13.7	105%	2%	0.42	19.9	18.9	103%	20.9	20.2	101%	2%
AROCLORS																
1242	19.9 U								23.6 U							
1248	19.9 U								23.6 U							
1254	19.9 U	157	139	113%	153	137	112%	1%	23.6 U	214	189	113%	232	202	115%	1%
1260	19.9 U								23.6 U							
SURROGATE I	RECOVERIES (%)															
PCB103	82.1	86.0			85.4				87.7	41.6		2	42.7			
PCB198	99.7	103			101				104	47.4			49.8			
	ENDED SOLIDS (mg/L)															
TSS																
U Not detec	ted at or above DL show	wn.														
	ation is less than 5x blan															
	AQC limits (SIS 40-1209		5D)												·	
		Bottle "d" was	•	Poeticido M	SAMSB				(B) NOTE	Bottle "d" was	e used for	Posticido M	SAMSB			
	NOTE.	Dome u was	useu 101	- caucide Ma					NOTE:	boule u was	s useu ior	resuciue Ma				

Bottle "c" was used for Aroclor 1254 MSA/MSB

<sup>9</sup> NOTE: Bottle "d" was used for Pesticide MSA/MSB Bottle "b" was used for Aroclor 1254 MSA/MSB

1529 West Sequim Bay Road Sequim, WA 98382-9099

360/681-3643

UNITED HECKATHORN Pesticides in Water Samples Received 3/8/02

				•		
La	uritzen - South	DUP			DUP	
MSL Code	1780-2c	1780-2c R2		1780-2b	1780-2b R2	
STATION NO	303.2	303.2		303.2	303.2	
	Total	Total	RPD	Dissolved	Dissolved	RPD
Matrix	Water	Water		Water	Water	
Extraction Date	03/08/02	03/08/02		03/09/02	03/09/02	
Dilution	1x	1x		1x	1x	
Analytical Batch	1	1		1	1	
Unit	ng/L	ng/L	%	ng/L	ng/L	%
2,4'-DDE	0.09 U	0.09 U	NA	0.10 U	0.10 U	NA
Dieldrin	0.50	0.44	13%	0.26	0.36	32% #8
4,4'-DDE	0.19	0.23	19%	0.09 B	0.13 B	36% #8
2,4'-DDD	0.10 U	0.10 U	NA	0.11 U	0.12 U	NA
4,4'-DDD	0.83	0.98	17%	0.56	0.79	34% #8
2,4'-DDT	0.04 U	0.27	NA	0.05 U	0.05 U	NA
4,4'-DDT	0.49	0.63	25%	0.27	0.47	<b>54%</b> #8
AROCLORS						
1242	25.9 U	26.7 U		29.1 U	30.8 U	
1248	25.9 U	26.7 U		29.1 U	30.8 U	
1254	25.9 U	26.7 U		29.1 U	30.8 U	
1260	25.9 U	26.7 U		29.1 U	30.8 U	
SURROGATE RECO	VERIES (%)	χ.				
PCB103	80.0	84.2		89.5	74.4	
PCB198	104	103		115	78.9	

TOTAL SUSPENDED SOLIDS (mg/L)

TSS

U Not detected at or above DL shown

B Concentration is less than 5x blank value

# Outside QAQC limits (SIS 40-120%R; RPD <30%D)

& Sample concentration <10x MDL

PROJECT:	Heckathorn Biomonitoring Year 5
PARAMETER:	Pesticides, PCBs, and Total Lipids
LABORATORY:	Battelle/Marine Sciences Laboratory, Sequim, Washington
MATRIX:	Tissues
SAMPLE CUSTODY:	Five mussel tissue samples were received on 3/8/02. All samp

**CUSTODY:** Five mussel tissue samples were received on 3/8/02. All samples were received in good condition. Samples were received in the same cooler as water samples received on the same day. The cooler temperature on arrival was 5.8°C. Mussels were shucked in the wet laboratory, placed in clean glass jars, and returned to the chemistry laboratory for analysis on 3/11/02. The cooler temperature on arrival was 2.3°C. Mussel samples were then assigned a Battelle Central File (CF) identification number (1782) and were entered into Battelle's log-in system.

. . .. .. ..

#### QA/QC DATA QUALITY OBJECTIVES:

					Detectio	<u>on Limits</u>
Analista	Extraction Method	Analytical Method	Range of	Relative	Target	Achieved
Analyte		Method	<u>Recovery</u>	<u>Precision</u>	<u>(ng/g wet)</u>	<u>(ng/g wet)</u>
2,4'-DDE	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.13
Dieldrin	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.29
4,4'-DDE	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.52
2,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	<b>±30%</b>	2	0.19
4,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.18
2,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.26
4,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	0.36
PCB Aroclor 1242	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
PCB Aroclor 1248	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
PCB Aroclor 1254	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	6.84
PCB Aroclor 1260	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
Total Lipids	CHCl <sub>3</sub>	Gravimetric	NA	±30%	NA	NA

ND Only Aroclor 1254 was detected.

#### **METHOD:**

Tissue samples for analysis of chlorinated pesticides and PCBs were processed according to Battelle SOP MSL-O-009, *Extraction and Clean-Up of Sediments and Tissues for Semivolatile Organics Following the Surrogate Internal Standard Method*, which is derived from NOAA NS&T and EPA methods with modifications from Krahn et al. (1988). Tissue samples were macerated and extracted with methylene chloride. Interferences were removed using an aluminum/silicon column chromatography step followed by a high-performance liquid chromatography (HPLC) clean-up according to SOP MSL-O-006, *HPLC Cleanup of Sediment and Tissue Extracts for Semivolatile Pollutants*. Sample extracts were then transferred to cyclohexane and analyzed by capillary-column (DB-1701) gas chromatography with electron-capture detection (GC/ECD) according to SOP MSL-O-004, *Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection*, which is based on EPA Method 8081 (EPA 1986).

Total lipids were determined according to the Bligh et al. (1959) method, modified to accommodate a smaller sample size. Lipids were extracted from separate aliquots of tissue samples using chloroform and the lipid weight obtained gravimetrically.

-----

HOLDING TIMES:	Samples were collected on 3/5/02 and held at $4^{\circ}C \pm 2^{\circ}C$ until mussels were shucked and placed into sample containers. Samples were frozen on receipt at the chemistry laboratory on 3/8/02. Samples were extracted on 4/8/02. GC analysis was conducted from 4/11/02 to 4/14/02. Lipid extractions were conducted
	on 4/16/02.

**DETECTION** LIMITS: Detection limits were determined by a previously conducted MDL study where replicates were analyzed and the standard deviation was multiplied by the Student's-t value for the number of replicates.

Sample-specific detection limits are calculated using the achieved detection limit and the sample weight.

METHODOne method blank was analyzed with the set of samples. 2,4'-DDE; 4,4'-DDE;BLANKS:4,4'-DDD; 2,4'-DDT; and PCB Aroclor 1254 were undetected in the blank.<br/>Dieldrin, 2,4'-DDD, and 4,4'-DDT were detected in the blank at concentrations less<br/>than 5 times their MDLs.

**BLANK SPIKES:** Two blank samples (reagents only, carried through all sample preparation processes) were spiked with 5 ng/g Dieldrin and 4,4'-DDT, and 50 ng/g Aroclor 1254. Blank spike recoveries of the three spiked analytes of interest ranged from 68% to 104%, and were within the target range of 40%-120%.

**REPLICATES:** One tissue sample [1780-7(20212-YSM-02)] was analyzed in duplicate for the analytes of interest. Precision of duplicate analysis is determined by calculating the relative percent difference (RPD) of replicate results. RPDs of all analytes of interest ranged from 1% to 10%, and were all within the QC limits of ±30%.

Sample 1780-8 (20212-YSM-02) was analyzed in duplicate for lipids. Precision of the duplicate lipid analysis was within the QC limits of  $\pm 30\%$  (4% RPD).

MATRIX SPIKES: A matrix spike and matrix spike duplicate pair was analyzed using sample 1780-9 (20212-YSM-04) spiked with 5 ng/g Dieldrin and 4,4'-DDT, and 50 ng/g Aroclor 1254. Recoveries of the three spiked analytes of interest ranged from 66% to 104%, and were within the target range of 40%-120% in both the MS and MSD.

Replicate precision of the MS/MSD analysis, expressed as the RPD between the MS and MSD, was within the QC criteria of  $\pm 30\%$  for dieldrin (9%); 4,4'-DDT (6%); and Aroclor 1254 (1%).

**SURROGATE RECOVERIES:** Chlorinated compounds PCBs 103 and 198 were added to each sample during the preparation step as surrogates to assess the efficiency of the extraction procedure. Surrogate recoveries were within the target range of 40%-120%, ranging from 67.8% to 108%.

#### **REFERENCES:**

Bligh, E.G., and W.J. Dyer. 1959. A Rapid Method of Total Lipid Extraction and Purification. *Canadian Journal of Biochemistry and Physiology*. 37:8 911-917.

Krahn, M.M, CA Wigren, R.W. Pearce, S.K. Moore, R.G. Bogar, W. D. McLeod, Jr., S.L. Chan, and D.W. Brown. 1988. *New HPLC Cleanup and Revised Extraction Procedures for Organic Contaminants*. NOAA Technical Memorandum MNFS F/NWC-153. Standard Analytical Procedures of the NOAA National Facility, 1988. National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, WA.

U.S. EPA. 1986 (Revised 1990). *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846.* 3rd ed. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

### Deviation Documentation Form 20212-D-001

STUDY NUMBER Project No. 2021 Project Manager:	2-D-001
Project Title: Heck	athorn Monitoring Year 5
Entered by: <u>ES</u>	Barrows Date: 6-24-02
[ ] a miscellane	
Description:	Tissue and Passive Samplers were analyzed 4 weeks after collection; recommended holding time for organics analysis is 2 weeks after collection.
Impact on Project:	Mussels were frozen upon collection and remained frozen until mussels were measured, shucked, and weighed. Sample jars containing shucked mussel tissues were frozen immediately. Passive samplers (polyethylene sheets exposed to study area) were frozen on arrival at the laboratory to accommodate sample collection schedules and facilitate batching sample processing in the laboratory. Freezing samples as a method of preservation for extended periods of time (i.e., up to one year) is an acceptable practice for organics analysis and should have no impact on the results of the analysis.
APPROVED BY:	

Project Manager or Study Director

Date

File in project notebook or study archive Send a copy to the MSL QA Officer

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

## UNITED HECKATHORN

Pesticides in Tissues

MSL Code	1780-6	1780-7	1780-8	1780-9	1780-10
STATION NO	20212-YSM-01	20212-YSM-02	20212-YSM-03	20212-YSM-04	20212-YSM-05
LOCATION	NA	NA	NA	NA	NA
Matrix	Tissue	Tissue	Tissue	Tissue	Tissue
Wet Wt (g)	21.6	21.4	20.6	19.9	20.5
Extraction Date	04/08/02	04/08/02	04/08/02	04/08/02	04/08/02
Percent Lipids (WW)	0.76	0.61	0.84	0.54	0.68
Percent Lipids (DW)	8.65	7.44	8.57	7.31	8.58
Percent Dry Wt	8.79	8.20	9.80	7.39	7.93
Dilution	1	· <b>1</b>	10	1	e <b>1</b>
Analytical Batch	1	1	1	<b>1</b>	1
Unit (wet wt)	ng/g	ng/g	ng/g	ng/g	ng/g
2,4'-DDE	0.12 U	0.66	3.22	0.21	0.13 U
Dieldrin	0.68	2.93	17.0	0.62	1.16
4,4'-DDE	4.67	28.8	45.9	6.27	10.8
2,4'-DDD	1.41	13.0	43.5	2.20	3.48
4,4'-DDD	0.17 U	30.4	86.8	6.31	12.1
2,4'-DDT	0.24 U	25.0	48.9	2.79	3.82
4,4'-DDT	3.13	41.5 D5	82.1	5.79	9.47
AROCLORS					
1254	38.2	101 D5	113	42.0	55.7
SURROGATE RECOV	'ERIES (%)				
PCB103	77.6	85.8	92.2	67.7	85.4
PCB198	90.1	92.9	96.1	72.9	101

M Mean used to calculate QC

U Not detected at or above DL shown

ND Analyte not detected

D5 Diluted 5x

NOTE: Sample 1780-8 (20212-YSM-02) was analyzed in duplicate for Lipids (0.87 percent lipids; 4% RPD)

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

#### **UNITED HECKATHORN**

Pesticides in Tissues

		BSA			BSB				DUP	
MSL Code	Blank3	Blank	Spike	Percent	Blank	Spike	Percent	1780-7	1780-7	
STATION NO			•					20212-YSM-02	20212-YSM-02	
LOCATION		Spike A	Amount	Recovery	Spike B	Amount	Recovery			RPD
Matrix	Tissue	Tissue			Tissue			Tissue	Tissue	
Wet Wt (g)	NA	NA			NA			21.4	20.6	
Extraction Date	04/08/02	04/08/02			04/08/02			04/08/02	04/08/02	
Percent Lipids (WW)	NA	NA			NA			0.61	0.61	
Percent Lipids (DW)	NA	NA			NA			7.44	7.44	
Percent Dry Wt	NA	NA			NA NA			8.20	8.20	
Dilution	NA	NA			NA			1	1	
Analytical Batch	1	1			1			. 1	. 1	
Unit (wet wt)	ng/g	ng/g	ng/g	%	ng/g	ng/g	%	ng/g	ng/g	%
2,4'-DDE	0.13 U	0.29	NS	NA	0.28	NS	NA	0.66	0.67	2%
Dieldrin	0.30	3.73	5.00	69%	3.68	5.00	68%	2.93	2.95	1%
4,4'-DDE	0.52 U	0.52 U	NS	NA	0.52 U	NS	NA	28.8	26.8	7%
2,4'-DDD	0.42	0.19 U	NS	NA	0.19 U	NS	NA	13.0	11.8	10%
4,4'-DDD	0.18 U	0.18 U	NS	NA	0.18 U	NS	NA	30.4	27.7	9%
2,4'-DDT	0.26 U	0.26 U	NS	NA	0.26 U	NS	NA	25.0	23.3	7%
4,4'-DDT	0.28	5.48	5.00	104%	5.29	5.00	100%	41.5	D5 39.9 D	5 4%
AROCLORS					Ç					
1254	6.84 U	49.3	50.0	85%	48.3	50.0	83%	101	D5 101 D	5 0%
÷.										
SURROGATE RECOVERIES (%	<u>6)</u>									
PCB103	92.3	89.2			91.5			85.8	75.9	
PCB198	99.0	103			108			92.9	88.1	

NS Not spiked

B.16

NA Not applicable/available

D5 Diluted 5x

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

UNITED HECKATHORN Pesticides in Tissues

		MSA			MSB			
MSL Code	1780-9	1780-9	Spike	Percent	1780-9	Spike	Percent	
STATION NO	20212-YSM-04	20212-YSM-04			20212-YSM-04			
LOCATION		Spike A	Amount	Recovery	Spike B	Amount	Recovery	RPD
Matrix	Tissue	Tissue			Tissue			
Wet Wt (g)	19.9	20.3			20.2			
Extraction Date	04/08/02	04/08/02			04/08/02			
Percent Lipids (WW)	0.54	NA			NA			
Percent Lipids (DW)	7.31	NA			NA			
Percent Dry Wt	7.39	NA			NA			
Dilution	1	1			1			
Analytical Batch	1	1			1			
Unit (wet wt)	ng/g	ng/g	ng/g	%	ng/g	ng/g	%	%
2,4'-DDE	0.21	0.13 L	J NS	NA	0.13 U	NS	NA	
Dieldrin	0.62	4.27	5.02	73%	3.88	4.92	66%	9%
4,4'-DDE	6.27	6.20	NS	NA	6.23	NS	NA	
2,4'-DDD	2.20	1.91	NS	NA	1.82	NS	NA	
4,4'-DDD	6.31	6.05	NS	NA	5. <b>9</b> 7	NS	NA	
2,4'-DDT	2.79	2.43	NS	NA	2.52	NS	NA	
4,4'-DDT	5.79	11.0	5.02	104%	10.6	4.92	<del>9</del> 8%	6%
AROCLORS								
1254	42.0	82.9	50.2	81%	82.4	49.2	82%	1%
SURROGATE RECOVERIES (								
PCB103	67.8	77.3			90.3			
PCB198	72.9	82.3			104			

U Not detected at or above DL shown

NS Not spiked

NA Not applicable/available

## **PASSIVE SAMPLER QA/QC SUMMARY**

PROJECT:	Heckathorn Biomonitoring Year 5
PARAMETER:	Pesticides, PCBs
LABORATORY:	Battelle/Marine Sciences Laboratory, Sequim, Washington
MATRIX:	Semi-permeable membrane devices (SPMD)

**SAMPLE CUSTODY:** Eight SPMD samples were received in two deliveries on 3/8/02 and 3/19/02. All samples were received in good condition. The cooler temperature on arrival of the first shipment was 5.8°C; the second shipment was 2°C. SPMD samples were then assigned a Battelle Central File (CF) identification number (1782) and were entered into Battelle's log-in system, then frozen until analysis.

#### QA/QC DATA QUALITY OBJECTIVES:

Analyte	Extraction <u>Method</u>	Analytical <u>Method</u>	Range of <u>Recovery</u>	Relative Precision	<u>Detect</u> Target (ng/g wet)	<u>ion Limits</u> Achieved <u>(ng/g wet)</u>
2,4'-DDE	MeCl₂	GC-ECD	40-120%	±30%	2	1.82
Dieldrin	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
4,4'-DDE	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
2,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
4,4'-DDD	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
2,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
4,4'-DDT	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	2	1.82
PCB Aroclor 1242	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
PCB Aroclor 1248	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
PCB Aroclor 1254	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	36.4
PCB Aroclor 1260	MeCl <sub>2</sub>	GC-ECD	40-120%	±30%	20	ND
ND Only Araclar 125	A was detected	1				

ND Only Aroclor 1254 was detected.

METHOD:

SPMD samples for analysis of PCBs as Aroclors were processed according to Battelle SOP MSL-O-009, *Extraction and Clean-Up of Sediments and Tissues for Semivolatile Organics Following the Surrogate Internal Standard Method*, which is derived from NOAA NS&T and EPA methods with modifications from Krahn et al. (1988). Approximately 0.5 g of SPMD sample material was combined with hexane and sealed in a glass jar with a Teflon-lined lid for 2 days. Interferences in the extract were removed using an alumina/silica column chromatography step. Sample extracts were then transferred to cyclohexane and analyzed by capillary-column (DB-1701) gas chromatography with electroncapture detection (GC/ECD) according to SOP MSL-O-004, *Analysis of Polychlorinated Biphenyls and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection*, which is based on EPA Method 8081 (EPA 1986).

The initial analysis of sample 1782-8 (PS-8") showed concentrations of chlorinated compounds too high to quantitate even when diluted 50x and 500x. A smaller mass of SPMD material was reextracted and reanalyzed.

Results of SPMD and poly bag analyses were reported in units of total ng Aroclor.

# PASSIVE SAMPLER QA/QC SUMMARY

HOLDING TIMES:	Seven of the eight samples were collected on 3/5/02; one additional sample was collected on 3/14/02. Samples were held at $4^{\circ}C \pm 2^{\circ}C$ and shipped by overnight courier to the chemistry laboratory. Samples were frozen on receipt at the chemistry laboratory on 3/8/02 and 3/19/02, and held frozen until analysis. Samples were extracted on 4/8/02. GC analysis was conducted from 4/11/02 to 4/14/02 and 4/30/02.
DETECTION LIMITS:	Detection limits were determined by a previously conducted MDL study where replicates were analyzed and the standard deviation was multiplied by the Student's-t value for the number of replicates. Achieved detection limits for Aroclor 1254 were higher than target MDL. Where Aroclor 1254 was detected, sample concentrations were clearly higher than the DL; therefore, the achieve MDL has no affect on the data.
METHOD BLANKS: BLANK SPIKES:	Sample-specific detection limits are calculated using the achieved detection limit and the sample weight. One method blank was analyzed with the set of samples. All analytes of interest were undetected in the blank. With the initial analysis (batch 1), one blank sample (reagents only, carried through all sample preparation processes) was spiked with 91 ng/g Dieldrin and 4,4'-DDT, and 909 ng/g Aroclor 1254. Blank spike recovery of the three spiked analytes of interest ranged from 65% to 108%, and were within the target range of 40%-120%.
	A second set of blank spikes was analyzed with the reanalysis of sample 1782-8 (batch 2), spiked at higher analyte levels: 19,200 ng/g Dieldrin and 4,4'-DDT, and 192,000 ng/g Aroclor 1254. Blank spike recoveries of the three spiked analytes of interest ranged from 60% to 98%, and were within the target range of 40%-120%.
REPLICATES:	One SPMD sample [1782-1(303.1)] was analyzed in duplicate for the analytes of interest. Precision of duplicate analysis is determined by calculating the relative percent difference (RPD) of replicate results. RPDs of all analytes of interest ranged from 1% to 22%, and were all within the QC limits of $\pm$ 30%.
	Replicate precision of the batch 2 blank spike A and blank spike B analyses, expressed as the RPD between BS A and BS B, ranged from 0% to 26%; all were within the QC limits of $\pm$ 30%.
SURROGATE RECOVERIES:	Chlorinated compounds PCBs 103 and 198 were added to each sample during the preparation step as surrogates to assess the efficiency of the extraction procedure. Surrogate recoveries among all sample analyses were within the target range of 40%-120%, ranging from 58.7% to 107%.
REFERENCES:	Krahn, M.M, CA Wigren, R.W. Pearce, S.K. Moore, R.G. Bogar, W. D. McLeod, Jr., S.L. Chan, and D.W. Brown. 1988. <i>New HPLC Cleanup and Revised Extraction</i> <i>Procedures for Organic Contaminants.</i> NOAA Technical Memorandum MNFS F/NWC-153. Standard Analytical Procedures of the NOAA National Facility, 1988. National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, WA.
	U.S. EPA. 1986 (Revised 1990). <i>Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846.</i> 3rd ed. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

# **PASSIVE SAMPLER QA/QC SUMMARY**

Deviation Documentation Form 20212-D-002

STUDY NUMBER: Project No. 20212 Project Manager:	-D-001			
Project Title: Hecka	thorn Monitoring Year 5			
Entered by: <u>ES E</u>	Barrows	Date:	6-24-02	
[ ] a miscellaneo	om Protocol, Work Plan or QA F from SOP	lan (give title	<b>)</b>	
Description:	Mass in grams of SPMDs (Pas time of sample extraction/prep estimated to be between 0.5 a each sample weight in calculat	aration. Wei nd 0.6 g. A v	ghts of each SPMD were	
Impact on Project:	No impact on project. Sample representation of the sample s expected ranges.			-
APPROVED BY:				-
	Project Manager or Study Direc	tor	Date	
	File in project noteboo	ok or study a	archive	

Send a copy to the MSL QA Officer

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

UNITED HECKATHORN Pesticides in SPMDs (passive water samplers)

MSL Code	1782-1	1782-2	1782-3	1782-5	
STATION NO	303.1	303.4	303.2	303.3	
	Richmond	Sante Fe	Lauritzen	Lauritzen	
LOCATION	Channel	Channel	South	North	
Matrix	SPMD	SPMD	SPMD	SPMD	
Wet Wt (g)	0.55	0.55	0.55	0.55	
Extraction Date	04/08/02	04/08/02	04/08/02	04/08/02	
Dilution	1	1	1	10	
Analytical Batch	· 1	1	1	1	
Unit (wet wt)	ng/g SPMD	ng/g SPMD	ng/g SPMD	ng/g SPMD	
2,4'-DDE	1.98	4.95	7.46	35.9	
Dieldrin	9.31	23.9	97.3	478	
4.4'-DDE	13.4	50.7	256	454	
2,4'-DDD	14.1	47.1	194	730	
4,4'-DDD	35.9	115	558	1380	
2,4'-DDT	5.61	27.4	188	685	
4,4'-DDT	12.0	57.8	501	1220	
AROCLORS					
1254	122	182	1160	1520	
SURROGATE RECO	VERIES (%)				
PCB103	58.7	62.7	59.0	76.6	
PCB198	66.0	79.0	80.9	82.5	

M Mean used to calculate QC

U Not detected at or above DL shown

ND Analyte not detected

1529 West Sequim Bay Road Sequim, WA 98382-9099 360/681-3643

UNITED HECKATHORN

Pesticides in SPMDs (passive water samplers)

				BSA				DUP	
MSL Code							1782-1	1782-1	
STATION NO		Blank	SPMD Blank	SPMD Blank	Spike	Percent	303.1	303.1	
							Richmond	Richmond	
LOCATION		· · · · · · ·		Spike A	Amount	Recovery	Channel	Channel	RPD
Matrix		SPMD	SPMD	SPMD			SPMD	SPMD	
Wet Wt (g)		NA	0.55	0.55			0.55	0.55	
Extraction Date		04/08/02	04/08/02	04/08/02			04/08/02	04/08/02	
Dilution		1	1	1			1	1	
Analytical Batch		1	1	1			1	· 1 ·	,
Unit (wet wt)	<u> </u>	g/g SPMD	ng/g SPMD	ng/g SPMD	ng/g SPMD	%	ng/g SPMD	ng/g SPMD	%
2,4'-DDE		1.82 U	1.82 U	4.97	NS	NA	1.98	2.47	22%
Dieldrin		1.82 U	2.08	58.8	90.9	65%	9.31	9.50	2%
4,4'-DDE		1.82 U	1.82 U	4.47	NS	NA	13.4	13.9	4%
2,4'-DDD		1.82 U	1.82 U	1.82 U	NS	NA	14.1	13.9	1%
4,4'-DDD		1.82 U	1.82 U	2.31	NS	NA	35. <del>9</del>	36.7	2%
2,4'-DDT		1.82 U	1.82 U	1.82 U	NS	NA	5.61	6.36	13%
4,4'-DDT		1.82 U	2.38	97.9	90.9	108%	12.0	13.0	8%
AROCLORS									
1254		36.4 U	36.4 U	856	909	94%	122	128	5%
									· )
SURROGATE RE	COVERIES (%)								,
PCB103		84.4	76.3	78.6			58.7	58.9	
PCB198		94.7	85.1	85.2			66.0	69.4	

U Not detected at or above DL shown

NS Not spiked

-

NA Not applicable/available

# APPENDIX C

MUSSEL SHELL LENGTH RAW DATA

Station	303.1	303.2	303.3	303.4	303.6
	<b>D</b> 1 1 -	<b>.</b>	Lauritzen	a –	
<b>T</b>	Richmond Inner	Lauritzen Chennel/		Santa Fe	
Location	Harbor Channel	Mouth	End	Channel/End	Parr Canal
Battelle Code	20212-Y5M-01	20212-Y5M-02	20212-Y5M-03		20212-Y5M-05
1	6.88	7.16	6.42	7.00	6.31
2	6.49	6.18	6.22	5.74	5.23
3	5.91	6.01	5.30	6.34	5.73
4	7.08	6.97	5.52	6.34	4.78
5	7.09	6.64	6.27	6.74	5.56
6	6.90	7.08	5.94	6.93	6.26
7	6.39	6.96	5.94	7.05	6.54
8	6.87	6.03	6.49	6.44	4.95
9	7.14	6.26	5.44	7.03	5.82
10	6.94	6.63	5.68	6.50	4.83
11	7.12	4.91	6.06	6.48	5.79
12	6.91	7.06	5.67	6.12	5.91
13	6.24	6.11	4.93	5.35	5.41
14	6.05	7.16	5.57	5.79	6.16
15	6.09	4.86	5.53	5.21	5.87
16	5.93	7.23	6.23	4.88	6.27
17	6.46	6.35	5.93	5.32	6.66
18	5.86	5.97	5.87	6.69	5.79
19	6.84	6.11	5.22	6.27	5.75
20	6.59	6.27	5.67	6.71	5.62
21	6.18	6.42	6.05	6.65	6.20
22	6.86	6.50	5.92	6.78	5.92
23	6.04	7.37	5.32	6.02	4.92
24	6.45	6.75	6.46	5.46	6.17
25	6.63	6.57	5.67	5.49	5.36
26	5.35	5.95	5.84	7.57	5.75
27	6.80	5.10	5.17	7.86	6.01
28	6.75	6.47	5.13	7.77	5.24
29	6.22	7.00	5.12	7.52	5.85
30	6.02	4.69	5.44	7.09	6.17
31	6.51	6.38	6.37	7.86	5.42
32	5.00	6.10	5.83	7.89	5.73
33	4.84	6.83	5.88	7.60	5.44
34	5.10	6.38	6.08	7.31	6.45
35	5.45	6.59	5.80	7.48	5.67
36	4.78	7.00	5.05	8.05	6.45
	4 75	6 19	5.28	7.16	6.21
37 38	4.75 5.26	6.19 6.17	5.28 5.12	7.16 7.47	6.21 6.59

# Resident Mussels Only, Year 5, 2002

	•	. ,			
Station	303.1	303.2	303.3	303.4	303.6
			Lauritzen		
	Richmond Inner	Lauritzen Chennel/	Chennel/	Santa Fe	
Location	Harbor Channel	Mouth	End	Channel/End	Parr Canal
Battelle Code	20212-Y5M-01	20212-Y5M-02	20212-Y5M-03	20212-Y5M-04	20212-Y5M-05
40	5.10	6.44	5.59	7.10	5.86
41		6.36	5.40		6.47
42			5.94		5.49
43			5.47		5.10
44			5.81		5.51
45			5.37		5.98
46			5.69		5.80
47			6.27		6.32
48			6.55		6.23
49			6.28		6.08
50			5.38		5.13
Min	4.75	4.69	4.93	4.88	4.78
Max	7.14	7.37	6.55	8.05	6.66
Med	6.32	6.42	5.75	6.76	5.84
Average Length: (cm)	6.18	6.39	5.75	6.72	5.82
sd length	0.73	0.63	0.43	0.85	0.48
Average wt			_		
(g/individual)	14.7	14.8	10.2	14.6	10.1

# Resident Mussels Only, Year 5, 2002 (continued)

### DISTRIBUTION

### No. of

### **Copies**

### <u>OFFSITE</u>

No. of

# <u>Copies</u>

## <u>ONSITE</u>

- 5 C. White, SFD-8-1
  U. S. Environmental Protection Agency Region IX
  75 Hawthorne Street
  San Francisco, CA 94105
- A. Lincoff
   U. S. Environmental Protection Agency Region IX Laboratory
   1337 S. 46<sup>th</sup> Street, Building 201
   Richmond, CA 94804
- L. D. Antrim Olympic Coast National Marine Sanctuary 138 W. First St. Port Angeles, WA 98362

- 1 Information Release Office K1-06
- 5 N. P. Kohn
- 1 R. K. Kropp