

TECHNICAL REPORT 1938  
May 2006

**Storm Water Toxicity  
Evaluation Conducted at  
Naval Station San Diego,  
Naval Submarine Base San Diego,  
Naval Amphibious Base Coronado,  
and Naval Air Station North Island**

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# EXECUTIVE SUMMARY

## BACKGROUND

This report describes results of a study to evaluate the toxicity of industrial storm water discharges from U.S. Navy facilities bordering San Diego Bay. The study was conducted to support a request from the San Diego Regional Water Quality Control Board to develop a scientifically based acute toxicity threshold for industrial storm water discharges that can be applied to National Pollutant Discharge Elimination System (NPDES) permits. Current NPDES storm water permits at Navy facilities include a toxicity requirement that states: “...*undiluted storm water runoff associated with industrial activity shall not produce less than 90% survival 50% of the time, and not less than 70% survival, 10% of the time, using standard test species and protocol.*” This requirement is based on Whole Effluent Toxicity (WET) testing that the Environmental Protection Agency (EPA) identifies as “a useful parameter for assessing and protecting against impacts upon water quality and designated uses caused by the aggregate toxic effects of the discharge of pollutants” (EPA, 1991a). Thus, the study focused on the use of WET test methods and data evaluations.

## GOAL

The goal of this study was to develop a robust dataset of storm water and receiving water toxicity that can be used to support a scientifically based acute toxicity threshold for industrial storm water discharges from Navy facilities. The technical approach used three simultaneous measurement components to evaluate industrial storm water toxicity and impacts to San Diego Bay waters. The three components included the following:

1. Toxicity and chemistry measurements in storm water (end-of-pipe)
2. Toxicity and chemistry measurements in receiving waters
3. Storm water plume mapping

## SAMPLING

The study evaluated storm discharges and receiving waters during 11 storm events from 2002 to 2005. Data were collected from 14 drainage areas at Naval Station San Diego, Naval Submarine Base San Diego, Naval Amphibious Base Coronado, and Naval Air Station North Island. The drainage areas monitored were representative of the various industrial activities occurring on all four bases.

A total of 136 discrete samples were collected during this study, including 51 first-flush (collected during the first hour of flow) and flow-weighted composite storm water samples. It also included 85 receiving water samples collected immediately outside outfalls before, during, and after storm events. A total of 333 toxicity tests were performed on these samples.

Samples were analyzed using multiple toxicity testing endpoints, including the two acute tests allowed in the permit, 96-hour survival of *Atherinops affinis* (topsmelt) larvae, and *Americamysis bahia* (mysid) juveniles. An additional toxicity endpoint evaluated the 48-hour normal embryo-larval development of *Mytilus galloprovincialis* (mussel), an indigenous species to San Diego Bay. This mussel test provides one of the most sensitive endpoints available for evaluating marine waters. These three test species were also used in a Toxicity Identification Evaluation (TIE) to identify the causative agents of toxicity. Samples were analyzed for a range of contaminants of concern, including a suite of total and dissolved metals, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides. Seventeen plume mapping surveys, including an on-site floating bioassay laboratory study, were conducted before, during, and after storm events.

## RESULTS

**Toxicity and Chemistry Measurements in Storm Water.** The study established that acute storm water toxicity measured at the end-of-pipe was highly variable, spanning the full range of impact, from 0 to 100% survival of topsmelt and mysids. The toxicity of first-flush storm water samples, representing the discharge at one moment in time, was higher than in composite samples that were representative of the entire discharge. First-flush samples failed to meet the 90% survival requirement in the NPDES permit 58% of the time. Composite samples failed 25% of the time. However, the 90% survival requirement in the permit does not follow WET data evaluation methods in identifying when a sample is acutely toxic or not. When using WET methods, including t-testing and consideration of method variability, 30% (versus 58%) of first-flush samples and 7% (versus 25%) of composite samples were identified as acutely toxic. The toxicity identification evaluation and chemistry data identified copper and zinc as the primary toxicants of concern, although surfactants were identified in some samples.

**Toxicity and Chemistry Measurements in Receiving Waters.** Less than 1% of 202 receiving water toxicity tests exhibited toxicity. The lack of relationship between the measurements of toxicity in first-flush samples with toxicity observed in the receiving environment was a result of limited receiving water exposure conditions.

**Storm Water Plume Mapping.** The mapping surveys and the special floating bioassay study clearly showed that Navy storm water discharges and their influence on receiving waters were limited in magnitude, minimal in their spatial extent, and very short-lived. Thus, toxicity measured in first-flush storm water overestimates the exposure conditions measured in the receiving water and thereby overestimates the potential for toxic impacts.

## SUMMARY

In summary, this study provides one of the most extensive datasets on storm water runoff conducted, effectively characterizing the bounds of variability inherent in these types of discharges and their impacts to receiving water quality. Using multiple lines of evidence, the data showed that first-flush storm water can be acutely toxic, primarily as a result of copper and zinc concentrations in the discharge. The total storm discharge, represented by composite samples, was generally less toxic and had lower contaminant concentrations. Most importantly, there was no relationship between toxicity measured in storm water and toxicity measured in the receiving water. These results show that WET testing on storm water as required in the permit cannot be used to infer toxicity in the receiving environment.

## RECOMMENDATIONS

This study was conducted to support a scientifically based acute toxicity threshold for storm water discharges. To ensure that an acute toxicity threshold for storm water discharges will accurately identify and be protective of water-quality impacts in the receiving environment, the proposed Navy alternative toxicity threshold should include the following:

- The use of appropriate EPA WET test methods and data evaluation when declaring a test result as toxic
- Acknowledgement of WET method variability and considerations of minimum detection limits in declaring toxic results
- Consideration of realistic exposure conditions when using WET testing to infer toxicity in the receiving water

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## LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
BAT	Best Available Technology Economically Achievable
BCT	Best Conventional Pollutant Control Technology
BMP	Best Management Practice
CCC	Criteria Continuous Concentration
CMC	Criteria Maximum Concentration
CNRSW	Commander Navy Region Southwest
CoCs	Contaminants of Concern
COMP	Composite
CVAA	Cold Vapor Atomic Absorption Spectrometry
CVAF	Cold Vapor Atomic Fluorescence Spectrometry
DDT	Dichlorodiphenyltrichloroethane
DOC	Dissolved Organic Carbon
DQO	Data Quality Objectives
EC50	Effect Concentration (50%)
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
ERM	Effects Range Mean
FF	First-flush
FIAS	Flow Injection Atomic Spectrometer
GFAA	Graphite Furnace Atomic Absorption Spectrometry
HMW	High Molecular Weight
HSB	Hypersaline brine
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ICP-OES	Inductively Coupled Argon Plasma Optical Emission Spectrometer
LC50	Lethal Concentration (50%)
LMW	Low Molecular Weight
LOEC	Lowest-Observable-Effect-Concentration
MBAS	Methylene Blue Activated Substances
MDL	Method Detection Limit
MESC	Marine Environmental Survey Capability
NAB	Naval Amphibious Base Coronado



NAV	Naval Station San Diego
NAVFACENGCOM	Naval Facilities Engineering Command
NFESC	Naval Facilities Engineering Service Center
NI	Naval Air Station North Island
NOEC	No Observed Effect Concentration
NPDES	National Pollutant Discharge Elimination System
NPS	Non-point Source
NS&T	National Status and Trends
PAH	Polynuclear Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PMSD	Percent Minimum Significant Difference
PSU	Practical Salinity Units
PWC	Public Works Center
RF	Radio Frequency
RSD	Relative Standard Deviation
SSC San Diego	Space and Naval Warfare Systems Center San Diego
SUB	Naval Submarine Base San Diego
SWRMC	South West Regional Maintenance Center
TAC	Test Acceptability Criteria
TIE	Toxicity Identification Evaluation
TMDL	Total Maximum Daily Load
TPCB	Total Polychlorinated Biphenyl
TSS	Total Suspended Solids
TU <sub>A</sub>	Acute Toxic Unit
UVF	Ultra-Violet Fluorescence
WET	Whole Effluent Toxicity
WQS	Water Quality Standard

# 1. INTRODUCTION

This report describes results of a study to evaluate the toxicity of industrial storm water discharges from U.S. Navy facilities bordering San Diego Bay. The study was conducted by the Environmental Sciences and Applied Systems Branch at the Space and Naval Warfare Systems Center San Diego (SSC San Diego) at the request of Commander Navy Region Southwest (CNRSW). The request was made after CNRSW received a National Pollutant Discharge Elimination System (NPDES) permit (CA0109363) from the San Diego Regional Water Quality Control Board for the Naval Submarine Base San Diego on 11 September 2002, with the following two provisions:

1. *“For the Submarine Base facility, effective 4 years after the adoption of this Order, in a 96-hour static or continuous flow bioassay (toxicity) test, undiluted storm water runoff associated with industrial activity shall not produce less than 90% survival 50% of the time, and not less than 70% survival, 10% of the time, using standard test species and protocol.”*
2. *“During the 4-year period before the effective date of the toxicity limit set forth in paragraph a of this Specification, the U.S. Navy shall conduct a study of the toxicity in storm water discharges from all areas of SUBASE which industrial activities are undertaken and shall recommend a scientifically valid survival rate for acute exposure to discharges of storm water from industrial areas at SUBASE. The study may include a Toxicity Identification Evaluation (TIE), or a Toxicity Reduction Evaluation (TRE).”*

These same requirements were adopted within the NPDES permits for three other Navy facilities on the bay: Naval Station San Diego, Naval Amphibious Base Coronado, and Naval Air Station North Island, which were permitted during the next 6 months.



## 2. BACKGROUND

The toxicity requirement in the permits is based on Whole Effluent Toxicity (WET) testing. WET testing was identified by the Environmental Protection Agency (EPA) as “a useful parameter for assessing and protecting against impacts upon water quality and designated uses caused by the aggregate toxic effects of the discharge of pollutants” (EPA’s Technical Support Document for Water Quality-based Toxics Control [EPA, 1991a]). On the basis of results obtained in EPA’s Complex Effluent Toxicity Testing Program and other reviewed studies (cited in EPA, 1991a), the EPA concluded that the control of toxicity is a valid approach for protecting ambient water quality and receiving water impact. They also concluded that “impact from toxics would only be suspected where effluent concentrations after dilution are at or above toxicity effect concentrations.” WET testing has been applied to mixing of continuous industrial discharges with receiving waters, but does not provide direction on its application for short exposure discharges such as those produced by storm water. The current permits do not consider if storm water effluent concentrations after dilution are at or above toxicity effect concentrations.

The permit requirement is based on short-term or acute toxicity testing. Acute WET tests use standardized protocols to evaluate short-term toxicity by exposing test organisms for 96-hour or less and measuring lethality as the endpoint. Tests also exist that are designed to evaluate chronic toxicity, which is typically defined as a longer term test in which sublethal effects such as fertilization, growth, or reproduction are measured on very sensitive life stages of test organisms (e.g., embryos). In WET tests, a chosen test species is exposed to an effluent sample (often at various levels of dilution) within a test chamber for a specified duration. At the end of the exposure period, the test effect (lethality, development, etc.) is evaluated and compared to results in a control sample to determine if the effluent was toxic or not. The current permits do not consider comparisons to control samples as a means of establishing when a sample is toxic or not toxic.

Various quality assurance/quality control (QA/QC) measures are applied to WET methods to minimize test method variability and ensure that the tests produce meaningful results. These measures apply to effluent sampling and handling, test organism source and condition, test conditions, instrument calibration, replication, the use of reference toxicants, recordkeeping, and data evaluations. Test method variability is a key component when evaluating toxicity data and declaring the result as toxic or non-toxic. Guidance on method variability and the use of minimum significant difference (MSD) was developed by EPA in 2000 (EPA, 2000). The MSD represents the smallest difference that can be distinguished between the response of the control organisms and the response of the organisms exposed to the effluent. As such, the MSD is a minimum detection limit for toxicity tests. The current permit requirement does not consider test method variability.



### **3. STUDY GOAL**

The goal of this study was to develop a robust dataset of storm water and receiving water toxicity that can be used to support a scientifically based acute toxicity threshold for industrial storm water discharges from Navy facilities. Implicit in this goal is the requirement that the toxicity threshold accurately ensures protection against impacts upon receiving water quality and its designated uses. To meet this goal, the study included an extensive characterization of storm water toxicity and its causes. It also included a comparable characterization of surrounding receiving waters, including an evaluation of exposure conditions. Together, these data were used to assess toxicity thresholds based on the observed relationship between toxicity measured in storm water discharges and in receiving waters. To ensure that the widest range of conditions was represented, measurements were made during multiple storm events from multiple drainage areas and in waters adjacent to all four Navy bases. Multiple toxicity endpoints and a suite of contaminants of concern (CoCs) were evaluated in storm water and receiving waters. Receiving water conditions around each base were evaluated before, during, and after storm events to evaluate exposure conditions and the spatial and temporal extent of storm water plumes.



## 4. TECHNICAL APPROACH

The technical approach used three simultaneous measurement components to evaluate industrial storm water toxicity and impacts to San Diego Bay waters. The three components included toxicity and chemistry measurements in storm water, toxicity and chemistry measurements in receiving waters, and storm water plume mapping. These lines of evidence are shown schematically in Figure 1 and graphically in Figure 2. The goal of conducting these measurements simultaneously was to be able to directly relate observations made in storm discharges to water quality impacts observed in the receiving environment.

The first component was to collect storm water samples before their discharge (end-of-pipe) into the receiving environment and analyze them for toxicity and chemistry. Two types of storm water samples were collected; first-flush (FF) storm water samples, collected during the first hour of flow as required in the permits, and flow-weighted composite (COMP) samples, acquired throughout an entire storm event. These discrete samples were analyzed for multiple toxicity endpoints, including two acute tests allowed in the NPDES permit: 96-hour survival of *Atherinops affinis* (topsmelt) larvae and *Americamysis bahia* (mysid) juveniles. An additional toxicity endpoint evaluated was the 48-hour normal embryo-larval development of *Mytilus galloprovincialis* (mussel), an indigenous species to San Diego Bay. This mussel test provides one of the most sensitive endpoints available for evaluating marine waters. The storm water samples were also analyzed for a suite of CoCs, including total and dissolved metals, polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and chlorinated pesticides that included dichlorodiphenyltrichloroethane (DDT) and its metabolites, and isomers of chlordane. Ancillary measurements included dissolved organic carbon (DOC) and total suspended solids (TSS). A Toxicity Identification Evaluation (TIE) was also conducted to evaluate the causative agents of observed toxicity.

One goal of these measurements was to evaluate the magnitude of toxicity as measured in first-flush samples as required in the NPDES permit and compare it to the magnitude of the toxicity represented by the discharges of an entire storm event represented by composite samples. A second goal was to evaluate the magnitude of the contaminants of concern relative to acute water quality standards to help identify the toxic agents.

The second measurement component was to collect and analyze receiving water samples for toxicity and chemistry. Discrete samples were collected immediately outside the points of storm water discharge before, during (simultaneous with storm water sample collection), and after storm events. Samples were also collected a distance away from the discharge points to evaluate gradients of impact in the receiving water. Bay samples were analyzed for the same toxicity endpoints and CoCs as the storm water samples. The goal of this measurement component was to evaluate the magnitude of toxic response directly in the receiving water resulting from the storm water discharges. This approach eliminates extrapolating exposure conditions and integrates impacts from all sources, not just storm water. CoCs measured in receiving waters were also compared to chronic water quality standards to assess their role in observed toxicity.

The third measurement component was to evaluate exposure conditions in receiving waters by mapping the spatial and temporal distribution of storm water plumes as they mixed with bay waters. Receiving waters were monitored outside outfalls for seawater salinity, temperature, turbidity, and ultraviolet oil fluorescence (UVF) before, during (simultaneous with storm water sample collection), and after storm events using the Navy's Marine Environmental Survey Capability (MES-C), a real-time data acquisition and processing system. These data were used to evaluate plume magnitude and



extent as a function of time to better understand the exposure conditions produced by storm discharges.

A variation on the three simultaneous measurement components was to deploy a shipboard bioassay laboratory system immediately outside an outfall to conduct receiving water toxicity testing under actual exposure conditions. The MESOC onboard the RV ECOS was used as the measurement and data acquisition platform. Simultaneous toxicity and chemistry measurements were conducted as on all other occasions but in this instance, bay water toxicity analyses were performed by exposing organisms directly to actual receiving water conditions outside the outfall for the test duration. The goal of this one-time effort (Special Floating Bioassay Study) was to measure the actual exposure conditions present outside a storm water discharge location, compare toxicity results using standard laboratory measurements with those made *in situ*, and to evaluate its time-varying toxic and chemical impact on the receiving water.

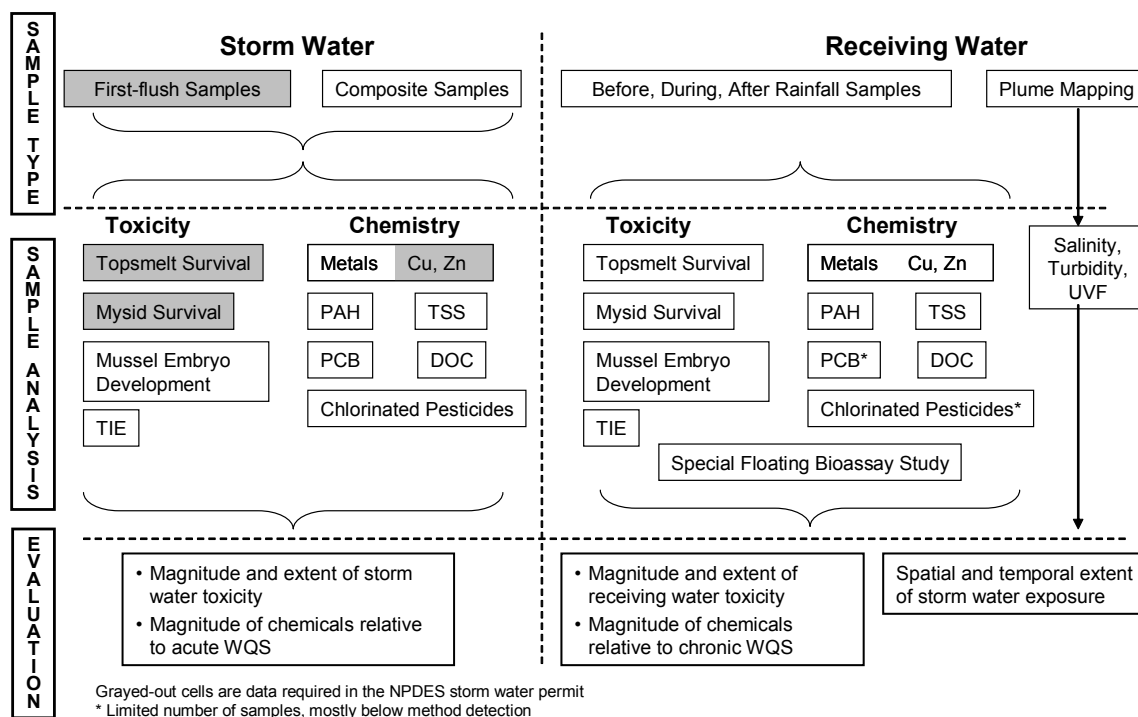


Figure 1. Schematic of technical approach that included simultaneous toxicity and chemistry measurements in storm water, toxicity and chemistry measurements in receiving waters, and storm water plume mapping.

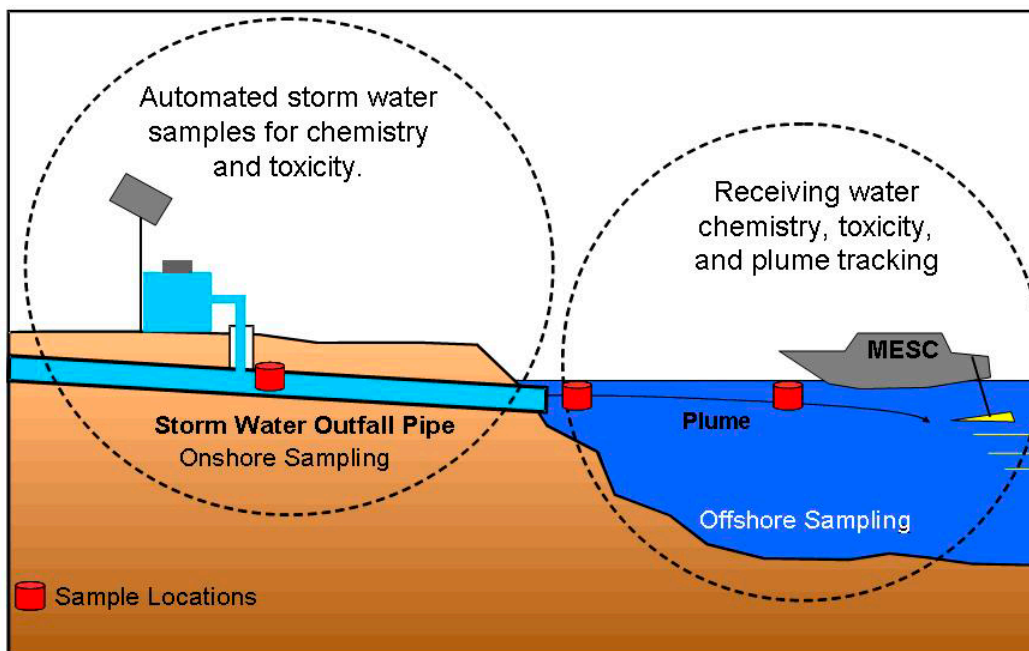


Figure 2. Graphical schematic for the technical approach that included simultaneous toxicity and chemistry measurements in storm water, toxicity and chemistry measurements in receiving waters, and storm water plume mapping. Receiving water sampling was conducted using the Marine Environmental Survey Capability (MESC).



## **5. TECHNICAL REVIEW**

A technical team was put together to help guide the sampling design and plans, and also evaluate results. The team included participants from the City of San Diego (Ruth Kolb), Port of San Diego (Eileen Maher), Southern California Coastal Water Research Project (Ken Schiff), Southwest Marine Shipyard (Shaun Halvax), U.S. Environmental Protection Agency (EPA) Region IX (Debra Denton), and U.S. Fish and Wildlife Service (Scott Sobiech). In addition to reviewing and commenting on sampling plans, the team met mid-way through the project to review results and provide comments and guidance on continuing work. Periodic project briefs and discussions with Regional Water Board staff were also conducted during the first 2 years of the project. Three of the technical review team members provided comments on the draft version of this report. Comments and responses to comments from these reviews along with those from two independent reviewers are included in Appendix I of this report.



## 6. METHODS

### 6.1 SAMPLING SUMMARY

The toxicity investigation was conducted by SSC San Diego during the October through May wet seasons from 2002 through 2005. During that time, 11 storms were sampled with rainfall totals ranging from 0.1 inch up to a record 3.4 inches (Table 1). A 12th sampling event captured only a pre-storm condition. Antecedent dry periods (rainfall <0.1 inch) ranged from 5 days up to a record dry period of 6 months (183 days), which was captured during the first-flush of the year storm SDB4. A total of 14 different industrial storm water drainage areas were sampled at four bases including four piers (Table 1). The drainage areas sampled ranged in size from 0.5 to 75 acres. The four bases included Naval Station San Diego (NAV), Naval Submarine Base San Diego (SUB), Naval Amphibious Base Coronado (NAB), and Naval Air Station North Island (NI) (Figure 3).

A total of 136 samples were collected and analyzed for toxicity and/or chemistry, though not every sample was analyzed for all components. Table 1 summarizes the samples collected and the analyses performed in chronological order. These tables, organized by base, are repeated in Appendix A. The sampling total was comprised of 51 storm water samples collected from the end-of-pipe (outfall) and included 33 first-flush samples (as required in the permit) and 18 full-storm, flow-weighted composite samples. The total also included 85 bay samples collected immediately outside outfalls before (27), during (35), and after (23) storm events. These bay sampling locations were nominally sited directly outside the point of discharge. At most locations, the samples were collected in the top 2 feet of the water column within a few feet of the discharge point. At a few sites, the outfall discharged under a pier or onto the shoreline before reaching the bay. In these few instances, bay samples were collected up to 50 feet away from the actual discharge point. The exact sampling locations are described later under each site description. Several receiving water samples were also collected from stations located a short distance away from the outfall discharge to see if a gradient in chemistry or toxicity could be detected. Seventeen plume mapping surveys were conducted before, during, or after storm events (Figure 4). Note that discrete samples collected during the SDB4 storm event were collected during the first 0.1-inch rainfall, though a total of 1.7 inches of rain fell during the next 3 days. Plume mapping was conducted during the later part of the rainfall event. Plume mapping was conducted only before and during (not after) storms SDB6 and SD7 because of logistical constraints.

The amounts and type of data collected during each storm sampling event varied with available resources, storm specifics, logistical constraints, and particular data needs. In a couple of instances, the sampling was opportunistic to capture a particular type of sample(s) such as the first-flush of the year sample or to capture a unique bay condition after a large amount of rainfall had occurred. In some instances, the sampling was limited to a single type of sample to meet a specific data need such as during the TIE sampling. The special floating bioassay study was also conducted during one storm (SDB45) event to monitor bay conditions outside an outfall for 96 hours to evaluate toxicity under true exposure conditions (Katz and Rosen, 2005). While the amount and type of data collected for each storm varied, the overall data collection was designed to meet the project goal of producing a robust dataset to characterize storm water toxicity and impacts to San Diego Bay.

The acronyms listed for each base above were used to uniquely identify samples collected from each base. The full sample identifier consisted of the base name acronym, sample location based on outfall number, storm event name, and sample type. Base name acronyms were described above.

However, the acronyms used by the toxicity laboratory performing the TIE were slightly different. An introductory description of the differences is provided in the TIE reports provided in Appendices E and F. The differences were as follows: NAV = NAVSTA, SUB = SUBASE, NAB = NAB, and NI = NASNI. Sample locations included storm water outfalls (OF), receiving water samples (Bay), or pier samples (PR). Storm events were given a unique identifier (Table 1). Sample types included first-flush (FF), composite (Comp), and bay samples collected before (PRE), during (DUR), and after (AFT) storm events (SDB1, SDB2...). Examples for sample naming conventions used throughout the study and included in the data appendices are as follows:

NAV-OF9-SDB1-FF = Naval Station San Diego Outfall 9, Storm SDB1, First-Flush

NAB-BAY9-SDB4-AFT = Naval Amphibious Base Coronado, Bay sample outside outfall 9, Storm SDB4, After storm

Table 1. Chronological summary of storms sampled, rainfall totals, antecedent dry period, and type of sampling. Discrete samples collected during the SDB4 storm event were collected during the first 0.1 inch of rainfall, as noted in the table, though mapping surveys started a day later with additional rainfall amounts.

Start Date	Storm Event	Navy Base	Rainfall Total (inches)	Antecedent Dry Period (days)*	Sampling
07 November 2002	SDB1	NAV	0.23	60	Onshore, Offshore, Mapping
24 February 2003	SDB2	NAV/SUB	0.99	10	Onshore, Offshore, Mapping
11 December 2003	SDB2A	SUB	0.00	NA	Offshore
02 February 2004	SDB3	SUB	0.46	8	Onshore, Offshore, Mapping
18 February 2004	TIE1	NAV/SUB	0.19	14	Onshore
26 February 2004	TIE1A	SUB	>3	NA	Offshore
17 October 2004	SDB4	NAV/SUB/NAB/NI	0.1	183	Onshore, Offshore, Mapping <sup>†</sup>
27 October 2004	SDB45	NAV	3.4	5	Onshore, Offshore, Mapping
10 January 2005	SDB5	NAV/SUB/NAB/NI	>6	NA	Offshore
10 February 2005	SDB6	NAB/NI	1.6	12	Onshore, Offshore, Mapping
19 March 2005	TIE2	NAB/NI	0.07	13	Onshore, Offshore
27 April 2005	SDB7	NAB/NI	0.44	34	Onshore, Offshore, Mapping

\* Previous rainfall < 0.1", amount typically required to generate flow.

<sup>†</sup> Mapping surveys were started a day later when a larger storm developed

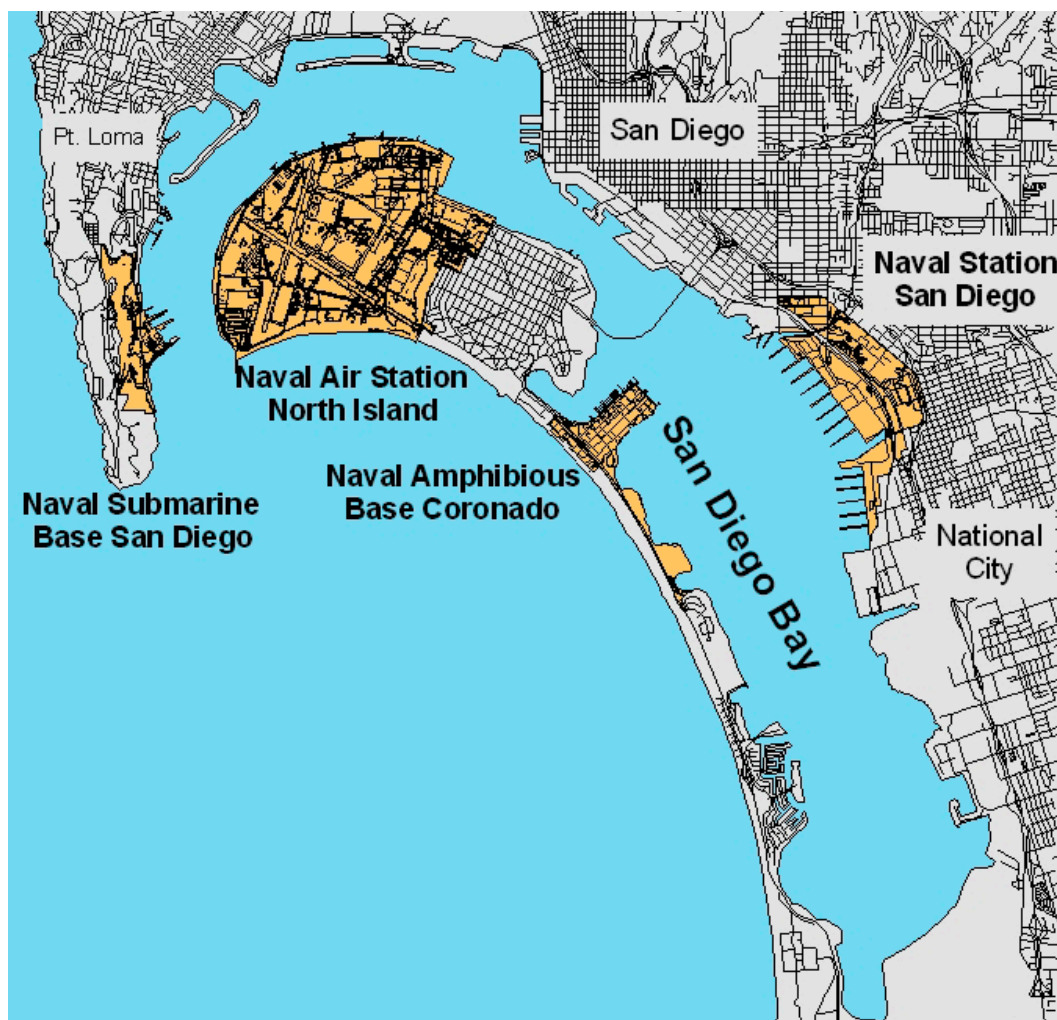


Figure 3. Navy bases bordering San Diego Bay sampled during the study, including Naval Station San Diego, Naval Submarine Base San Diego, Naval Amphibious Base Coronado, and Naval Air Station North Island.



Table 2. Chronological sampling and analysis summary. An “X” denotes analysis performed. Sample naming conventions were described above.

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
11/7/2002	NAV	SDB1	OF 9	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	OF 11	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	OF 14	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	Bay	PRE				X			X			
	NAV	SDB1	Bay 9	PRE	X	X	X		X					
	NAV	SDB1	Bay 9	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 9	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 11	PRE	X	X	X		X					
	NAV	SDB1	Bay 11	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 11	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 14	PRE	X	X	X		X					
	NAV	SDB1	Bay 14	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 14	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 14A	PRE	X	X	X		X					
	NAV	SDB1	Bay 14A	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 14A	AFT	X	X	X	X	X		X			
2/24/2003	NAV	SDB2	PR 5	FF	X	X	X	X	-		X	X		
	NAV	SDB2	PR 5	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	PR 6	FF	X	X	X	X	-		X	X		
	NAV	SDB2	PR 6	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 9	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 9	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 11	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 11	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 14	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 14	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	Bay 9	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 9	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 9	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	AFT	X	X	X	X	-		X			
	SUB	SDB2	OF 11B	FF	X	X	X	X	-		X	X		
	SUB	SDB2	OF 24	FF	X	X	X	X	-		X	X		
	SUB	SDB2	OF 26	FF	X	X	X	X	-		X	X		
	SUB	SDB2	Bay 11B	PRE	X	X	X	X	-		X			
	SUB	SDB2	Bay 11B	DUR	X	X	X	X	-		X			
	SUB	SDB2	Bay 24	DUR	X	X	X	X	-		X			
	SUB	SDB2	Bay 26	DUR	X	X	X	X	-		X			
12/11/2003	SUB	SDB2A	Bay 11B	PRE	X	X	X							
	SUB	SDB2A	Bay 23CE	PRE	X	X	X							
	SUB	SDB2A	Bay 26	PRE	X	X	X							
2/2/2004	SUB	SDB3	OF 11B	FF	X	X			X	X	X			X
	SUB	SDB3	OF 11B	COMP	X	X	X	X	X	X	X	X	X	
	SUB	SDB3	OF 23 C&E	FF	X	X	X		X	X	X			X
	SUB	SDB3	OF 23 C&E	COMP	X	X	X	X	X	X	X	X	X	
	SUB	SDB3	OF 26	FF	X	X	X		X	X	X			X
	SUB	SDB3	OF 26	COMP	X	X		X	X	X	X	X	X	X
	SUB	SDB3	Bay 11B	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 11B	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 11B	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	AFT	X	X	X		X	X	X			X

- Lost

Table 2. Chronological sampling and analysis summary. An “X” denotes analysis performed. Sample naming conventions were described above. (cont)

Sample Dates	Base	Storm	Outfall	Sample Type	Menidia	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
2/18/2004	NAV	TIE1	OF 9	FF	X	X	X	T						
	NAV	TIE1	OF 11	FF	X	X	X	T						
	NAV	TIE1	OF 14	FF	X	X	X	T						
2/18/2004	SUB	TIE1	OF 11B	FF	X	X	X	T						
	SUB	TIE1	OF 23 C&E	FF	X	X	X	T						
	SUB	TIE1	OF 26	FF	X	X	X	T						
2/26/2004	SUB	TIE1A	Bay 11B	AFT			X							
	SUB	TIE1A	Bay 23 C&E	AFT			X							
	SUB	TIE1A	Bay 26	AFT			X							
10/17/2004	NAV	SDB4	OF 14	FF	X	X	X		X					X
	ALL <sup>+</sup>	SDB4	Bay	PRE	X	X	X		X					X
	NAV	SDB4	Bay 14	DUR	X	X	X		X					X
10/17/2004	SUB	SDB4	OF 11B	FF	X	X	X		X					X
	SUB	SDB4	Bay 11B	DUR	X	X	X		X					X
10/17/2004	NAB	SDB4	OF 9	FF	X	X	X		X					X
	NAB	SDB4	Bay 9	DUR	X	X	X		X					X
10/17/2004	NI	SDB4	OF 23A	FF	X	X	X		X					X
	NI	SDB4	Bay 23A	DUR	X	X	X		X					X
10/26/2004	NAV	SDB45	OF 14	FF	X	X	X	X	X	X	X	X	X	
	NAV	SDB45	OF 14	COMP		X	X	X	X	X	X	X	X	
	NAV	SDB45	Bay 14	PRE	X	X	X		X	X				X
	NAV	SDB45	Bay 14	DUR1*	X	X	X		X	X				X
	NAV	SDB45	Bay 14	DUR2					X	X				X
	NAV	SDB45	Bay 14	DUR3					X	X				X
	NAV	SDB45	Bay 14	DUR4					X	X				X
	NAV	SDB45	Bay 14	AFT1					X	X				X
	NAV	SDB45	Bay 14	AFT2					X	X				X
	NAV	SDB45	Bay 14	AFT3					X	X				X
1/10/2005	NAV	SDB5	Bay 14	AFT	X	X	X							
	SUB	SDB5	Bay 11B	AFT	X		X							
	NAB	SDB5	Bay 9	AFT	X	X	X							
	NI	SDB5	BAY 23A	AFT			X							
	na	SDB5	Downtown	AFT	X	X	X							
2/10/2005	NAB	SDB6	OF 9	FF	X	X	X		X	X	X	X	X	X
	NAB	SDB6	OF 9	COMP	X	X	X	X	X	X	X	X	X	
	NAB	SDB6	OF 18	FF	X	X	X		X	X	X	X	X	X
	NAB	SDB6	OF 18	COMP				X	X	X	X	X	X	
	NAB	SDB6	Bay 9	PRE	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 9	DUR	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 18	PRE	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 18	DUR	X	X	X		X	X	X	X	X	X
	NI	SDB6	OF 23A	FF	X	X	X		X	X	X	X	X	
	NI	SDB6	OF 26	FF	X	X	X		X	X	X	X	X	X
	NI	SDB6	OF 26	COMP	X	X	X	X	X	X	X	X	X	
	NI	SDB6	BAY 23A	PRE	X	X	X		X	X	X	X	X	X
	NI	SDB6	BAY 23A	DUR	X	X	X		X	X	X	X	X	X
	NI	SDB6	Bay 26	PRE	X	X	X		X	X	X	X	X	X
	NI	SDB6	Bay 26	DUR	X	X	X		X	X	X	X	X	X
3/19/2005	NAB	TIE2	OF 9	FF	X	X	X	T						
	NAB	TIE2	OF 18	FF	X	X	X	T						
	NAB	TIE2	Bay 9	DUR	X	X	X							
	NAB	TIE2	Bay 18	DUR	X	X	X							
	NI	TIE2	OF 23A	FF	X	X	X	T						
	NI	TIE2	OF 26	FF	X	X	X	T						
	NI	TIE2	Bay 23A	DUR	X	X	X							
	NI	TIE2	Bay 26	DUR	X	X	X							
4/27/2005	NAB	SDB7	OF 9	FF	X				X	X	X			X
	NAB	SDB7	OF 9	COMP	X				X	X	X	X	X	
	NAB	SDB7	OF 18	FF	X				X	X	X			X
	NAB	SDB7	OF 18	COMP	X				X	X	X	X	X	
	NAB	SDB7	Bay 9	PRE	X		X		X	X	X			X
	NAB	SDB7	Bay 9	DUR	X		X		X	X	X			X
	NAB	SDB7	Bay 18	PRE	X		X		X	X	X			X
	NAB	SDB7	Bay 18	DUR	X		X		X	X	X			X
	NI	SDB7	OF 23A	FF	X				X	X	X	X	X	
	NI	SDB7	OF 26	FF	X				X	X	X	X		X
	NI	SDB7	OF 26	COMP	X				X	X	X	X	X	
	NI	SDB7	BAY 23A	PRE	X		X		X	X	X			X
	NI	SDB7	BAY 23A	DUR	X		X		X	X	X			X
	NI	SDB7	Bay 26	PRE	X		X		X	X				X
	NI	SDB7	Bay 26	DUR	X		X		X	X	X			X

+ Taken off SSC-SD Pier

\* *ex situ* toxicity

T Analyzed by toxicity lab

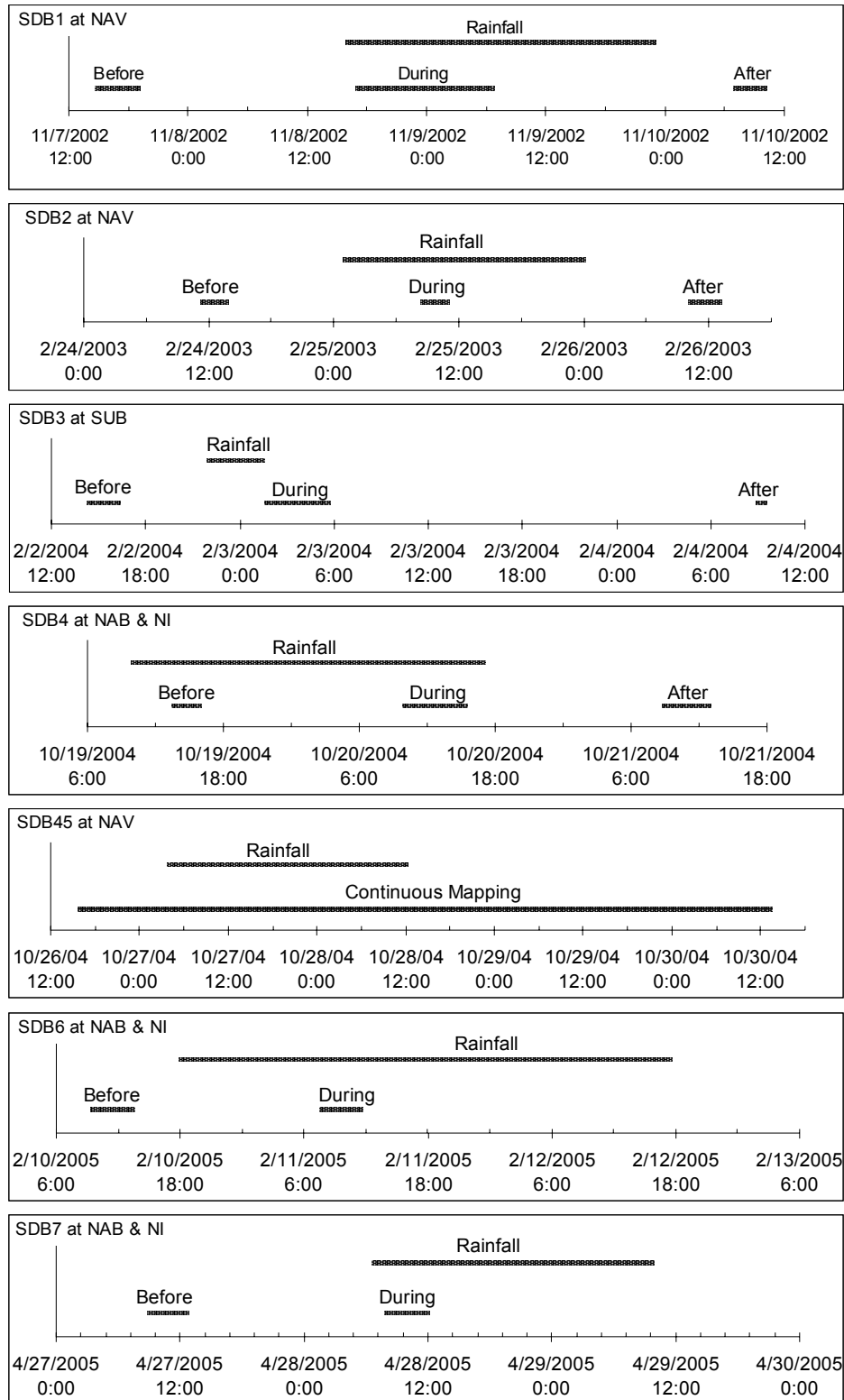


Figure 4. Summary timetable of 17 plume mapping surveys conducted before, during, and after rainfall events. The floating bioassay system was deployed during the SDB45 storm event.

## 6.2 MONITORING SITES

The drainage areas evaluated at each base were chosen on the basis that they contain some industrial activities as identified by the CNRSW Water Program Manager, Mr. Rob Chichester. All industrial drainage areas implement best available technology economically achievable (BAT) for toxic and non-conventional pollutants and best conventional pollutant control technology (BCT) for conventional pollutants through the use of Best Management Practices (BMP) as required in the Navy's Storm Water Pollution Prevention Plan. Placement of the monitoring site within a drainage area was based on the ability to safely access the site at all times, that the physical configuration of the outfall was appropriate for automated monitoring equipment and for measuring flow, and that the site was minimally impacted from tide water intrusion. Because most, if not all, storm drain outfalls at these bases are subject to tide water intrusion, most monitoring sites were moved upstream from their point of discharge to the bay to minimize the likelihood of tidal intrusion during sampling. Though the monitoring sites were placed upstream of the discharge point, they still represented over 90% of the drainage area. Even though sites were moved upstream of their discharge point, most remained affected by tidal intrusion during high tides. In all, the drainage areas represented about 221 acres. This area is approximately 10% of the total industrial acreage at these bases (Table 3). The drainage areas were all made up of greater than 90% impervious surface. The following sections describe the specific drainage acreages monitored at each of the four bases.

Table 3. Storm water outfall monitoring site sampling acreages.

Monitoring Site	Drainage Area (acres)	Sampled Area (acres)	Area Sampled (%)
<b>NAV</b>			
Outfall 9	16.6	15.4	93%
Outfall 11	30.8	28.0	91%
Outfall 14	53.3	49.1	92%
Pier 5	1.7	1.7	100%
Pier 6	1.9	1.9	100%
Total	104.3	96.1	92%
<b>SUB</b>			
Outfall 11B	21.3	19	90%
Outfall 23C	0.7	0.7	100%
Outfall 23E	0.5	0.5	100%
Sierra Pier 26	2.5	2.5	100%
November Pier 24	0.7	0.7	Not known
Total	25.8	23.7	92%
<b>NAB</b>			
Outfall 18	6.3	6.3	100%
Outfall 9	5.3	5.3	100%
Total	11.6	11.6	100%
<b>NI</b>			
Outfall 23A	5.7	5.7	100%
Outfall 26	73.9	68.0	92%
Total	79.6	73.7	93%

### 6.2.1 Naval Station San Diego Sites

Naval Station San Diego is located on the eastern shore of mid-San Diego Bay (Figure 3). The base is just south of downtown San Diego and adjacent to National City. The base is the largest surface force support installation in the nation, providing shore support, living quarters, and pier-side berthing services for approximately 60 Pacific Fleet Surface Force ships. The base has approximately 50 tenant commands, the three largest of which include the Public Works Center (PWC), the South West Regional Maintenance Center (SWRMC), and the Fleet Training Center. The base population is more than 35,000 military and 7,000 civilians.

The facility is composed of approximately 1029 acres, about 90% of which is made up of impervious surface. Its 14 piers provide about 12 miles of berthing space. There are 38 industrial drainage areas on the base. Most of these drainages directly discharge to San Diego Bay. Approximately 280 acres are identified as having industrial activities that include fuel storage and dispensing, hazardous substance storage, materials storage, metal fabrication, painting, a recycling collection center, repair and maintenance (general), sandblasting, a scrap metal yard, ship support services, vehicle repair and maintenance. Well over 50% of base acreage is paved roads or used for parking.

CNRSW chose five drainage areas to represent industrial storm water discharges to the center pier area region. This region is due for a sediment Total Maximum Daily Load (TMDL) evaluation in the near future, and the data derived from this study were planned for use in that investigation. Figure 5 shows the five drainage areas, their outfalls, drainage conveyance systems, and sampling locations. Two of the drainages include piers that have multiple drains along their entire length. Table 3 shows the drainage areas for each area. Figure 6 shows an example mapping track used to evaluate the magnitude and extent of storm water plumes in the receiving water. The 104 acres of drainage area evaluated represents about 37% of the base's total acreage identified as industrial. About 90% of the drainage areas evaluated were actually monitored by placing sampling locations close to where the outfalls discharge to the bay. The following paragraphs describe each monitoring site setup. The drainage areas sampled do not have any storm water run-on from non-Navy sources.

**Outfall 9.** Outfall 9 (OF9) enters the bay just north of Pier 5. The monitoring location was at the corner of Bainbridge and Brinser Streets, just north of the Graving Dock, about 100 feet from the discharge point through the quay wall. The outfall drains 16.6 acres, virtually all of which is impervious surface. This monitoring location was estimated to effectively sample 93% of the drainage area. Industrial facilities in this drainage area include the SWRMC shops: auxiliary machine shop, maintenance shops, and transportation and maintenance shop. The outfall is tidally influenced with bay water reaching the monitoring location at a tide stage of 3.8 feet. The pipe diameter on the upstream side of the catch basin was 20 inches, though silt covered the bottom 3.4 inches.

Onshore monitoring equipment was set up on the sidewalk next to a bus stop shelter, with the rain gauge placed on top of the shelter (Figure 7). Sensor cables and a sample line were run across the sidewalk under a mound of mortar where it entered into a curb drain that met with the main flow line. The outfall was accessible through a manhole in the middle of the street. The sensors were placed ~3 feet upstream of the manhole and catch basin opening, with the flow sensor pointing upstream to optimize its signal strength. The sensors were placed on top of the silted in section and area-flow calculations were adjusted to account for this altered pipe area. Offshore samples were collected immediately outside the discharge pipe as it came through the quay wall, within 2 feet of the pipe opening.

**Outfall 11.** Outfall 11 (OF11) enters the bay between Piers 5 and 6. The monitoring location was located at the western corner of Building 84 at the Graving Dock, about 500 feet from the discharge point through the quay wall. The outfall drains ~31 acres, all of which is impervious surface. This monitoring location was estimated to effectively sample 91% of the drainage area. When the Graving Dock is active, about half, 40% the area, is sealed from draining to this outfall as a result of storm water best management practices (BMP). Industrial facilities in this drainage area include an SWRMC corrosion control shop, antenna repair shop, and maintenance shop, and PWC ship-to-shore shops. The outfall is tidally influenced, with bay water reaching the monitoring location at a tide stage of 4.3 feet. The pipe diameter was 36 inches, though the bottom 3.3 inches was covered with gravel.

Onshore monitoring equipment was set up next to Building 84, with the rain gauge placed on top of the building (Figure 8). The outfall was accessible through a grated catch basin next to the building. The sensors were placed ~ 3 feet upstream of the catch basin opening, with the flow sensor pointing upstream to optimize its signal strength. The sensors were placed on top of the gravel section and area-flow calculations were adjusted to account for this altered pipe area. When the Graving Dock was active, the catch basin opening was well sealed around the sensor and sampling lines. Offshore samples were collected immediately outside the discharge pipe as it came through the quay wall, within 2 feet of the pipe opening.

**Outfall 14.** Outfall 14 (OF14) enters the bay between Piers 6 and 7. The monitoring site was located in a large parking lot bordering Wooden Street across from the Defense Logistics Agency Building, about 650 feet from the discharge point through the quay wall. The outfall drains ~53 acres, virtually all of which is impervious surface. This location was estimated to effectively sample 92% of the drainage area. Industrial facilities in this drainage area include a PWC vehicle maintenance and a divers' storage facility. The outfall is tidally influenced with bay water reaching the monitoring location at a tide stage of 3 feet. The pipe diameter on the upstream side of the catch basin was 36 inches, though the bottom 1.6 inches was covered with gravel.

Onshore monitoring equipment was set up inside concrete barriers placed around the manhole (Figure 9). The sensors were placed ~ 3 feet downstream of the manhole opening, with the flow sensor pointing upstream to optimize its signal strength. The sensors were placed on top of the gravel section and area-flow calculations were adjusted to account for this altered pipe area. Offshore samples were collected immediately outside the discharge pipe as it came through the quay wall, within 2 feet of the pipe opening. This site was monitored during the special floating bioassay study (SD45). Bay samples were also collected at a station, designated 14A, approximately 500 feet out from the outfall pipe.

**Pier 5.** Pier 5 (PR5) is approximately 1,260 feet long and 60 feet wide, with a total surface area of 1.7 acres. Storm water drains through ~ 350 separate concrete scuppers along the sides of the crowned pier. The high number of drains did not lend itself to autosampling, so samples were manually collected from about 20% of the drains along the entire length of the pier and composited to obtain a sample representative of the entire pier. Standard operations on the pier include material handling of sanitary waste, bilge water waste, loading equipment and supplies, drum and hazardous waste removal, recycling bins, and trash collection. The drains were not tidally influenced. Offshore samples were not collected that were specific to the pier discharge, though plume mapping was conducted around the pier area.

**Pier 6.** Pier 6 (PR6) is approximately 1375-feet long and 60-feet wide, with a total surface area of 1.9 acres. Storm water drains through ~ 120 separate small drains imbedded in the concrete surface. The high number of drains did not lend itself to autosampling, so samples were manually collected

from about 20% of the drains along the entire length of the pier and composited to obtain a sample representative of the entire pier. Standard operations on the pier include the same material handling operations already discussed for Pier 5 above. Offshore sampling was conducted around the outside of the pier. The drains were not tidally influenced. Offshore samples were not collected that were specific to the pier discharge, though plume mapping was conducted around the pier area.

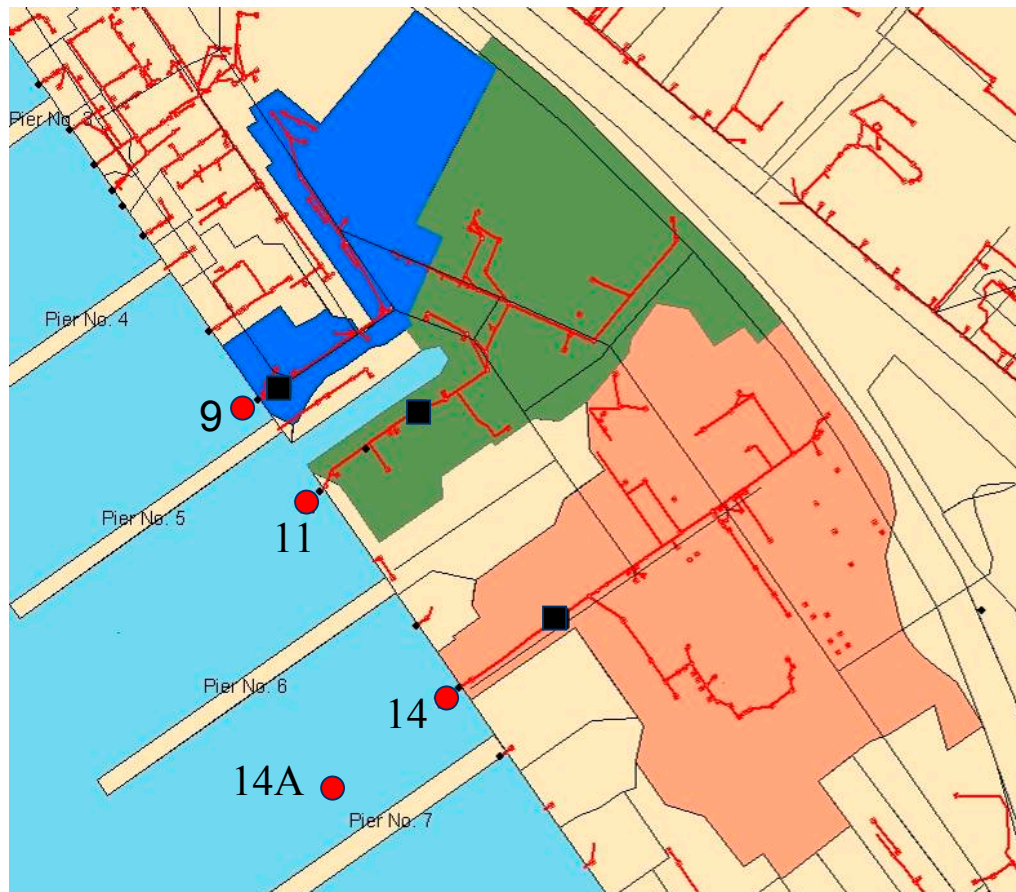


Figure 5. Detail of Naval Station San Deigo drainage areas, including storm water outfall locations and conveyance systems. Onshore storm water monitoring locations are identified by the black squares. Receiving water locations are identified by the red circles and labeled with the associated outfall number. Drains along Piers 5 and 6 were also monitored. Position of offshore sampling locations is approximate because of the map scale.

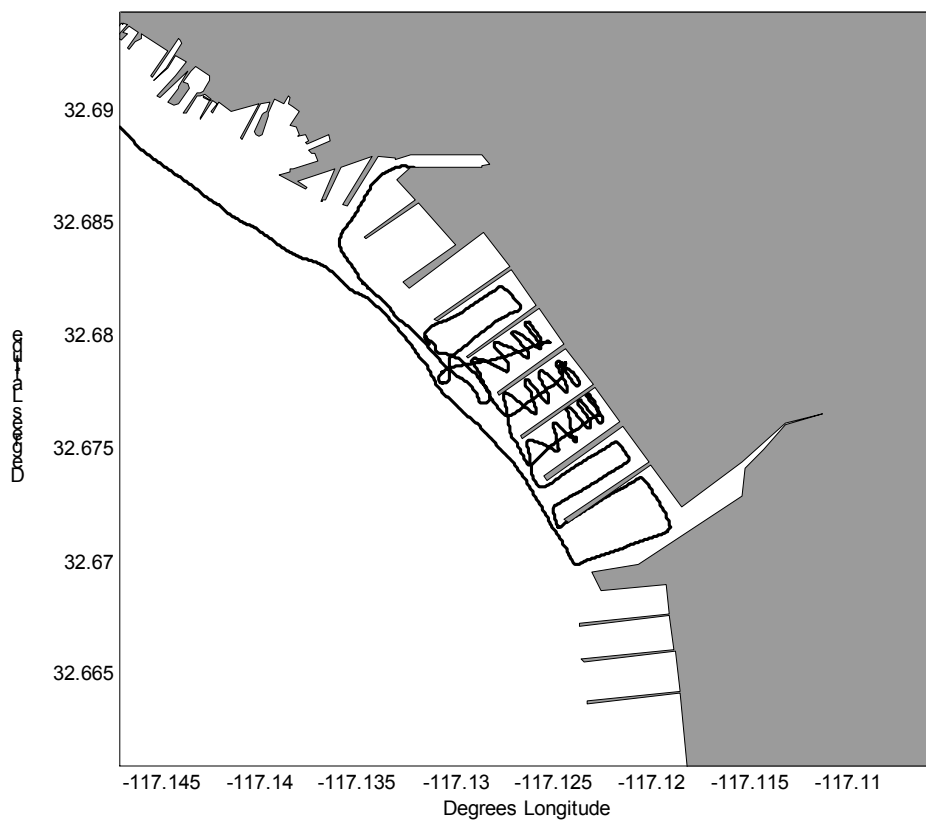


Figure 6. Example storm water plume mapping track used during storm event SDB1 at Naval Station San Diego. The track was repeated before, during, and after storm events. All plume mapping tracks are shown in Appendix G.



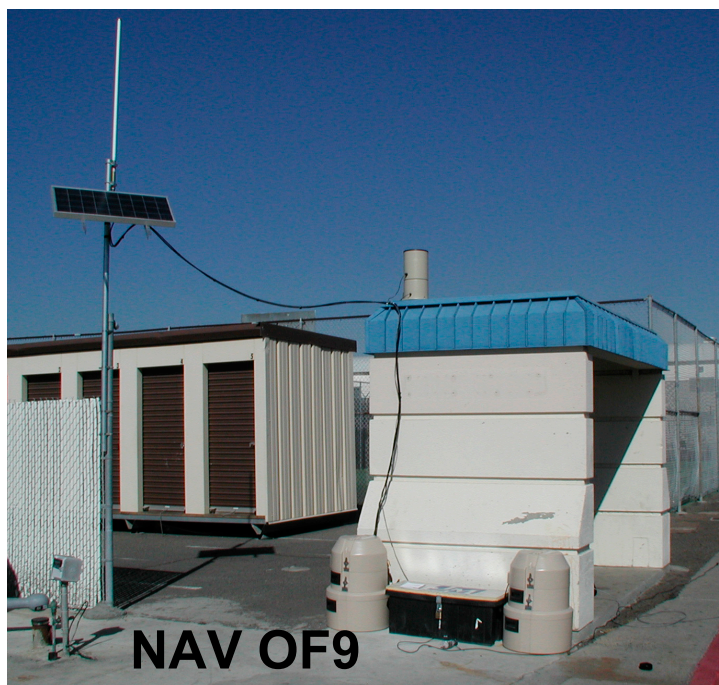


Figure 7. Naval Station San Diego storm water monitoring location for outfall 9. Automated samplers, rain gauge, power and communications systems are also shown.



Figure 8. Naval Station San Diego storm water monitoring location for outfall 11. The rain gauge was placed on top of Building 84 in the background. The solar power panel and RF link were attached to the light pole next to the building. The short distance between the building and the grate was secured by traffic cones to protect the sample line and cabling. The inset at the right shows plywood covering the catch basin when the Graving Dock was active.



Figure 9. Naval Station San Diego storm water monitoring location for outfall 14. The site was located in a parking lot about 650 feet from the discharge point through the quay wall. The barriers were provided by the base to provide a secure monitoring area.

### 6.2.2 Naval Submarine Base San Diego

Naval Submarine Base San Diego is on the Point Loma peninsula, which forms the western boundary of the entrance to San Diego Bay from the Pacific Ocean. The base provides pier-side berthing and support services for submarines of the U.S. Pacific Fleet. The base is home to Commander, Third Fleet; Commander, Submarine Squadron Eleven; Commander, Submarine Development Squadron Five; and Commander, Military Sealift Command Pacific, as well as six attack submarines, the Third Fleet Flagship, and Submarine Training Center Detachment.

The base comprises 316 acres, but the majority of the industrial facilities are on approximately 30 acres around its pier area (Figure 10). Most of this acreage is made up of impervious surface. The base has three main piers identified as November, Mike, and Sierra. There are 11 different industrial drainage areas on the base. Industrial activities on the base include a fuel depot, hazardous substance storage, materials storage, a recycling collection center, repair and maintenance (general), ship support services, an air compressor, and a steam plant. A high percentage of the base is paved roads or used for parking. The drainage areas sampled do not have any storm water run-on from non-Navy sources.

Five drainage areas were chosen by CNRSW to represent industrial storm water discharges from the base. Figure 10 shows the drainage areas, their outfalls, drainage conveyance systems, and sampling locations. Two of the drainages include piers that have multiple drains along their entire length. Table 3 shows the drainage areas for each area. Figure 11 shows an example mapping track used to evaluate the magnitude and extent of storm water plumes in the receiving water. A total of 26 acres of industrial drainage area was evaluated. About 90% of the drainage areas evaluated were

actually monitored by placing sampling locations close to where the outfalls discharge to the bay. The following paragraphs describe each monitoring site setup.

**Outfall 11B.** Outfall 11 (OF11) enters the bay under Sierra Pier. The monitoring location was located at the northeast corner of the base's parking structure, approximately 280 feet from its discharge point under Sierra Pier. The outfall drains about 21 acres, nearly all of which is impervious surface. This location was estimated to effectively sample 90% of the drainage area. Industrial facilities in this drainage area include an air compressor plant, fire fighting facility, wet trainer, and waterfront operations storage. The outfall is tidally influenced with bay water reaching the monitoring location at a tide stage of ~ 4.1 feet. The pipe diameter was 26 inches.

Onshore monitoring equipment was set up in a parking space enclosed by barriers similar to Naval Station San Diego outfall 14 (Figure 9). The rain gauge was placed on the ground within a few feet of the sampling system. The outfall was accessible through a grated catch basin. Monitoring sensors were placed ~ 3 feet downstream of the catch basin opening, with the flow sensor pointing upstream to optimize its signal strength. Offshore samples were collected at the northwest corner of Sierra Pier. This sampling position was approximately 50 feet away from the discharge pipe, which enters underneath the pier.

**Outfall 23CE.** Outfalls 23C and 23E (OF23CE) were sampled together. These drainage areas are roughly 0.5 acres, each of impervious surface, and are next to each other along the waterfront north of Mike Pier (Figure 10). The waterfront edges of these areas are bermed by about a ½-foot-high asphalt curb. A pipe with a ball valve extends through the berm in each area. The valve can be manually opened to allow storm water to flow over the rip-rap border before its entry to the bay, though it usually remains closed. The onshore monitoring location was located on the bay side of the two valves. The two valves were tied together using Teflon<sup>®</sup> tubing connected to an automated sampler. The autosampler system was used to manually collect storm water samples from the two sites and to measure rainfall. Industrial facilities in this drainage area include a bilge and oily wastewater treatment system, periscope maintenance facility, and a ship spares storage area. The outfall was not tidally influenced. The pipe diameter going through the berm was approximately 3 inches. Offshore samples were collected from the surface water within 5 feet of the rip-rap that forms the base borders and half-way between the two discharge locations.

**Outfall 24, November Pier.** Outfall 24 (OF24) is one of many drains located along the length of November Pier. Because the pier was not numbered, the designator for this outfall was its outfall (OF) number rather than its pier number (PR), as was used at Naval Station San Diego. The sampling location used to manually collect one first-flush storm water sample was approximately 170 feet out on the north side of the pier. The pier is approximately 540 feet long and 60 feet wide, with a total surface area of ~ 0.7 acres. The area of the pier represented by the single sampling location is not known. Standard operations on the pier include material handling of sanitary waste, bilge water waste, loading equipment and supplies, drum and hazardous waste removal, recycling bins, and trash collection. The drains were not tidally influenced. The pier drain was sampled by pumping water as it flowed across a Teflon<sup>®</sup> sheet using a peristaltic pump with Teflon<sup>®</sup> tubing. Offshore samples were collected off the side of the pier below the drain using the same pumping system. A float was attached to the tubing to ensure the sample was collected at a depth of 2 feet.

**Outfall 26, Sierra Pier.** Outfall 26 (OF26) is one of many drains located along the length of Sierra Pier. Because the pier was not numbered, the designator for this outfall was its outfall (OF) number rather than its pier number (PR), as was used at Naval Station San Diego. The center drain at the 525-foot marker collected first-flush storm water samples. Full-storm composite samples were manually collected from about 20% of the drains along the entire length of the pier and composited



to obtain a sample representative of the entire pier, which at approximately 1000-feet long by 110-feet wide, has a total surface area of ~2.5 acres. Samples were pumped from plastic funnel inserts that had a siphon tube that allowed water to flow through the drain while maintaining a constant 0.5-L volume.

Standard operations on the pier include material handling of sanitary waste, bilge water waste, loading equipment and supplies, drum and hazardous waste removal, recycling bins, and trash collection. Offshore sampling was conducted off the side of the pier immediately to the west of the ARCO dry dock. The drains were not tidally influenced. Offshore sampling was conducted immediately next to the south side of the pier adjacent to the ARCO dry dock. An additional sample was also collected at a site designated 26A, approximately 100 feet out from the end of Sierra Pier.

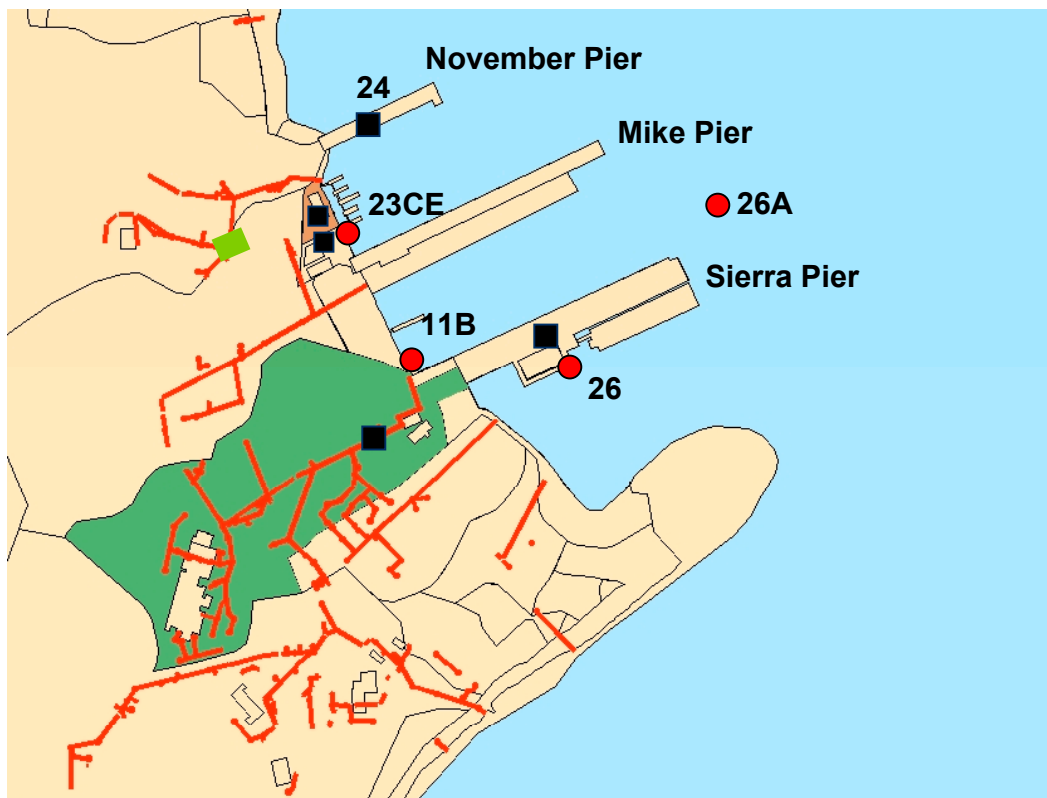


Figure 10. Detail of Naval Submarine Base San Diego drainage areas, including storm water outfall locations and conveyance systems. Onshore storm water monitoring locations are identified by the black squares, though samples were also collected from multiple drains along Sierra Pier for composite samples. Receiving water sample locations are identified by the red circles and labeled with the associated outfall number. Position of offshore sampling locations is approximate because of the map scale.

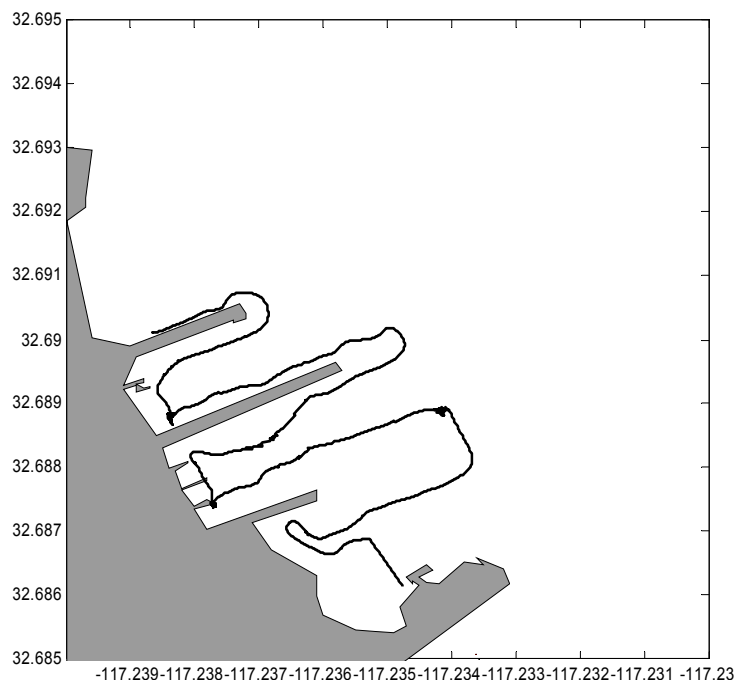


Figure 11. Example storm water plume mapping track used during storm event SDB2 at Naval Submarine Base San Diego. The track was repeated before, during, and after storm events. All plume mapping tracks are shown in Appendix G.

### 6.2.3 Naval Amphibious Base Coronado Sites

Naval Amphibious Base Coronado is on a strip of land that juts into the bay from the west side at about its midpoint from the mouth (Figure 3). The base is a major shore command, supporting 27 tenant commands, and is the West Coast focal point for special and expeditionary warfare training and operations. The amphibious base houses Commander Naval Surface Force, U.S. Pacific Fleet, responsible for the training, maintenance and crews of the approximately 90 ships of the Pacific Fleet, and Commander Naval Special Warfare Command, U.S. Pacific Fleet. Also located there are most of the Naval Expeditionary and Naval Special Warfare units of the Pacific Fleet as well as the Navy Parachute Team, the Leap Frogs.

The base currently occupies ~1,000 acres, including 257 beach-front acres leased from the State of California along the Pacific Ocean. The majority of the Activity is on a rectangular-shaped area constructed with fill material extending from the original peninsula into the bay. The topography of the Activity is very flat, with an average elevation of about 10 feet above mean sea level. Most of the acreage is made up of impervious surface. The drainage areas sampled do not have any storm water run-on from non-Navy sources.

The base has 53 industrial drainage areas. Approximately 88 acres are identified as having industrial activities that include fuel storage and dispensing, hazardous substance storage, materials storage, a recycling collection center, repair and maintenance (general), ship support services, an air compressor, and a steam plant. A high percentage of the base is paved roads or used for parking.

CNSRW chose two drainage areas to represent industrial storm water discharges from the base. Figure 12 shows the drainage areas, their outfalls, drainage conveyance systems, and sampling locations. Figure 13 shows an example mapping track used to evaluate the magnitude and extent of

storm water plumes in the receiving water. The nearly 12 acres of drainage area evaluated represents about 14% of the base's total acreage identified as industrial. The entire drainage areas were evaluated by placing sampling locations at the end of the discharge pipes. Offshore sampling was conducted immediately outside the pipe discharge to the bay. The following paragraphs describe each monitoring site setup.

**Outfall 9.** Outfall 9 (OF9) enters the bay near the southeast corner of the base in a barge maintenance yard. The outfall drains ~ 5.3 acres, all of which is impervious surface. The monitoring site was right along the quay wall (Figure 14), thus sampling was representative of the entire drainage area other than what might discharge as sheet runoff. Industrial facilities in this drainage area include an abrasive blast facility and a boat-fitting and sail-loft building. The outfall is tidally influenced with bay water reaching the monitoring location at a tide stage of 4.8 feet. The pipe diameter was 13 feet. Monitoring sensors were placed ~ 3 feet upstream of the end of the pipe with the flow sensor pointing upstream. Offshore sampling was conducted immediately outside the discharge pipe as it came through the quay wall.

**Outfall 18.** Outfall 18 (OF18) enters the bay near the northwest corner of the base in a small grassy area along the beach (Figure 15). The outfall drains ~6.3 acres, most of which is impervious surface. The monitoring site was at the end of the outfall pipe that exited the rip-rap at the shore edge. Thus, sampling was representative of the entire drainage area other than what might discharge as sheet runoff. Industrial facilities in this drainage area include a vehicle and boat maintenance facility and a hazardous materials storage and handling area. The outfall was tidally influenced, with bay water reaching the monitoring location at a tide stage of 6.4 feet, a very high tide condition. The pipe diameter was 18 feet. A funnel with a siphon tube was attached at the end of the outfall pipe to provide a consistent volume for the sampling pump (Figure 16). Monitoring sensors were placed ~ 3 feet upstream of the end of the pipe, with the flow sensor pointing upstream. Offshore sampling was conducted immediately outside the region of rip-rap. During the SDB4 and TIE2 rain events, samples were collected from shore within 5 feet of the discharge. During the SDB6 and SDB7 sampling events, the samples were collected by boat and because of shallow water, the distance from the discharge was between 30 and 50 feet away.

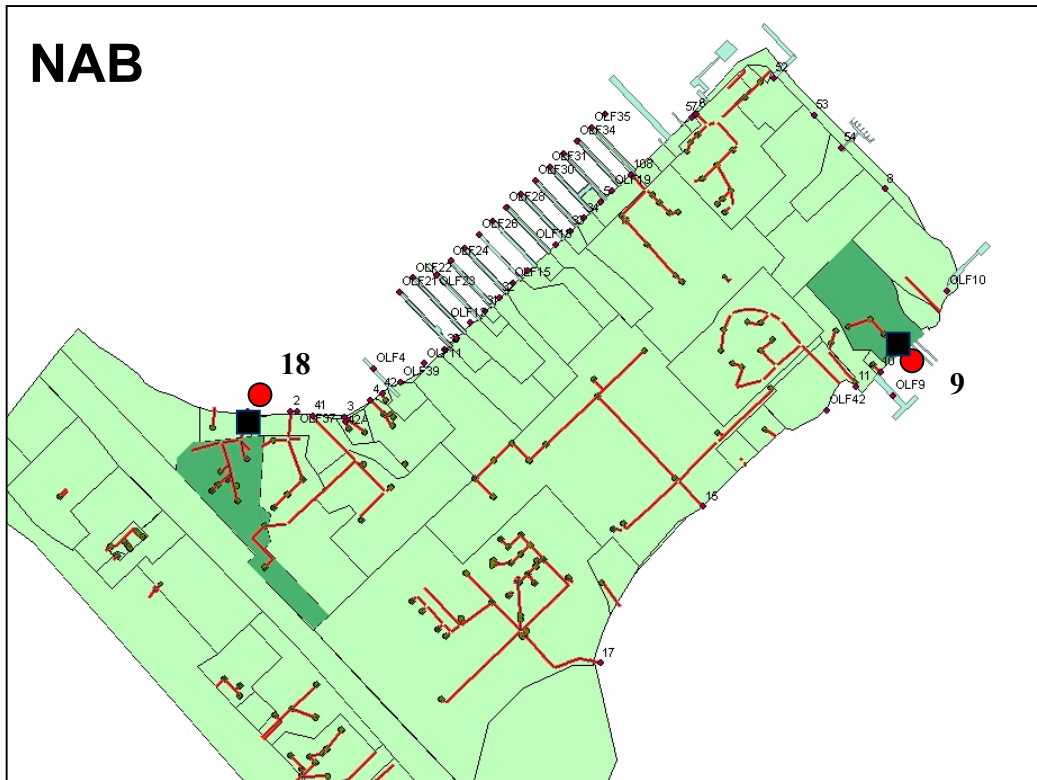


Figure 12. Detail of Naval Amphibious Base Coronado drainage areas, including storm water outfall locations and conveyance systems. Onshore storm water monitoring locations are identified by the black squares. Receiving water sample locations are identified by the red circles and labeled with the associated outfall number. Position of offshore sampling locations is approximate because of the map scale.

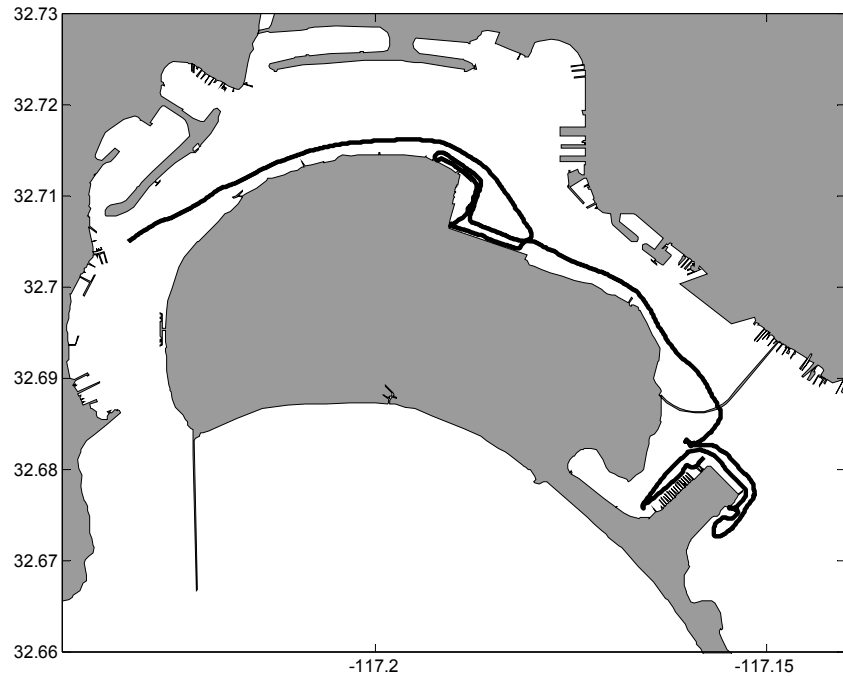


Figure 13. Example storm water plume mapping track used before storm event SDB6 for Naval Amphibious Base Coronado and Naval Air Station North Island. The track was repeated before and during storm events. All plume mapping tracks are shown in Appendix G.



Figure 14. Naval Amphibious Base Coronado storm water monitoring location for outfall 9. The site was located in a barge maintenance area right at the quay wall.



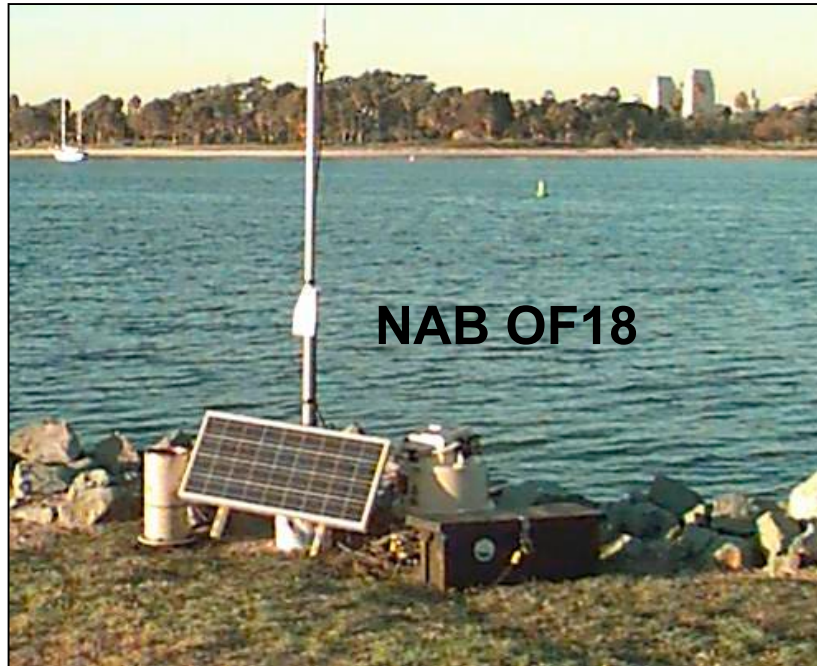


Figure 15. Naval Amphibious Base Coronado storm water monitoring location for outfall 18. The site was located within a small grassy area along a beach bordering the bay.



Figure 16. Sampling setup at Naval Amphibious Base Coronado outfall 18. Storm water was sampled as it flowed through the funnel setup, which maintained a continuous 0.5-L volume using the attached siphon tube.

#### 6.2.4 Naval Air Station North Island Sites

Naval Air Station North Island is the bulk of the land mass that forms the western perimeter of San Diego Bay (Figure 3). The Air Station is headquarters for six major military flag staffs, including Commander Naval Air Force, U.S. Pacific Fleet, responsible for maintenance and training of all naval aircraft and aircraft carriers in the Pacific Fleet; Commander Third Fleet, responsible for the defense of the western approaches to the U.S. and the direction of joint, combined, intertype, and fleet exercises in the eastern Pacific; Commanders Carrier Group One and Seven; and Commanders Cruiser Destroyer Group One and Five. With all the ships in port, the population of the base is over 30,000 active duty, selected reserve military, and civilian personnel.

The base occupies 2,800 acres, of which 2,400 acres are land area and 400 acres are water (tidelands around the island). Approximately 80% of the base land area is impervious to storm water. There are 54 industrial drainage areas on the base. Approximately 2,040 acres are identified as having industrial activities that include fuel storage and dispensing, hazardous substance storage, materials storage, metal fabrication, painting, a recycling collection center, repair and maintenance (general), sandblasting, a scrap metal yard, ship support services, aircraft support and maintenance facilities, and vehicle repair and maintenance.

CNRSW chose two drainage areas to represent industrial storm water discharges to the center pier area region. Figure 17 shows the two drainage areas, their outfalls, drainage conveyance systems, and sampling locations. Table 3 shows the drainage areas for each area. Figure 13 shows an example mapping track used to evaluate the magnitude/extent of storm water plumes in the receiving water. The nearly 80 acres of drainage area evaluated represents about 4% of the base's total industrial acreage. About 93% of the drainage areas evaluated were actually monitored by placing sampling locations close to where the outfalls discharge to the bay. Sampled drainage areas do not have any storm water run-on from non-Navy sources. The following describe each monitoring site setup.

**Outfall 23A.** Outfall 23A (OF23A) enters the bay along the north-south carrier pier. The outfall was located in a parking area behind the Port Operations building, adjacent to one of the carrier piers (Figure 17). Because the catch basin grate was located in a thoroughfare, the site was sampled manually. The outfall drains ~5.7 acres, all of which is impervious surface. The monitoring site was representative of the entire drainage area. Industrial facilities in this drainage area include a water-front operations facility and a boom storage facility. It is not known whether bay water tidally influences the outfall, as this event was not observed during sampling events. The pipe diameter was estimated as 18 feet (the grating was not removed). Offshore sampling was conducted immediately outside the discharge pipe as it came through the quay wall along the carrier pier.

**Outfall 26.** Outfall 26 (OF26) enters San Diego Bay at the corner formed by two carrier piers (Figure 17). The monitoring site was along the fence line that secured a steam plant (Figure 18). The outfall drains ~74 acres, which is impervious surface. Samples collected at this monitoring site were representative of about 92% the entire drainage area. Industrial facilities include aircraft maintenance hangars, a PWC storage warehouse, a spray paint booth and sandblasting facility, an air compressor plant, and a Navy primary standards laboratory flow calibration facility. The outfall is tidally influenced, with bay water reaching the monitoring location at a tide stage of 3.2 feet. The pipe diameter was 48 inches. Monitoring sensors were placed ~3 feet upstream of the manhole, with the flow sensor pointing upstream. Offshore sampling was conducted as close to the discharge pipe as it came into the bay through the quay wall and rip-rap along the shoreline. During the SDB4 and TIE2 rain event, samples were collected from shore within 5 feet of the discharge. During the SDB6 and SDB7 sampling events, the samples were collected by boat and because of shallow water, the distance from the discharge was between 30 and 50 feet away.



## 6.3 SAMPLE COLLECTION METHODS

### 6.3.1 Design Storm Criteria

The goal of the project was to sample during typical rainfall conditions for the region. Seasonal rainfall for the immediate region averages about 10 inches, with 85% of it falling between November and March (<http://www.wrh.noaa.gov/sgx/climate/san-san.htm>) (NOAA, 2004). The historical data plotted as a cumulative frequency diagram (Figure 19) shows that a rainfall total of 0.25 inches or less represents nearly half of all rainfall events while up to a 0.5-inch rain total represents 68% of all storms. About 16% of all storms have rainfall totals greater than 1 inch.

The design storm used in this study was a rainfall total of at least 0.25 inch within a 24-hour time frame, with an antecedent dry period of 7 days. Given the inexact nature of weather predictions and the limited storm weather window in San Diego, the design storm was chosen primarily on the need to have sufficient time and runoff volume for sampling rather than on trying to obtain data during a specific loading condition. The permits specify only that grab samples be collected during scheduled facility operating hours during the first hour of discharge (flow measurement is not required) when preceded by at least 7 working days without storm water discharge. Unlike the NPDES permit requirement, sampling during this study was conducted on a 24-hour/7-day-per-week basis.

A decision to sample a storm was based on a better than 50% likelihood of rainfall (probability of measurable precipitation) and quantitative rainfall amount  $>0.25$  inch, predicted by the San Diego office of the National Weather Service. The type of storm and its likelihood of meeting the predictions also played a role in the decision process. The purpose of these decision criteria was to help ensure that a full collection sequence could be completed once a decision to sample was made. The decision to end a storm (cease sampling) was made when there was no more storm flow and there was little likelihood for more significant rainfall, based on radar and satellite storm tracking.

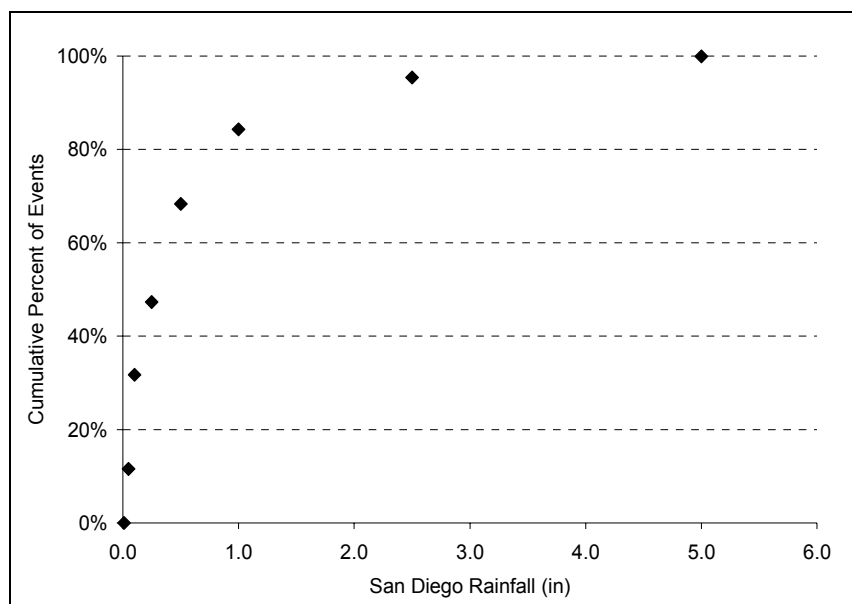


Figure 19. Cumulative frequency distribution plot of historical rainfall data for San Diego (Lindbergh Field). The plot shows rainfall totals for storm events occurring during the October–April rainy season. The plot represents percentages derived from over 15,000 records See the following website: <http://www.wrh.noaa.gov/sgx/climate/san-san.htm>

### 6.3.2 Onshore Storm Water Sampling

Onshore monitoring included the collection of first-flush and/or full-storm composite storm water samples from outfall locations using an automated sampler (American Sigma 900) or manual methods. The automated samplers also measured rainfall, storm water flow velocity and level in the discharge pipe, and conductivity data. These data were stored on the automated samplers as well as telemetered to SSC San Diego using radio frequency (RF) communications. Pictures of the automated systems have been shown in previous figures (e.g., Figure 15).

**First-Flush.** First-flush storm water samples were grabs collected during the first hour of storm flow by pumping water from the outfall using the automated sampling system pumps or similar but separate peristaltic pumps. At a few locations, a pre-cleaned plastic bucket was used to collect water as it exited the pipe before reaching the bay. In all cases, first-flush samples represented undiluted storm water discharge, similar to the requirement in the NPDES permit. The PR5 and PR6 pier samples collected at Naval Station San Diego were pumped from water that had pooled on top of a Teflon<sup>®</sup> sheet placed over part of the drain. The Naval Submarine Base San Diego outfall 26 samples were pumped from pre-cleaned funnels placed inside the drains that allowed water to continuously flow to the bay but maintained a volume of 0.5 L similar to the one used at the end of Amphibious Base Coronado outfall 18 (Figure 16). Sample water was usually pumped directly into the glass containers that were sent for toxicological or chemical analysis. In some instances, as a result of logistical constraints, an intermediate set of pre-cleaned glass bottles was filled and the sample transferred to bottles that were sent for analysis. All samples were stored at 4°C until processed for analysis, except for DOC samples, which were frozen.

**Composite.** Composite storm water samples were collected as a function of rainfall throughout a storm event using the automated sampling system. Though not included in the NPDES permit, composite sampling was initiated to characterize the total storm water discharge. Earlier work with the samplers indicated that sample collection triggered on rainfall was equivalent to flow-weighted sampling (Figure 20). Composite samples collected in this manner accurately represented the entire discharge. Between 250- and 535-mL aliquots were collected during each triggering event (rainfall = 0.01 inch). The volume and number of samples per bottle chosen for collection were preprogrammed based on the predicted rainfall total, the sample volume required for analysis, and number of aliquots considered representative of the predicted storm (CALTRANS, 2000). The volume of sample necessary to accomplish all toxicity and chemistry testing was 11 L. There were only a couple of instances when there was insufficient composite sample volume to fulfill all the analysis requirements. In those instances, the number of toxicity test species or number of dilutions were reduced. Samples were collected into pre-cleaned 4-L glass bottles. When all four bottles were filled, a second set was placed into the sampler and the sampling resumed. No sample collection occurred during the time it took to switch out bottles, download data, and restart the sampling program, a period of roughly 15 to 20 minutes. Composite samples collected on the piers and at Naval Submarine Base San Diego outfall 23CE were manually collected as a function of time. All samples were stored at 4°C until processed for analysis, except for DOC samples, which were frozen.

**Sample Processing.** Sample processing was done as soon as practical, but typically within 24 hours of collection. First-flush samples collected into intermediate bottles in the field were brought back to the lab and split into the final bottles used for analysis. The process typically involved splitting water from two 4-L bottles into multiple containers for metals, DOC, TSS, and organics. Each bottle was shaken and then poured to fill about half the volume of the receiving bottle based on visual inspection. The second bottle was then shaken and poured to fill the remaining volume needed. The sample remaining in the original bottles was used for the toxicity analyses.



Each of the samples used to produce the composite sample were checked for conductivity, temperature, oxygen, and pH by removing a small aliquot before compositing. The samples were also weighed when there were more than five full composite sample bottles to assist in the compositing process. If there were less than five full bottles, the entire contents of the samples in each bottle were added to a pre-cleaned 5-gal carboy. If more than five bottles were collected, a partial sample from each bottle based on weight was placed into the carboy. The bottles were stirred before and during transfers to minimize any losses of particulates. The full composite sample was then distributed from the carboy to individual chemistry bottles using a Teflon<sup>®</sup> hose siphon. The sample remaining in the 5-gal carboy was used for the toxicity analyses. Samples were stored at 4°C until analyzed, except for DOC samples, which were frozen.

### **6.3.3 Offshore Receiving Water Sampling**

As described previously, offshore monitoring included collecting surface bay water samples directly outside of outfalls before, during, and after storm events. Some samples were also collected a distance away from the outfalls to evaluate toxicity and chemistry gradients. Sample locations were described earlier under site descriptions. Sample collection locations were usually determined visually but were recorded by the MESC navigation system. The discrete samples were collected from a boat-mounted pumping system or by sampling from shore using a peristaltic pump, or in a few instances, for logistical reasons, with a pre-cleaned bucket. Sampling by boat was performed using either a submersible stainless steel and Teflon<sup>®</sup> pump or a peristaltic pump. Both types of pumps used Teflon<sup>®</sup> hoses to deliver surface seawater to pre-cleaned sample bottles. The intake hoses were set at a depth of ~2 feet for collection. In all cases, water was pumped for at least 2 minutes before collecting the sample. Water was delivered directly to the sample bottles sent for analysis.

As a result of logistical constraints, receiving waters were occasionally sampled from shore. When this was done, only locations directly outside the outfalls were collected. In most cases, a peristaltic pump and Teflon<sup>®</sup> hose were used to obtain surface seawater. In a few instances, a pre-cleaned bucket was used. The pump system was outfitted with a small buoy and weight setup to ensure the sample was collected at a depth of about 2 feet. Bucket sampling provided a sample collected from the top 2 feet of the water column (cf. at a depth of 2 feet). Sample water was delivered to a set of intermediate pre-cleaned bottles and then placed on ice at 4°C until processed, except for DOC samples, which were frozen.

### **6.3.4 Plume Mapping**

Offshore plume mapping was performed using the MESC real-time data acquisition and processing system designed and built by the U.S. Navy (Lieberman, Clavell, and Chadwick, 1989; Chadwick and Salazar, 1991; Katz and Chadwick, 1993). MESC was deployed onboard the 40-foot Navy research vessel (RV) ECOS or on a 20-foot survey craft, depending on availability. The primary MESC real-time measurement parameter for evaluating storm water plume magnitude and extent was salinity, though sample depth temperature, light transmission, and ultraviolet oil fluorescence were also evaluated. A Trimble Model 4000RLII differential global positioning system was used to acquire real-time position data. SeaBird Inc. Model 911 CTD was used to measure salinity, temperature, and sample depth. Oil fluorescence was measured using a Turner Designs Inc. Model 10AU fluorometer in flow-through mode. Light transmission was measured using a SeaTech 25-cm path-length transmissometer. Sensors were towed off the side of the vessel or run in flow-through mode by pumping water from the towed package to the onboard sensors.

The MESC was used to map out the above parameters as close in to the outfall pipe discharge location as possible, usually within a few feet of the discharge pipe, and expanded out to cover larger

regions of the facility before, during, and after storm events. A few locations such as Submarine Base outfall 11B discharged under a pier and the closest sampling point was about 50 feet away. Outfalls NAB18 and NI26 discharged into shallow water that limited the ability to map closer than about 30 to 50 feet away, depending on tide height. Track lines varied with each survey to accommodate sample collections and wide-area plume mapping coverage. Most data were collected in the top 1 meter of the water column, though vertical profiles were also run periodically to evaluate plume depths at various locations in the survey area. When plume sizes were sufficiently large enough to track at depth, vertical tow-yos were run in which the sensors were raised and lowered through the top 10 meters of the water column as the boat was moving, and thus provided wide-area coverage of plume depth. The nominal along-track resolution when traveling at 5 knots was about 0.5 meter. The nominal depth resolution when performing tow-yos or vertical profiles was ~0.1 meter.

The objective for collecting MESC data was to develop maps of the areal extent of storm water plumes developed during events and to see how they dissipate with time. The salinity data were also used to quantify the magnitude of the freshwater input. While sampling plans included conducting multiple transects throughout storm events, waterside security measures and resources allowed for a more limited set of surveys. The set typically included a survey before the start of rainfall (typically <24 hours before), one or two surveys during storm water discharge, and one survey about 24 hours after rainfall had stopped. The data collected on each of these surveys were used to produce interpolated spatial maps that allowed evaluation of the area of impact through time. Interpolated maps of salinity were used to quantify the relative amount of freshwater derived from the storm discharge.

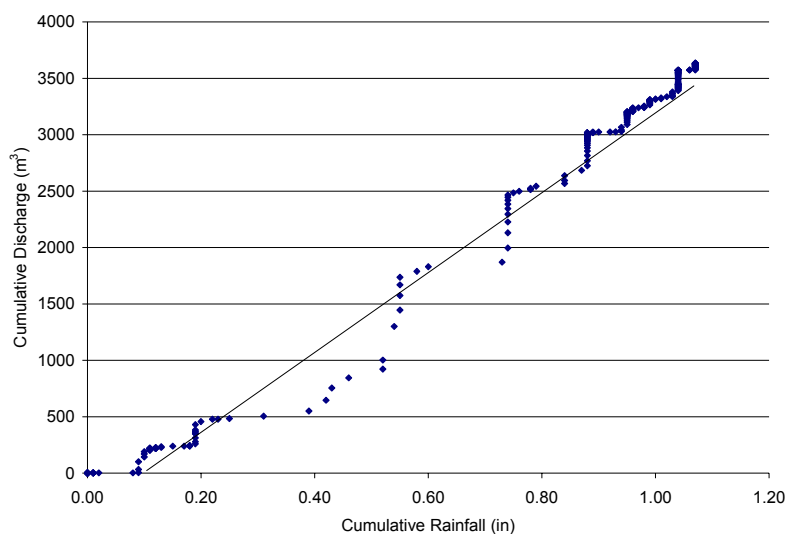


Figure 20. Relationship between rainfall and discharge volume during one storm at Naval Submarine Base San Diego outfall 11B. The good correlation validated the use of rainfall as a trigger for composite sampling for the four Navy facilities. The relationship is not expected to hold for regions with appreciable amounts of non-impervious surface.

### 6.3.5 Special Floating Bioassay Laboratory Study

A special floating bioassay laboratory study was conducted in October 2004 to monitor the receiving environment throughout an entire storm event and evaluate impacts under actual exposure conditions immediately outside the point of discharge. The storm event was a record rainfall total for October at 3.4 inches over a 2-day period. To perform this task, a flow-through bioassay system was

placed aboard the RV ECOS along with the MESC real-time monitoring system. Monitoring was performed outside of Naval Station San Diego outfall 14 over a 4-day period from 26 to 30 October 2004. The ECOS with MESC system was tied up on the quay wall just outside the outfall so that its sensors and water intake system were directly in line with the outfall pipe discharge, about 5 meters away from the quay wall. The MESC sensors and water intake were placed at about 1-meter depth, though the full water column to about a depth of 7 meters was periodically evaluated. Surface salinity, temperature, sample depth, light transmission, pH, and oil fluorescence data were collected every 4 seconds. Two trace metal analyzers, using anodic stripping voltammetry techniques (Zirino, Lieberman, and Clavell, 1978) were used to measure dissolved copper and zinc about every 15 minutes. The MESC's trace-metal, clean Teflon<sup>®</sup> seawater pumping system was used to supply surface seawater to the bioassay flow-through system at a rate of about 10 L/min, and to collect discrete samples for chemical analysis before, during (four samples), and after (three samples) the storm event. First-flush and full-storm composite storm water samples were collected from the discharge during the storm event using the techniques already described above.

The bioassays were conducted with topmelt, mysids, and mussel embryos. Two treatments were conducted, one under flow-through conditions and the other a "floating" control to assess any impacts associated with being in the field. Test organisms were held in clean, seawater-leached 400-mL polyethylene containers that were placed into a water bath (Figure 21). Matching lids with cutouts were used to prevent organism ejection during boat movement, yet allow access for water flow and feeding. Control (static) and flow-through chambers contained 250 mL of seawater at all times. The MESC flow-through system provided water to a PVC grid fitted with adjustable valves to regulate water flow to individual chambers. Overflow ports on flow-through chambers measured approximately 2 cm and were covered with a 300- $\mu$ m PeCap mesh. The flow rate resulted in an average of 15 turnovers per hour. Seawater overflow from the exposure chambers filled the water bath to approximately 5 cm in height to help insulate against temperature shift. Control chambers were filled with clean, filtered, natural seawater from the research pier at Scripps Institution of Oceanography. One renewal of the control water was performed for 96-hour exposures, while 48-hour exposures were not renewed. Topmelt and mysids swam freely in the chambers, while mussel embryos were contained in 5-cm-diameter polycarbonate drums with 20- $\mu$ m Nitex<sup>®</sup> mesh on each side, as described in Phillips et al., 2004.

Six replicates of 10 mysids, 8 replicates of 5 topmelt, and 6 replicates of 150 mussel embryos were used for each treatment. Mysid and topmelt exposures were 96 hours while mussel exposures were 48 hours. Organisms were acclimated to expected testing temperatures in the exposure chambers over approximately 1 hour and carefully transported to the water bath system aboard the RV ECOS. All topmelt and mysids were fed twice daily with freshly hatched *Artemia* nauplii. MESC sensors were used to monitor temperature, pH, and salinity for all flow-through chambers, and a HOBO<sup>®</sup> data logger was used to monitor temperature in static controls and the water bath. Dissolved oxygen was also monitored hourly in all chambers using a YSI oxygen meter.

Individual outfall and receiving water toxicity and chemistry results are described in the Naval Station San Diego results section. The real-time monitoring data results are included in the discussion. The full results of this special study are described in a Marine Technology Society Oceans 2005 proceedings paper (Katz and Rosen, 2005), Appendix H.





Figure 21. Flow-through bioassay setup aboard RV ECOS. Water was continuously dripped into each of the treatment beakers containing topsmelt, mysids, or mussel embryo larvae.

## 6.4 TOXICITY TESTING

### 6.4.1 Topsmelt (*Atherinops affinis*) and Mysid (*Americamysis bahia*) Survival

**Test organisms.** Both species were purchased from Aquatic Biosystems of Fort Collins, Colorado, and shipped overnight to SSC San Diego or Nautilus Environmental. Topsmelt were 7 to 9 days old, and mysids were 1 to 2 days old on the shipping date. Upon arrival, water quality (temperature, salinity, dissolved oxygen, pH) was measured. Organisms were then provided aeration, fed with freshly hatched brine shrimp nauplii (*Artemia*), and assessed for overall health. Partial water changes took place over the next 1 to 2 days to slowly acclimate the organisms to testing conditions. Dilution water used for water changes consisted of 0.45- $\mu$ m filtered, natural seawater collected from Scripps Institution of Oceanography's pier. Salinity was adjusted by no more than 2 psu per 24-hour period. Mysids and topsmelt were held at  $20 \pm 1^\circ\text{C}$  during holding and all phases of testing.

**Test Design.** Because storm water effluent samples were generally freshwater, the salinity was increased to approximately 32 psu, which generally coincided with ambient bay water salinity and the requirements of the marine test species. For the topsmelt and mysid tests, the salinity was adjusted with addition of synthetic sea salts (Crystal Sea Marine Mix, a.k.a. Forty Fathoms, Bioassay Grade). Effluent samples were subsequently serially diluted with water collected before the storm (PRE water) and adjacent to the appropriate storm water outfall to produce three to five concentrations of effluent for dose-response determinations. Receiving water samples were tested without dilution and did not require any salinity adjustment.

Topsmelt tests were conducted in 400-mL glass beakers containing 200 mL of test material. Five topsmelt were distributed to each of four replicates for each treatment. Mysid tests were conducted in 300-mL glass beakers containing 200 mL of test material. Ten mysids were distributed to each of three replicates for each treatment. Test solutions were brought up to the testing temperature before introduction of test organisms. Test organisms were randomly selected from holding tanks and carefully added to test chambers using a 5-mL plastic pipette with the bottom 0.5 cm cut off to prevent injury to organisms. Test solutions were then mixed and gently added to the test chambers. Upon test

initiation, test chambers were covered with a clear acrylic plate to prevent evaporation. All tests were 96-hour, static-renewal exposures, with a single renewal at 48 hours.

**Controls.** Pre-storm receiving water was used as the primary control water and as diluent for all the dilution series tests. In addition, filtered Scripps seawater and artificial salt mixtures were used as negative controls, and conducted alongside the pre-storm and storm water samples. Artificial salt controls consisted of deionized water and an appropriate amount of Crystal Sea Marine Mix to achieve a salinity of ~32 psu. The reference toxicant, copper sulfate, was used as a positive control. Reference toxicant tests were used to assess laboratory performance and batch sensitivity, and were performed alongside most storm water exposures. Up to six copper treatments (concentration range: 25 to 400 µg/L) were prepared from Scripps seawater and a measured copper sulfate stock solution.

**Observations and Maintenance.** Observations and removal of mortalities were made daily. Water quality parameters (salinity, DO, temperature, and pH) were recorded in one replicate per treatment daily. Dissolved oxygen in some mysid beakers occasionally dropped below 4 mg/L. In such instances, all beakers for that test were aerated. Test organisms were fed with freshly hatched *Artemia* nauplii twice daily, resulting in approximately 100 and 80 *Artemia* per organism per day or mysids and topsmelt, respectively.

#### **6.4.2 Mussel (*Mytilus galloprovincialis*) Embryo-Larval Development**

**Test Organisms.** Adult mussels were purchased from Carlsbad Aquafarm in Carlsbad, California. Animals were shipped overnight on ice or picked up by SSC San Diego staff and transported by car in an ice chest. Mussels were spawned on the day of arrival at the laboratory.

**Test Design.** For the mussel exposures, hypersaline brine (HSB), prepared by concentrating filtered, natural seawater collected from Scripps Pier was used to increase storm water sample salinity to ~32 psu. This dilution of the storm water effluent samples resulted in a maximum test concentration below 100%, generally around 60%. The brined solutions were then serially diluted with baseline water collected before a storm event (PRE) near the appropriate outfall to create a total of six test concentrations, including the control (e.g., 0, 6.25, 12.5, 25, 50, 60%). Depending on the test date, four or five replicates of each concentration were tested. Test chambers were seawater-leached 20-mL glass scintillation vials, which were filled with 10 mL of test solution. Tests were initiated by addition of approximately 20 embryos/mL test solution within 4 hours of fertilization.

**Test Procedure.** Approximately 30 to 50 mussels were induced to spawn by heat shock, which involved heating seawater 5 to 10°C above ambient temperature. As mussels began to spawn, they were segregated into 200-mL beakers containing 15°C, filtered seawater. After approximately 30 minutes of spawning, gametes were rinsed with seawater using a series of mesh screens. Upon verification of quality eggs (assessed by color, shape, and absence of germinal vesicles or signs of deterioration) and sperm (assessed by high degree of motility) under the microscope, three of the best quality egg stocks were individually fertilized with a sperm mixture collected from several males. After ~10 minutes, the mixtures were each poured through a 20-µm screen to remove sperm and rinsed with filtered seawater. Clean, fertilized eggs were allowed to develop in an environmental chamber for approximately 2 hours. The embryo suspension that appeared to have the highest proportion of dividing eggs was selected for density determination under a microscope. The appropriate volume needed to achieve a density of 15 to 20 embryos/mL was added via pipette to test chambers. Test vials were held in a temperature-controlled light chamber with a 16-hour light: 8-hour dark photo period. Water quality (dissolved oxygen, pH, temperature, salinity) was measured daily.

**Controls.** Filtered Scripps seawater and brine were used as negative controls and conducted alongside storm water samples. Brine controls consisted of deionized water and an appropriate amount of HSB to achieve a salinity of ~32 psu, and were used to assess any effects associated with the brine solution. The reference toxicant, copper sulfate, was used as a positive control. Reference toxicant tests were used to assess laboratory performance and batch sensitivity, and were performed alongside most storm water exposures. Up to six copper treatments (concentration range: 2.9 to 17.2 µg/L) were prepared from Scripps seawater and a measured copper sulfate stock solution.

**Test Termination.** Following 48 hours of exposure, tests were terminated by adding of 1 mL of concentrated formaldehyde to each vial. An inverted microscope was then used to quantify the proportion of normally developed, D-shaped (prodissoconch) larvae in the test vials. This task was achieved by evaluating a minimum of 100 larvae. The endpoint used for this test was the proportion of normal larvae to abnormal larvae (% normal development).

#### 6.4.3 Statistical Evaluations

When evaluating the quality of toxicity results, bay water data were compared to the Scripps water control, while effluent data were compared to the relevant un-manipulated pre-storm bay water sample. Because bay water samples were not typically collected for the TIE studies, salt or brine controls were used in making statistical comparisons for those tests. Statistical analyses for storm water effluent, receiving water, and reference toxicant tests were performed using Toxcalc<sup>®</sup> Scientific Software, Version 5.0. The data were arcsin square root transformed before analysis. Shapiro–Wilk’s Test was used to test for normality, while Bartlett’s Test was used to confirm equality of variance. Depending on whether or not analysis of variance assumptions were met, Dunnett’s Multiple Comparison Test, Steel’s Many One Rank Test, or Bonferroni’s t-Test was used to determine differences between the control and each test concentration, as described in step-wise procedures (e.g., flow charts) outlined in EPA (2002). These hypothesis tests provided the no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC). Where dose responses were observed, median effect concentrations such as the concentration causing 50% mortality (LC50) or a 50% effect (EC50) were calculated using the Maximum Likelihood-Probit or Trimmed Spearman–Karber point estimate methods, in that order of preference. Two sample t-tests ( $\alpha = 0.05$ ) were also used to determine statistical differences between control means and individual treatments and receiving water samples, in accordance with EPA (2002). The PMSD (percent minimum significant difference), an indicator of within-test variability and test method sensitivity, and CVs (coefficient of variation) were also calculated using the Toxcalc<sup>®</sup> software.

#### 6.4.4 Toxicity Data QA/QC

Toxicity testing was performed by SSC San Diego’s in-house toxicity laboratory and by Nautilus Environmental. Both laboratories are certified by the State of California, and have internal quality assurance (QA) plans. Topsmelt (*Atherinops affinis*) and mysid (*Americamysis bahia*) tests followed guidance provided by the U.S. EPA’s fifth edition of “Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms” (EPA, 2002). These test organisms were identified for use by inference in the NPDES permit. Mussel (*Mytilus galloprovincialis*) tests were guided by American Society for Testing and Materials (ASTM) protocols for conducting acute toxicity tests with marine bivalves (ASTM, 1999). Although the mussel test is not a requirement in the Navy’s storm water permit, it was included as an indigenous species to San Diego Bay that would provide a sensitive endpoint for evaluating bay waters. Quality Assurance/Quality Control parameters for the toxicity tests were based on the contents of these documents. Results were assessed for sample holding time and holding temperature, testing methods, water quality conditions, negative control response, and positive control response (Table 4). Laboratory

controls were performed concurrently with each assay, and nearly all assays were conducted with a concurrent reference toxicant test (minimum monthly requirement) as a means of confirming test organism quality and proper laboratory technique.

Test acceptability criteria (TAC) were  $\geq 90\%$  survival in controls for the topsmelt and mysid tests, and  $\geq 70\%$  normal development of resulting mussel larvae (Table 5). Any failure to meet the TAC resulted in invalidation of all sample data associated with that test. Data quality objectives (DQOs) were also evaluated on a case-by-case basis to determine if any excursions from the targeted range might be cause to invalidate the data. Excursions from the DQOs were flagged, and then assessed using a combination of decision criteria. For example, if the dissolved oxygen concentration briefly dipped below 4 mg/L at 48 hours, but mortality had occurred before the incident, the excursion was considered inconsequential.

There were a few deviations from the guidance documents, which were mostly a result of the attempt to match the laboratory study with conditions relevant to San Diego Bay. Test salinity was targeted at salinities typical of the bay ( $\sim 32$  psu). In addition, the testing temperature for mussels in one survey (SDB45) was adjusted to a higher, but also acceptable, temperature ( $18^{\circ}\text{C}$ ) to complement concurrent field exposures (e.g., floating laboratory bioassay). Due to supply issues with topsmelt, the first TIE study used inland silversides (*Menidia beryllina*), which were tested at  $25^{\circ}\text{C}$ , acceptable according to the guidance (EPA, 2002). A difference between the maximum and minimum temperature of more than  $3^{\circ}\text{C}$  within a test was weighed more heavily than temperature excursions slightly outside (e.g.,  $<1^{\circ}\text{C}$ ) the targeted temperature range, which is also in accordance with the guidance (EPA, 2002).

Table 4. Toxicity testing QA/QC objectives.

Parameter	Topsmelt Survival	Mysid Survival	Mussel Larval Development
Sample holding time	< 36 hours	< 36 hours	< 36 hours
Sample holding temperature	$4 \pm 2^{\circ}\text{C}$	$4 \pm 2^{\circ}\text{C}$	$4 \pm 2^{\circ}\text{C}$
Organism acclimation period	> 24 hours	> 24 hours	NA
Organism age at test initiation	9-15 days	2-5 days	1-4 hours
Negative control response	$\geq 90\%$ survival	$\geq 90\%$ survival	$\geq 70\%$ normal development
Copper reference toxicant test	LC50 within 2 SD of control chart mean	LC50 within 2 SD of control chart mean	EC50 within 2 SD of control chart mean
Water quality parameters:			
Temperature	$20 \pm 1^{\circ}\text{C}$ ; max/min deviation no > $3^{\circ}\text{C}$	$20 \pm 1^{\circ}\text{C}$ ; max/min deviation no > $3^{\circ}\text{C}$	$15 \pm 2^{\circ}\text{C}$
Salinity	32 psu $\pm$ 10%	32 psu $\pm$ 10%	32 psu $\pm$ 10%
Dissolved oxygen	>4.0 mg/L	>4.0 mg/L	>4.0 mg/L
pH	6.0-9.0	6.0-9.0	6.0-9.0

## 6.5 TOXICITY IDENTIFICATION EVALUATION (TIE)

Toxicity Identification Evaluations (TIE) were performed by Nautilus Environmental, LLC. One set of samples was collected by SSC San Diego from Naval Station San Diego outfalls 9, 11, and 14; naval Submarine Base San Diego outfalls 11B, 23CE, and 26; Naval Amphibious Base Coronado outfalls 9 and 18; and Naval Air Station North Island outfalls 23A and 26. These outfalls sampled corresponded to those outfalls focused on in the study. The selection of storm events sampled for TIEs was based only on logistical constraints.

The TIE consisted of baseline toxicity tests with topsmelt or inland silversides (*Menidia beryllina*), mysids, and mussel embryos. The baseline toxicity tests performed on samples collected at Naval Station San Diego and Naval Submarine Base San Diego were performed using inland silversides because topsmelt were unavailable from the supplier. The TIE evaluation using silversides in this step is not expected to be any different than having used topsmelt. Phase I manipulations included ethylenediaminetetraacetic acid (EDTA) additions to test for toxicity attributable to cationic metals and a solid phase extraction with a C18 column to test for toxicity attributable to non-polar organics. An aeration step was added for TIEs performed at samples collected from the Naval Amphibious Base Coronado and the Naval Air Station North Island to assess toxicity from volatile compounds. Phase II manipulations, dependent on the outcome of Phase I results included copper and zinc mixture studies to address samples exhibiting metals toxicity. They also included methanol extraction of the C18 column for samples exhibiting toxicity to non-polar organics. For the later TIE samples collected at Naval Amphibious Base Coronado and Naval Air Station North Island, an aeration foam add-back was also performed during this phase. Phase III TIE manipulations included copper and zinc toxicity studies, studies with mixtures of copper and zinc; comparison of sample metal concentrations with available literature values, statistical comparisons of predicted and actual TUs present in the samples, and comparisons of species sensitivity.

## 6.6 CHEMISTRY

Before the start of the study at Naval Station San Diego, a review of historical data were used to derive the contaminants of concern. Three sources of data were used to identify potential CoCs. These included data from The State of California's Bay Protection Toxic Cleanup Program (Fairey et al., 1996), a sediment quality report for the base (Chadwick et al., 1999), and historical storm water monitoring records. The list of CoCs used at the start of this study included copper, zinc, silver, mercury, lead, PAH, and PCB. As the study expanded to other bases, the list of CoCs grew to include chlorinated pesticides, as these were identified as CoCs for sediment TMDLs.

A full suite of total and dissolved metals were analyzed by Battelle Marine Sciences Laboratories (Sequim, WA). While the suite included the five metals identified as CoCs above, contractual requirements eventually resulted in the analysis of a suite of 14 metals described below. Some samples were analyzed for total and dissolved copper and zinc in-house by SSC San Diego. A suite of 48 PAH analytes, 31 PCB congeners, and 29 chlorinated pesticides were analyzed by Battelle Ocean Sciences (Duxbury, MA). DOC analyses were performed by Applied Marine Sciences (League City, TX). TSS analyses were performed in-house by SSC San Diego.

### 6.6.1 TSS

Total suspended solids analyses were performed at SSC San Diego. The analysis was performed using standard protocols developed at the University of New Hampshire, Jackson Estuarine Laboratory, by R. Langan in 1992. In summary, the samples were filtered using pre-dried/pre-weighed nitrate cellulose filters (GFC) with a 1.2- $\mu$ m nominal pore retention. The suspended solids filters were dried in an oven (preset at 90 to 120°C) for 24 hours and weighed again. The TSS concentration was determined by calculating the difference between the filter weights (before/after filtration),

divided by the total volume filtered. An attempt to make a simplification in the filtration step during survey SDB2 resulted in data that could not be used. The nominal MDL was 0.1 mg/L.

### **6.6.2 DOC**

DOC analyses were added to the suite of analytes in the study during the third storm event. Dissolved organic carbon analyses were performed by Applied Marine Sciences (League City, TX), using EPA method 415.1. Samples were filtered through a 0.45- $\mu$ m filter, and acidified to pH 2 with hydrochloric acid before being converted to carbon dioxide by catalytic combustion or wet chemical oxidations. The carbon dioxide formed was measured directly by an infrared detector. The amount of carbon dioxide was proportional to the concentration of carbonaceous material in the sample. The nominal MDL was 0.01 mg/L.

### **6.6.3 Metals**

Most samples were analyzed for 14 total and dissolved metals at Battelle Marine Sciences Laboratories (Sequim, WA), though some were analyzed for only total and dissolved copper and zinc at SSC San Diego. Once samples were returned to the laboratory, they were filtered through 0.45- $\mu$ m glass fiber filters and acidified to pH  $\leq$ 2 using ULTREX-grade nitric acid before further analysis. Storm water samples analyzed at Battelle were directly analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) or by cold vapor atomic fluorescence spectrometry (CVAF) or cold vapor atomic absorption spectrometry (CVAA) for Hg according to Battelle SOP MSL-I-013, Total Mercury in Aqueous Samples by CVAF, which is derived from EPA Method 1631.

Seawater samples were preconcentrated using iron and palladium in accordance with the Battelle SOP MSL-I-025, Methods of Sample Preconcentration, which is derived from EPA Method 1640. The sample preconcentration was submitted for analysis by ICP-MS or Inductively Coupled Argon Plasma Optical Emission Spectrometer (ICP-OES) and graphite furnace atomic absorption spectrometry (GFAA). Seawater samples were analyzed by ICP-MS in accordance with Battelle SOP MSL-I-022, Determination of Elements in Aqueous and Digestate Samples by ICP-MS. This method is based on two EPA Methods: 200.8 and 1638. Analytes reported from the preconcentrated seawater samples include cadmium, chromium, copper, nickel, and lead.

Analytes reported from the direct analysis of the seawater samples include aluminum, iron, manganese, tin, and zinc. Silver was analyzed in the iron-palladium preconcentrate by GFAA following Battelle SOP MSL-I-029, Determination of Metals in Aqueous and Digestate Samples by GFAA, which is derived from EPA Method 200.9. Seawater samples were analyzed by hydride generation flow injection atomic spectroscopy (FIAS) for arsenic and selenium according to Battelle SOP MSL-I-030, Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS.

Total and dissolved copper and zinc samples were also analyzed at SSC San Diego using EPA methods 200.12, 200.9, and 289.2 for trace metals in seawater by GFAA (also see EPA, 1991b). Comparable QA/QC to Battelle's labs was conducted for these analyses. For these analyses, the data validation steps were conducted by the laboratory manager.

### **6.6.4 PAH**

Water samples were extracted for 48 PAH analytes following general National Status and Trends (NS&T) methods (NOAA, 1993). The 16 priority pollutant PAHs measured are identified in Table 6. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with Recovery Internal Standard (RIS) compounds, and split quantitatively for the required analyses. Extracts were analyzed using gas

chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using RIS compounds. The nominal MDL was 1 ng/L.

### 6.6.5 PCB

Water samples were extracted for 31 PCB congeners following general National Status and Trends(NS&T) methods (NOAA, 1993). The sum of these congeners multiplied by a factor of two is comparable to the total PCBs (TPCB) measured as the sum of Arochlors® (SFBRWQCB, 2004; NOAA, 1993) used for water quality standards. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through a alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS, and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using RIS compounds. The nominal MDL was 1 ng/L.

### 6.6.6 Pesticides

Samples were extracted for 29 chlorinated pesticides following general NS&T methods (NOAA, 1993). Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through a alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the RIS compounds. The nominal MDL was 1 ng/L.

Table 5. List of total and dissolved metals analyzed with associated method detection limit.

Metal	ID	MDL (ug/L)
Aluminum	Al	2.31
Iron	Fe	2.51
Chromium	Cr	0.10
Manganese	Mn	0.03
Nickel	Ni	0.05
Copper	Cu	0.45
Zinc	Zn	0.12
Arsenic	As	0.12
Selenium	Se	1.47
Silver	Ag	0.02
Cadmium	Cd	0.04
Tin	Sn	0.50
Lead	Pb	0.01
Mercury	Hg	0.00015

Table 6. PAH analyte list with identifiers. Grayed-out analytes are included in the priority pollutant PAH list. The nominal MDL was 1 ng/L.

Analyte	ID	Analyte	ID
Naphthalene	<b>C0N</b>	Dibenzothiophene	<b>C0D</b>
C1-Naphthalenes	<b>C1N</b>	C1-Dibenzothiophenes	<b>C1D</b>
C2-Naphthalenes	<b>C2N</b>	C2-Dibenzothiophenes	<b>C2D</b>
C3-Naphthalenes	<b>C3N</b>	C3-Dibenzothiophenes	<b>C3D</b>
C4-Naphthalenes	<b>C4N</b>	C4-Dibenzothiophenes	<b>C4D</b>
2-Methylnaphthalene	<b>2MN</b>	Fluoranthene	<b>FLANT</b>
1-Methynaphthalene	<b>1MN</b>	Pyrene	<b>PYR</b>
Biphenyl	<b>BIP</b>	C1-Fluoranthenes/Pyrenes	<b>C1F/P</b>
2,6-dimethylnaphthalene	<b>26N</b>	C2-Fluoranthenes/Pyrenes	<b>C2F/P</b>
Acenaphthylene	<b>ACEY</b>	C3-Fluoranthenes/Pyrenes	<b>C3F/P</b>
Acenaphthene	<b>ACE</b>	Benzo(a)anthracene	<b>BAA</b>
2,3,5-trimethylnaphthalene	<b>235N</b>	Chrysene	<b>C0C</b>
Dibenzofuran	<b>DBF</b>	C1-Chrysenes	<b>C1C</b>
Fluorene	<b>C0F</b>	C2-Chrysenes	<b>C2C</b>
C1-Fluorenes	<b>C1F</b>	C3-Chrysenes	<b>C3C</b>
C2-Fluorenes	<b>C2F</b>	C4-Chrysenes	<b>C4C</b>
C3-Fluorenes	<b>C3F</b>	Benzo(b)fluoranthene	<b>BBF</b>
Anthracene	<b>C0A</b>	Benzo(j/k)fluoranthene	<b>BKF</b>
Phenanthrene	<b>C0P</b>	Benzo(e)pyrene	<b>BEP</b>
C1-Phenanthrenes/Anthracenes	<b>C1P/A</b>	Benzo(a)pyrene	<b>BAP</b>
C2-Phenanthrenes/Anthracenes	<b>C2P/A</b>	Perylene	<b>PER</b>
C3-Phenanthrenes/Anthracenes	<b>C3P/A</b>	Indeno(1,2,3-cd)pyrene	<b>INDENO</b>
C4-Phenanthrenes/Anthracenes	<b>C4P/A</b>	Dibenz(a,h)anthracene	<b>DAA</b>
1-Methylphenanthrene	<b>1MP</b>	Benzo(g,h,i)perylene	<b>BGP</b>



Table 7. List of PCB congeners and IDs. Nominal MDL was 1 ng/L.

PCB Congener	ID
PCB8 - 2,4'-Dichlorobiphenyl	CI2(8)
PCB18 - 2,2',5'-Trichlorobiphenyl	CI3(18)
PCB28 - 2,4,4'-Trichlorobiphenyl	CI3(28)
PCB44 - 2,2',3,5'-Tetrachlorobiphenyl	CI4(44)
PCB49 - 2,2',4,5'-Tetrachlorobiphenyl	CI4(49)
PCB52 - 2,2',5,5'-Tetrachlorobiphenyl	CI4(52)
PCB66 - 2,3',4,4'-Tetrachlorobiphenyl	CI4(66)
PCB77 - 3,3',4,4'-Tetrachlorobiphenyl	CI4(77)
PCB87 - 2,2',3,4,5'-Pentachlorobiphenyl	CI5(87)
PCB101 - 2,2',4,5,5'-Pentachlorobiphenyl	CI5(101)
PCB105 - 2,3,3',4,4'-Pentachlorobiphenyl	CI5(105)
PCB114 - 2,3,4,4',5-Pentachlorobiphenyl	CI5(114)
PCB118 - 2,3',4,4',5-Pentachlorobiphenyl	CI5(118)
PCB123 - 2',3,4,4',5-Pentachlorobiphenyl	CI5(123)
PCB126 - 3,3',4,4',5-Pentachlorobiphenyl	CI5(126)
PCB128 - 2,2',3,3',4,4'-Hexachlorobiphenyl	CI6(128)
PCB138 - 2,2',3,4,4',5'-Hexachlorobiphenyl	CI6(138)
PCB153 - 2,2',4,4',5,5'-Hexachlorobiphenyl	CI6(153)
PCB156 - 2,3,3',4,4',5-Hexachlorobiphenyl	CI6(156)
PCB157 - 2,3,3',4,4',5'-Hexachlorobiphenyl	CI6(157)
PCB167 - 2,3',4,4',5,5'-Hexachlorobiphenyl	CI6(167)
PCB169 - 3,3',4,4',5,5'-Hexachlorobiphenyl	CI6(169)
PCB170 - 2,2',3,3',4,4',5-Heptachlorobiphenyl	CI7(170)
PCB180 - 2,2',3,4,4',5,5'-Heptachlorobiphenyl	CI7(180)
PCB183 - 2,2',3,4,4',5,6-Heptachlorobiphenyl	CI7(183)
PCB184 - 2,2',3,4,4',6,6'-Heptachlorobiphenyl	CI7(184)
PCB187 - 2,2',3,4',5,5',6-Heptachlorobiphenyl	CI7(187)
PCB189 - 2,3,3',4,4',5,5'-Heptachlorobiphenyl	CI7(189)
PCB195 - 2,2',3,3',4,4',5,6-Octachlorobiphenyl	CI8(195)
PCB206 - 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	CI9(206)
PCB209 - 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	CI10(209)

Table 8. List of chlorinated pesticides. Nominal MDL was 1 ng/L.

Analyte	Analyte
2,4'-DDD	chlorpyrifos
2,4'-DDE	oxychlordane
2,4'-DDT	dieldrin
4,4'-DDD	endosulfan I
4,4'-DDE	endosulfan II
4,4'-DDT	endosulfan sulfate
aldrin	endrin
$\alpha$ -chlordane	endrin aldehyde
$\gamma$ -chlordane	endrin ketone
cis-nonachlor	heptachlor
trans-nonachlor	heptachlor epoxide
$\alpha$ -BHC	Hexachlorobenzene
$\beta$ -BHC	methoxychlor
$\delta$ -BHC	Mirex
Lindane	

#### 6.6.7 Chemistry Data QA/QC

Chemical analyses were performed in-house and by Battelle's Ocean Sciences and Marine Sciences laboratories, in Duxbury, Massachusetts, and Sequim, Washington, respectively. All analyses were performed using standard NS&T low-detection methods with appropriate QA/QC controls including method blanks, blank-spikes, matrix spikes, duplicates, and standard reference. A key component of the chemistry analyses was to use low-detection methods to minimize the possibility of not detecting an analyte. Battelle Laboratories have consistently provided very low detection methods for chemical analyses made in freshwater and seawater matrices. The nominal method detection limit (MDL) for individual organic compounds was 1 ng/L, though it was determined early, that even with this very low MDL, PCB and chlorinated pesticides would not be detected in receiving water samples. Because of this situation, PCB and pesticides were measured in only a few bay water samples, while metals and PAH were measured in storm water and bay water samples. For the most part, the PCB and pesticides were only measured in composite storm water samples. Table 5 though Table 8 show the full list of chemical analytes. Table 9 shows the QA/QC objectives for the chemical analyses.

Battelle validates their data in three steps. First, by the analyst who generated the data, then by a Reporting group that finalizes the data tables, and then by a QC Chemist group that validates and reviews the full final data package. Their "checklist" is as follows:

- Review work plan:
- Review QC checklist:
- Review title page and original custody records:
- Ensure samples bracketed by calibration standards:
- Review all pertinent miscellaneous documentation:
- Validate QIS standard amounts:
- Check preparation records:

- Review IC check exceedances:
- Review instrument chemist documentation:
- Validate data tables:
- Ensure proper method was used to quantify:
- Review integrations:
- Review calibration exceedances:
- Review chemical reasonableness:
- Review calibration standard amounts:
- Control charts review:

The QC Chemist's group provided the most rigorous and thorough review of the data, including auditing 100% of sample preparation and analytical data packages against SOPs and project plans, validating and verifying analysis test codes, preparing and distributing audit reports, approving data packages on behalf of the Laboratory Manager, and maintaining control charts of key laboratory performance data. Additionally, 10% of the final data packages were audited by an independent QA unit. A project manager also performed a final review of the data before and after the final review and audit. Narrative QA/QC reports with each dataset are included in Appendix D.

Table 9. Sample quality assurance and quality control parameters for chemical sampling and analyses.

Parameter	Metals	TSS	DOC	Organics
Sample Processing Holding Time	2 days	7 days	7 days	7 days
Sample Analysis Holding Time	90 days	90 days	28 days	40 days
Sample Holding Temperature	4°C	4°C	4°C	4°C
Reference Method	CVAF; FIAS; GFAA; ICP/MS or ICP-OES*	UNH-JEL	EPA 415.1	General NS&T
Field Blank	>10 x MDL or <5 x blank	NA	NA	NA
Method Blank	<3 x MDL	NA	<20%	<5 x MDL
Surrogate Recovery	50-150%	NA	<25%	40-120%
Lab Control Standard (LCS) /Matrix Spike (MS) Recovery	50-150%	NA	<20%	40-120%
Standard Reference Material	≤20%	NA	≤20%	≤30%
Sample Replicate/Relative Precision (relative difference)	≤30%	<20%	<20%	≤30%
Method Detection Limits	0.01;0.05;0.2;0.5;1;10;50 µg/L <sup>†</sup>	0.1 mg/L	0.01 mg/L	0.09-1.93

Notes:

Sample Replicate/Relative Precision from matrix spike and matrix spike duplicate

Standard reference material for analytes >5x MDL

LCS/MS for target spike >5x native concentrations

\* Method-Hg; As,Se; Ag; Ni,Cu,Cd,Pb,Mn,Zn,Sn,Cr,Fe,Al

<sup>†</sup> MDL-Hg; Ni,Cu,Cd,Pb; Se; Mn,Zn,As, Ag,Sn; Cr; Fe; Al

## 6.7 DATA EVALUATION

Toxicity, chemistry, and plume mapping results were described for each base, with the combined results evaluated later in the discussion section. Though the evaluation included some comparisons amongst the bases, the study was not designed to, and did not, collect sufficient data to statistically compare outfalls or evaluate variability as a result of antecedent dry weather, rainfall total, or intensity. Most data were presented in summary tables and graphics. Individual data values and associated QA/QC were provided in the appendices.

### 6.7.1 Toxicity Data Benchmarks

Toxicity data were characterized for each base using basic statistical evaluations including minimum, mean, maximum, and relative standard deviation (standard deviation/mean expressed as

percent; RSD). Both the topsmelt and mysid tests in first-flush storm water samples are used to meet the NPDES permit requirements. Therefore, these test results were evaluated using the 90% survival 50% of the time, as well as the 70% survival 10% of the time, criteria. Though not required in the permit, composite storm water samples were also evaluated for toxicity relative to these benchmarks to compare how samples representative of the whole discharge relate to first flush. Mussel test results, which are also not required in the permit, were appropriately evaluated by statistically comparing treatment results to the relevant controls.

Storm water toxicity data were also characterized using no observed effect concentration (NOEC) data derived from the dilution series tests. The NOEC represents the highest effect concentration in the dilution series that is not significantly different from the control response. The NOEC is determined very similarly to t-tests, except that multiple treatments (dilutions) are involved, as opposed to comparisons between only two samples (control and one treatment). The NOEC is thus an indicator of the receiving water concentration, once mixed with storm water, which does not result in a toxic effect. The dilution series tests were run with pre-storm bay water as the diluent to ensure that the results would account for any added background toxicity as well as any assimilative capacity of receiving waters to mitigate toxicity.

Individual toxicity test result quality was evaluated using the minimum significant difference (MSD), which is defined as “the smallest difference between the control and another test treatment that can be determined as statistically significant in a given test, and the PMSD, which is the MSD represented as a percentage of the control response” (EPA, 2000). As such, the PMSD provides a measure of test method variability and toxicity test quality.

Receiving water toxicity tests for all species were evaluated by statistically comparing results to the relevant control (Scripps natural seawater). Both absolute values for survival and normal development data were described as well as values relative to control.

The evaluation of toxicity in the discussion section considered combined results of the topsmelt and mysids tests (they are interchangeable from a permit perspective), comparison of results amongst bases, as well as an overall quantification of results combined from all tests from all bases. This assessment included a quantification of test result outcomes that are declared as “toxic” based on (1) meeting the permit requirement of either 90% or 70% survival, (2) a t-test that identifies a test result as statistically significant different from its associated control treatment, and (3) exceeding the 90<sup>th</sup> percentile PMSD. This discussion is critical to understanding the impact of using the current permit requirement for declaring a toxic result compared to established, reproducible quantification of WET test results.

#### **6.7.2 TIE Evaluation**

TIE evaluations were developed by the contract toxicity laboratory, Nautilus Environmental, LLC. The evaluations described in the report are based on summaries of the full reports shown in appendices E and F.

#### **6.7.3 Chemistry Data Benchmarks**

Chemical concentration data were characterized for each base using basic statistical descriptions including minimum, mean, maximum, and relative standard deviation. In addition to quantifying the range in chemical concentrations, the chemistry data were compared to water quality benchmarks throughout the results and discussion sections. The permit has performance goals for first-flush sample concentrations for total copper and zinc. Therefore, their concentrations measured in first-flush samples were compared to their performance goals of 63.6 and 117 µg/L, respectively. Other CoCs were compared to aquatic life water quality standards (WQS), where available, to assess their

magnitude relative to levels, below which, are considered protective of acute or chronic toxicity (EPA, 1991a). Chemicals measured in storm water were compared to EPA's aquatic life chronic maximum concentrations, which are the acute Water Quality Standards for the State of California (EPA, 2000a). The acute criterion is the appropriate benchmark for these short-lived discharges. Chemicals measured in receiving waters were compared to EPA's chronic continuous concentrations, which are the chronic Water Quality Standards for the State of California (EPA, 2000b). The chronic criterion is the appropriate benchmark for these samples that may represent longer-term conditions (before storm samples) as well as those occurring during short-term storm water exposures.

The dissolved phase of the metal was used when comparing metals concentrations to WQS standards. The comparison for dissolved mercury data was to the human health WQS of 0.05 µg/L because the acute WQS for mercury is currently "reserved" (EPA, 2000b). PAH, PCB, and most chlorinated pesticides measured in this study do not have published aquatic life acute or chronic WQS. Where available, PAH and PCB data were compared to minimum toxicity thresholds published in the literature. Seventy publications were reviewed for toxicity threshold data, with 28 containing unique citations specific to 13 PAH analytes, PCBs and pesticides (these references are specially cited in the Bibliography). Of these, the extensive review paper of Scannell, Duffy Perkins, and O'Hara (2005) was used to identify most of the minimum acute and chronic thresholds for individual PAH analytes to fish and invertebrates. Three additional papers (Kuhn and Lussier, 1987; Schimmel, Thursby, Heber, and Chammas, 1989; and Thursby, Berry, and Champlin, 1989) were used to identify a minimum acute or chronic threshold for another three PAH analytes. These PAH thresholds also include levels associated with toxic effects after ultraviolet light activation. Acute and chronic PCB thresholds were derived from EPA (1987) and EPA (2000b). These thresholds are for PCBs defined as the sum of Arochlors<sup>®</sup>. The sum of identified toxic thresholds for total PCBs was measured as the sum of Arochlors<sup>®</sup>. This measure of total PCB is approximately comparable to the sum of congeners\*2 (NOAA Environmental Monitoring and Assessment Program [EMAP]; NOAA, 1989). Table 10 and Table 11 provide the chemical benchmark levels used for chemical concentration data comparisons made throughout the report.

#### **6.7.4 Plume Mapping Evaluation**

Plume mapping results were evaluated by visual inspection of spatial maps of salinity, turbidity, and ultraviolet-fluorescence generated before, during, and after storm event conditions. Quantitation of the maximum percentage of storm water present during or after a storm event was calculated by comparing the minimum salinity observed during a storm survey relative to the average salinity measured during the pre-storm survey:

$$\text{Max Storm Water (\%)} = ((\text{Ave Salinity Before} - \text{Minimum Salinity During}) / \text{Ave Salinity Before}) * 100$$

Table 10. Aquatic life water quality standards (EPA, 2000a) used as chemical benchmarks for metals and pesticide data comparisons. Storm water concentrations were compared to acute WQS, while receiving water data were compared to chronic WQS. Dissolved metal concentrations were compared to benchmarks. Total copper and total zinc in storm water samples were also compared to their permit performance goals of 63.7 and 117 µg/L, respectively.

Analyte	Acute WQS <sup>1</sup> (µg/L)	Chronic WQS <sup>1</sup> (µg/L)	NPDES Permit <sup>2</sup> (µg/L)
Arsenic	69	36	
Cadmium	42	9.3	
Chromium	1100	50	
Copper	4.8	3.1	63.6
Lead	210	8.1	
Mercury	0.05	0.05	
Nickel	74	8.2	
Selenium	290	71	
Silver	1.9		
Zinc	90	81	117
2,4'-DDD			
2,4'-DDE			
2,4'-DDT			
4,4'-DDD			
4,4'-DDE			
4,4'-DDT	130	1	
aldrin	1300		
a-chlordane	90*	4*	
g-chlordane			
a-BHC			
b-BHC			
d-BHC			
Lindane			
cis-nonachlor			
trans-nonachlor			
chlorpyrifos	11	5.6	
oxychlordane			
dieldrin	710	1.9	
endosulfan I	34	8.7	
endosulfan II	34	8.7	
endosulfan sulfate			
endrin	37	2.3	
endrin aldehyde			
endrin ketone			
heptachlor	53	3.6	
heptachlor epoxide	53	3.6	
Hexachlorobenzene			
methoxychlor			
Mirex			

<sup>1</sup> Dissolved metal

<sup>2</sup> Total Metal

\* Used for sum of a- and g-chlordane

Table 11. Aquatic life water quality chemical benchmarks used for PAH and PCB. The values are based on minimum concentration thresholds derived from a review of the literature. Storm water concentrations were compared to acute thresholds while receiving waters were compared to chronic thresholds. The literature source citation is shown in the last column.

Analyte	Minimum Acute Literature Threshold (ng/L)	Minimum Chronic Literature Threshold (ng/L)	Minimum Threshold Citation
Naphthalene	510000	-	Scannell et. al., 2005
2-Methylnaphthalene	600000	-	Scannell et. al., 2005
1-Methylnaphthalene	1900000	-	Scannell et. al., 2005
2,6-dimethylnaphthalene	80000	-	Scannell et. al., 2005
2,3,5-trimethylnaphthalene	320000	-	Scannell et. al., 2005
Acenaphthene	460	63990	Schimmel et al., 1989-acute Thursby et al., 1989-chronic
Fluorene	320000	-	Scannell et. al., 2005
Phenanthrene	370000	8129	Scannell et. al., 2005-acute Kuhn and Lussier, 1987-chronic
Anthracene	3600	82000	Scannell et. al., 2005
1-Methylphenanthrene	300000	-	Scannell et. al., 2005
Fluoranthene	1090	810	Scannell et. al., 2005
Pyrene	230	910	Scannell et. al., 2005
Chrysene	1000000	-	Scannell et. al., 2005
Benzo(a)pyrene	1000000	-	Scannell et. al., 2005
Dibenz(a,h)anthracene	1000000	-	Scannell et. al., 2005
TPCB*	10000	30	EPA, 1987-acute EPA, 2000-chronic

\* TPCB is the sum of arachlors  $\cong$  2\*sum of congeners

## 7. RESULTS

### 7.1 DATA QUALITY

#### 7.1.1 Toxicity Data

Twelve storms were sampled for toxicity evaluation. Only in one instance (mussels during storm event SDB1) did failure of meeting the test acceptability criteria result in invalidating the test. Therefore, no samples from that dataset were used in this study. Samples were processed for testing immediately upon arrival in the laboratory, or the morning after collection, thus the 36-hour holding time was always met. In all cases, all species met the relevant acclimation period. With some minor exceptions, most other data quality objectives were met throughout the study, and a summary for each test species is provided. Except where noted, deviations were deemed inconsequential to the results of the study based on the decision-making criteria outlined previously.

**Topsmelt.** Laboratory (Scripps natural seawater) and salt controls always exceeded the 90% minimum survival criterion for test acceptability (range = 95 to 100%). All concentrations causing 50% lethality (LC50) for copper reference tests fell within two standard deviations of each laboratory's mean. Nautilus reference toxicant EC50s fell within SSC San Diego's control chart limits for SSC San Diego, suggesting similar performance between the two laboratories. The pH was always within the objectives. Only one dissolved oxygen concentration (0.1% of measurements) momentarily fell below 4 mg/L, which was immediately corrected with gentle aeration. The maximum and minimum temperature never varied by more than 3°C. Temperature did fall slightly outside the targeted temperature range 23% of the time, but this exceedance was by less than 1°C for all but one sample. The DQO for salinity was met for all samples, with average minimum and maximum salinities of 31.6 and 34.3 psu, respectively.

**Mysids.** Laboratory (Scripps natural seawater) and salt controls always exceeded the 90% minimum survival criterion for test acceptability (range = 93 to 100%). All concentrations causing 50% lethality (LC50) for copper reference tests fell within two standard deviations of each laboratory's mean. Nautilus reference toxicant EC50s fell within SSC San Diego's control chart limits for SSC San Diego, suggesting similar performance between the two laboratories. The pH always fell within the DQO. A total of 13 measurements (1.4% of total) indicated a dissolved oxygen concentration of less than 4.0 mg/L. Most D.O. excursions were associated with SDB2 and TIE2 samples early in the exposure, and corrective action (aeration) was taken immediately, resulting in acceptable levels for the remainder of the tests. Temperature never varied by more than 3°C, as required. Temperature did fall outside the targeted temperature range 13% of the time, but the exceedance was by less than 1°C for 98% of those samples. Average salinity minimum and maximums were 31.8 and 34.5 psu, respectively, with less than 1% of values falling outside the range designated by the DQOs.

**Mussels.** Laboratory (Scripps natural seawater) and brine controls always exceeded the 70% minimum percentage normal development criterion for test acceptability (range = 80 to 98%). This does not include data from SDB1, which was not included in the final analysis of this study due to low control performance. All concentrations causing a 50% effect (EC50) for copper reference tests fell within two standard deviations of each laboratory's mean. Nautilus reference toxicant EC50s generally fell within SSC San Diego's control chart limits for SSC San Diego, suggesting similar performance between the two laboratories. The Cu reference test EC50 associated with TIE2, however, was 23% higher than SSC San Diego's control chart range. The pH always fell within the DQO. Three measurements (1.1% of total) indicated that dissolved oxygen concentration was low. However, analysis of the data indicated these values did not impact the results of the tests. Temperature never fell outside the targeted range. Salinity was below the DQO (by less than 1 psu) for 2.8%



of the measurements, which coincided with a lower targeted salinity for these particular tests (SDB5 and SDB6), where 30 psu was sought instead of 32 psu. The lower salinity is considered acceptable for this endpoint (EPA, 1995).

### 7.1.2 Chemistry Data

For the most part, the chemistry data quality met the data QA/QC objectives set forth at the beginning of this study. All samples were maintained at holding temperatures before analysis and all samples were processed in the required holding times. The TSS data for the SDB2 storm were compromised in processing and could not be used for further evaluation. DOC analyses met all QA/QC requirements. The metals data met all QA/QC objectives for matrix spikes and recoveries, blanks, replicates, method detection limits, and standard reference materials. Nearly all metal concentrations were measured above MDLs. Silver, selenium, and tin were occasionally not detected above their respective MDLs. Non-detect results were reported as the MDL value and were qualified in the appendices.

The PAH data met QA/QC objectives with the following exceptions. Initial analysis of sample NAV-OF14-SD45-FF (Battelle ID S5983) for SDB45 yielded low surrogate recoveries. The archived non-fractionated extract for this sample was reprocessed and reanalyzed outside of the 40-day holding time. These data were qualified with a “T” in the data tables. Analysis of sample OF-NAB9-SDB6-FF (Battelle ID S7118) for storm SDB6 yielded percent recoveries for surrogate compounds naphthalene-d8 and chrysene-d12 outside of the laboratory control limits specified by the method (40 to 120% recovery). The chromatography and calculations were reviewed and no discrepancies were found. The exceedances were qualified with an “N” in the data tables and no further corrective action was taken. For SDB7, percent recovery for surrogate compound naphthalene-d8 in sample OF-NI26-SDB7-FF was outside of the laboratory control limits. Chromatography and calculations were reviewed with no discrepancies found. The sample preparation records indicate an emulsion formed during the extraction of this sample and the extract had difficulty passing through the alumina cleanup column. The exceedance was qualified with an “N” and no further corrective action was taken. Concentrations of analytes making up the list of priority pollutant PAHs were above their respective MDLs in storm water samples 93% of the time while the same analytes in seawater sample were above MDLs 43% of the time. Non-detect results were reported as the MDL value. Summations were computed using one-half MDL values. MDLs ranged up to a maximum of 1.6 ng/L.

PCB data met all QA/QC requirements with the following exceptions. Storm SDB1 PCB extracts were reanalyzed after the 40-day holding time due to cross contamination of the procedural blank caused by the previous run of a standard. The associated QA/QC of the second analysis appeared good and was reported. The PCB analysis on samples collected during storm SDB2 was not dual-column confirmed, thus these data used only a single-column analysis. No corrective action was taken, and these data were flagged with a “NC” qualifier in the data tables. The value for C17(180) was above normal calibration limits and the value was estimated and qualified with an “E”. The matrix spike and matrix spike duplicate run with samples collected during the SD45 storm event yielded analyte recoveries between 121 and 129%, outside the laboratory control limit of 40 to 120%. Chromatography and calculations were reviewed and no discrepancies were found. The exceedances were qualified with an “N” in the data tables. Samples for the SDB45 storm were prepared for analysis as a single analytical batch and were extracted within 7 days of sample collection. However, extracts were not analyzed within the 40-day holding time. These data were qualified with a “T” in the data tables.

Chlorinated pesticides data met all QA/QC requirements. Over 90% of all analytes were below their MDL in storm water and bay water samples. Summations were computed using ½ MDL values. MDLs ranged up to a maximum of 2.2 ng/L.

### 7.1.3 Plume Mapping Data

The plume mapping objective of spatially mapping salinity variations as a result of freshwater plumes emanating from all four bases was met on all occasions. However, base security limitations (e.g., floating barriers) precluded continuously monitoring plume development that could be used to capture tidal variations. The salinity data collected were adequate to quantify the magnitude of the freshwater input as well. Vertical profile data used to evaluate plume depths were sufficient to look at large-scale conditions, but insufficient to evaluate any fine structure that might develop near the sea surface. All measurement parameters were not available on all surveys, but the key parameter, salinity, was successfully measured on all occasions.

## 7.2 NAVAL STATION SAN DIEGO

### 7.2.1 Storm Water Toxicity

Nineteen storm water outfall samples were tested, not necessarily for all species, for toxicity at Naval Station San Diego, including samples collected during the special floating bioassay laboratory study. Figure 22 shows the 100% storm water effluent toxicity data. A statistical summary of the results are provided in Table 12, with all data provided in Appendices B and C. The composite sample collected at outfall 9 during storm SDB1 was only run at the 50% effluent concentration and was therefore not plotted in the figure. Included in topsmelt data are results from three first-flush tests conducted with the inland silverside (*Menidia beryllina*) due to the inability to acquire topsmelt for that sampling event (TIE1). Based on the LC50 for zinc, silversides are expected to be more sensitive to metals than topsmelt (Cardin, 1985). However, the data were combined because both fish species are applicable under the permit.

In general, topsmelt and mysids responded similarly to outfall samples, both averaging 75% survival in the undiluted storm water effluent. First-flush samples, however, were more toxic than composites, averaging about 60% survival compared to 93% in composite samples. Some of this toxicity reduction was probably a result of tide water partially ( $\leq 30\%$ ) mixing into the outfall composite sample. For topsmelt, 60% of first-flush samples would have failed the 90% survival requirement, compared with a 14% failure rate for composites. Similarly, mysids failed 70% of the time when tested in first-flush samples, and failed only 13% of the time with the composites. Topsmelt and mysids in first-flush samples would have failed the 70% survival requirement 40% and 50% of the time, respectively. All the composite samples would have passed the 70% requirement.

For Naval Station San Diego samples, 67% of NOECs for combined topsmelt and mysid in first-flush and composite samples were 100% storm water effluent. Three of the 36 dilution series results for first-flush samples had a NOEC of 10%, one first-flush sample from Pier 5 had a NOEC less than 10%, and one composite sample had a NOEC of 50%. These data suggest that with the exception of one sample, a receiving water mixture with less than a 10% storm water fraction would result in no observable toxicity.

Mussel larvae were more sensitive than the permitted species in outfall samples, with an overall average of 27% normal development in undiluted storm water effluent (maximum effluent concentrations ranged between 70% and 81% because of brine addition). Because this bioassay is not included in the permit, the 90% requirement does not apply. Relative standard deviations of the toxicity data indicated four to six times more variability in first-flush samples compared to composites. This variability commonly occurs as toxicity increases, but also may be due to the

variability associated with collecting grab samples versus composite samples. In addition, mussel data were considerably more variable than topsmelt and mysid data for all sample types. NOECs for mussels ranged from 10 to 65% (the maximum effluent concentration tested), though one sample had a NOEC of <6.25%. These data suggest that with the exception of one sample, a receiving water mixture with less than a 10% storm water fraction would result in no observable toxicity.

This study was not designed to, and did not, collect sufficient data to statistically contrast and compare outfalls. Data were insufficient to evaluate variability as a result of antecedent dry weather, storm rain totals, or storm intensity. However, a qualitative review of the data showed that the highest toxicity was observed for samples collected at outfall 11 and pier 5 during SDB2. The next most toxic samples were from pier 6 during SDB2 and from outfall 14 collected during the first flush of the year sampling (SDB4). However, outfalls 11 and 14 showed considerable variability during multiple samplings indicating that there are factors beyond the general activities occurring within a drainage area that control the outcome.

As described earlier method variability in toxicity testing is an important consideration for evaluating results.

Table 13 shows the PMSD for Naval Station San Diego industrial storm water dilution series toxicity tests, including baseline TIE results. PMSD values ranged from 8 to 32% for topsmelt and averaged 16%. PMSD for mysid tests ranged from 3 to 15 and averaged 8%. The mussel embryo-larval development tests ranged from 3 to 25% and averaged 9%. The mysid results all fell well within EPA guidelines for test acceptability (EPA, 2000). The topsmelt and mussel data also met the PMSD test acceptability criteria for comparable endpoints (inland silverside survival and mussel survival and normal development). These differences are described later in the discussion section.

### **7.2.2 Receiving Water Toxicity**

Twenty-eight receiving water samples were tested, not necessarily for all species, for toxicity at Naval Station San Diego. No toxicity was observed for topsmelt or mysids in bay water samples. Survival was very high ( $\geq 90\%$ ) for topsmelt and mysids exposed to bay waters. All topsmelt and mysid receiving water data were statistically indistinguishable from lab controls ( $p < 0.05$ ). Mussel larval development in bay water samples averaged 89% overall, and with one exception, was not statistically different from controls. The exception was for a sample collected outside outfall 14 during a first-flush of the year event (SDB4) after a record 6-month antecedent dry period. Toxicity results in the floating laboratory study showed a similar lack of observable effects to all species as those conducted previously using standard laboratory bioassays.

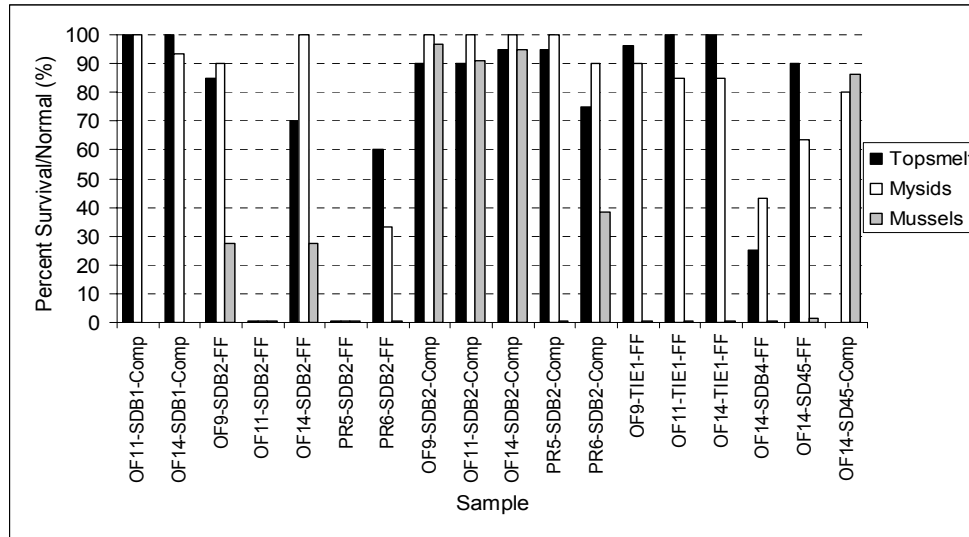


Figure 22. Topsmelt and mysid survival and normal mussel embryo-larval development in 100% storm water effluent collected from first-flush (FF) and composite (Comp) samples at Naval Station San Diego.

Table 12. Statistical summary of toxicity data in Naval Station San Diego first-flush (FF) or composite (Comp) undiluted storm water or in receiving water (Bay) samples. Results are expressed as percent survival for topsmelt and mysids and as percent normal embryo-larval development for mussels. “# <90% and % Failing” refers to the number and percentage of samples that did not meet the 90% survival criterion in the permit.

NAV	Topsmelt Survival (%)			Mysid Survival (%)			Mussel Normal Development (%)		
	FF	Comp	Bay	FF	Comp	Bay	FF	Comp	Bay
<i>n</i>	10	8*	28	10	9*	28	10	6	16
Min	0	75	90	0	80	97	0	0	8
Mean	63	92	96	59	95	100	5	68	89
Max	100	100	100	100	100	100	28	97	97
RSD	64	9	4	64	8	1	217	58	25
# <90%	6	1	NA	7	1	NA	NA	NA	NA
% FAILING	60%	14%	NA	70%	13%	NA	NA	NA	NA

NA Not applicable

\* One sample was run only at maximum 50% effluent

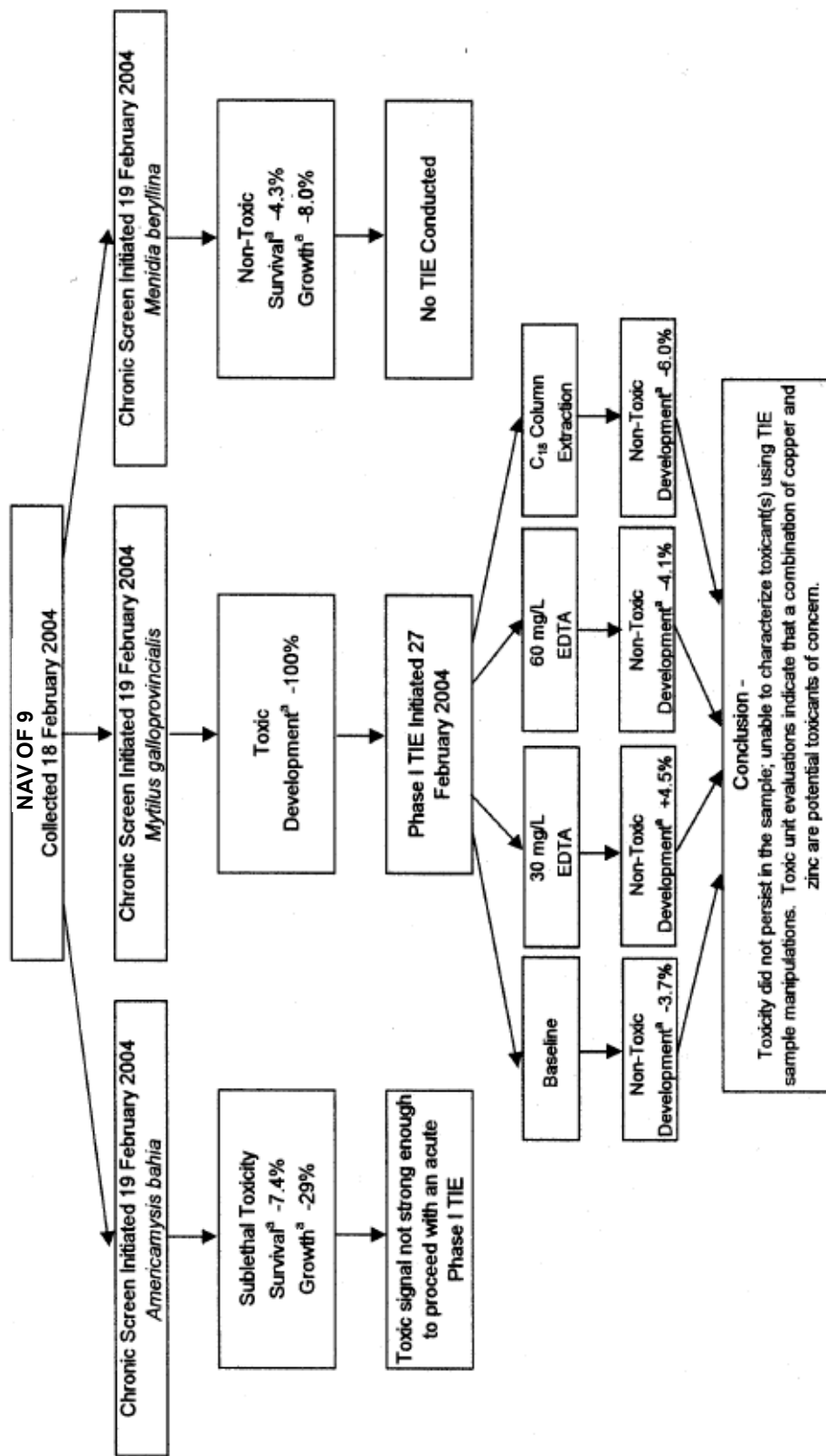
Table 13. Percent Minimum Significant Difference (PMSD) for Naval Station San Diego toxicity tests.

PMSD	Topsmelt	Mysids	Mussels
<i>n</i>	18	16	12
Min (%)	8	3	3
Mean (%)	16	8	9
Max (%)	32	15	25

### 7.2.3 TIE

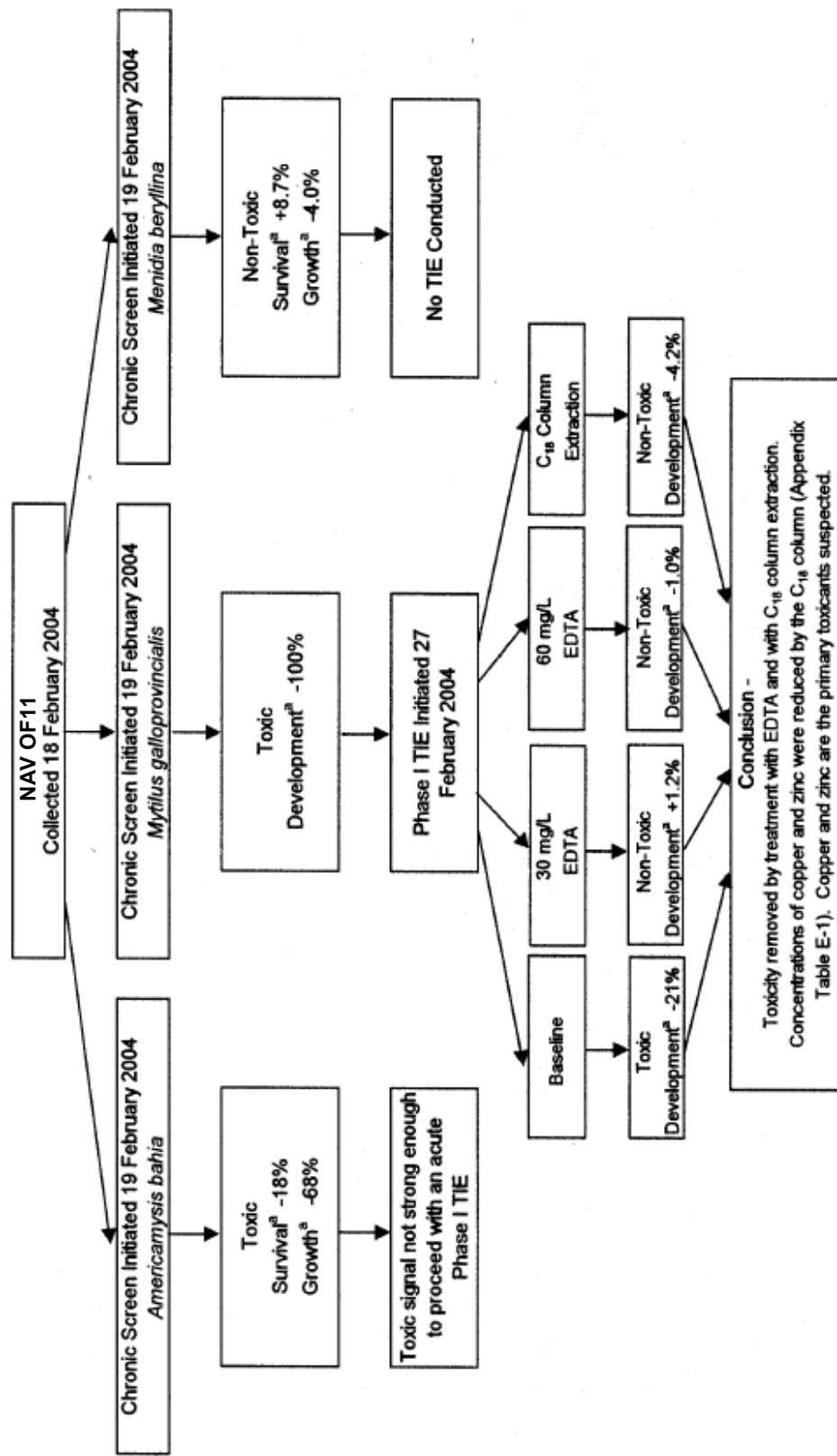
A Toxicity Identification Evaluation was performed on first-flush storm water samples collected from each of the three outfalls at Naval Station San Diego during the storm event on 18 February 2004. First-flush samples were collected at the start of a very low rainfall event in which only 0.19 inches of rainfall fell. The report for this effort is included as Appendix E. Inland silversides (*Menidia beryllina*) were used in lieu of topmelt in these tests because topmelt were unavailable from the supplier. It is expected that the results for inland silversides would have been the same for topmelt. Figure 23 through Figure 25 show the manipulations performed for each outfall sample.

Toxicity screening results showed that there was insufficient toxicity to inland silversides or to mysids to perform a TIE for any of the outfall samples. It is expected that the results would have been similar using topmelt. TIEs were therefore conducted only using the mussel embryo-larval development tests. The TIE results identified copper and zinc as the primary causes of toxicity in all three outfall samples at Naval Station San Diego. For outfall 9 and outfall 11, copper and zinc were present at concentrations that were sufficient to be the causative agents in those samples. The sample at outfall 14 had insufficient amounts of copper or zinc to individually cause toxicity, but taken together, the two chemicals were in sufficient quantity to cause toxicity. The Phase III TIE established that copper and zinc were additive in their toxicity.



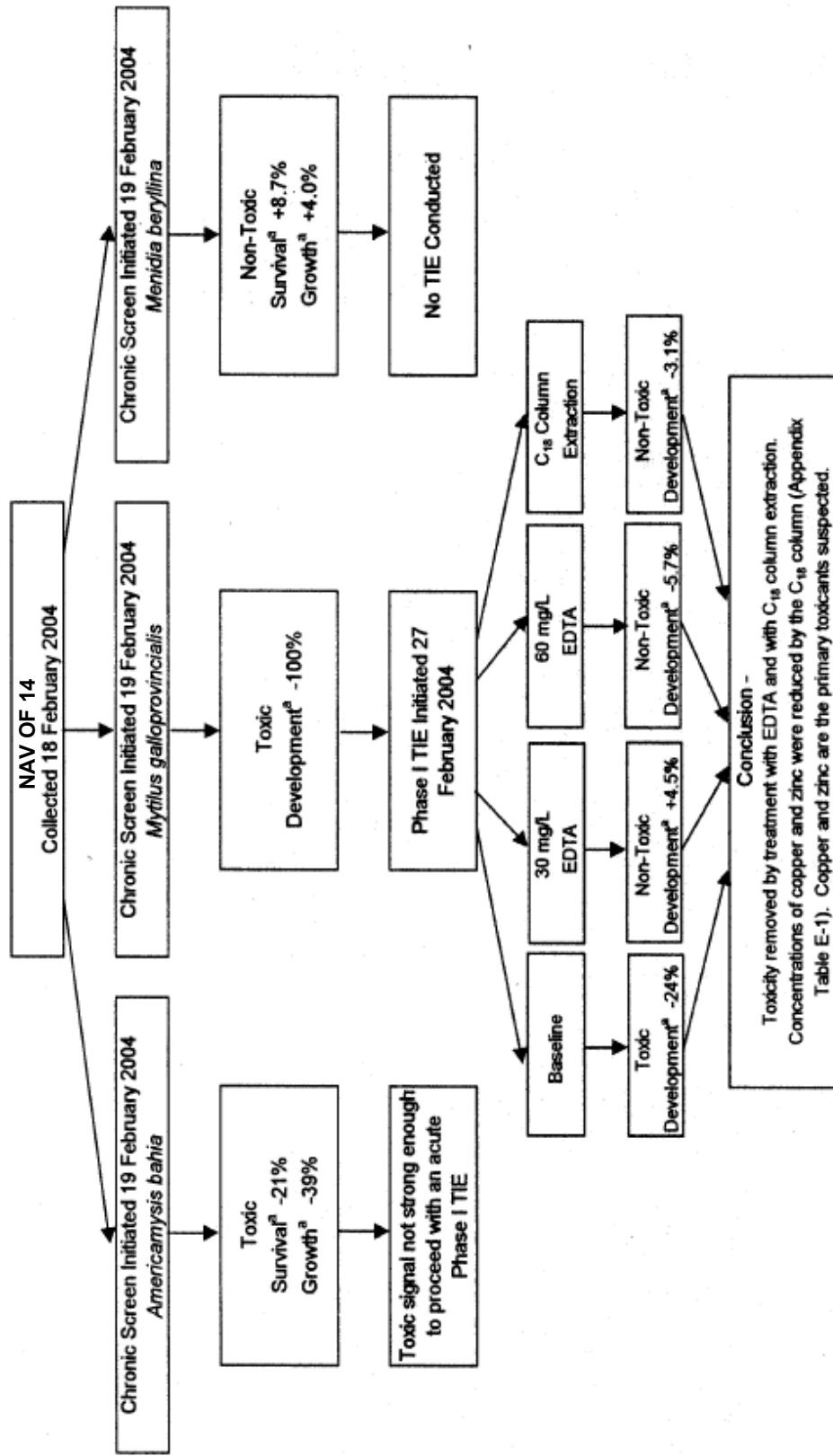
<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 23. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Station San Diego outfall 9.



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 24. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Station San Diego outfall 11.



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 25. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Station San Diego outfall 14.



### 7.2.4 Chemistry

**TSS/DOC.** A total of 28 and 10 samples were analyzed for TSS and DOC, respectively, at Naval Station San Diego. Table 14 shows a statistical summary of the TSS and DOC data. Appendix D shows all individual sample data. TSS in storm water ranged from ~60 to over 800 mg/L and averaged about 233 mg/L. On average, first-flush samples had higher TSS concentrations than composite samples, though the loss of TSS data during the second storm sampling limits this comparison. The first-flush samples also showed a considerably higher variability than the composite samples, as described by the relative standard deviation (RSD). The maximum TSS level was measured in the first-flush samples collected during the first-flush of the year storm event (SDB4) in October 2004. Bay samples were about an order of magnitude lower in TSS than the outfall samples and ranged from ~1 to 21 mg/L, with an average of 2.6 mg/L. The average value for bay samples collected before the storm increased about a factor of three during the storm and then decreased back to pre-storm conditions in the “after” samples showing the ephemeral nature of the storm derived particles in the water column. The “during” samples were considerably more variable than the other bay samples showing the variable nature of plumes.

The DOC data came exclusively from samples collected during a single storm event (SDB45) in October 2004 because DOC analyses were not added to the suite of analysis until the third storm event (SDB3). DOC in the composite sample was about a factor of two higher than in the first-flush sample, and about a factor of 10 higher than the average bay water sample. Elevated DOC in storm water runoff is expected from solubilization of terrigenous organic matter (SFERMP, 1994). The higher DOC in composite samples might indicate that there is a lag time in the discharge of organic compounds in storm water. Bay water “during” samples averaged about 30% higher than the pre-storm and post-storm samples, indicating storm water as a source of DOC to the bay.

Table 14. Statistical summary of TSS and DOC data at Naval Station San Diego. Sample types include first-flush (FF) and composite (Comp) outfall samples as well as receiving water (Bay) samples collected before, during, and after storm events.

TSS (mg/L)	Outfalls		Bay		
	FF	Comp	Before	During	After
n	2	4	6	9	7
Min	61	79	0.8	0.7	0.5
Mean	450	125	1.3	4.4	1.3
Max	839	170	1.8	21	2.9
RSD	122%	30%	24%	144%	77%
DOC (mg/L)					
n	1	1	1	4	3
Min				0.61	0.62
Mean	6.0	12	0.91	1.23	0.91
Max				1.73	1.3
RSD	NA	NA	NA	44%	42%

**Metals.** Forty-seven samples were analyzed for total and dissolved metals at Naval Station San Diego, which included 16 outfall samples and 31 receiving water samples. Of the total, 11 were analyzed for only copper and zinc. Appendix D shows all individual sample data.

Table 15 shows a statistical summary of the outfall metals data for Naval Station San Diego. The table data are summarized by first-flush and composite samples and by total and dissolved metals. The data show considerable variability of the individual metals spanning a range of ~25% to 180% for both the dissolved and total metal. Variability was typically about the same or lower in composite samples than in first-flush samples.

Nearly all total copper (71%) and all total zinc concentrations in first-flush storm water samples were above their respective performance goals in the NPDES permit of 63.6 and 117 µg/L. Only dissolved copper and zinc were elevated in outfall samples above their respective acute saltwater water quality standards of 4.8 and 90 µg/L, respectively, with the remaining dissolved metals all well below WQS (EPA, 2000a). This also includes dissolved mercury data that were compared to the human health WQS of 0.05 µg/L because the acute WQS for mercury is currently “reserved” (EPA, 2000a). Dissolved copper and zinc exceeded their acute WQS by a maximum factor of 36 and 27, respectively in first-flush samples. The comparable ratio in composite samples was reduced to 12 and 9, respectively.

Maximum total copper and zinc concentrations measured in the outfalls were 240 and 3600 µg/L, respectively. These levels were measured in the first-flush of the year sample (SDB4) at outfall 14 (Figure 26). This result matches the observation for TSS and DOC (note: no other chemicals were measured in SDB4 samples). The lowest copper and zinc levels were in the composite sample collected at outfall 14 during the second storm event SDB2. Except for one sample, total copper and zinc concentrations were higher in first-flush samples than their paired composite samples (Figure 26). Dissolved copper and zinc concentrations were always higher in first-flush samples though this was not the case for all metals. Tidal mixing (<38%) inside the outfall pipe was at least a partial explanation for the reduction in some of the composite sample concentrations.

Copper and zinc ranged from about 30 to over 90% and averaged ~60% as the dissolved phase metal in first-flush and composite samples. First-flush samples showed a slightly higher amount of the dissolved phase metal than observed in composite samples, indicating a potential lag of particles in the storm discharge.

Table 16 shows a statistical summary of the bay seawater sample data. Appendix D shows all individual sample data. The variability in these data was generally lower than observed in storm water samples with the exception of zinc. As was observed for storm water, bay water concentrations of copper (14 µg/L) and zinc (182 µg/L) were highest in samples collected during the first-flush of the year storm event (SDB4). This sample was one of only two receiving water samples in the study to exhibit mussel larvae toxicity. These concentrations represent about a factor of three for copper and 10 for zinc above typical levels. They also represent a reduction from first-flush levels by a factor of about 20. The concentrations of copper and zinc in this sample also exceeded chronic WQS (no other metals were analyzed in this sample). All other bay water metals were measured at concentrations well below their respective chronic WQS. Additionally, copper exceeded its chronic WQS of 3.1 µg/L (EPA, 2000b) in nearly all samples as a result of chronic sources, presumably from hull coating leachate or other bay sources. This was supported by copper concentrations that were not always higher in “during” samples than were measured in pre- or post-storm samples. Dissolved zinc concentrations measured during storm events were higher than those measured in pre-storm samples, except in one instance. The predominant phase of copper and zinc in seawater was as the dissolved metal, averaging about 70% for copper and 97% for zinc. Thus, these metals in bay waters tended toward the dissolved phase of the metal compared to the outfall discharge.

Table 15. Statistical summary of first-flush (FF) and composite (Comp) outfall (OF) metals data at Naval Station San Diego. Values for the total and dissolved metal are shown. NPDES performance goals and acute WQS are also shown. Grayed-out cells are values equal to the MDL.

OF FF Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	6	7	6	6	7	6	6	6	6	6	6	6	6	6
Min	0.052	45.3	4.06	0.0056	314	179	1.18	0.99	3.33	426	22.4	7.2	0.149	0.21
Mean	0.148	107.5	22.5	0.0348	945	1332	2.01	2.14	6.72	1943	78.7	11.6	0.59	0.82
Max	0.229	244	43.8	0.0629	3631	2640	3.20	5.49	13.7	3940	131	17.2	1.30	1.44
RSD	47%	70%	56%	68%	126%	71%	42%	81%	55%	68%	45%	36%	86%	50%
NPDES Performance Goal		63.6			117.0									
OF FF Dissolved (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	6	7	6	6	7	6	6	6	6	6	6	6	6	6
Min	0.006	18.9	0.37	0.0027	175	11	0.37	0.39	0.80	19	14.4	3.7	0.087	0.09
Mean	0.021	62.3	2.5	0.0059	614	22	1.09	1.47	1.65	46	36.7	7.3	0.48	0.21
Max	0.029	177	11.8	0.0133	2453	40	2.04	4.97	3.6	161	82	17.2	1.33	0.50
RSD	43%	92%	182%	65%	133%	51%	55%	119%	65%	121%	63%	67%	107%	77%
OF Comp Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	9	9	9	9	9	6	6	6	6	6	6	6	6	6
Min	0.063	28.9	6.50	0.0151	200	722	1.33	0.659	4.70	1149	31.5	4.48	0.035	0.536
Mean	0.132	72.8	15.9	0.0660	393	1244	1.72	1.06	7.88	1986	49.7	6.85	0.167	0.903
Max	0.247	136	23.5	0.2662	969	2618	2.39	2.27	12.9	4481	72	11.2	0.53	1.13
RSD	52%	55%	38%	118%	63%	56%	25%	58%	35%	63%	31%	37%	109%	24%
OF Comp Dissolved (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	9	9	9	9	9	6	6	6	6	6	6	6	6	6
Min	0.004	7.2	0.16	0.0018	68	8	0.81	0.244	1.12	18	5.9	1.66	0.035	0.060
Mean	0.012	28.8	0.4	0.0052	252	22	1.14	0.40	3.01	45	14.3	2.42	0.167	0.213
Max	0.025	60	0.6	0.0123	776	40	1.72	0.67	10.0	71	25	4.1	0.36	0.50
RSD	49%	77%	38%	79%	98%	53%	30%	42%	115%	54%	44%	38%	82%	75%
WQS Acute (µg/L)	1.9	4.8	210		90		69	42	1100			74	290	

Table 16. Statistical summary of total and dissolved bay seawater metals data at Naval Station San Diego. Values for the total and dissolved metal are shown. Chronic WQS are also shown. Grayed-out cells are values equal to the MDL.

Bay Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	21	31	21	21	31	2	2	2	2	2	2	2	2	2
Min	0.015	3.50	0.140	0.001	8.42	74.9	1.15	0.105	1.75	129	10.7	1.93	0.044	0.201
Mean	0.025	5.87	0.275	0.002	20.2	91.0	1.16	0.107	1.86	141	11.6	2.00	0.049	0.227
Max	0.058	20.5	0.629	0.004	238	107	1.17	0.109	1.96	152	12.5	2.06	0.054	0.253
RSD	37%	48%	55%	31%	202%	NA	NA	NA	NA	NA	NA	NA	NA	NA
Bay Dissolved (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	21	31	21	21	31	2	2	2	2	2	2	2	2	2
Min	0.010	3.00	0.054	0.001	7.70	2.32	1.11	0.100	0.219	88.5	9.01	1.17	0.035	0.228
Mean	0.021	4.17	0.085	0.002	18.0	8.01	1.12	0.103	0.231	107	9.51	1.19	0.050	0.232
Max	0.033	14.1	0.137	0.005	182	13.7	1.13	0.106	0.242	125	10.0	1.21	0.064	0.235
RSD	32%	45%	20%	67%	171%	NA	NA	NA	NA	NA	NA	NA	NA	NA
WQS Chronic (µg/L)		3.1	8.1		81		36	9.3	50			8.2	71	

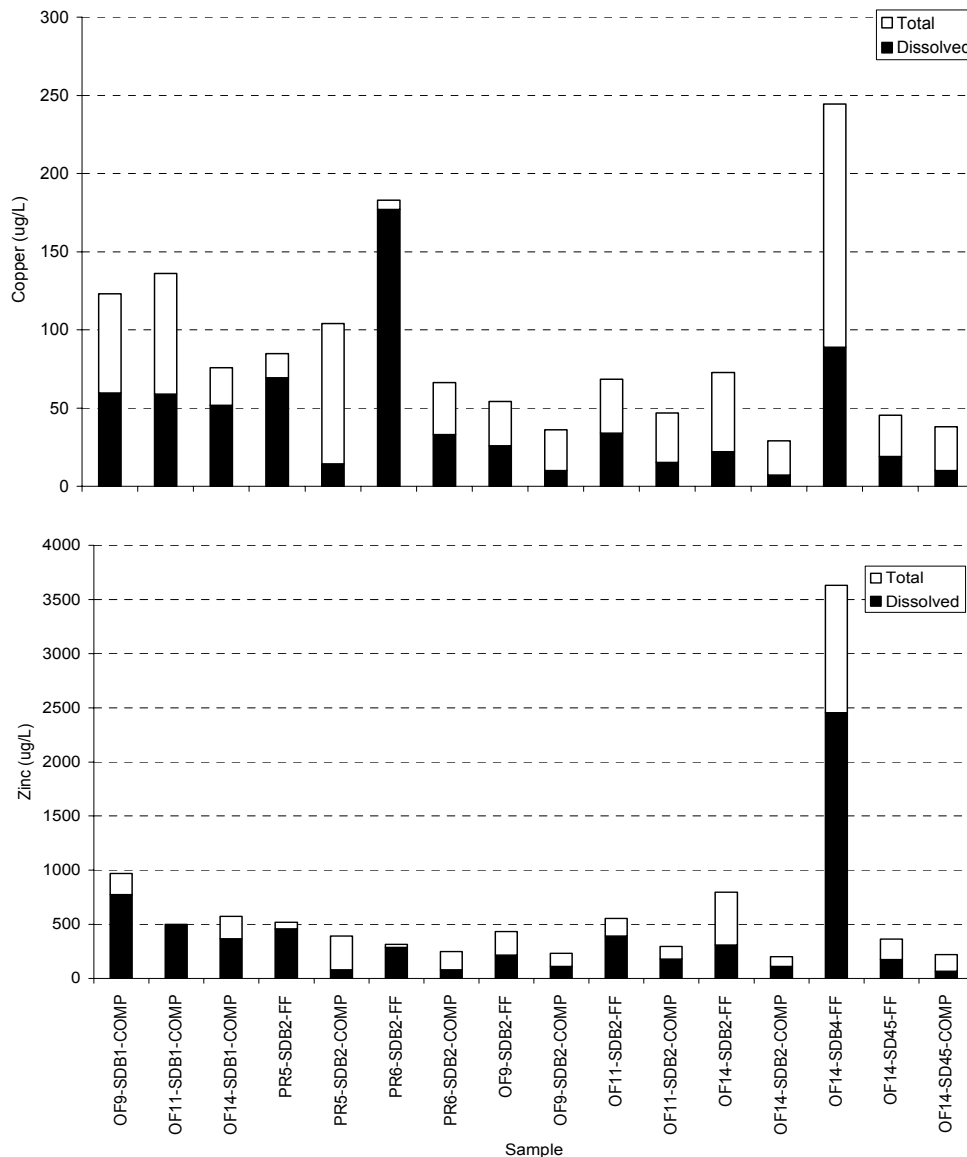


Figure 26. Total and dissolved copper and zinc concentrations measured in Naval Station San Diego first-flush (FF) and composite (Comp) outfall samples.

**PAH.** Thirty-six samples were analyzed for PAH at Naval Station San Diego. This total includes 15 outfall samples and 21 receiving water samples. Table 17 shows a statistical summary of storm water and bay water samples that is based on the summation of the 16 priority pollutant PAH data. Appendix D shows all individual sample data. The sum of priority pollutant PAH concentrations in outfall samples ranged from ~60 to 2,160. Only about 3% of these PAHs were below a MDL, which ranged from 0.33 to 1.6 ng/L, depending on the specific analyte. Analytes not detected were given a value equal to one-half the MDL in the summation. The highest level was found in the first-flush sample collected from outfall 11 during the second storm event SDB2. First-flush samples were not always higher than their corresponding composite sample, even though their average concentration (738 ng/L) was about 35% higher (471 ng/L).

Average summed priority pollutant PAH concentrations in bay water samples were relatively low, ranging from 20 to 246 ng/L and averaged 52 ng/L. These levels were about an order of magnitude lower than measured in composite outfall samples. About 45% of these PAH analytes in bay water samples were below a MDL. Analytes not detected were given a value equal to one-half the MDL in the summation.

Acute or chronic WQS for PAHs do not exist. A review of the literature identified minimum acute and chronic thresholds for individual PAH analytes to fish and invertebrates (Table 11). The minimum acute level for pyrene in one first-flush sample collected from outfall 11 during the second storm event SDB2 was exceeded by 70%. All the receiving water samples contained PAH concentrations below the minimum chronic threshold value shown in Table 11.

Figure 27 shows the average relative composition of the PAH in first-flush and composite samples. Figure 28 shows a comparable plot for bay water samples. These distributions were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type: first-flush, composite, or bay sample. The PAH distribution in first-flush and composite samples were very similar. The main differences were the relatively lower naphthalenes and higher methylated fluorenes in the first-flush samples. Both sample types had compositions that were consistent with a predominantly low-level petrogenic (fuel) and minor pyrogenic (combustion) source. The composite samples had a relatively higher petrogenic component. Receiving water PAH compositions were very similar in samples collected before, during, and after storm events. These samples had a distinctly different composition than that of storm water with a distribution more characteristic of weathered petrogenic and pyrogenic source.

Table 17. Statistical summary of priority pollutant PAH data at Naval Station San Diego. The summation used one-half the MDL for analytes not detected in the sample. Sample types include first-flush (FF) and composite (COMP) outfall samples as well as receiving water (Bay) samples collected before (PRE), during (DUR), and after (AFT) storm events.

Sum Priority Pollutant PAH (ng/L)	Outfalls		Bay		
	FF	COMP	PRE	DUR	AFT
n	6	9	5	8	8
Min	62	93	20	28	28
Average	738	471	31	50	66
Max	2156	977	45	77	246
RSD	102%	62%	36%	38%	115%

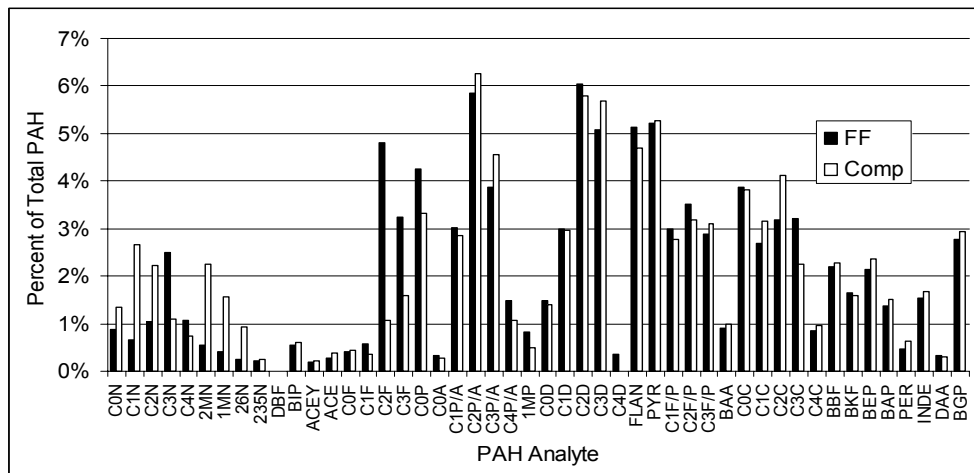


Figure 27. Average PAH composition in first-flush (FF) and composite (Comp) samples at Naval Station San Diego. The averages were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type (first-flush or composite). Table 6 shows analyte IDs.

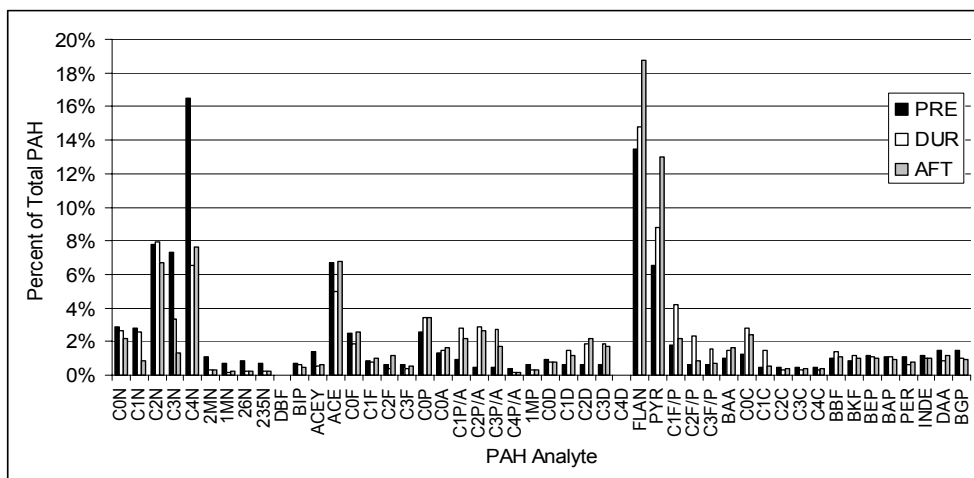


Figure 28. Average PAH composition in receiving waters before (PRE), during (DUR), and after (AFT) storm events at Naval Station San Diego. Table 6 shows analyte IDs.

**PCB.** Fifteen outfall samples were analyzed for PCB congeners at Naval Station San Diego. Table 18 shows a statistical summary of storm water of PCB data. No seawater PCB analyses were conducted because historical analyses showed levels typically all below detection even with MDLs of 1 ng/L. Appendix D shows all individual sample data. The sum of PCBs was calculated by summing all of the individual congeners in a sample. Congeners not detected were give a value equal to one-half the MDL, which ranged from 0.1 to 1.8 ng/L, depending on the congener. The sum of PCBs averaged 50 ng/L in first-flush samples and 19 ng/L in composite samples. Though the sum of PCBs in first-flush samples was three times higher than levels found in composite samples, the difference was not statistically significant at the 95% confidence level because the results were highly variable. The variations can be seen in Figure 29. All samples contained total PCB concentrations well below

the minimum acute threshold value of 10,000 ng/L described earlier under chemical benchmarks (EPA, 1987).

Table 18. Statistical summary of PCB data at Naval Station San Diego. “Sum PCB” is the summation of all congeners measured in the sample. The summation used one-half the MDL for congeners not detected in the sample. Sample types include first-flush (FF) and composite (COMP) outfall samples. The minimum acute threshold described earlier is also shown.

Sum PCB (ng/L)	Outfalls	
	FF	COMP
n	6	9
Min	6.9	4.0
Average	50	19
Max	154	35
RSD	111%	62%
Acute Threshold	10000	

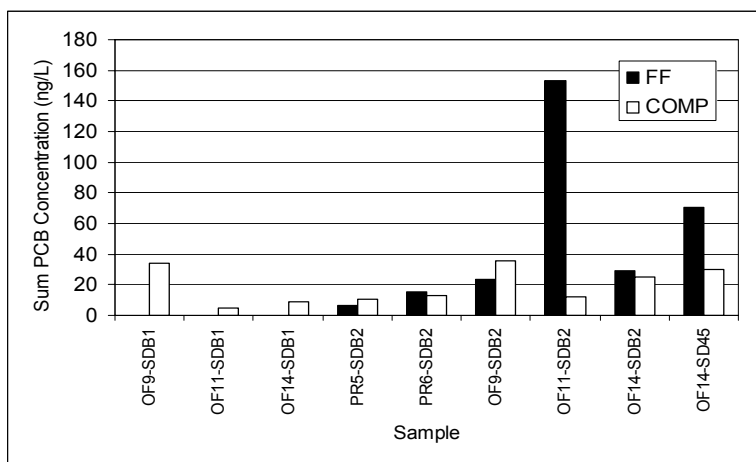


Figure 29. Summed PCB concentrations for first-flush (FF) and composite (COMP) outfall samples at Naval Station San Diego. The summation used one-half the MDL for congeners not detected in the sample.

**Pesticides.** Table 19 shows chlorinated pesticides data analyzed in two storm water samples collected at Naval Station San Diego. Pesticide analyses were added later in the study and no seawater pesticide analyses were conducted because of detection limit considerations. The two samples analyzed were collected as part of the SD45 storm event (Floating Bioassay Laboratory Study). A total of only nine analytes were detected in the two samples above a MDL, which ranged between 0.2 and 1.9 ng/L, depending on the analyte. The lack of detectable data precludes a meaningful evaluation of differences between first-flush and composite samples. However, 4',4' DDE, 4'4' DDT, a-chlordane, and trans-nonachlor were higher in first-flush samples than their paired composite sample. All the pesticides measured in storm water samples were below acute WQS.

Table 19. Chlorinated pesticide data measured in one first-flush (FF) and one composite (COMP) outfall sample at Naval Station San Diego outfall 14. Grayed-out cells are values equal to the MDL. Acute WQS are also shown.

Pesticide	Outfalls		Acute WQS (ng/L)
	OF14-SD45-FF (ng/L)	OF14-SD45-COMP (ng/L)	
2,4'-DDD	0.99	0.62	
2,4'-DDE	0.84	0.52	
2,4'-DDT	0.59	0.37	
4,4'-DDD	1.16	1.49	
4,4'-DDE	1.62	1.1	
4,4'-DDT	4.12	0.45	130
aldrin	0.48	0.3	1300
a-chlordane	2.16	1.67	
g-chlordane	0.49	0.31	90
a-BHC	0.42	0.26	
b-BHC	0.58	0.36	
d-BHC	0.47	0.3	
Lindane	0.6	1.49	
cis-nonachlor	0.79	0.49	
trans-nonachlor	2.03	1.44	
oxychlordane	0.48	0.3	
dieldrin	0.93	0.58	710
endosulfan I	0.33	0.21	34
endosulfan II	0.84	0.53	34
endosulfan sulfate	0.79	0.49	
endrin	0.92	0.57	37
endrin aldehyde	1.03	0.65	
endrin ketone	1.08	0.68	
heptachlor	0.72	0.45	53
heptachlor epoxide	1.92	1.2	53
Hexachlorobenzene	1.01	0.63	
methoxychlor	1.19	0.74	
Mirex	0.75	0.47	

### 7.2.5 Plume Mapping

Plume mapping was performed at Naval Station San Diego in November 2002 (SDB1) and February 2003 (SDB2). Figure 4 shows the timetable of the surveys and rainfall. Figure 30 shows example spatial maps of surface salinity from surveys made before, during, and after storm event SDB2. Appendix G shows spatial plots for all parameters measured for all surveys. Rainfall for this storm totaled about an inch. The salinity plots show that the storm water plumes during the storm were limited to an area immediately along the shoreline. Evidence of the plume extent was observed with most other parameters, particularly light transmission, which is a measure of the particle loading. Vertical cross-sections of salinity collected during the storm event showed that the plumes were limited to a maximum depth of 2 meters (Figure 31). The plume depth decreased with distance away from the shoreline until there was no evidence of it ~300 meters from the quay wall. Most parameters, particularly the “after” storm survey, showed a very slight reduction in salinity out to the ends of the piers. This reduction in salinity was a result of an unexpected short but intense rain squall



that occurred during the survey. The effects of this squall rainfall can clearly be seen in the “after” plot, where a freshwater plume was observed discharging from Chollas Creek bordering the north side of the base.

The maximum fraction of storm water in the receiving water as measured by the reduction in salinity was 4%. This value was calculated as described earlier by comparing the minimum salinity measured during a storm event to the average salinity measured on the pre-storm survey. The maximum value was measured right along the quay wall.

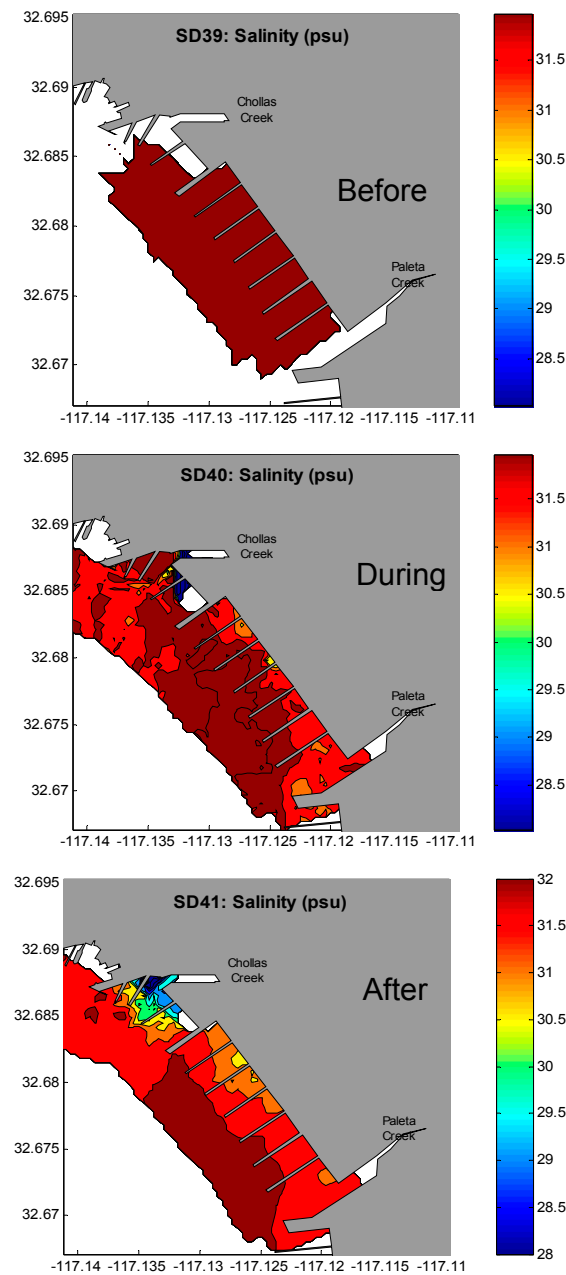


Figure 30. Surface salinity mapping before, during, and 24 hours after a storm event (SDB2) at Naval Station San Diego.

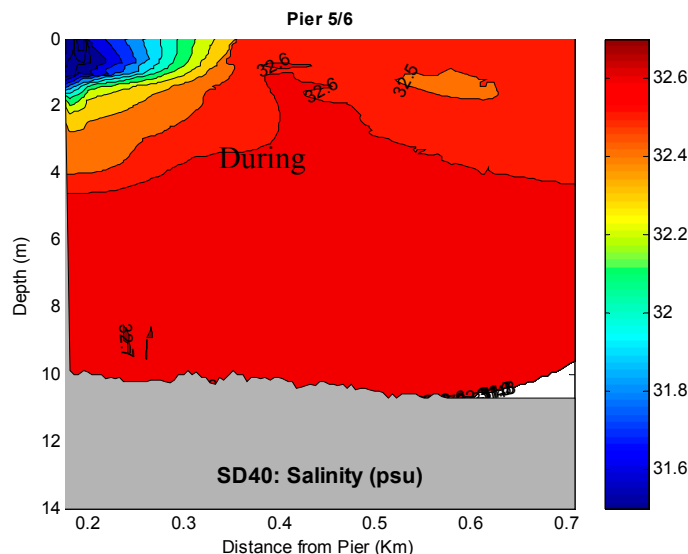


Figure 31. Vertical cross section of salinity between piers 5 and 6 (outside of outfall 9) during storm event SDB2 at Naval Station San Diego.

## 7.3 NAVAL SUBMARINE BASE SAN DIEGO

### 7.3.1 Storm Water Toxicity

Thirteen storm water outfall samples were tested, not necessarily for all species, for toxicity at Naval Submarine Base San Diego. Figure 32 shows the 100% storm water effluent toxicity data. A statistical summary of the results are provided in Table 20, with all data provided in Appendices B and C. Similar to Naval Station San Diego results, the three TIE tests conducted with the inland silverside (*Menidia beryllina*) were counted in the topsmelt results. In general, topsmelt and mysids responded similarly to outfall samples, averaging 91 and 80% survival in the undiluted effluent. First-flush and composite samples did not differ in toxicity, averaging 85% survival for both sample types, with low RSDs observed for both species. Though survival was relatively high, 40% of first-flush samples and 33% of composite samples would have failed the 90% survival requirement when tested with topsmelt. When mysids were used, failure rates were substantially higher, with 70 and 100% of samples resulting in <90% survival for first-flush and composite samples, respectively. Topsmelt in first-flush samples would not have failed the 70% survival requirement, though mysids would have failed 20% of the time. All the composite samples would have passed the 70% requirement.

For Naval Submarine Base San Diego samples, 96% of NOECs (combined for topsmelt and mysids) were 100% storm water effluent. Three of the 26 dilution series test results run on first-flush samples had a NOEC of 50% and two of the composite samples had a NOEC of 50%. These data suggest that a receiving water mixture with less than a 50% storm water fraction would result in no observable toxicity.

Mussel larvae were more sensitive than the permitted species in outfall samples, with an overall average of <2% normal development in undiluted storm water effluent (maximum effluent concentrations ranged between 58 and 65% because of brine addition). Because this bioassay is not included in the permit, the 90% requirement does not apply. The mysid and mussel toxicity data were more variable in first-flush samples than in composite samples. A qualitative review of the data showed that the highest toxicity was observed in the first-flush sample collected from outfall 11B during the

first flush of the year sampling (SDB4). Though the study was not designed to compare outfalls, a qualitative review of paired data showed that toxicity in samples from the Naval Submarine Base San Diego outfalls were similar, though there was a slight increase observed for outfall 23CE during the TIE1 sampling. NOECs for mussels ranged from 10 to 33%, though one sample had a NOEC of <6.25%. With the exception of this one sample, a receiving water mixture with less than a 10% storm water fraction would result in no observable toxicity.

As described earlier, method variability in toxicity testing is an important consideration for evaluating results. Table 21 shows the PMSD for Naval Submarine Base San Diego industrial storm water dilution series toxicity tests, including baseline TIE results. PMSD values ranged from 6 to 24% for topsmelt and averaged 13%. PMSD for mysid tests ranged from 4 to 13 and averaged 9%. The mussel embryo-larval development tests ranged from 8 to 19% and averaged 13%. The mysid results all fell well within EPA guidelines for test acceptability (EPA, 2000). The topsmelt and mussel data also met the PMSD test acceptability criteria for comparable, endpoints (inland silverside survival and mussel survival and normal development). These differences are described later in the discussion section.

### 7.3.2 Receiving Water Toxicity

Twenty-four receiving water samples were tested, not necessarily for all species, for toxicity at Naval Submarine Base San Diego. No toxicity was observed in bay water samples. Survival was very high for topsmelt and mysids exposed to bay waters, with a combined average survival of 98%. All topsmelt and mysid bay water data were statistically indistinguishable from lab controls ( $p < 0.05$ ). Mussel larval development in all samples averaged 87% and was not statistically different from controls.

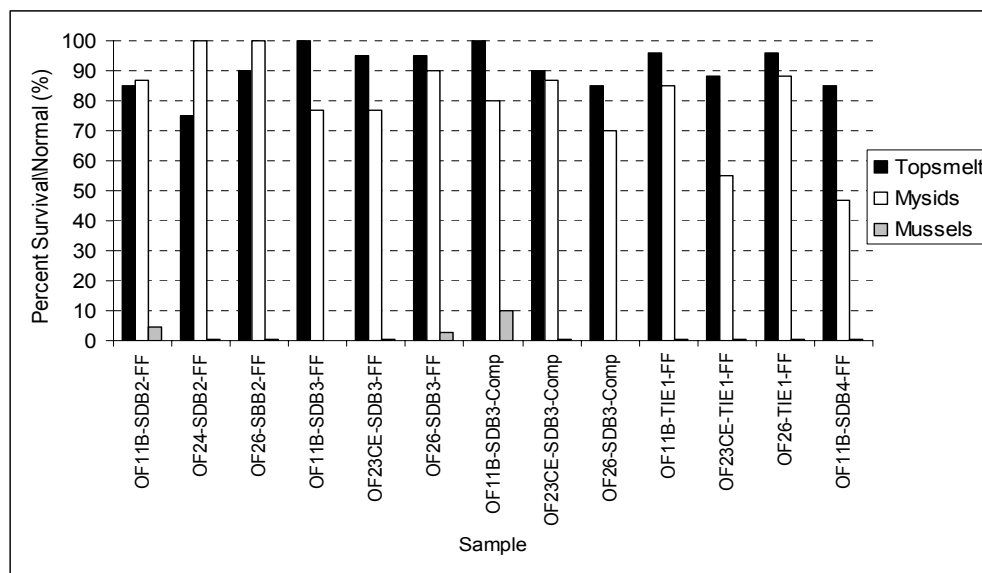


Figure 32. Topsmelt and mysid survival and normal mussel embryo-larval development in 100% storm water effluent collected from first-flush (FF) and composite (Comp) samples at Naval Submarine Base San Diego.

Table 20. Statistical summary of toxicity data in Naval Submarine Base San Diego first-flush (FF) or composite (Comp) undiluted storm water or in receiving water (Bay) samples. Results are expressed as percent survival for topsmelt and mysids and as percent normal embryo-larval development for mussels. “# <90% and % Failing” refers to the number and percentage of samples that did not meet the 90% survival criterion in the permit.

SUB	Topsmelt Survival (%)			Mysid Survival (%)			Mussel Normal Development (%)		
	FF	Comp	Bay	FF	Comp	Bay	FF	Comp	Bay
<i>n</i>	10	3	21	10	3	20	9	2	24
Min	75	85	90	47	70	93	0	0	86
Mean	91	92	97	80	79	99	1	5	92
Max	100	100	100	100	87	100	4	10	97
RSD	8	8	4	22	11	2	199	NA	4
# <90%	4	1	NA	7	3	NA	NA	NA	NA
% FAILING	40%	33%	NA	70%	100%	NA	NA	NA	NA

NA Not applicable

Table 21. Percent Minimum Significant Difference (PMSD) for Naval Submarine Base San Diego toxicity tests.

PMSD	Topsmelt	Mysids	Mussels
<i>n</i>	13	12	11
Min (%)	6	4	8
Mean (%)	13	9	13
Max (%)	24	13	19

### 7.3.3 TIE

A Toxicity Identification Evaluation was performed on first-flush samples collected from each of the three outfalls at Naval Submarine Base San Diego during the storm event on 18 February 2004. First-flush samples were collected at the start of a very low rainfall event in which only 0.19 inches of rainfall fell. Appendix E includes the report for this effort. Inland silversides (*Menidia beryllina*) were used in lieu of topsmelt in these tests because topsmelt were unavailable from the supplier. It is expected that the results for inland silversides would have been the same for topsmelt. Figure 33 through Figure 35 show the manipulations performed for each outfall sample.

Toxicity screening results showed that there was insufficient toxicity to inland silversides or to mysids to perform a TIE at outfall 11B or outfall 26. Therefore, TIEs were conducted only using the mussel embryo-larval development tests at these two outfalls. The sample from outfall 23CE was sufficiently toxic to mysids, so the TIE for this sample was conducted with mussel embryos and mysids.

The TIE showed copper as the toxic agent in all three outfall samples. Zinc was identified as an additional causative agent in two of the outfalls, 23CE and 26. In the case of 23CE, zinc was the toxic agent for mussels and mysids. An additional compound identified by the toxicity laboratory that may have caused additive toxicity at outfall 11B was a non-polar organic compound called nonylphenol (see addendum report of Appendix E). Nonylphenol is a surfactant (or wetting agent) that is a degradation product from a broader class of surfactant compounds known as nonylphenol ethoxylates

common in paints, resins and protective coatings, pest control products, and various cleaning products. The toxicity laboratory identified this as a likely additive causative agent based on their historical data. However, after the evaluation was completed, EPA published an acute saltwater aquatic life criterion for nonylphenol as 7.0 µg/L (EPA, 2006). The concentration of 0.18 µg/L nonylphenol estimated in the samples was below this toxic threshold and suggests it may not have been a causative agent for toxicity measured in the sample.

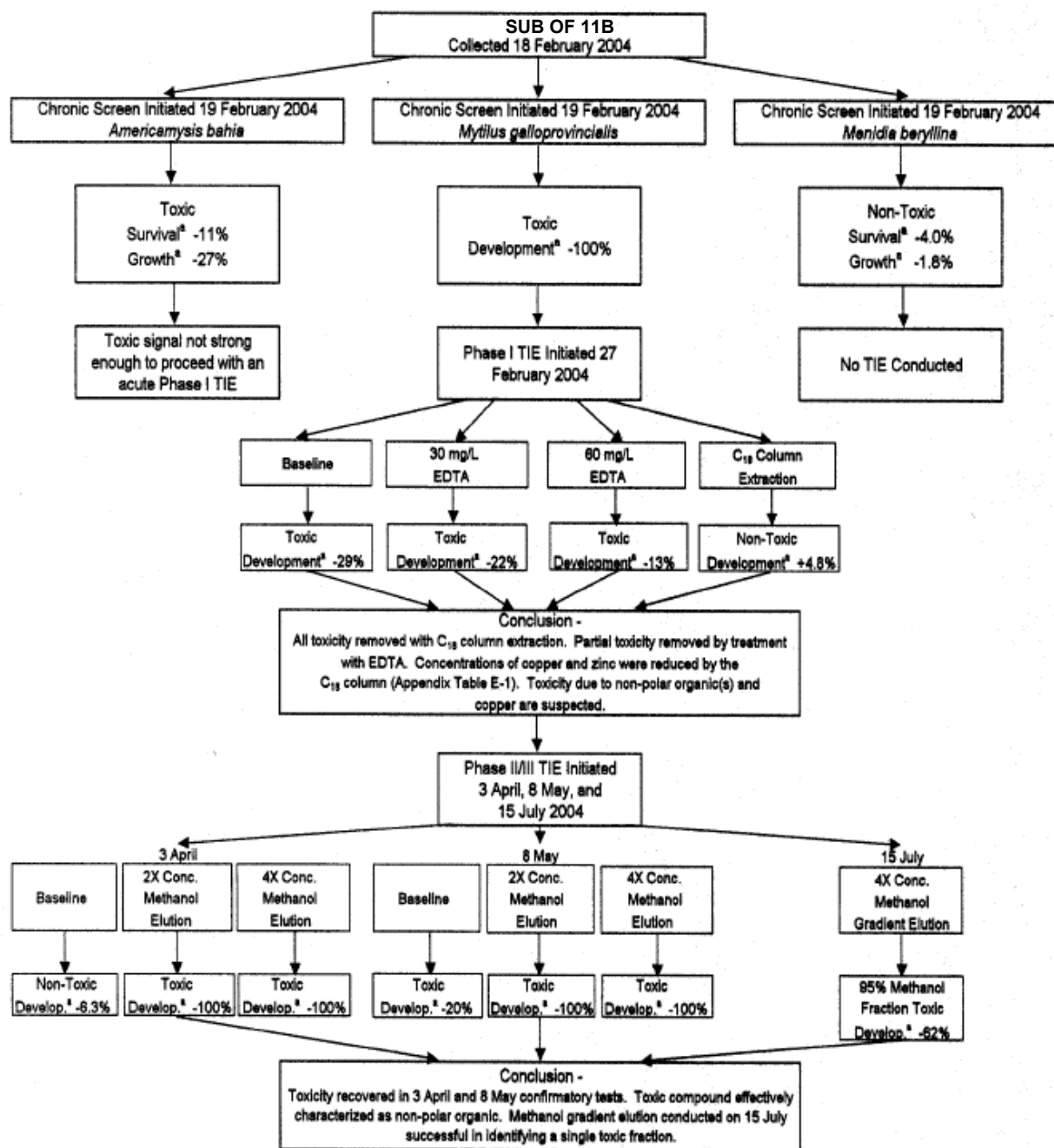
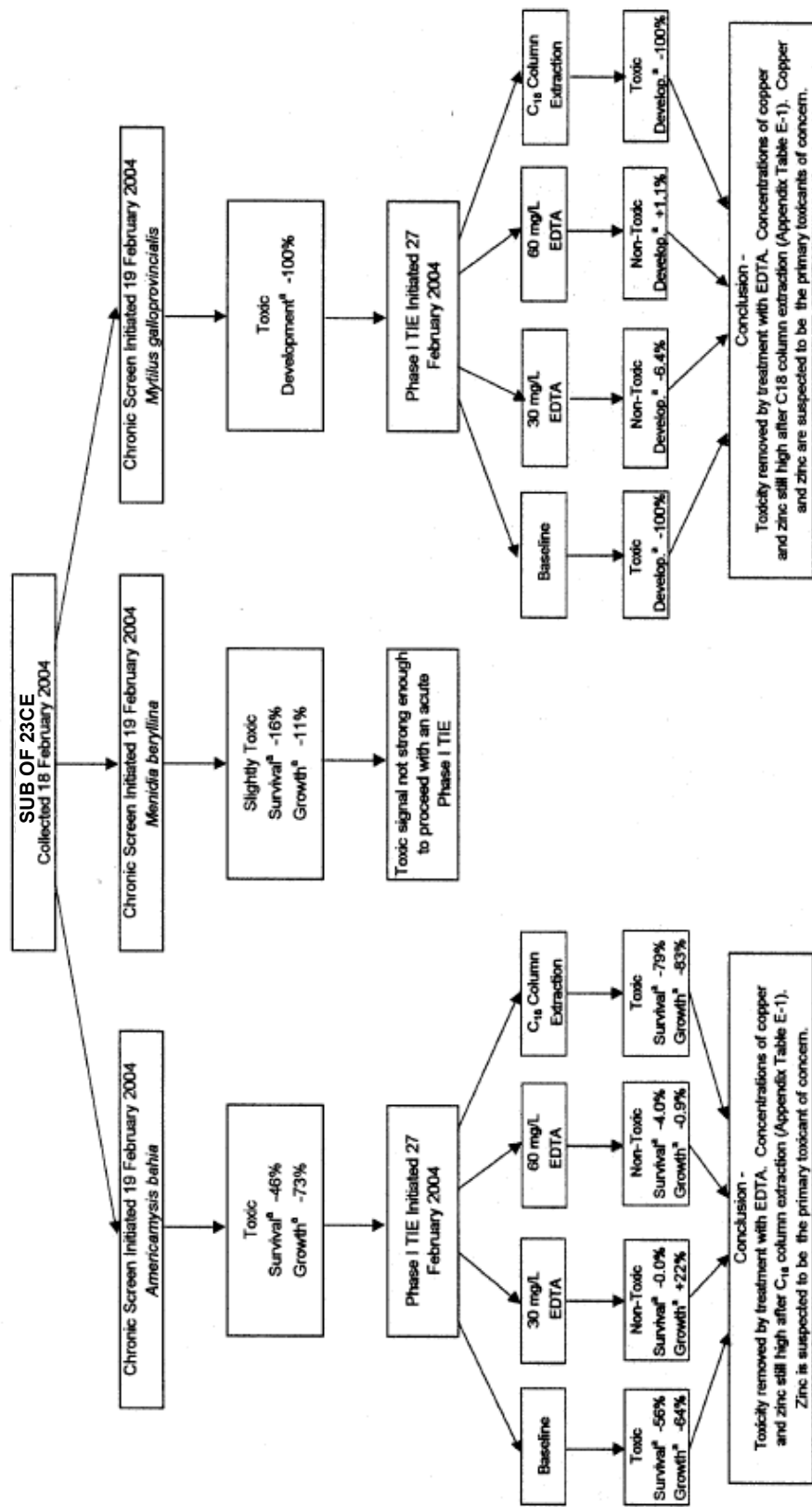
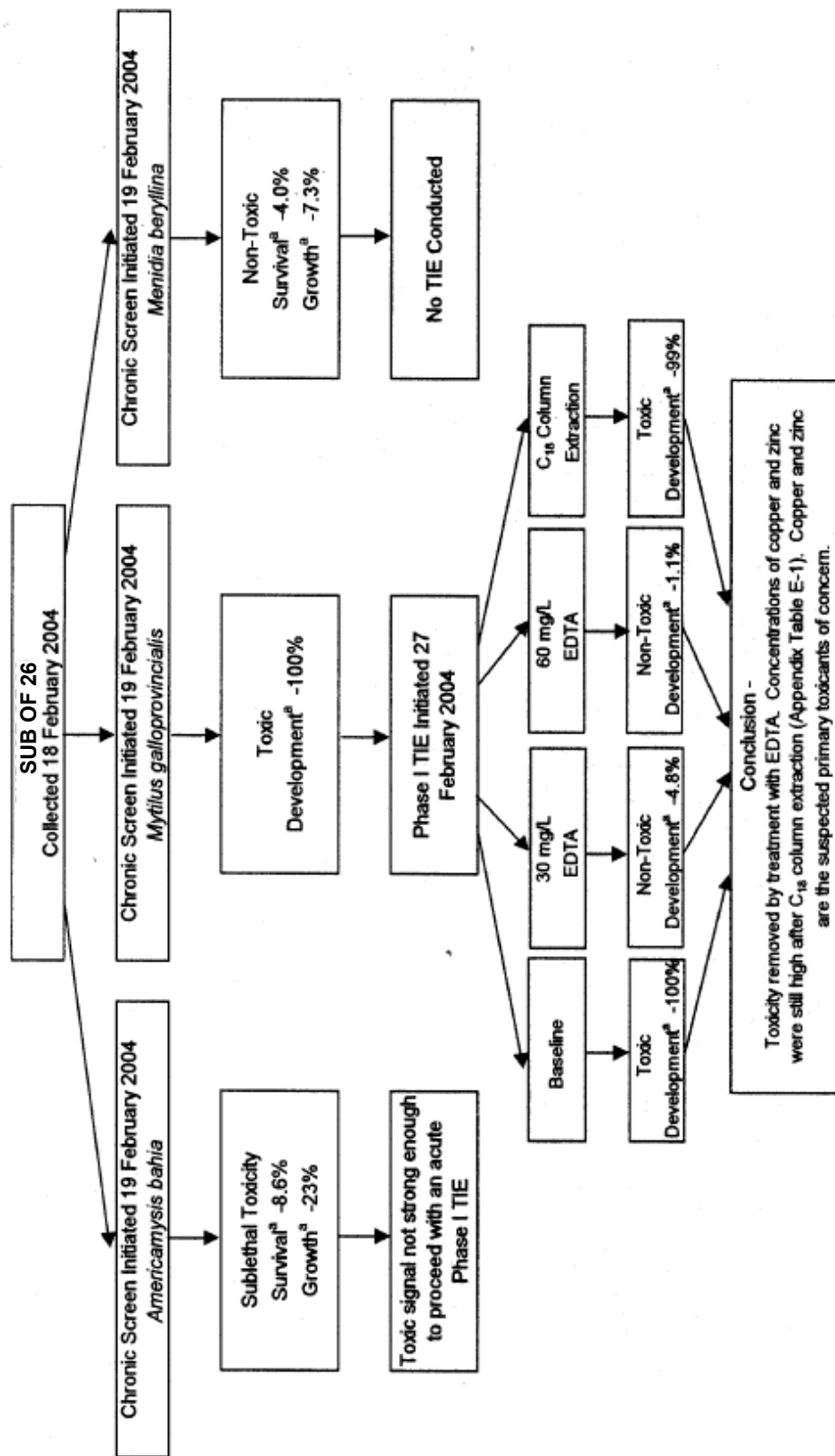


Figure 33. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Submarine Base San Diego outfall 11B.



\* Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 34. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Submarine Base San Diego outfall 23CE.



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 35. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Submarine Base San Diego outfall 26.

### 7.3.4 Chemistry

**TSS/DOC.** A total of 20 and 18 samples were analyzed for TSS and DOC, respectively, at Naval Submarine Base San Diego. Table 22 shows a statistical summary of the TSS and DOC data for Naval Submarine Base San Diego. Appendix D shows all individual sample data. TSS in storm water ranged from ~21 to over 150 mg/L and averaged about 60 mg/L. These levels were about a factor of five lower than those observed at Naval Station San Diego. On average, first-flush samples had higher TSS concentrations than composite samples. The first-flush samples also showed a considerably higher variability than the composite samples as described by the relative standard deviation (RSD). The maximum TSS level was measured in the first-flush samples collected during the first-flush of the year storm event (SDB4) in October 2004. This level was also observed for Naval Station San Diego measurements. Bay samples were about an order of magnitude lower in TSS than the outfall samples, ranged from ~2 to 9 mg/L, and averaged 2.2 mg/L. The average value for bay samples collected before the storm increased about 30% during the storm and then decreased back to pre-storm conditions in the “after” samples. The “during” samples were considerably more variable than the other bay samples.

The DOC data came exclusively from samples collected during a single storm event (SDB3) February 2004, as this measurement was added later in the study. DOC levels in outfall samples were about the same as measured at Naval Station San Diego. Composite samples were about a factor of two higher in DOC than first-flush samples. This was also the case for samples collected at Naval Station San Diego and suggests a lag time in the discharge of organic compounds during storm events. Receiving water samples ranged between 0.5 and 0.8 mg/L DOC before, during, and after the storm event and were about a factor of 10 to 20 lower in DOC than outfall samples.

Table 22. Statistical summary of TSS and DOC at Naval Submarine Base San Diego. Sample types include first-flush (FF) and composite (Comp) outfall samples as well as receiving water (Bay) samples collected before, during, and after storm events.

TSS (mg/L)	Outfalls		Bay		
	FF	Comp	Before	During	After
n	4	3	4	5	4
Min	37	21.2	2.2	2.1	2.4
Mean	68	57	2.8	3.7	3.0
Max	153	97	3.4	8.6	3.7
RSD	82%	66%	20%	74%	23%
DOC (mg/L)					
n	3	3	4	4	4
Min	4.5	11.3	0.5	0.5	0.5
Mean	8.3	12.2	0.7	0.6	0.6
Max	11	13	0.8	0.7	0.8
RSD	42%	7%	19%	16%	21%

**Metals.** Twenty-eight samples were analyzed for total and dissolved metals at Naval Submarine Base San Diego, which included 11 outfall samples and 17 receiving water samples. Of those, 18 were analyzed for only copper and zinc. Table 23 shows a statistical summary of the outfall metals data. The appendices show all individual sample data. The table data are summarized by first-flush and composite samples and by total and dissolved metals. The data show variability of the individual metals spanning a range of ~4% to 135% for the dissolved and total metal. Copper and



zinc concentrations were about double the average storm water value in samples collected during the first-flush of the year (SDB4) storm event. This result matches the observation for TSS and DOC (no other chemicals measured in SDB4 samples).

Nearly all total copper (71%) and all total zinc concentrations in first-flush storm water samples were above their respective performance goals in the NPDES permit of 63.6 and 117  $\mu\text{g/L}$ . Only dissolved copper and zinc were elevated in outfall samples above their respective acute saltwater water quality standards of 4.8 and 90  $\mu\text{g/L}$ , respectively, with the remaining dissolved metals all well below WQS (EPA, 2000b). The comparison made for mercury was to the human health WQS of 0.05  $\mu\text{g/L}$ , as discussed previously. Dissolved copper and zinc exceeded their acute WQS by a maximum factor of 19 and 14, respectively, in first-flush samples. The comparable ratio in composite samples was 29 and 6, respectively.

Maximum total copper and zinc concentrations measured in the outfalls were 149 and 1290  $\mu\text{g/L}$ , respectively. The highest total zinc concentration was measured in the first-flush of the year sample (SDB4) at outfall 11B (Figure 36). However, the highest total copper concentration was measured in the composite sample collected from outfall 26 on Sierra Pier. Composite samples were always higher in copper than their corresponding first-flush samples (Figure 36). However, there was no consistent pattern for zinc for dissolved or total metal.

Copper and zinc ranged from about 41 to 59% and averaged ~48% as the dissolved phase metal in first-flush and composite samples. First-flush samples showed a slightly higher amount of dissolved phase copper than observed in composite samples, indicating a potential lag of particles in the storm discharge. The phase of zinc between sample types was not as consistent.

Table 24 shows a statistical summary of the bay seawater sample data. Appendix D shows all individual sample data. The variability in these data was generally higher than observed in storm water samples, a result not seen at Naval Station San Diego. Most of this variation appeared to be more related to stage of the tide than to storm condition. As was observed for storm water, bay water dissolved concentrations of copper and zinc were highest in the SDB4 sample collected at outfall 11B during the first-flush of the year. Concentrations were 5.5 and 53  $\mu\text{g/L}$ , respectively, and represent an increase above typical concentrations by a factor of 3 and 7, respectively. This was the only bay water sample in which a metal concentration exceeded a chronic WQS. In this instance, dissolved copper was a factor of 1.8 above the WQS.

Table 23. Statistical summary of first-flush (FF) and composite (Comp) outfall metals data at Naval Submarine Base San Diego. Values for the total and dissolved metal are shown. NPDES performance goals and acute WQS are also shown. Grayed-out cells are values equal to the MDL.

OF FF Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	3	7	3	3	7	3	3	3	3	3	3	3	3	3
min	0.056	20.4	9.9	0.0067	130	453	1.23	0.56	3.44	750	22.60	6.58	0.24	0.44
mean	0.101	95.0	22.6	0.0129	554	1317	1.31	0.97	5.09	2424	120	11.9	0.27	0.55
max	0.152	149	43.5	0.0253	1291	3040	1.46	1.26	6.23	5770	306	16.6	0.30	0.69
RSD	48%	54%	81%	83%	77%	113%	10%	38%	29%	120%	135%	42%	12%	22%
NPDES Performance Goal		63.6			117.0									
OF FF Dissolved (µg/L)														
n	3	7	3	3	7	3	3	3	3	3	3	3	3	3
min	0.010	15.1	0.184	0.0034	59.3	18.60	0.45	0.17	0.51	15.3	11.0	3.30	0.10	0.04
mean	0.014	45.2	0.376	0.0056	358	25.6	0.91	0.43	1.09	34.2	22.7	7.53	0.21	0.08
max	0.017	92.6	0.575	0.0098	1255	32.9	1.14	0.65	1.59	53.6	44.8	11.8	0.28	0.14
RSD	24%	68%	52%	65%	126%	28%	44%	57%	50%	56%	84%	56%	46%	63%
OF COMP Total (µg/L)														
n	3	4	3	3	4	3	3	3	3	3	3	3	3	3
min	0.040	24.9	7.8	0.0166	123	529	1.09	0.24	4.79	1980	48.7	6.76	0.26	0.50
mean	0.059	118	13.4	0.0257	458	1423	2.60	1.28	5.89	2497	72.3	7.92	0.48	0.64
max	0.072	216	20.1	0.0432	792	2190	4.62	2.60	6.71	3210	89.7	9.31	0.63	0.87
RSD	28%	86%	47%	59%	60%	59%	70%	94%	17%	26%	29%	16%	41%	32%
OF COMP Dissolved (µg/L)														
n	3	4	3	3	4	3	3	3	3	3	3	3	3	3
min	0.009	15.2	0.400	0.0074	37.4	9.05	0.72	0.09	0.89	30.9	11.1	3.14	0.20	0.50
mean	0.015	74.5	0.554	0.0165	286	14.9	2.18	0.46	1.21	32.0	23.6	4.03	0.36	0.50
max	0.026	142	0.742	0.0265	505	18.2	4.31	0.86	1.80	33.5	35.9	5.76	0.65	0.50
RSD	66%	90%	31%	58%	68%	34%	86%	83%	42%	4%	53%	37%	69%	0%
WQS Acute (µg/L)	1.9	4.8	210		90		69	42	1100			74	290	

Table 24. Statistical summary of total and dissolved bay seawater metals data for Naval Submarine Base San Diego. Values for the total and dissolved metal are shown. Chronic WQS are also shown.

Bay Total (µg/L)	Ag	Cu	Pb	Hg	Zn
n	4	17	4	4	17
min	0.013	0.55	0.11	0.001	1.19
mean	0.015	2.02	0.24	0.003	8.6
max	0.018	10.5	0.56	0.010	71
RSD	19%	113%	92%	128%	193%
Bay Dissolved (µg/L)					
n	4	17	4	4	17
min	0.022	0.34	0.054	0.001	1.17
mean	0.026	1.30	0.064	0.006	7.4
max	0.030	5.5	0.083	0.013	53
RSD	13%	91%	20%	97%	165%
WQS Chronic (µg/L)		3.1	8.1		81

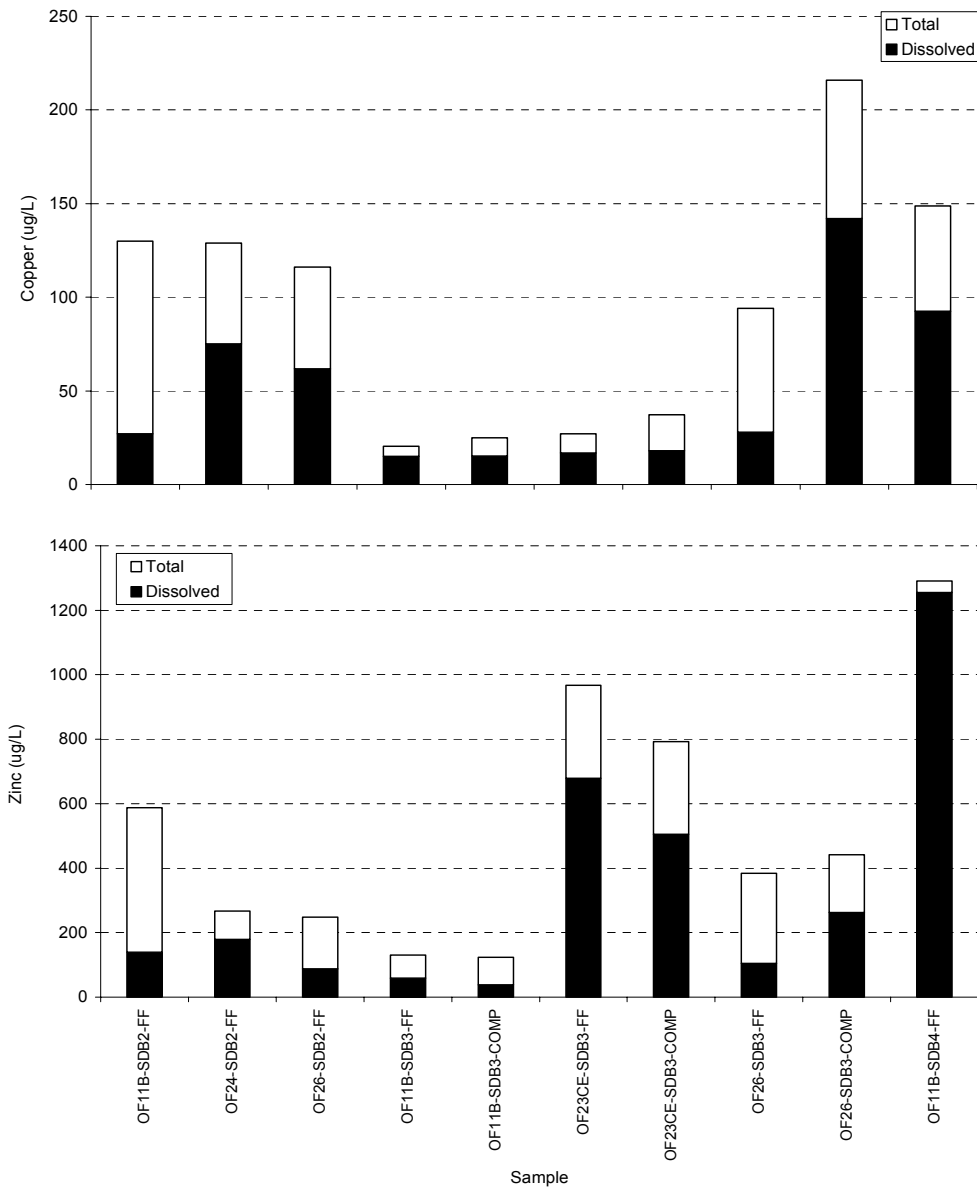


Figure 36. Total and dissolved copper and zinc concentrations measured in Naval Submarine Base San Diego first-flush (FF) and composite (Comp) outfall samples.

**PAH.** Twenty-five samples were analyzed for PAH at Naval Submarine Base San Diego. Of this total, nine samples were collected from outfalls and 16 were collected in receiving waters. Table 25 shows a statistical summary of storm water and bay water samples that is based on the summation of the 16 priority pollutant PAH data. Appendix D shows all individual sample data. The sum of priority pollutant PAH concentrations in outfall samples ranged from 94 to 325 ng/L and averaged about 220 ng/L. This average was less than half that observed in samples collected at Naval Station San Diego. All priority pollutant PAH analytes were detected above the MDL that ranged from 0.28 to 1.5 ng/L, depending on the specific analyte. The highest level was found in the first-flush sample collected from outfall 23CE during the SDB3 storm event. First-flush samples were not always higher than their corresponding composite sample.

Average summed priority pollutant PAH concentrations in receiving water samples were relatively low, ranging from 9 to 194 ng/L and averaged 31 ng/L. These levels were about a factor of five lower than levels measured in composite outfall samples. About 11% of these PAH analytes in receiving water samples were below the MDL. Analytes not detected were given a value equal to one-half the MDL in the summation.

All the storm water samples contained PAH concentrations below the minimum acute thresholds identified in Table 11. All the receiving water samples had PAH at levels below the minimum chronic threshold values in the same table.

Figure 37 shows the average relative composition of the PAH in first-flush composite samples. Figure 38 shows a comparable plot for bay water samples. These distributions were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type; first-flush, composite, or bay sample. The PAH distribution in first-flush and composite samples were very similar, with only very minor variations. Both sample types had compositions that were consistent with a predominantly low-level weathered petrogenic source and a minor pyrogenic (combustion) source. Receiving water PAH compositions were very similar in samples collected before, during, and after storm events. They had a distinctly different composition than that of storm water, having a distribution more characteristic of weathered pyrogenic source.

Table 25. Statistical summary of priority pollutant PAH data at Naval Submarine Base San Diego. The summation used one-half the MDL for analytes not detected in the sample. Sample types include first-flush (FF) and composite (Comp) outfall samples as well as receiving water (Bay) samples collected before (PRE), during (DUR), and after (AFT) storm events.

Sum Priority Pollutant PAH (ng/L)	Outfalls		Bay		
	FF	COMP	PRE	DUR	AFT
n	6	3	5	7	4
Min	94	137	8.8	9.0	14
Average	213	219	28	41	18
Max	325	314	58	194	21
RSD	42%	41%	70%	165%	16%

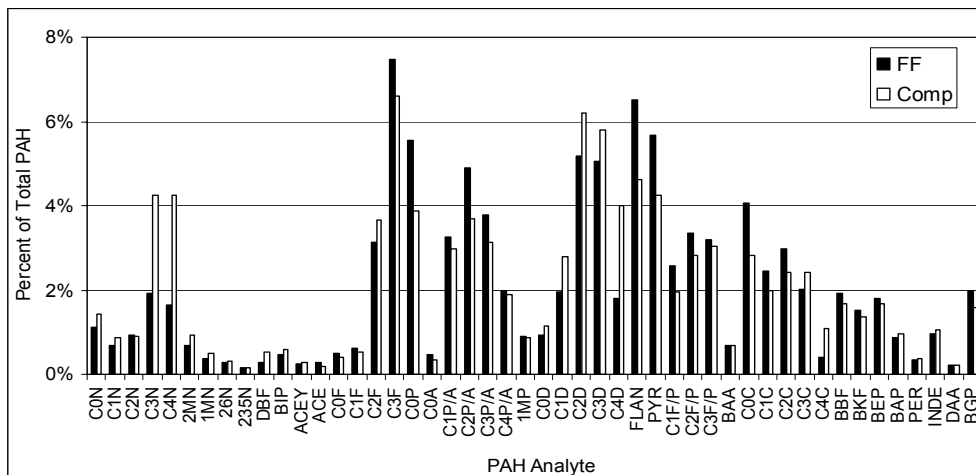


Figure 37. Average PAH composition in first-flush (FF) and composite (Comp) samples at Naval Submarine Base San Diego. The averages were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type (first-flush or composite). Table 6 shows analyte IDs.

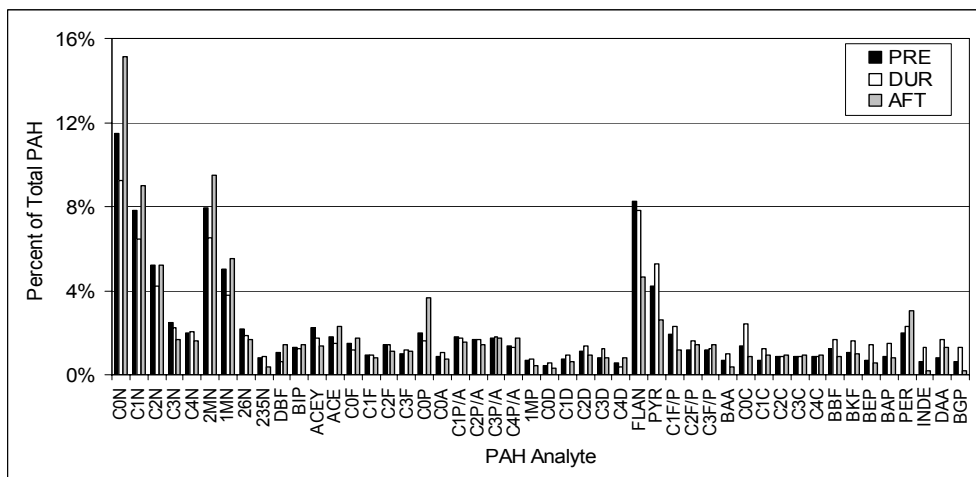


Figure 38. Average PAH composition in receiving waters before (PRE), during (DUR), and after (AFT) storm events at Naval Submarine Base San Diego. Table 6 shows analyte IDs.

**PCB.** Six outfall samples were analyzed for PCB congeners at Naval Submarine Base San Diego. Table 26 shows a statistical summary of storm water PCB data. No seawater PCB analyses were conducted. Appendix D shows all individual sample data. The sum of PCBs was calculated by summing all the individual congeners in a sample. Those congeners not detected were given a value equal to one-half the MDL, which ranged from 0.1 to 1.8 ng/L, depending on the congener. The sum of PCBs averaged 8.3 ng/L in first-flush storm water samples and 3.3 ng/L in composite samples, though the samples were not collected from the same outfalls during the same storms. Nearly 90% of these totals were a result of non-detect data. PCB levels measured in outfalls all fell below the minimum acute toxicity thresholds (EPA, 1987).

Table 26. Statistical summary of PCB at Naval Submarine Base San Diego. “Sum PCB” is the summation of all congeners measured in the sample. The summation used one-half the MDL for congeners not detected in the sample. Sample types include first-flush (FF) and composite (COMP) outfall samples. The acute toxicity benchmark is also shown.

Sum PCB (ng/L)	Outfalls	
	FF	COMP
n	3	3
min	4.1	2.4
mean	8.3	3.3
max	12	5.0
RSD	49%	45%
Acute Threshold	10,000	

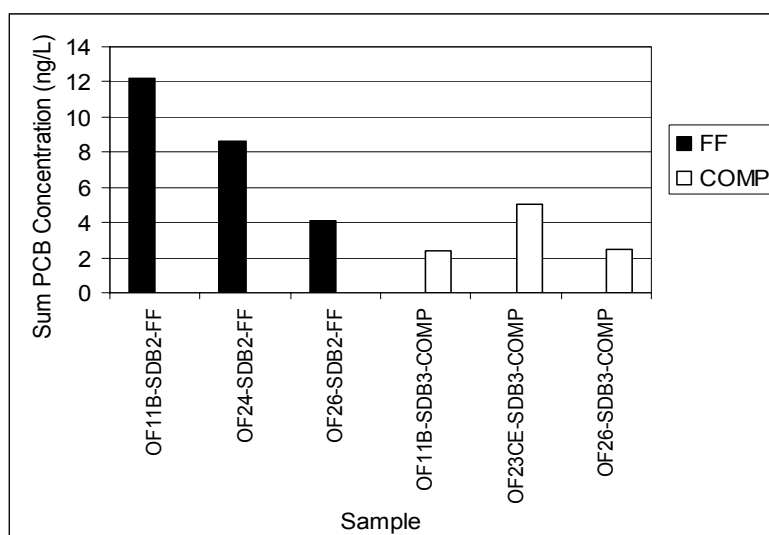


Figure 39. Summed PCB concentrations for first-flush (FF) and composite (COMP) outfall samples at Naval Submarine Base San Diego.

**Pesticides.** Three outfall composite samples were analyzed for chlorinated pesticides at Naval Submarine Base San Diego. All pesticides measured in these samples were below detection limits ranging from 0.21 to 2.2 ng/L. These concentrations were well below acute WQS shown in Table 10.

### 7.3.5 Plume Mapping

Plume mapping was performed once at Naval Submarine Base San Diego in February 2004 (SDB3). Figure 4 shows the timetable of the surveys and rainfall. Figure 40 shows spatial maps of surface salinity from surveys made before, during, and after the storm event. Appendix G shows spatial plots for all parameters measured during these surveys. Rainfall for this storm totaled about a half-inch. The salinity plots show that the storm water plumes were limited to an area immediately along the shoreline. Evidence of the plume extent was observed with most other mapping parameters. Water quality conditions around the base measured 24 hours after the storm event had returned to pre-storm conditions. The lack of any measurable plume feature at that time was a result of the limited spatial extent of the plume to begin with as well as the more effective tidal mixing near the mouth of the bay. The maximum fraction of storm water in the receiving water as measured by the reduction in salinity was 5%. This maximum value was measured right along the shoreline.

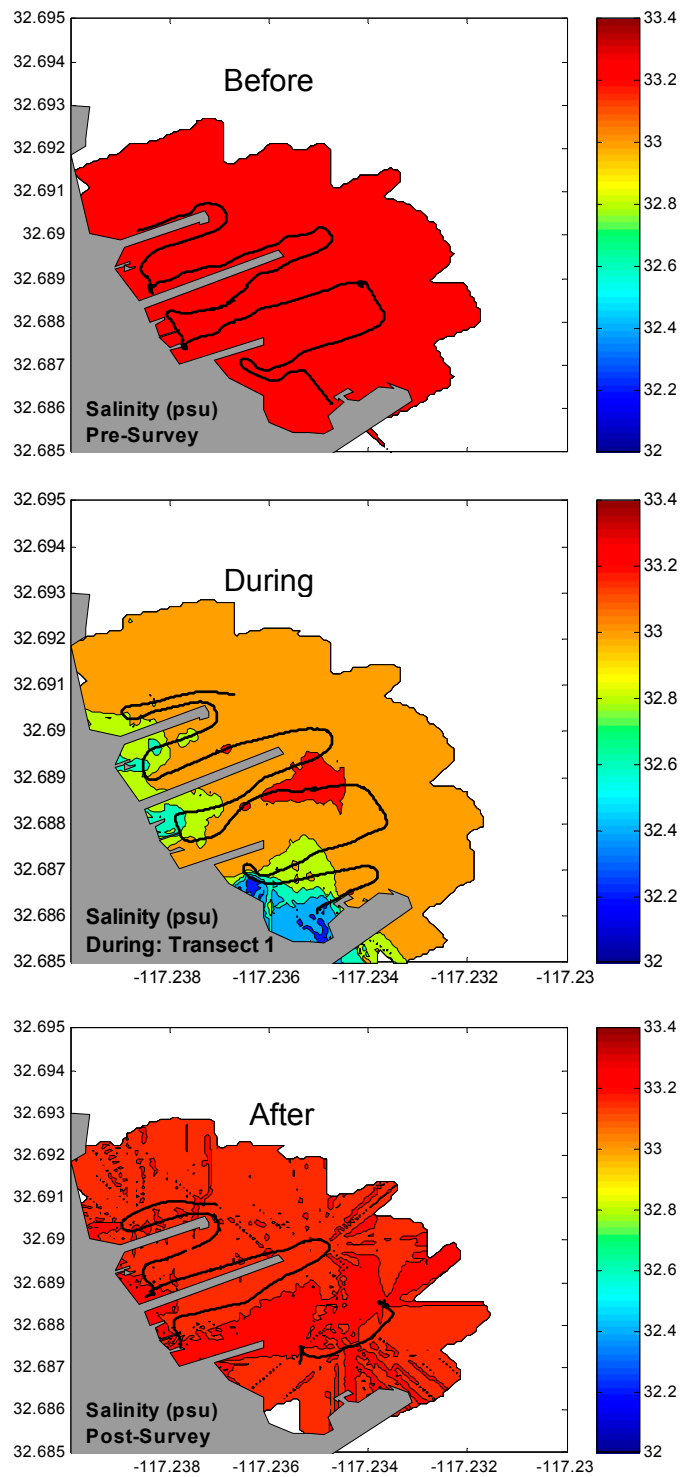


Figure 40. Surface salinity mapping before, during, and after a storm event (SDB3) at Naval Submarine Base San Diego.

## **7.4 NAVAL AMPHIBIOUS BASE CORONADO**

### **7.4.1 Storm Water Toxicity**

Ten storm water outfall samples were tested, not necessarily for all species, for toxicity at Naval Amphibious Base Coronado. Figure 41 shows the 100% storm water effluent toxicity data. A statistical summary of the results are provided in Table 27, with all data provided in Appendices B and C.

Overall, topsmelt were less sensitive than mysids, with average survival rates of 66 and 46% in the undiluted first-flush effluent, respectively. Although the average survival in composite samples was higher than in first-flush samples, a review of the paired results (Figure 41) shows no clear difference. For topsmelt, 43% of the first-flush samples would have failed the 90% survival requirement, while 33% of composites would have failed. Mysids failed the requirement in 80% of the first-flush samples, but passed in the single composite sample tested.

For Naval Amphibious Base Coronado samples, 56% of NOECs (combined for topsmelt and mysids) were 100% storm water effluent. Two of the 16 dilution series results had a NOEC of 12.5% and one of the composite samples had a NOEC of 50%. These data suggest that a receiving water mixture with less than a 12% storm water fraction would result in no observable toxicity.

Mussel larvae were much more sensitive than the topsmelt or mysids in outfall samples, with no observations of any normal larvae in the highest concentration of storm water effluent tested for any sample. Because this bioassay is not included in the permit, the 90% requirement does not apply. Topsmelt and mysids in first-flush samples would have failed the 70% survival requirement 33 and 60% of the time, respectively. All but one of the composite samples would have passed the 70% requirement for both species. Mussel larvae were much more sensitive than the permitted species in outfall samples, with no observations of any normal larvae in the highest concentration of storm water effluent tested for any sample. Though the study was not designed to compare outfalls, a qualitative review of paired data showed that toxicity in samples from the two outfalls was highly variable, with no clear pattern of relative magnitude of effects in one outfall versus the other. Three mussel-test NOECs were 12.4% effluent. Another two tests had NOECs of <12.4% and one had a NOEC of <6.25%. These data suggest that with the exception of two samples, a receiving water mixture with less than a 6% storm water fraction would result in no observable toxicity.

As described earlier, method variability in toxicity testing is an important consideration for evaluating results. Table 28 shows the PMSD for Naval Amphibious Base Coronado industrial storm water dilution series toxicity tests, including baseline TIE results. PMSD values ranged from 9 to 18% for topsmelt and averaged 14%. PMSD for mysid tests ranged from 6 to 29% and averaged 16%. The mussel embryo tests ranged from 3 to 7% and averaged 4%. The mysid results all fell well within EPA guidelines for test acceptability (EPA, 2000). The topsmelt and mussel data also met the PMSD test acceptability criteria for comparable, endpoints (inland silverside survival and mussel survival and normal development). These differences are described later in the discussion section.

### **7.4.2 Receiving Water Toxicity**

Twelve receiving water samples were tested, not necessarily for all species, for toxicity at Naval Amphibious Base Coronado. No toxicity was observed for topsmelt or mysids in bay water samples. Survival was very high for topsmelt and mysids exposed to bay waters, with a combined average survival of 98%. All topsmelt and mysid bay water data were statistically indistinguishable from lab controls ( $p < 0.05$ ). Mussel larval development in receiving water samples averaged 87% overall and, with one exception, was also not statistically different from controls. The exception was for a sample collected outside outfall 18 during a first-flush of the year event (SDB4) after a record 6-month antecedent dry period.



Table 27. Statistical summary of toxicity data in Naval Amphibious Base Coronado first-flush (FF) or composite (Comp) undiluted storm water or in receiving water (Bay) samples. Results are expressed as percent survival for topsmelt and mysids and as percent normal embryo-larval development for mussels. “# <90% and % Failing” refers to the number and percentage of samples that did not meet the 90% survival criterion in the permit.

NAB	Topsmelt Survival (%)			Mysid Survival (%)			Mussel Normal Development (%)		
	FF	Comp	Bay	FF	Comp	Bay	FF	Comp	Bay
<i>n</i>	7	3	12	5	1	8	5	1	12
Min	0	60	90	0	90	97	0	0	4
Mean	66	83	98	46	90	99	0	0	87
Max	100	100	100	90	90	100	0	0	98
RSD	69	25	3	93	NA	2	0	NA	30
# <90%	3	1	NA	4	0	NA	NA	NA	NA
% FAILING	43%	33%	NA	80%	0%	NA	NA	NA	NA

NA Not applicable

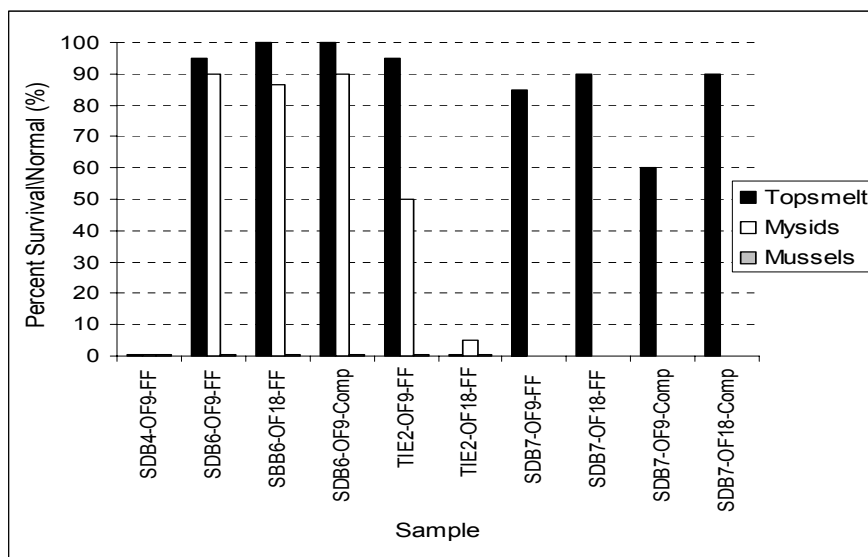


Figure 41. Topsmelt and mysid survival and normal mussel embryo-larval development in 100% storm water effluent collected from first-flush (FF) and composite (Comp) samples at Naval Amphibious Base Coronado.

Table 28. Percent Minimum Significant Difference (PMSD) for Naval Amphibious Base Coronado toxicity tests.

PMSD	Topsmelt	Mysids	Mussels
<i>n</i>	7	6	6
Min (%)	9	6	3
Mean (%)	14	16	4
Max (%)	18	29	7

### 7.4.3 TIE

A Toxicity Identification Evaluation was performed on first-flush samples collected from each of the two outfalls at Naval Amphibious Base Coronado during the storm event on 19 March 2005. First-flush samples were collected during a very minimal rainfall event in which only 0.07 inches of rainfall fell. The TIE was performed by Nautilus Environmental LLC, San Diego. Appendix F includes the report for this effort. The TIE consisted of baseline acute toxicity tests with topsmelt, mysids, and mussel embryos.

Toxicity screening results showed that there was sufficient toxicity (>20% relative to control) to perform a TIE with mysids and mussel embryos at outfall 9 and with all three test species at outfall 18. Figure 42 and Figure 43 show the manipulations performed for each outfall sample.

The cause of toxicity to mysids and to mussel embryo-larval development at outfall 9 was copper and zinc. While copper was the primary toxicant to the mussels, it was not clear which toxicant was the primary cause of toxicity to mysids. The cause of toxicity to mussel embryos at outfall 18 was copper and zinc in combination with surfactants. Surfactants were also the primary cause of toxicity to mysids and possibly the cause of toxicity to topsmelt in this sample. The surfactants were not uniquely identified but were attributed to a class of compounds called methylene blue activated substances (MBAS). Though the toxicity data for these compounds is limited, Nautilus Environmental LLC has previously identified these compounds as having toxicity at concentrations above 1 mg/L. The sample collected from outfall 18 had a MBAS concentration of 1.9 mg/L.

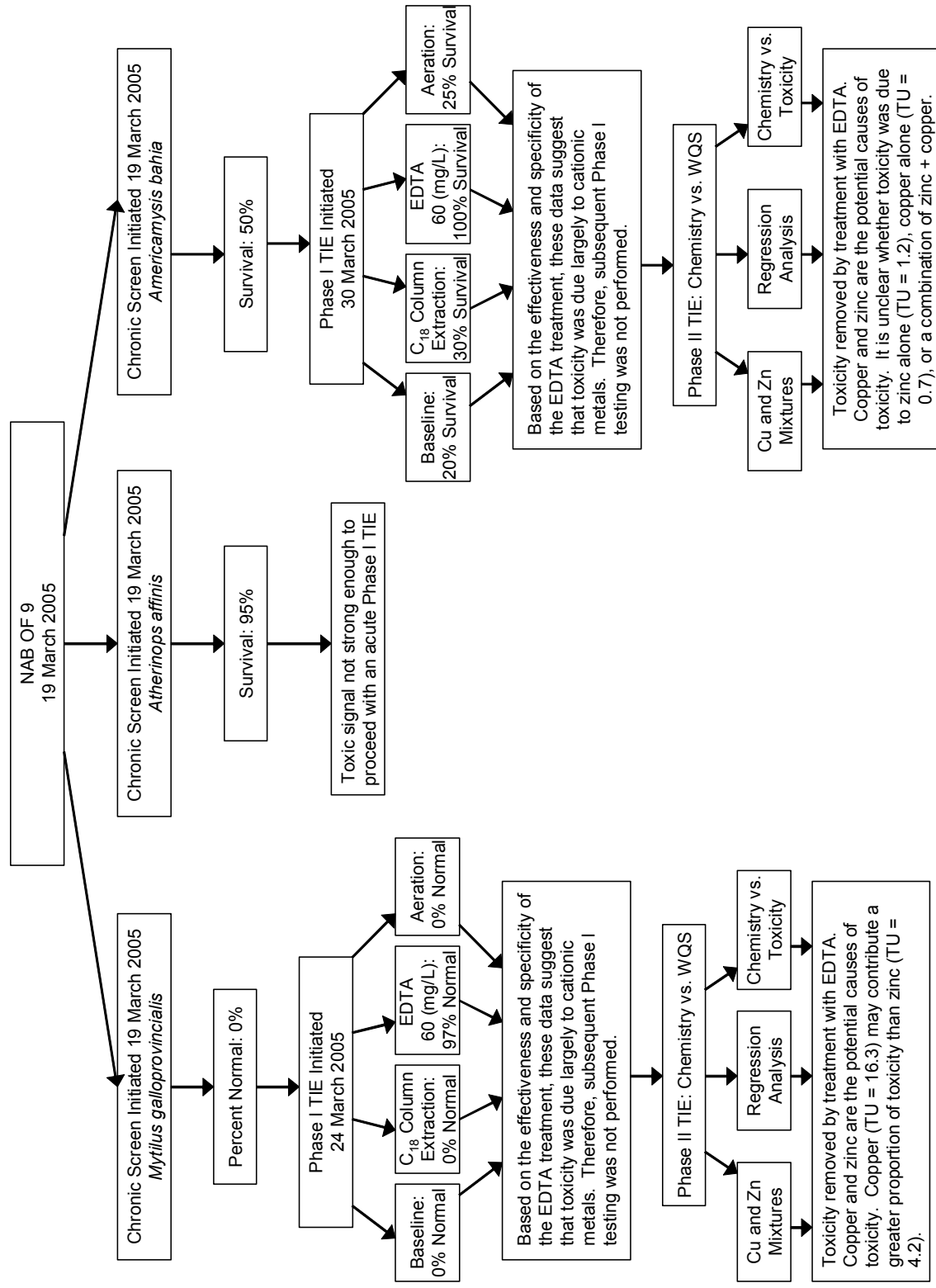


Figure 42. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Amphibious Base San Diego outfall 9.

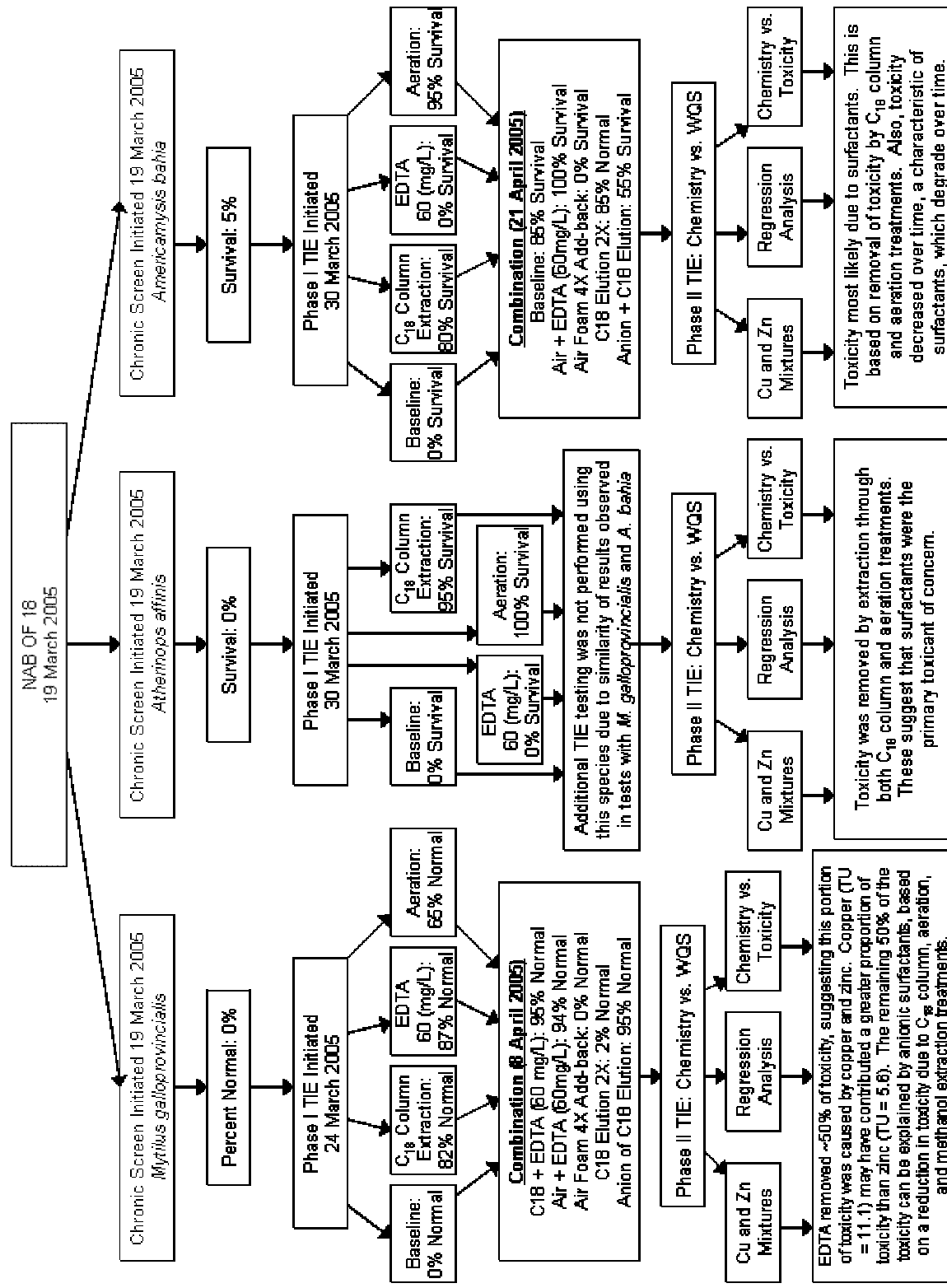


Figure 43. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Amphibious Base outfall 18.

#### 7.4.4 Chemistry

**TSS/DOC.** A total of 18 and 16 samples were analyzed for TSS and DOC, respectively, at Naval Amphibious Base Coronado. No after-storm samples were collected or analyzed. Table 29 shows a statistical summary of the TSS and DOC data. Appendix D shows all individual sample data. TSS in storm water ranged from ~6 to over 230 mg/L and averaged about 60 mg/L. On average, composite samples had higher TSS concentrations than first-flush samples, which is opposite to observations at Naval Station San Diego and Naval Submarine Base San Diego. However, the difference was not statistically significant at the 95% confidence level. First-flush samples showed similar variability to the composite samples as described by the relative standard deviation (RSD). The maximum TSS level was measured in a composite sample collected at outfall 18 during the SDB7 storm in April 2005. This level was unlike other outfall measurements that showed maximum TSS in first-flush samples collected during the first-flush of the year storm event (SDB4).

Bay sample TSS concentrations ranged from ~2 to 15 mg/L. On average TSS concentrations were about a factor of two higher than off Naval Station San Diego across the bay. Water depths along portions of the base are quite shallow and wind driven resuspension was observed during all storm event sampling. No after-storm bay samples were collected at Naval Amphibious Base Coronado. Average bay TSS values were about a factor of 10 less than the average in outfall samples. The maximum bay water TSS level was measured in the sample collected during the SDB7 storm event. TSS levels increased about a factor of two in samples collected during storms compared to samples collected before storms. This difference was statistically significant at the 95% confidence level.

DOC levels in outfall samples were about the same as found at the other bases, ~10 mg/L. Like the other bases, composite samples were almost always higher than their corresponding first-flush sample suggesting a lag time in the discharge of organic compounds during storm events. DOC concentrations in bay water samples were about a factor of 5 lower than found in outfall samples. These levels were about double the concentrations measured off Naval Station San Diego and Submarine Base San Diego.

Table 29. Statistical summary of TSS and DOC data at Naval Amphibious Base Coronado. Sample types include first-flush (FF) and composite (Comp) outfall samples as well as receiving water (Bay) samples collected before and during storm events.

TSS (mg/L)	Outfalls		Bay	
	FF	Comp	Before	During
n	5	4	4	5
Min	6	10.0	2.2	6.1
Mean	40	81	4	11
Max	130	234	6	15
RSD	133%	128%	106%	33%
DOC (mg/L)				
n	4	4	4	4
Min	7.8	5.4	1.6	1.7
Mean	9.1	11.7	1.7	2
Max	11.4	15.2	1.8	2
RSD	18%	39%	7%	19%

**Metals.** A total of 18 samples were analyzed for total and dissolved metals at Naval Amphibious Base Coronado, which included nine storm water and nine receiving water samples. All first-flush and bay water samples were analyzed for only copper and zinc. Table 30 shows a statistical summary of the outfall metals data. Appendix D shows all individual sample data. The data are summarized by first-flush and composite samples and by total and dissolved metals. The data show considerable variability of the individual metals spanning a range of ~25% to 190% for the dissolved and total metal. Copper and zinc variability were considerably lower in composite samples than in first-flush samples as was seen at Naval Station San Diego.

Half of the total copper and all total zinc concentrations in first-flush storm water samples were above their respective performance goals in the NPDES permit of 63.6 and 117 µg/L. Only dissolved copper and zinc were elevated in outfall samples above their respective acute saltwater water quality standards (WQS) of 4.8 and 90 µg/L, respectively, with the remaining dissolved metals all well below WQS (EPA, 2000a). The comparison made for mercury was to the human health WQS of 0.05 µg/L as discussed previously. Dissolved copper and zinc exceeded their acute WQS by a maximum factor of 35 and 79, respectively, in first-flush samples. The comparable ratio in composite samples was reduced to eight for both metals.

Maximum total copper and zinc concentrations measured in the outfalls were 668 and 8051 µg/L, respectively. These levels were measured in the first-flush of the year sample (SDB4) at outfall 9 (Figure 26) and represent the highest levels measured during the study. These maxima were a factor of four greater than the average and were in part, the reason for the relatively high variability as measured by the RSD. Dissolved copper and zinc concentrations were usually the similar or higher in composite samples than in first-flush samples (Figure 44).

Copper and zinc ranged from about 43 to 72% and averaged ~60% as the dissolved phase metal in first-flush and composite samples. First-flush samples showed a higher amount of the dissolved phase metal than observed in composite samples, indicating a potential lag of particles in the storm discharge.

Table 31 shows a statistical summary of the bay seawater copper and zinc data. All individual sample data. As was observed for storm water, receiving water concentrations of copper (17 µg/L) and zinc (176 µg/L) were highest in samples collected during the first-flush of the year storm event (SDB4). These concentrations represent about a factor of five for copper and eight for zinc above typical levels. The concentrations of copper and zinc in this sample also exceeded chronic WQS by factors of five and two, respectively. Additionally, copper exceeded its chronic WQS of 3.1 µg/L in two other samples collected during storm events. Dissolved zinc concentrations measured during storm events were higher than those measured in pre-storm samples. The predominant phase of copper and zinc in seawater was as the dissolved metal, averaging about 61% for copper and 75% for zinc. Thus, these metals in bay waters tended toward the dissolved phase of the metal compared to the outfall discharge.

Dissolved copper exceeded its chronic WQS in three seawater samples collected during storm events. Dissolved zinc exceeded its WQS in a single sample collected during the SDB4 storm event. This sample was one of only two receiving water samples in the study to exhibit mussel larvae toxicity. The maximum elevation above a WQS was about a factor of six for copper and a factor of two for zinc. The average bay sample was ~65% as the dissolved metal.

Table 30. Statistical summary of first-flush (FF) and composite (Comp) storm water metals data at Naval Amphibious Base Coronado. Values for the total and dissolved metal are shown. NPDES performance goals and acute WQS are also shown. Grayed-out cells are values equal to the MDL.

OF FF Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n		5			5									
min		33.3			137									
mean		170			1925									
max		668			8051									
RSD		163%			178%									
NPDES Performance Goal		63.6			117.0									
OF FF Dissolved (µg/L)														
n		5			5									
min		17.6			134									
mean		59.4			1617									
max		172			7134									
RSD		107%			191%									
OF COMP Total (µg/L)														
n	4	4	4	4	4	4	4	4	4	4	4	4	4	4
min	0.040	44.4	3.21	0.0071	214	192	2.28	0.55	2.11	832	26.1	2.45	1.47	0.50
mean	0.074	80.0	11.3	0.0121	830	1625	8.28	1.46	5.48	3406	113	7.10	17.4	0.67
max	0.125	108	23.0	0.0201	1832	4717	23.4	2.91	11.1	6550	197	11.60	52.4	0.90
RSD	56%	41%	79%	49%	85%	129%	123%	73%	77%	88%	69%	62%	139%	27%
OF COMP Dissolved (µg/L)														
n	4	4	4	4	4	4	4	4	4	4	4	4	4	4
min	0.040	26.2	0.13	0.0019	101	13.2	1.20	0.32	0.57	14.3	8.6	1.27	1.47	0.50
mean	0.040	33.8	0.35	0.0034	329	22.1	6.99	0.57	1.02	55.1	49.6	4.41	16.5	0.50
max	0.040	40.0	0.85	0.0046	709	46.4	20.2	1.04	1.60	145	95.9	8.68	48.8	0.50
RSD	0%	19%	96%	34%	84%	73%	128%	56%	45%	110%	75%	70%	136%	0%
WQS Acute (µg/L)	1.9	4.8	210		90		69	42	1100			74	290	

Table 31. Statistical summary of total and dissolved bay seawater metals data at Naval Amphibious Base Coronado. Chronic WQS are also shown.

Bay Total (µg/L)	Cu	Zn
n	9	9
min	3.05	8.51
mean	7.65	55.4
max	22.9	256
RSD	89%	143%
Bay Dissolved (µg/L)		
n	9	9
min	2.01	6.19
mean	4.79	38.3
max	17.4	176
RSD	106%	141%
WQS Chronic (µg/L)	3.1	81

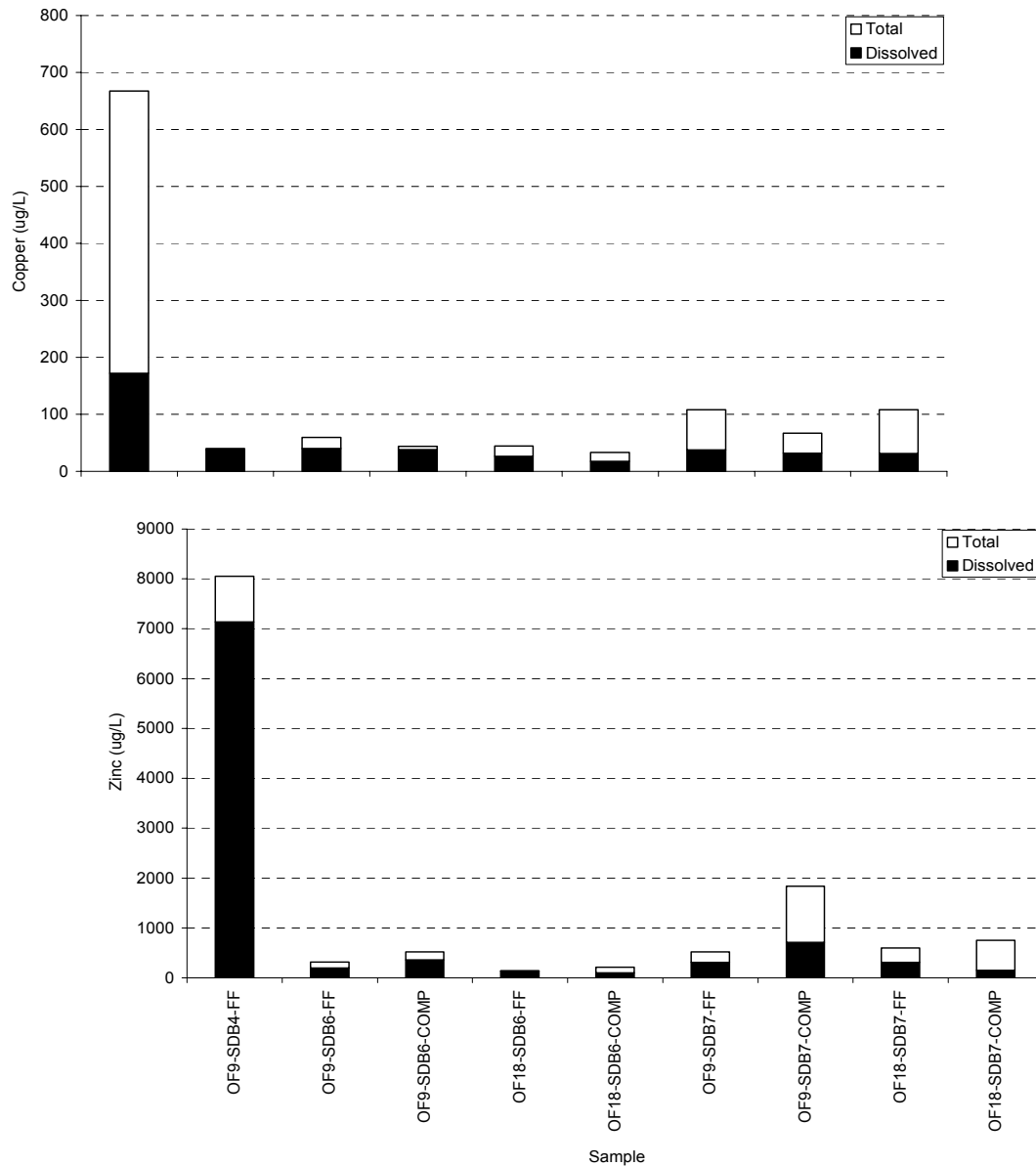


Figure 44. Total and dissolved copper and zinc concentrations measured in Naval Amphibious Base Coronado first-flush (FF) and composite (Comp) storm water outfall samples. Values for the total and the dissolved phase of the metal are shown.



**PAH.** A total of 16 samples were analyzed for PAH at Naval Amphibious Base Coronado. This total includes eight storm water outfall and eight receiving water samples. Table 32 shows a statistical summary of the storm water and seawater priority pollutant PAH data. Appendix D shows all individual sample data. The sum of priority pollutant PAH concentrations in storm water samples ranged from ~30 to 735 ng/L. About 19% of these PAHs were below a MDL, which ranged from 0.4 to 1.5 ng/L, depending on the specific analyte. Analytes not detected were given a value equal to one-half the MDL in the summation. The highest level was found in the composite sample collected from outfall 18 during storm event SDB7. This sample was also elevated in TSS and DOC. PAH levels in first-flush samples were always lower than in corresponding composite samples. The difference was about a factor of two.

Average summed priority pollutant PAH concentrations in receiving water samples relatively low, ranging from 12 to 94 ng/L and averaged 45 ng/L. About 25% of the PAH analytes in bay water samples were below a MDL. While the average receiving water PAH concentration was a factor of five lower than the average composite value, the bay water sample collected outside outfall 18 during the SDB7 storm event was actually higher than its corresponding outfall samples (FF and COMP). This suggests another source of PAH to the bay that was not sampled.

All the storm water samples contained PAH concentrations below the minimum acute thresholds identified in Table 11. All the receiving water samples had PAH at levels below the minimum chronic threshold values in the same table.

Figure 45 shows the average relative composition of the PAH in first-flush and composite samples. Figure 46 shows a comparable plot for bay water samples. These distributions were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type: first-flush, composite, or bay sample. The PAH distribution in first-flush and composite samples were very similar. Both sample types had compositions that were consistent with a predominantly low-level petrogenic and minor pyrogenic source. Receiving water PAH compositions were very similar in samples collected before and during storm events. They had a distinctly different composition than that of storm water, having a distribution more characteristic of a highly weathered low concentration pyrogenic source.

Table 32. Statistical summary of priority pollutant PAH data at Naval Amphibious Base Coronado. The summation used one-half the MDL for analytes not detected in the sample. Sample types include first-flush (FF) and composite (Comp) storm water outfall samples as well as receiving water (Bay) samples collected before (PRE) and during (DUR) storm events.

Sum Priority Pollutant PAH (ng/L)	Outfalls		Bay	
	FF	COMP	PRE	DUR
n	4	4	4	4
Min	31	53	12	43
Average	124	327	22	68
Max	232	735	32	94
RSD	80%	99%	45%	32%

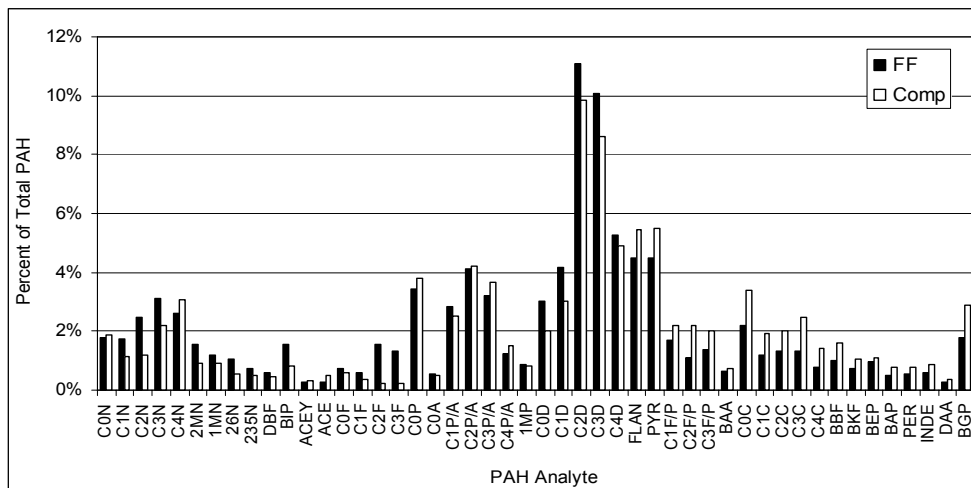


Figure 45. Average PAH composition in first-flush (FF) and composite (Comp) samples at Naval Amphibious Base Coronado. The averages were calculated by dividing each analyte by the total amount of PAH in a sample and then averaging by sample type (first-flush or composite). Table 6 shows analyte IDs.

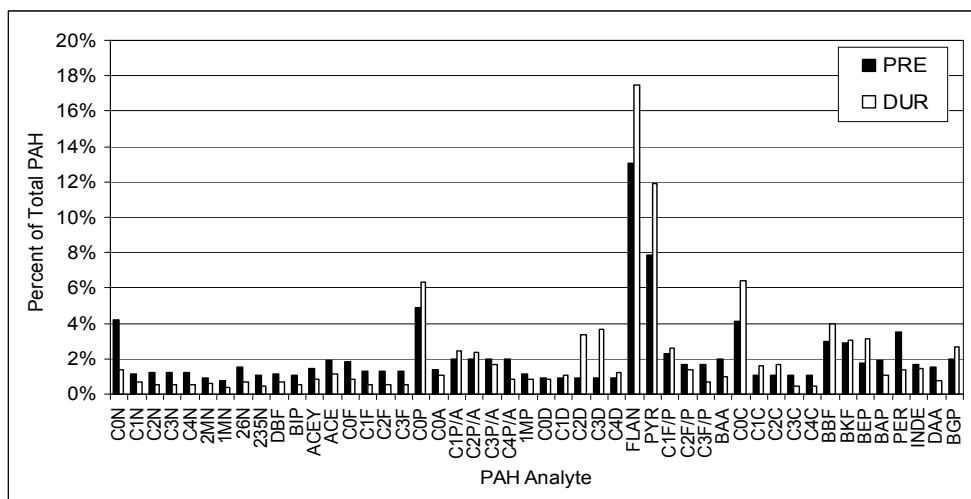


Figure 46. Average PAH composition in bay waters before (PRE) and during (DUR) storm events at Naval Amphibious Base Coronado. Table 6 shows analyte IDs.

**PCB.** Ten samples were analyzed for PCB at Naval Amphibious Base Coronado. The total includes six storm water outfall and four receiving water samples. Table 33 shows a statistical summary of PCB data. Appendix D shows all individual sample data. PCB concentrations in all but one storm water and bay water sample were non-detect, with the MDL ranging from 0.1 to 0.7 ng/L, depending on the congener. The composite sample collected at outfall 18 during storm SDB7 had a summed PCB concentration of 37 ng/L. This sample was also elevated in TSS, DOC, and PAH. PCB levels measured in storm water all fell well below the minimum acute toxicity threshold (EPA, 1987). PCB levels measured in receiving waters were all below chronic WQSC (EPA, 2000b).

Table 33. Statistical summary of PCB data at Naval Amphibious Base Coronado. “Sum PCB” is the summation of all congeners measured in the sample. The summation used one-half the MDL for congeners not detected in the sample. Sample types include first-flush (FF), composite (COMP) storm water outfall samples and bay samples collected before (PRE) and during (DUR) a storm event. Toxicity threshold benchmarks are also shown.

Sum PCB (ng/L)	Outfalls		Bay	
	FF	COMP	PRE	DUR
n	2	4	2	2
min	2.8	2.8	2.8	2.8
mean	2.8	13	2.8	2.8
max	2.8	37	2.8	2.8
RSD		126%		
Threshold	Acute 10,000		Chronic 30	

**Pesticides.** Ten samples were analyzed for chlorinated pesticides at Naval Amphibious Base Coronado, including six storm water outfall and four receiving water samples. Chlorinated pesticide concentrations in storm water samples were nearly all (93%) non-detect, with the MDL ranging from 0.2 to 1.6 ng/L, depending on the analyte (Table 34). All receiving water samples were non-detect. Appendix D shows all individual sample data. All storm water pesticide concentrations fell well below acute WQS, while all pesticide levels measured in receiving waters were below chronic WQS shown in Table 10.

Table 34. Chlorinated pesticide data collected at Naval Amphibious Base Coronado. Grayed-out cells contain values that were *above* the MDL, with all other data at the MDL. Sample types include first-flush (FF) and composite (Comp) storm water outfall samples. Acute WQS are also shown. The WQS shown for g-chlordane is actually for the sum of chlordane isomers.

Analyte (ng/L)	NAB- SDB6- OF9- FF	NAB- SDB6- OF18- FF	NAB- SDB6- OF9- COMP	NAB- SDB6- OF18- COMP	NAB- SDB7- OF9- COMP	NAB- SDB7- OF18- COMP	Acute WQS
2,4'-DDD	0.62	0.63	0.63	1.63	0.61	0.61	
2,4'-DDE	0.41	0.53	0.76	1.37	0.25	0.52	
2,4'-DDT	0.37	0.37	0.37	0.97	0.37	0.37	
4,4'-DDD	0.73	0.73	0.73	1.9	0.72	0.72	
4,4'-DDE	0.52	0.53	0.53	1.37	0.52	0.9	
4,4'-DDT	0.45	0.45	0.45	1.18	1.39	0.44	130
aldrin	0.3	0.3	0.3	0.79	1.65	0.3	1300
a-chlordane	0.29	0.29	0.29	0.76	0.34	0.28	90*
g-chlordane	0.31	0.31	0.31	0.81	0.3	0.3	
a-BHC	0.26	0.26	0.26	0.69	0.26	0.26	
b-BHC	0.36	0.36	0.36	0.95	0.36	0.36	
d-BHC	0.3	0.3	0.3	0.78	0.99	0.67	
Lindane	0.38	0.38	0.38	0.99	0.37	0.37	
cis-nonachlor	0.49	0.5	0.5	1.29	0.49	0.49	
trans-nonachlor	0.31	0.31	0.31	0.81	1.14	0.31	
Chlorpyrifos	0.39	0.39	0.39	1.02	0.39	0.39	11
oxychlordane	0.3	0.3	0.3	0.78	0.3	0.3	
dieldrin	0.58	0.59	0.59	1.53	0.58	0.58	710
endosulfan I	0.21	0.21	0.21	0.55	0.21	0.21	34
endosulfan II	0.53	0.53	0.53	1.38	0.52	0.52	34
endosulfan sulfate	0.5	0.5	0.5	1.3	0.49	0.49	
endrin	0.57	0.58	0.58	1.5	0.57	0.57	37
endrin aldehyde	0.65	0.65	0.65	1.7	0.64	0.64	
endrin ketone	0.68	0.68	0.68	1.78	0.67	0.67	
heptachlor	0.45	5.65	4.57	1.17	0.44	0.44	53
heptachlor epoxide	1.2	1.21	1.21	3.15	1.19	1.19	53
Hexachlorobenzene	0.63	0.64	0.64	1.65	0.62	0.62	
methoxychlor	0.75	0.75	0.75	1.76	0.74	5.28	
Mirex	0.47	0.48	0.48	1.24	0.47	0.47	

#### 7.4.5 Plume Mapping

Plume mapping was performed at Naval Amphibious Base Coronado on three occasions, during the SDB4, SDB6, and SDB7 storm events. Three surveys were conducted after the SDB4 storm event, which began with 0.1-inch rainfall on 17 October 2004. First-flush samples were collected at that time. The first plume mapping survey did not begin until the 18 October, when it became clear that the bulk of the storm was on its way. The “Pre”-SDB4 mapping survey was conducted as it began to rain on 18 October. The “During” surveys were conducted during the next 2 days, when up to 1.7 inches of rain fell over the time period. No “After” surveys were conducted because of logistical constraints.

Figure 47 shows spatial maps of surface salinity from surveys made before and during the SDB4 storm event. Figure 4 shows the timetable of the surveys and rainfall. Appendix G shows Spatial plots for all parameters measured during these surveys. The pre-storm plot captured a condition when some light drizzle had fallen before arrival. The “during” plot was produced from data collected on the third day of the storm after 1.7 inches of rain had fallen during heavy squall conditions. Because of the near continuous rainfall over several tide cycles, a large freshwater signature covered most of the inner portion of the bay during this survey, evidenced by the relatively lower salinity seen at the top right of the plot. The salinity distribution during the storm shows freshwater along the northern shore of the base, with a smaller signal on the southern shore. The minimum salinity was observed in the northwest corner of the base, just to the east of where the discharge from outfall 18 enters the bay, and where a number of relatively large drainages also discharge. The maximum reduction in salinity at this location (from 33.2 to 28.5) by freshwater input was 14%.

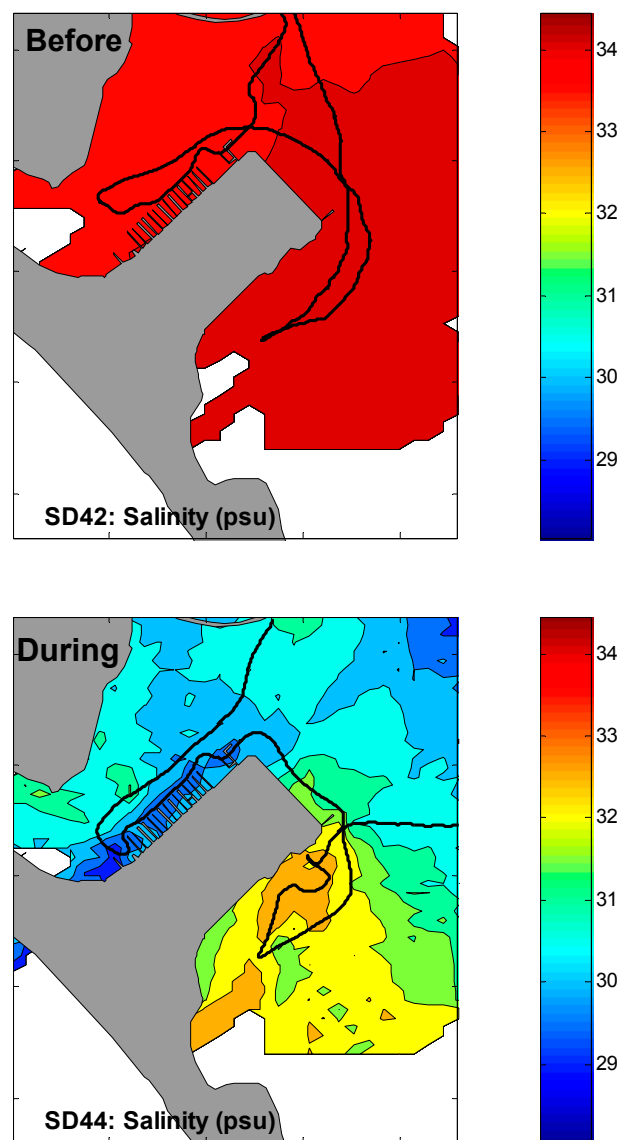


Figure 47. Surface salinity mapping before and during storm event (SDB4) at Naval Amphibious Base Coronado. There was no mapping performed after the storm.

## **7.5 NAVAL AIR STATION NORTH ISLAND**

### **7.5.1 Storm Water Toxicity**

Nine storm water outfall samples were tested, not necessarily for all species, for toxicity at Naval Air Station North Island. Figure 48 shows the 100% storm water effluent toxicity data. Table 35 provides a statistical summary of the results. Appendices B and C provide all toxicity data.

Overall, topsmelt appeared to respond similarly to mysids at these sites (Figure 48). First-flush samples ranged between 57 and 100% survival and averaged 83% for the two species. No mortality was observed in the composite samples. For topsmelt, 43% of the first-flush samples would have failed the 90% survival requirement, while no composites would have failed. Topsmelt and mysids in first-flush samples would have failed the 70% survival requirement 14% and 10% of the time, respectively. None of the composite samples would have failed the 70% requirement for both species.

For Naval Air Station North Island samples, 80% of NOECs (combined for topsmelt and mysids) were 100% storm water effluent. One of the 15 dilution series results run on first-flush samples had a NOEC of 25%. All the composite samples had a NOEC of 100%. These data suggest that a receiving water mixture with less than a 25% storm water fraction would result in no observable toxicity.

Mussel larval development was more sensitive and more variable than the permitted species in first-flush outfall samples that ranged from 0% to 89% normal development. The single composite sample tested with mussels did not significantly disrupt larval development. This sample also showed no toxicity to topsmelt or mysids. Though the study was not designed to compare outfalls, a qualitative review of paired data showed that toxicity in samples from the two outfalls was highly variable, with no clear pattern of relative magnitude of effects in one outfall versus the other. NOECs for mussels ranged from 6.25 to 69% (the maximum effluent concentration tested). These data suggest that a receiving water mixture with less than a 6% storm water fraction would result in no observable toxicity.

As described earlier, method variability in toxicity testing is an important consideration for evaluating results. Table 36 shows the PMSD for Naval Air Station North Island industrial storm water dilution series toxicity tests, including baseline TIE results. PMSD values ranged from 8 to 19% for topsmelt and averaged 14%. PMSD for mysid tests ranged from 5 to 15% and averaged 10%. The mussel embryo-larval development tests ranged from 2 to 5% and averaged 3%. The mysid results all fell well within EPA guidelines for test acceptability (EPA, 2000a). The topsmelt and mussel data also met the PMSD test acceptability criteria for comparable endpoints (inland silverside survival and mussel survival and normal development). These differences are described later in the discussion section.

### **7.5.2 Receiving Water Toxicity**

Thirteen receiving water samples were tested, not necessarily for all species, for toxicity at Naval Air Station North Island. Survival was very high for topsmelt and mysids exposed to bay waters, with a combined average survival of 98%. All topsmelt and mysid bay water data were statistically indistinguishable from lab controls ( $p < 0.05$ ). Mussel larval development was also very high, averaging 95%, with no samples being statistically lower than the controls.

Table 35. Statistical summary of toxicity data in Naval Air Station North Island first-flush (FF) or composite (Comp) undiluted storm water or in receiving water (Bay) samples. Results are expressed as percent survival for topsmelt and mysids and as percent normal embryo-larval development for mussels. “# <90% and % Failing” refers to the number and percentage of samples that did not meet the 90% survival criterion in the permit.

NI	Topsmelt Survival (%)			Mysid Survival (%)			Mussel Normal Development (%)		
	FF	Comp	Bay	FF	Comp	Bay	FF	Comp	Bay
<i>n</i>	7	2	12	5	1	8	5	1	13
Min	65	100	90	57	100	93	0	96	90
Mean	86	100	98	79	100	99	18	96	95
Max	100	100	100	97	100	100	89	96	98
RSD	14	NA	3	21	NA	3	224	NA	2
# <90%	3	0	NA	3	0	NA	NA	NA	NA
% FAILING	43%	0%	NA	60%	0%	NA	NA	NA	NA

NA Not applicable

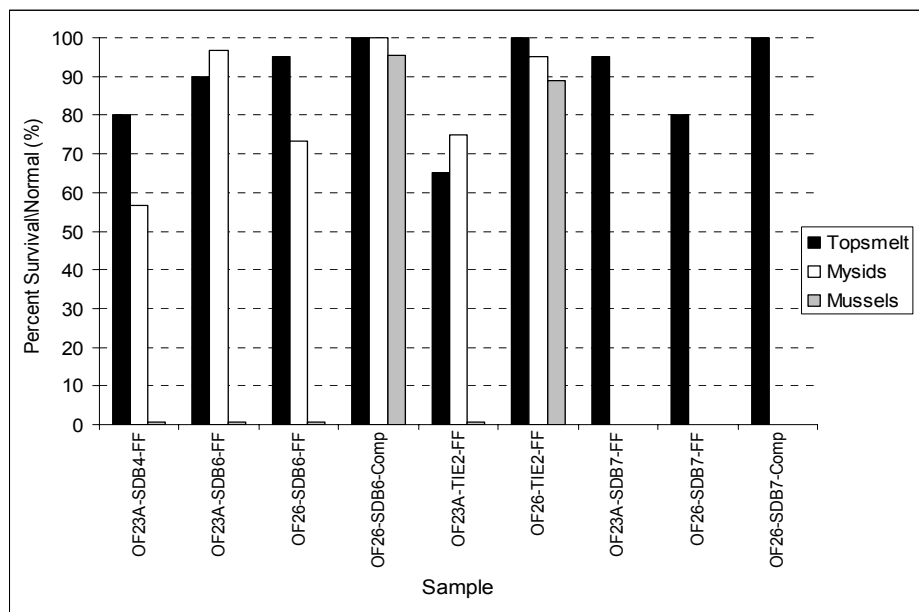


Figure 48. Topsmelt and mysid survival and normal mussel embryo-larval development in 100% storm water effluent collected from first-flush (FF) and composite (Comp) samples at Naval Air Station North Island.

Table 36. Percent Minimum Significant Difference (PMSD) for Naval Air Station North Island toxicity tests.

PMSD	Topsmelt	Mysids	Mussels
n	6	6	6
Min (%)	8	5	2
Mean (%)	14	10	3
Max (%)	19	15	5

### 7.5.3 TIE

A Toxicity Identification Evaluation was performed on first-flush samples collected from each of the two outfalls at Naval Air Station North Island during the storm event on 19 March 2005. First-flush samples were collected during a very minimal rainfall event in which only 0.07 inches of rainfall fell. The TIE was performed by Nautilus Environmental LLC, San Diego. The report for this effort is included as Appendix F. Figure 49 and Figure 50 show the manipulations performed for each outfall sample. Toxicity screening results showed that there was insufficient toxicity (>20% relative to control) to perform a TIE at outfall 26 with any species. A review of the water quality data made upon receipt of the samples indicated very high conductivity (21 mmhos/cm) and hardness (>1000) that likely played a role in minimizing toxicity. These values suggest that the samples may have been partially mixed with residual seawater in the catchment, though the sampling personnel did not observe this when sampling. Toxicity was sufficient to perform a TIE at outfall 23A with all three species. Figure 49 and Figure 50 also show the results of the TIE. The cause of toxicity to mysids and topsmelt at outfall 23A was surfactants. These were not uniquely identified, but were attributed to a class of MBAS compounds. Though the toxicity data for these compounds is limited, Nautilus Environmental LLC has previously identified these compounds at the toxicant agent at concentrations above the 1 mg/L found in this sample. The toxicant agents to mussel embryo development were a combination of copper and zinc (50%) and surfactants (50%). The TIE established that copper and zinc were additive in their toxicity.



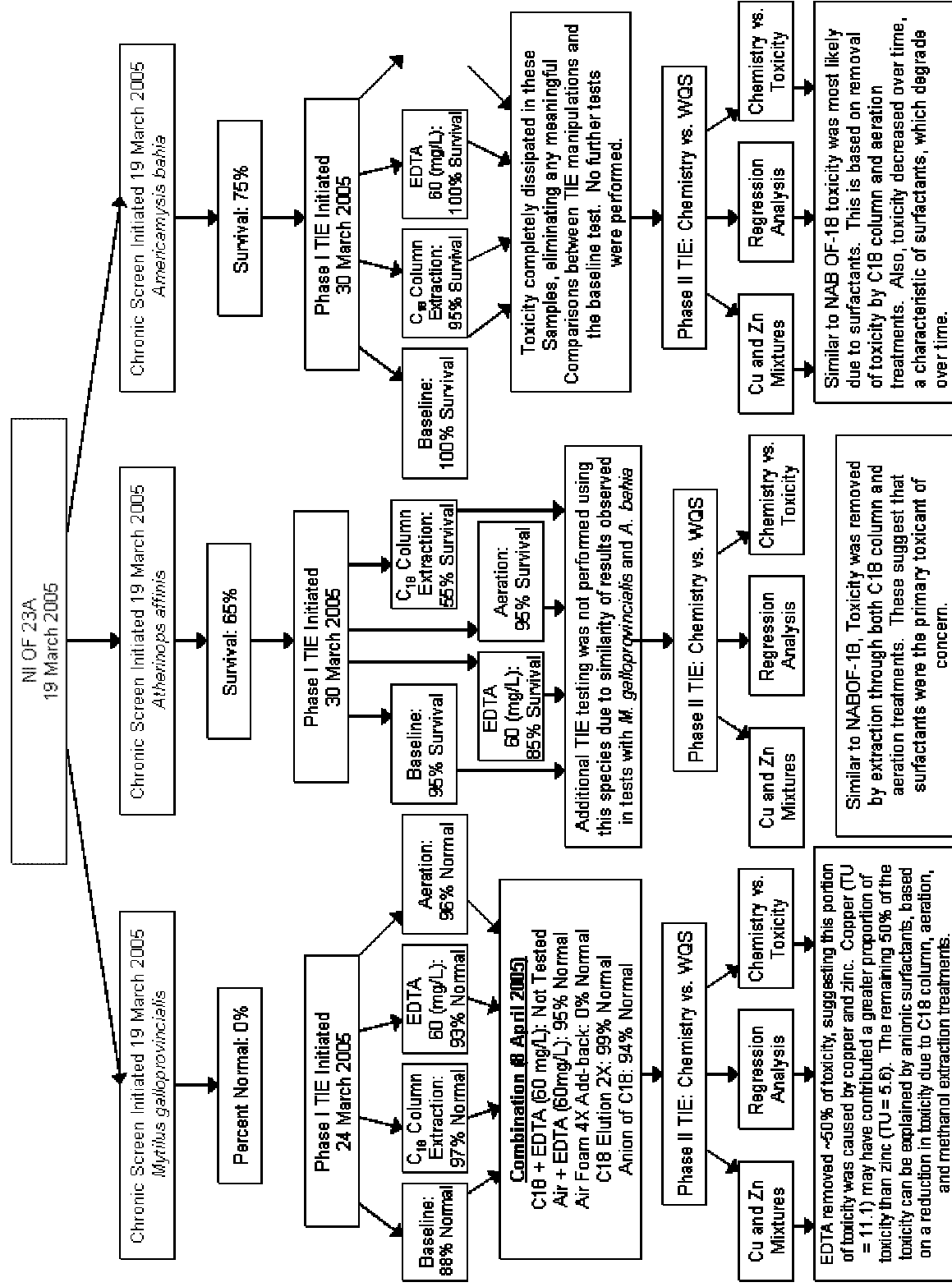


Figure 49. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Air Station North Island outfall 23A.

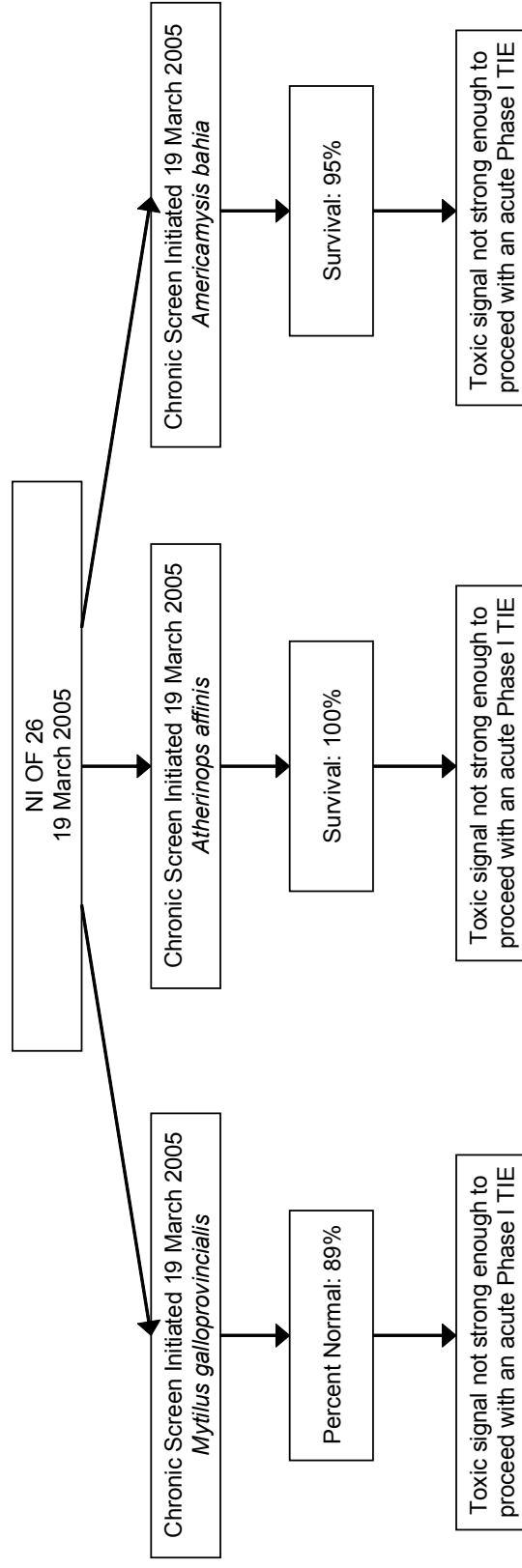


Figure 50. Flow diagram of TIE manipulations and outcome performed on first-flush sample collected from Naval Air Station North Island outfall 26.

### 7.5.4 Chemistry

**TSS/DOC.** A total of 16 and 14 samples were analyzed for TSS and DOC, respectively, at Naval Air Station North Island. Table 37 shows a statistical summary of the TSS and DOC data. Appendix D shows all individual sample data. TSS in storm water ranged from ~10 to over 200 mg/L and averaged about 90 mg/L. First-flush samples were slightly lower in TSS concentrations than corresponding composite samples, which is reflected in the averages. The maximum TSS level was measured in the first-flush sample collected at outfall 23A during the (SDB4) first-flush of the year storm event in October 2004. The second highest level of 162 mg/L was measured in the composite sample collected from outfall 26 during the SDB7 storm event in April 2005. Bay samples were an order of magnitude or more lower in TSS than the outfall samples, and ranged from ~3 to 13 mg/L. The average value for bay samples collected before the storm increased by 40% during storms, though this increase was driven primarily by one sample pair and was not statistically significant (95%).

DOC in first-flush samples was nearly a factor of 10 higher than in the composite samples. This is opposite of what was observed at the other bases. The highest level was measured in the composite sample at outfall 26 during the SDB7 storm event in April 2005. Receiving water samples had about the same DOC levels as the composite samples at roughly 3 mg/L. Bay water samples collected during storms averaged about 50% higher than the pre-storm samples though the increase was not statistically significant.

Table 37. Statistical summary of TSS and DOC data at Naval Air Station North Island. Sample types include first-flush (FF) and composite (Comp) storm water outfall samples as well as receiving water (Bay) samples collected before and during storm events.

TSS (mg/L)	Outfalls		Bay	
	FF	Comp	Before	During
n	5	2	4	5
Min	9.1	22	2.9	4.2
Mean	87	92	4.1	7.4
Max	201	162	5.5	12.7
RSD	97%	NA	29%	50%
DOC (mg/L)				
	FF	Comp	Before	During
n	4	2	4	4
Min	3.8	0.9	1.7	1.9
Mean	21	3.4	2.0	3.1
Max	49	6.0	2.4	4.3

**Metals.** Fifteen samples were analyzed for total and dissolved metals at Naval Air Station North Island, which included six storm water outfall and nine receiving water samples. Three of the outfall samples and all nine bay samples were analyzed for only copper and zinc. Table 38 shows a statistical summary of the outfall metals data. Appendix D shows all individual sample data. The data are summarized by first-flush and composite samples and by total and dissolved metals.

Nearly half of the total copper (40%) and all total zinc concentrations in first-flush storm water samples were above their respective performance goals in the NPDES permit of 63.6 and 117 µg/L. Only dissolved copper and zinc were elevated in outfall samples above their acute saltwater WQS, with the remaining dissolved metals all well below WQS (EPA, 2000b). The comparison made for mercury was to the human health WQS of 0.05 µg/L, as discussed previously. Dissolved copper and

zinc exceeded their acute WQS by a maximum factor of 15 and 9, respectively, in first-flush samples. The comparable ratio in composite samples was reduced to six for copper and was less than one for zinc (concentrations below WQS).

Maximum copper and zinc concentrations measured in storm water were 172 and 1,125 µg/L, respectively. These levels were measured in the first-flush of the year sample (SDB4) at outfall 23A (Figure 51). The next highest levels were observed in the composite sample collected at outfall 26 during the SDB7 storm event. This sample also had elevated TSS, DOC and metals. The amount of dissolved phase copper and zinc in outfall samples was quite variable, ranging from 9 to 79%. The relative amount of dissolved zinc in first-flush samples was higher than in paired composite samples but there was no consistent pattern for copper. Table 39 shows a summary of the bay seawater copper and zinc data. Appendix D shows all individual sample data. Bay water dissolved copper (5.2 µg/L) and zinc (21 µg/L) were highest in the sample collected outside outfall 23A during the first-flush of the year storm event (SDB4). This sample exceeded chronic WQS for copper, but not for zinc. The two outfall samples collected during the SDB6 storm event also had copper concentrations of 3.3 and 4.1 µg/L that exceeded the 3.1 µg/L WQS. All bay concentrations of zinc were below its chronic saltwater WQS. Similar to other areas of the bay, copper and zinc were found primarily in the dissolved phase (62 and 84%, respectively).

Table 38. Statistical summary of first-flush (FF) and composite (Comp) storm water metals data at Naval Air Station North Island. Values for the total and dissolved metal are shown. NPDES performance goals and acute WQS are also shown. Grayed-out cells are values equal to the MDL.

OF FF Total (µg/L)	Ag	Cu	Pb	Hg	Zn	Al	As	Cd	Cr	Fe	Mn	Ni	Se	Sn
n	2	5	2	2	5	2	2	2	2	2	2	2	2	2
min	0.04	33.4	3.78	0.012	129	290	0.648	0.55	1.47	388	15.1	3.83	1.47	0.5
mean	0.075	81.4	12.8	0.014	529	869	0.934	0.91	5.54	1473	29.7	7.815	1.47	1.48
max	0.109	172	21.9	0.016	1125	1448	1.22	1.26	9.61	2557	44.2	11.8	1.47	2.45
RSD	NA	73%	NA	NA	87%	NA	NA	NA	NA	NA	NA	NA	NA	NA
NPDES Performance Goal		63.6			117.0									
OF FF Dissolved (µg/L)														
n	2	5	2	2	5	2	2	2	2	2	2	2	2	2
min	0.04	3.69	0.201	0.004	33.4	11.1	0.208	0.06	0.295	12.4	0.15	1.41	1.47	0.5
mean	0.04	38.6	0.212	0.005	327	14.1	0.588	0.21	0.658	16.4	1.36	2.43	1.47	0.5
max	0.04	74.3	0.223	0.006	778	17.1	0.968	0.37	1.02	20.4	2.57	3.45	1.47	0.5
RSD	NA	70%	NA	NA	102%	NA	NA	NA	NA	NA	NA	NA	NA	NA
OF COMP Total (µg/L)														
n	2	2	2	2	2	2	2	2	2	2	2	2	2	2
min	0.072	41.0	10.8	0.021	87.3	540	2.62	1.14	3.65	756	51	5.93	1.61	0.74
mean	0.191	65.2	44.2	0.035	317	2147	7.06	3.75	11.9	3262	123	10.5	20.3	0.82
max	0.311	89.3	77.5	0.049	546	3753	11.5	6.35	20.2	5767	194	15.0	38.9	0.89
RSD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
OF COMP Dissolved (µg/L)														
n	2	2	2	2	2	2	2	2	2	2	2	2	2	2
min	0.04	18.9	0.512	0.0021	36.6	19.8	1.15	0.79	1.31	22.1	7.12	4.62	1.47	0.5
mean	0.04	24.0	1.01	0.0038	58.1	70.4	6.08	0.84	1.61	62.6	15.4	5.29	19.9	0.5
max	0.04	29.1	1.50	0.0055	79.5	121	11.0	0.88	1.90	103	23.6	5.95	38.3	0.5
RSD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
WQS Acute (µg/L)	1.9	4.8	210		90		69	42	1100			74	290	

Table 39. Statistical summary of total and dissolved bay seawater metals data at Naval Air Station North Island. Chronic WQS are also shown.

<b>Bay Total (µg/L)</b>	<b>Cu</b>	<b>Zn</b>
n	9	9
min	2.31	6.30
mean	5.10	15.5
max	9.7	29
RSD	49%	53%
<b>Bay Dissolved (µg/L)</b>		
n	9	9
min	1.68	5.06
mean	2.92	12.5
max	5.2	21
RSD	39%	46%
<b>WQS Chronic (µg/L)</b>	3.1	81

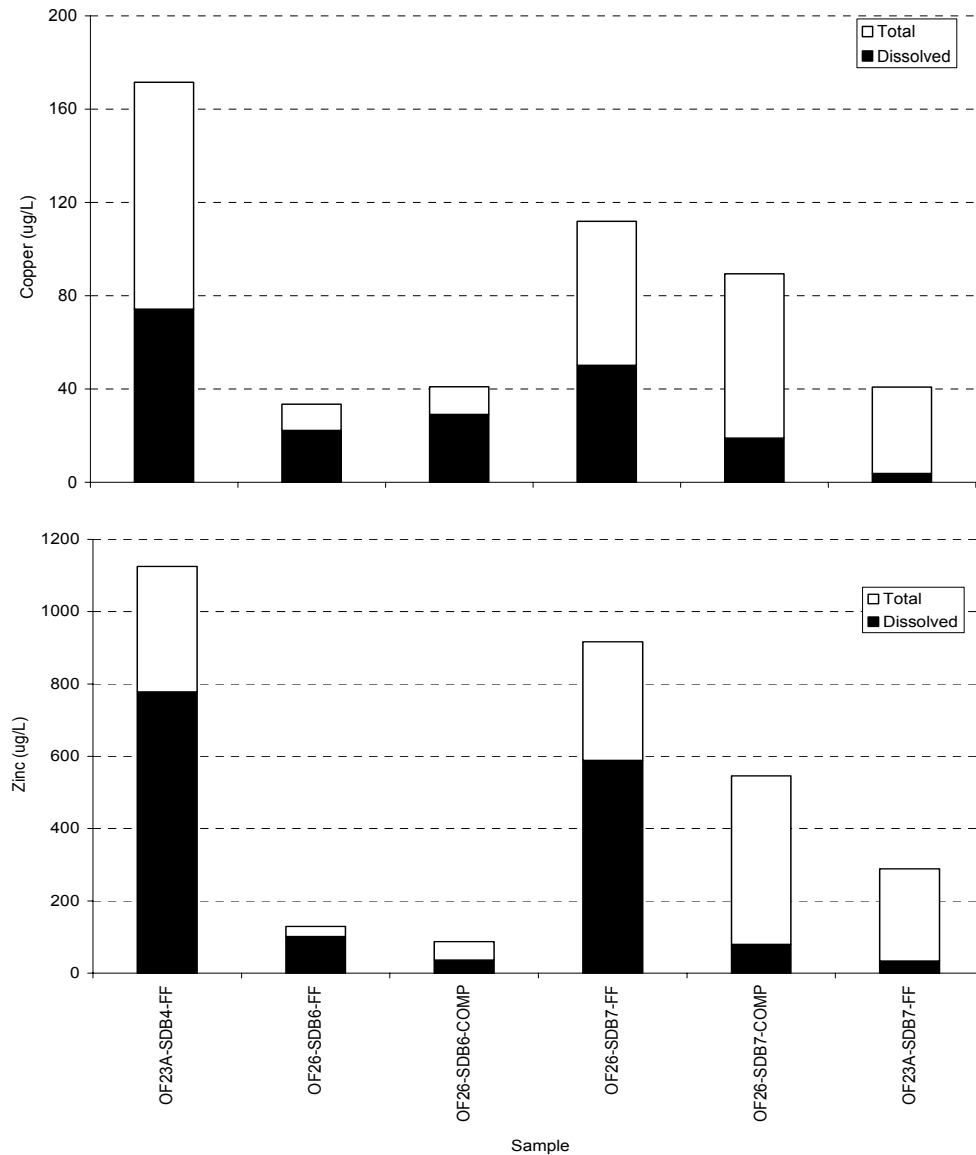


Figure 51. Total and dissolved copper and zinc concentrations measured in Naval Air Station North Island in first-flush (FF) and composite (Comp) storm water samples.

**PAH.** Thirteen samples were analyzed for PAH at Naval Air Station North Island. The total includes six storm water outfall and seven receiving water samples. Table 40 shows a statistical summary of storm water and bay water samples that is based on the summation of the 16 priority pollutant PAH data. Appendix D shows all individual sample data. The sum of priority pollutant PAH concentrations in outfall samples ranged from ~100 to 10,700 ng/L, the maximum value representing the highest level observed at any base in the study. This maximum concentration was measured in the composite sample collected from outfall 26 during the SDB7 storm event. The associated first-flush sample was nearly a factor of seven lower in PAH. The composite sample was also elevated in DOC, TSS, and metals. The data collected from outfalls and receiving water sites showed considerable variability (Figure 52).

Receiving water summed priority pollutant PAH ranged from 24 to 1369 ng/L. PAH in samples collected in bay samples outside OF23A before and during storm events was actually higher than levels measured in the associated first-flush storm water sample. PAH in first-flush, composite, and in bay water samples outside outfall 26, were quite variable from storm to storm. The observed variations were also not consistent with trends in one type of sample opposite to the trends observed in another. The reason for this high degree of variability is not known.

Only about 3% of priority pollutant PAHs in the outfall samples was below a MDL, which ranged from 0.4 to 1.5 ng/L, depending on the specific analyte. Analytes not detected were given a value equal to one-half the MDL in the summation. About 38% of priority pollutant PAH analytes in bay water samples were below a MDL.

Fluoranthene (one of four samples) and pyrene (four of four samples) exceeded minimum acute thresholds for individual PAH analytes shown in Table 11 at Naval Air Station North Island outfall 26. These included measurements made in two first-flush and two composite samples. All the receiving water samples contained PAH concentrations below the minimum chronic threshold values shown in Table 11.

The relative PAH composition of first-flush and composite samples collected from outfall 26 was nearly identical and showed a mixed petrogenic and pyrogenic source signal. There was a relatively higher petrogenic signal in the first-flush sample collected during the SDB6 storm event, though the corresponding composite sample was more similar to the other outfall samples. The relative PAH composition of first-flush samples collected from outfall 23A during the SDB6 storm event showed a relatively higher petrogenic signal than the first-flush sample collected during the SDB7 storm event. No composite samples were collected from this outfall because of logistical constraints.

Receiving water samples collected outside of both outfalls before the SDB6 storm event showed a nearly identical low-level mixture of pyrogenic and petrogenic PAH (Figure 55). Samples collected during both storm events had a similar PAH composition, though there was a slight elevation in phenanthrene, fluoranthene, pyrene, and chrysene in these samples. These samples had a distinctly different composition than that of storm water and did not appear to be altered appreciably by the storm discharge. The difference in composition suggests sources other than storm water may have been responsible for the observed variability.

Table 40. Statistical summary of the sum of priority pollutant PAH data at Naval Air Station North Island. The summation used one-half the MDL for analytes not detected in the sample. Sample types include first-flush (FF) and composite (Comp) storm water outfall samples as well as receiving water (Bay) samples collected before (PRE) and during (DUR) storm events.

Sum Priority Pollutant PAH (ng/L)	Outfalls		Bay	
	FF	COMP	PRE	DUR
n	4	2	3	4
Min	96	2204	11	24
Average	1784	6484	239	744
Max	5119	10764	692	1369
RSD	129%	NA	165%	74%

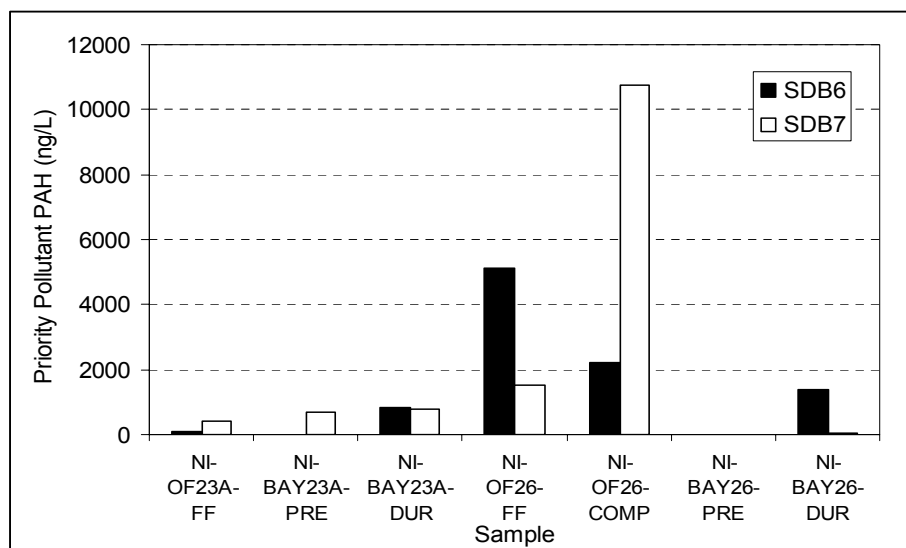


Figure 52. Summed priority pollutant PAH data for Naval Air Station North Island samples collected during storms SDB6 and SDB7. Analytes not detected were given a value equal to one-half the MDL in the summation. Sample types include first-flush (FF) and composite (COMP) outfall (OF) samples as well as bay (BAY) samples collected before (PRE) and during (DUR) storms.



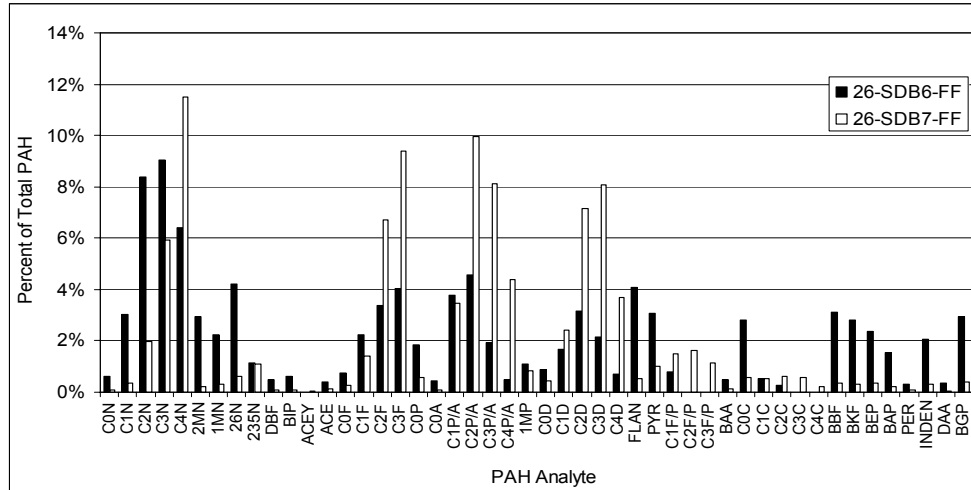


Figure 53. Relative PAH composition in first-flush samples collected from Naval Air Station North Island outfall 26 during the SDB6 and SDB7 storm events. Table 6 shows analyte IDs.

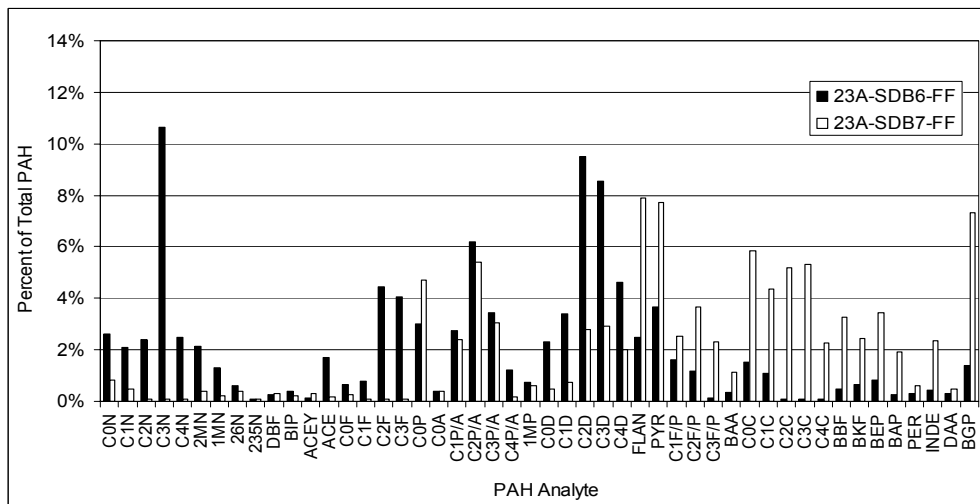


Figure 54. Relative PAH composition in first-flush samples collected from Naval Air Station North Island outfall 23A during the SDB6 and SDB7 storm events. Table 6 shows analyte IDs.

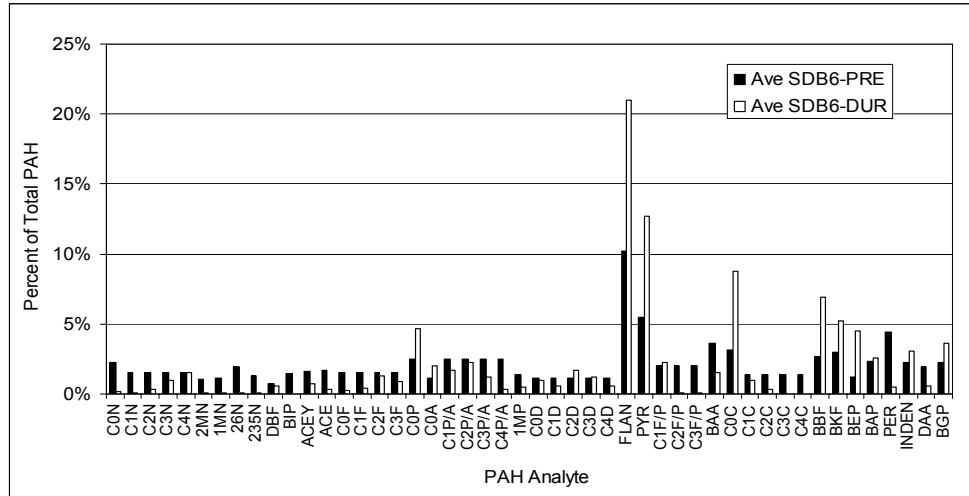


Figure 55. Average relative PAH composition in receiving water samples collected before and during the SDB6 storm event outside Naval Air Station North Island outfalls 23A and 26. Table 6 shows analyte IDs.

**PCB.** Nine samples were analyzed for PCB at Naval Air Station North Island. The total includes five storm water outfall and four receiving water samples. Table 41 shows a statistical summary of PCB data. Appendix D shows all individual sample data. The sum of PCB concentrations in storm water samples ranged from 2.9 ng/L (all congeners below detection) to a maximum of 742 ng/L. The maximum concentration was measured in the composite sample collected from outfall 26 during storm SDB7 and was the maximum found in any sample collected in the study. This sample was elevated in other contaminants as well. Except for this sample, nearly all PCB congeners were below or near the detection limit that ranged from 0.07 to 0.66 ng/L, depending on the congener. PCB levels measured in storm water all fell below the minimum acute toxicity thresholds (EPA, 1987).

Nearly all PCB congeners in receiving water samples were below detection. The maximum bay water summed PCB concentration calculated from these data was 4.4 ng/L. All values were below the chronic PCB WQS of 30 ng/L (EPA, 2000b).

Table 41. Statistical summary of PCB data at Naval Air Station North Island. "Sum PCB" is the summation of all congeners measured in the sample. The summation used one-half the MDL for congeners not detected in the sample. Sample types include first-flush (FF), composite (COMP) storm water outfall samples and bay samples collected before (PRE) and during (DUR) a storm event. Toxicity threshold benchmarks are also shown.

Sum PCB (ng/L)	Outfalls		Bay	
	FF	COMP	PRE	DUR
n	3	2	2	2
min	2.9	5.2	2.8	2.8
mean	4.4	374	3.2	3.6
max	6.0	742	3.6	4.4
RSD	34%	NA	NA	NA
Threshold	Acute 10,000		Chronic 30	

**Pesticides.** Nine samples were analyzed for chlorinated pesticides at Naval Air Station North Island. Table 42 shows these data. Appendix D shows all individual sample data. Though most analytes were below MDLs that ranged from 0.3 to 1.2 ng/L, depending on the analyte, the two composite samples collected at outfall 26 during the SDB6 and SDB7 storm events had multiple pesticides above detection limits. Pesticide levels were a maximum in the composite sample at outfall 26 during SDB7, consistent with other contaminants measured in the sample. Including these maximum concentrations, none of the chlorinated pesticides measured in storm water samples exceeded an acute WQS (Table 42).

All pesticide concentrations measured in receiving water samples were below detection except for four analytes in the sample collected during the SDB7 storm event outside outfall 26 (Table 42). This sample had a 4',4' DDT concentration that exceeded its chronic WQS (EPA, 2000b). The remainder of the analytes was below chronic WQS.

Table 42. Chlorinated pesticide data collected at Naval Air Station North Island . Grayed-out cells contain values that were *above* the MDL, with all other data at the MDL. Sample types include first-flush (FF) and composite (Comp) storm water samples, and receiving water (BAY) before (PRE) and during (DUR) storm event samples. Acute and chronic water quality standards are also shown. The WQS shown for g-chlordane is actually for the sum of chlordane isomers.

Pesticide (ng/L)	SDB6- OF23A- FF	SDB6- OF26- FF	SDB7- OF23A- FF	SDB6- OF26- COMP	SDB7- OF26- COMP	Acute WQC (ng/L)	SDB6- BAY23A- PRE	SDB6- BAY23A- DUR	SDB6- BAY26- PRE	SDB6- BAY26- DUR	Chronic WQS (ng/L)
2,4'-DDD	0.63	0.62	0.62	0.62	7.52		0.62	0.62	0.62	0.63	
2,4'-DDE	1.16	0.52	0.52	0.52	0.52		0.52	0.52	0.52	0.53	
2,4'-DDT	0.37	0.37	0.37	0.37	5.98		0.37	0.37	0.37	0.37	
4,4'-DDD	0.73	3	3	2.1	6.55		0.72	0.72	0.73	1.19	
4,4'-DDE	0.53	0.52	0.52	0.82	9.29		0.52	0.52	0.52	0.71	
4,4'-DDT	0.45	0.45	0.45	4.58	16.1	130	0.45	0.45	0.45	3.37	1
aldrin	0.3	0.3	0.3	0.3	0.3	1300	0.3	0.3	0.3	0.3	
a-chlordane	0.29	0.29	0.29	1.7	8.56		0.29	0.29	0.29	0.47	
g-chlordane	0.31	0.31	0.31	0.31	14.36	90	0.31	0.31	0.31	0.31	4
a-BHC	0.26	0.26	0.26	0.26	0.26		0.26	0.26	0.26	0.26	
b-BHC	0.36	0.36	0.36	0.36	0.36		0.36	0.36	0.36	0.36	
d-BHC	0.3	0.3	0.3	0.3	1.62		0.29	0.3	0.3	0.3	
Lindane	0.38	0.38	0.38	0.38	0.37		0.37	0.38	0.38	0.38	
cis-nonachlor	0.5	0.49	0.49	0.49	3.16		0.49	0.49	0.49	0.5	
trans-nonachlor	0.31	0.31	0.31	1.62	6.48		0.31	0.31	0.31	0.65	
Chlorpyrifos	0.39	0.39	0.39	0.39	0.39		0.39	0.39	0.39	0.39	
oxychlordane	0.3	0.3	0.3	0.3	0.3		0.3	0.3	0.3	0.3	
dieldrin	0.59	0.58	0.58	0.58	2.53	710	0.58	0.58	0.58	0.59	1.9
endosulfan I	0.21	0.21	0.21	0.21	0.21	34	0.21	0.21	0.21	0.21	8.7
endosulfan II	0.53	0.53	0.53	0.53	5.98	34	0.52	0.53	0.53	0.53	8.7
endosulfan sulfate	0.5	0.5	0.5	0.5	33.23		0.49	0.49	0.5	0.5	
endrin	0.58	0.57	0.57	0.57	0.57	37	0.57	0.57	0.57	0.58	23
endrin aldehyde	0.65	0.65	0.65	0.65	6.25		0.64	0.65	0.65	0.65	
endrin ketone	0.68	0.68	0.68	0.68	0.67		0.67	0.68	0.68	0.68	
heptachlor	8.67	0.45	0.45	0.45	0.44	53	0.44	0.45	0.45	0.45	36
heptachlor epoxide	1.21	1.2	1.2	1.2	1.19	53	1.19	1.2	1.2	1.21	36
Hexachlorobenzene	0.64	0.63	0.63	0.63	0.62		0.28	0.63	0.63	0.64	
methoxychlor	0.75	9.57	9.57	6.99	15.05		0.74	0.74	0.75	0.75	
Mirex	0.48	0.47	0.47	0.47	0.47		0.47	0.47	0.47	0.48	

### 7.5.5 Plume Mapping

Plume mapping was performed at Naval Air Station North Island on three occasions, during the SDB4, SDB6, and SDB7 storm events. Figure 4 shows the timetable of the surveys and rainfall. Three surveys were conducted during the SDB4 storm event. The event began with a 0.1-inch rainfall on 17 October 2004. First-flush samples were collected at that time. The first plume mapping survey did not begin until the 18 October, when it became clear that the bulk of the storm was on its way. The “Pre”-SDB4 mapping survey was conducted as it began to rain on the 18 October. The “During” surveys were conducted during the next 2 days, when up to 1.7 inches of rain fell over the time period. No “After” surveys were conducted because of logistical constraints.

Figure 56 shows spatial maps of surface salinity from surveys made before and during the SDB4 storm event. Appendix G shows spatial plots for all parameters measured during these surveys. The pre-storm plot captured a condition when some light drizzle had already fallen. The pre-storm plot captured a condition when some light drizzle had fallen before arrival. The “during” plot was produced from data collected on the third day of the storm after 1.7 inches of rain had fallen during heavy squall conditions. Because of the near continuous rainfall over several tide cycles, a large freshwater signature covered most of the inner portion of the bay during this survey, evidenced by the relatively lower salinity seen throughout the spatial map of the “during” survey. The salinity was generally lower during the storm, with a maximum decrease of about 6%. There was no clear evidence of freshwater plumes along the shoreline, with the lowest salinity observed further out from shore to the north and to the east of the base. This was consistent with the whole south bay showing a lower salinity after multiple days of rain. This overall decrease was about a 2% reduction in salinity.

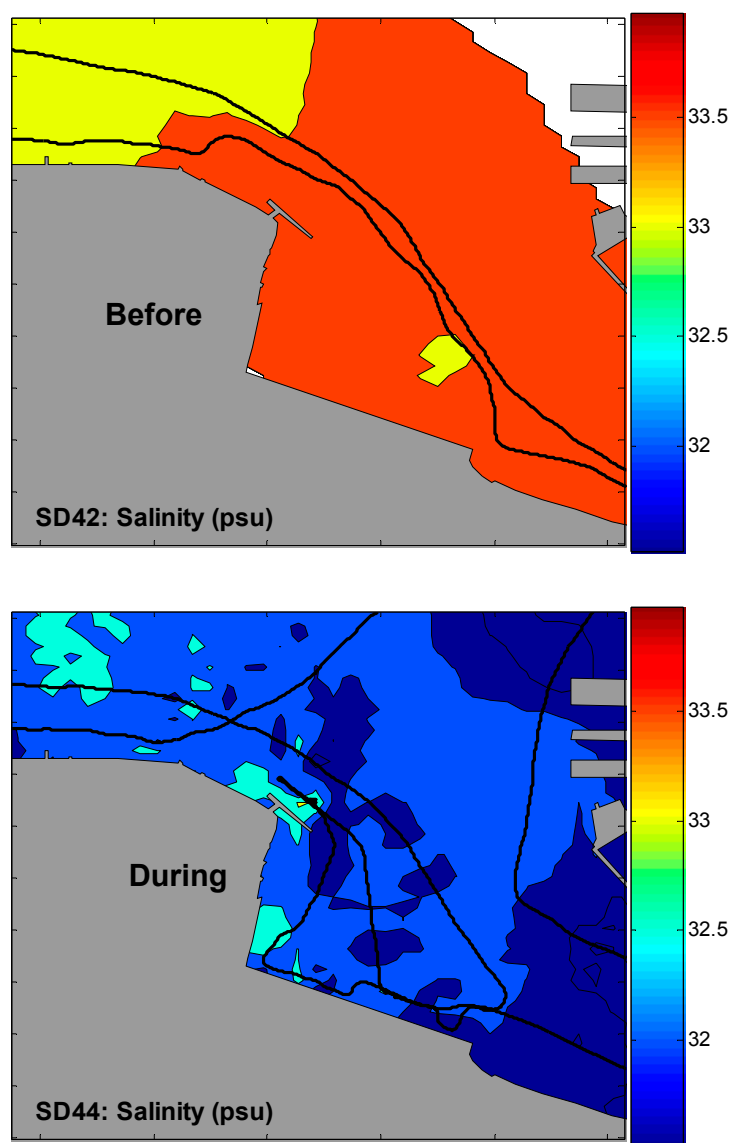


Figure 56. Surface salinity mapping before and during storm event (SDB4) at Naval Air Station North Island. There was no “after” storm mapping.

## 7.6 FLOATING BIOASSAY STUDY

Effluent toxicity, when adequately related to ambient conditions, can give a valid assessment of receiving water impact (EPA, 1991a). One method to link effluent WET tests to ambient impacts is to perform dilution series tests that bracket receiving water conditions to identify when there is no observable toxic impact. This method requires knowledge of receiving water exposure conditions. Two methods were used during this study to evaluate receiving water exposures. Plume mapping surveys conducted throughout this study provided large-scale, multiple snapshots of receiving water exposure conditions before, during, and after rainfall events. These large-scale snapshots showed that maximum exposures were in the range of 4 to 14%, were limited in size, and dissipated quickly. The second method, using a special floating bioassay system, provided a highly detailed characterization of actual exposure conditions.

As described earlier, the technical approach in this study was to simultaneously measure toxicity and chemistry in storm water and receiving waters. In this special effort, toxicity and chemistry of receiving waters were measured on site, immediately outside Naval Station San Diego outfall 14 (Figure 57) during the SDB45 storm event. The MESC was used to monitor water quality conditions and to supply surface seawater to multiple test organisms throughout a 96-hour period just before, during, and after the storm event. The WET tests were therefore performed using actual exposure conditions present outside the outfall and evaluated with the high-resolution measurement of actual water quality conditions. Results of this effort are fully detailed in Appendix H.

Like most other results observed throughout this study, storm water discharges showed some toxicity in storm water samples, with no toxicity observed in the tests conducted in the receiving water. In this case, first-flush storm water was significantly toxic to mysids (63% survival) and mussel larvae (1% normal development) in 100% storm water effluent, but not to topsmelt (90% survival). All chemicals measured in first-flush samples were below acute WQS or other benchmarks described in Table 10 and Table 11, except for dissolved copper (45 µg/L) and zinc (175 µg/L). Total zinc (362 µg/L) was also above the permit performance goal. The combination of copper and zinc combined was likely the cause of observed toxicity, though this cannot be confirmed.

No toxicity was observed in any receiving water toxicity tests. The reason for this can be seen in the bay monitoring data summarized in Figure 58. Though storm water discharge was sufficient to reduce salinity from its pre-storm value of 33.5 psu to near zero during the most intense rainfall periods, the low-salinity conditions were maintained for very short periods of time; on the order of minutes or tens of minutes. Over the full 96-hour exposure period, salinity averaged 32.4 psu, which translates into a storm water percentage that was less than 4%, with some portion of that reduction related to direct rainfall. Dissolved copper and zinc concentrations measured in receiving waters also showed short-lived variations. Maximum dissolved copper concentrations (5.5 µg/L) were 40% higher than pre-storm levels, while zinc concentrations (16 µg/L) peaked at a factor of two higher. These maximum levels were lower by factors of 8 and 23, respectively, from those measured in first-flush storm water. Though copper levels exceeded an acute WQS, the excursion was limited in duration. Copper did exceed chronic WQS throughout the period, though the levels, mostly below 4 µg/L, were below those observed to cause toxicity in receiving waters as a result of complexation reactions with DOC (Rosen, Rivera-Duarte, Kear-Padilla, and Chadwick, 2005; Arnold, 2005).

The data collected from this special study showed that storm discharges were rapidly mixed, even when the discharge was large enough to reduce salinity to near zero during the most intense conditions. Significant reductions in chemical concentrations occurred on the order of minutes or tens of minutes, thereby limiting plume exposure well below the 48- or 96-hour exposures used in standard

bioassays. The issue of limited exposure has previously been identified by Hall and Anderson, 1988; Katznelson et al., 1995; and Mancini and Plummer, 1986; all cited in Burton, Pitt, and Clark, 2000). Using 100% storm water effluent to evaluate toxicity at the end-of-pipe with 2- and 4-day exposure times greatly overestimates the actual exposure conditions observed in the receiving environment. There is presently no WET test guidance on how to evaluate short-term exposure conditions presented by storm water runoff.



Figure 57. RV ECOS tied up along Naval Station San Diego quay wall outside outfall 14 during the special floating laboratory bioassay conducted in October 2004. The sensors and pump intake were ~ 15 feet away from the outfall. Note sheet runoff over quay wall.

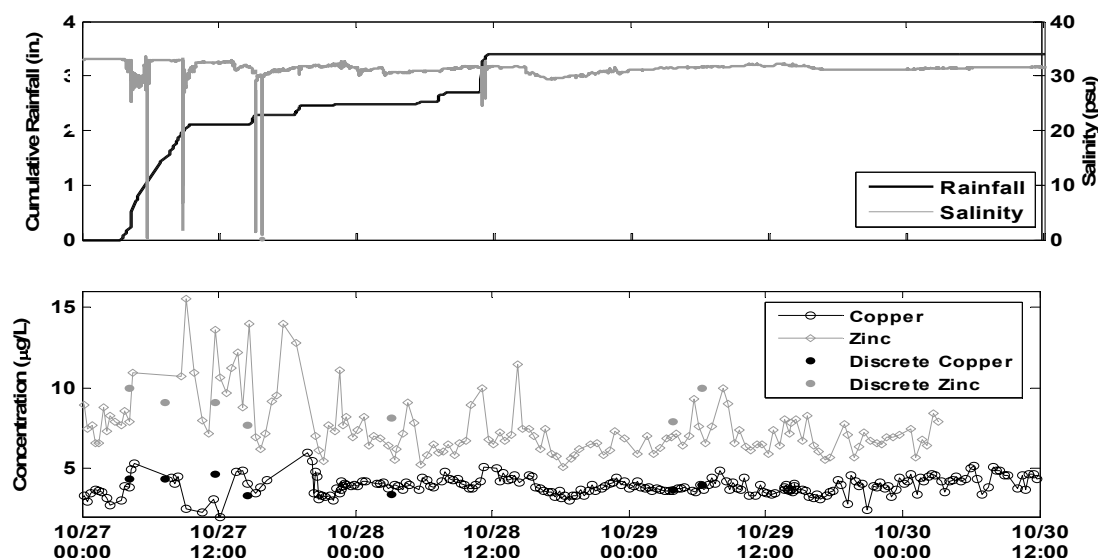


Figure 58. MESC full-storm monitoring data for receiving water salinity, cumulative rainfall (upper panel) and dissolved copper and zinc (lower panel) collected during the special floating bioassay laboratory study at Naval Station San Diego outfall 14. Dissolved copper and zinc data include results from the continuous trace metal analyzer (open symbols) and discrete samples analyzed.

As previously stated, the goal of this study was to develop a robust dataset of storm water and receiving water toxicity that can be used to support a scientifically based acute toxicity threshold for industrial storm water discharges from U.S. Navy facilities. Three simultaneous measurement components were used to meet these goals, including: toxicity and chemistry measurements in storm water discharges, toxicity and chemistry measurements in receiving waters, and plume mapping surveys to measure exposure conditions in receiving waters. These multiple lines of evidence were used to fully characterize storm water discharges and directly relate them to observed receiving water quality impacts.





## 8. DISCUSSION

The study was designed to collect a sufficient quantity of high-quality data that was representative of the full range of expected storm and discharge conditions. Therefore, the principal evaluation was based on sample data pooled from all four bases. Pooling the data provides the widest range in drainage sizes and activities, rainfall amounts, intensities, and antecedent dry weather, and the most complete range in toxicity and chemistry results. Though the evaluation also included some comparisons amongst the bases, the study was not designed to, and did not, collect, sufficient data to statistically compare outfalls or evaluate variability as a result of antecedent dry weather, rainfall total, or intensity.

Evaluation of this dataset included a discussion of how representative the collected data are of conditions expected to be found at Navy industrial sites. The magnitude and extent of storm water toxicity was evaluated using summary statistics, comparisons of first-flush and composite sample results, consideration of no observable effects concentrations, and comparisons by facility. The evaluation also includes a discussion of WET test methods used to identify a toxic result, including t-testing, percent minimum significant difference, and a comparison to the NPDES permit requirement. The causes of toxicity were focused on the toxicity identification evaluations and comparisons of chemistry results with effect levels. Impacts to receiving water quality were focused on the magnitude and extent of toxicity and chemistry observed in the receiving water, as well as on the magnitude, extent, and duration of storm water exposure conditions using results of the plume mapping and a special floating bioassay laboratory study.

The study captured nearly, if not the full range, of rainfall and discharge conditions likely to occur at these sites, and captured rainfall events that were slightly above normal historical daily rainfall totals (Figure 59). The study captured drought conditions between 2002 and 2004, followed by the third wettest season on record during the 2004 through 2005 wet season. Measurements made during this study included extrema in rainfall totals as well antecedent dry period. This included sampling at Naval Station San Diego during a record 3.5-inch rainfall in October 2004 and sampling the very first-flush of the year at all four bases after a record 183 days of antecedent dry conditions. Though first-flush sampling by its nature is independent of total rainfall for an event, composite samples were collected over a tenfold range in rainfall totals, from 0.23 inch during SDB1 to 2.1 inches during the special floating bioassay study SD45. Bay samples were collected over a slightly wider range of rainfall totals, capturing a condition after a 3-inch rainfall had fallen over 10 days (TIE1A) and a 6-inch rainfall had fallen during a 2-week period (SDB5), an amount comparable to 60% of a normal annual total storm input to the bay. These sampling conditions were representative of bay conditions that had a chance to accumulate and integrate sources and impacts.

The drainage areas and outfalls monitored during the study were chosen to be representative of the range in industrial areas of the bases that are reasonably similar at all four bases. The drainage areas monitored contained various industrial activities including, but not limited to, fuel storage and dispensing, hazardous substance storage, materials storage, metal fabrication, painting, recycling, vehicle repair and maintenance, sandblasting, scrap metal yards, and vehicle repair and maintenance. The drainages sampled had a wide range in size, from 0.5 to 75 acres. Though only 10% of the total industrial area of these bases was monitored, they contained the typical activities and land uses that are carried out at these bases. Comparing results amongst the bases provided a sense of how applicable these data were to other similar facilities.

The pooled data set provided ample toxicity, chemistry, and plume mapping data to perform a successful characterization and evaluation. A total of 136 discrete samples were collected during this

study. From these samples, 333 total toxicity tests were performed, including 131 tests conducted on storm water outfall samples and 202 tests performed on receiving waters. Most samples had all three bioassays performed, providing a wide range in species and endpoint sensitivities. Nearly all the outfall samples were run with three to five dilutions to evaluate the magnitude of toxicity and to calculate NOECs and PMSDs. Though only one set of TIE analyses were performed at each outfall, the analysis of four broad classes of chemicals consisting of as many as 124 total analytes in storm water samples provided a sufficient data suite to evaluate which contaminants were likely the cause of observed toxicity. The inclusion of data from 17 plume mapping surveys conducted before, during, and after storm events provided a quality dataset from which to evaluate magnitude, extent, and duration of receiving water impacts. Thus, the pooled data provide a robust scientific dataset that is representative of the range of storm and discharge conditions that are found at these facilities.

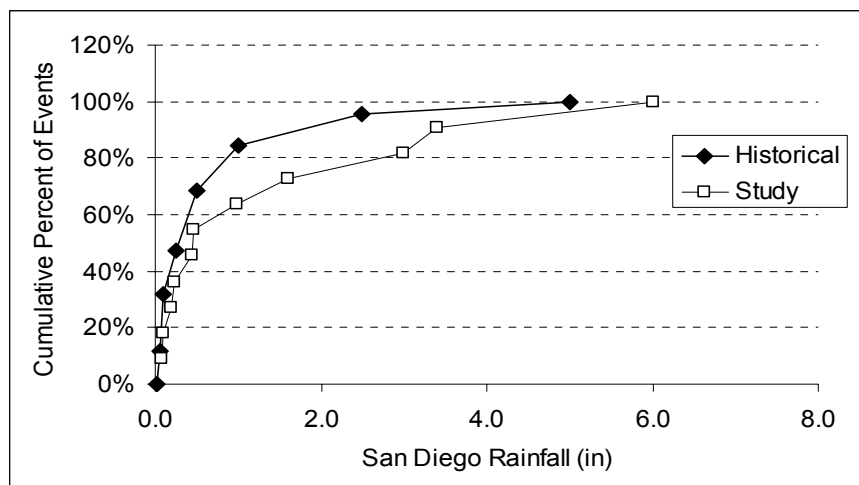


Figure 59. Historical daily rainfall data for San Diego (1948–1990) and rainfall data for storm events captured in this study.

## 8.1 STORM WATER TOXICITY

The toxicity requirement in the NPDES permit for all Navy bases bordering San Diego Bay is as follows:

“...in a 96-hour static or continuous flow bioassay (toxicity) test, undiluted storm water runoff associated with industrial activity shall not produce less than 90% survival, 50% of the time, and not less than 70% survival, 10% of the time, using standard test species and protocol.”

The topsmelt and mysid acute toxicity tests meet the NPDES requirement. The mussel embryolarval development test was added to the study because it is considered a chronic endpoint in WET testing (EPA, 1995) and provides one of the most sensitive endpoints available for assessing receiving water toxicity. Though not explicitly stated in the above requirement, the permit requires that samples of undiluted storm water runoff include only those collected during the first hour of flow (first-flush). Though composite samples are not collected as part of the permit process, they were collected during this study to provide data representative of the complete storm discharge for comparison to a grab sample that is representative of a single moment in time. Though mysids were generally more sensitive than topsmelt (Figure 60), results from both species were combined for

many of the following evaluations because they are interchangeable endpoints within the NPDES permit.

Ninety-two storm water samples were tested for acute toxicity using topsmelt or mysids (Table 43). This total included 64 first-flush and 28 composite tests. Overall, the toxicity of undiluted storm water measured in first-flush samples was higher, had a larger range, and was more variable than toxicity measured in composite samples (Figure 61). The acute toxicity of undiluted first-flush storm water discharging from the four Navy facilities ranged across the full extent possible, from 0 to 100%, and averaged 72% survival (RSD = 46%). Composite sample results showed a narrower range of results, 60 to 100%, and averaged 91% survival (RSD = 15%). These data take into account combined test results from the mysid and topsmelt bioassays. This general finding confirms that the initial volume discharged at the start of rainfall tends to be more toxic than the total volume that is discharged during a storm event. There were, however, a few instances where toxicity in first-flush samples equaled that in the corresponding composite sample.

The combined topsmelt and mysid results shown in Table 43 and Figure 60 show that 58% (37 of 64 tests) of first-flush samples failed the 90% survival threshold in the NPDES permit. Only 25% (7 of 28 tests) of composite samples would have failed this threshold if it applied. First-flush samples also did not meet the 70% permit threshold, failing 28% (8 of 64 tests) of the time, while composite samples failed this threshold once, representing 4% of samples. These failure rates were pooled for all bases over multiple years and may not necessarily be compared directly to permit requirements because the permit does not state specifically what “50% of the time” or “10% of the time” mean.

Though the permit sets a cutoff value at 90% survival as an acceptable result, it does not accurately identify results that would be declared acutely toxic using the standard statistical approach used in WET testing (EPA, 2002; Wang, Denton, and Shukla, 2000). The standard method to declare a test result as toxic is to statistically compare (t-test) the result to controls run with the test, provided the controls meet test acceptability criteria (EPA, 2002). Establishing a quantifiable difference between the control and treatment is fundamental to the issue of identifying toxicity. This is because of variations in organism quality and even small variations in testing procedures that affect within-test variability on a random basis. It is particularly important if control performance (e.g., survival) is allowed to vary within acceptable limits. As control performance varies, the statistical comparison will always evaluate the treatment response in the context of the actual control performance, and retain a consistent level of sensitivity regardless of the level of control survival. Using this standard method, 34% (22 of 64 tests) of first-flush samples were identified as toxic compared to the 58% identified by the permit cutoff value. The 90% survival requirement in the permit therefore classifies about 40% of test results as a failure, though they are not toxic using standard WET data evaluation procedures.

The observed reduction of acute toxicity in composite samples compared to first-flush samples indicates that the potential for toxic impact in receiving waters is less than might be predicted from the first-flush grabs alone. Because of the sampling method, there is no way to determine what percentage of the storm discharge was represented by first-flush samples. However, the potential for an acute impact generally declined with time and the volume of storm water discharged. This observation was at least partially responsible for limited toxicity observed in the receiving environment (Figure 61).

The dilution series tests performed on storm water effluent samples provided NOEC data that were used to estimate what receiving water concentrations, once entrained with storm water, would not show an adverse impact. As described previously, the NOEC represents the highest effect concentration in the dilution series that was not significantly different from the control response, and is thus

an indicator of the receiving water concentration, once mixed with storm water, which does not result in a toxic effect. The dilution series tests were run with pre-storm bay water as the diluent to ensure that the results would account for any added background toxicity that may be present in the bay as well as reflect any complexation capacity that receiving waters may have to mitigate toxicity.

The vast majority (75%) of storm water samples (first-flush and composite) had topsmelt and mysid NOEC values equivalent to 100% effluent. These samples were not significantly toxic and storm water discharges to the receiving environment would not have resulted in adverse impacts. The minimum NOEC for the remaining 25% of topsmelt and mysid results was 10%. This suggests that receiving waters with a storm water fraction less than 10% would not have an adverse impact. The fact that all 137 (Figure 61) receiving water samples were not toxic to either topsmelt or mysids indicates that the receiving water concentrations were always below a storm water fraction of 10%.

The chronic mussel embryo-larval development test was run on storm water primarily to compare with receiving water results. Results in undiluted storm water showed a similar degree of variability (0 to 89% normal development) as was seen in the acute tests and, as expected, showed a higher level of toxicity, averaging 5% normal development. About 10% of 40 mussel bioassays run with storm water had a NOEC equivalent to the maximum effluent concentrations tested, which ranged from 61 to 69% effluent. The minimum NOEC in any of the mussel dilution series tests was <6.25% effluent measured in the first-flush samples collected at three of the four bases during the first-flush of the year event (SDB4). These data indicate that receiving waters with a storm water fraction less than about 6% would show an adverse impact, though the exact amount was not determined. Two of these samples, at Naval Station San Diego and Naval Amphibious Base Coronado, did exhibit receiving water toxicity to mussels.

Overall storm water toxicity levels varied significantly from base to base, though the differences can only be attributed to differences in the specific drainage areas monitored rather than the bases taken as a whole. Figure 62 shows the combined toxicity results, including first-flush and composite samples for mysids and topsmelt, for each base. Toxicity decreased in the relative order NAB>NAV>NI~SUB. The differences between Naval Amphibious Base Coronado and all three of the other bases, as well as the difference between NAV and SUB, were statistically significant at the 95% confidence level.

Figure 62 shows how each base would measure up to meeting the “90%, 50% of the time” and the “70%, 10% of the time” permit requirement in first-flush samples. Only Naval Air Station North Island would have met the “90%, 50%” threshold if “50% of the time” was applied base by base. However, Naval Air Station North Island would have failed the “70%, 10%” threshold. Only Submarine Base Coronado would have met the “70%, 10%” threshold if applied on this basis. A comparable evaluation for composite storm water samples shows that all bases except Naval Amphibious Base Coronado would have met both permit thresholds. Naval Amphibious Base Coronado composite samples would not have met either of the two requirements.

Table 43. Toxicity data summary for first-flush and composite samples by base. Values include the number of tests conducted, the number of tests failing the NPDES benchmarks of 70% and 90%, the number of tests failing the 90% requirement and significantly different from controls using a t-test, and those that were outside the 90<sup>th</sup> percentile PMSD value for the test.

First-Flush Data (counts)						Composite Data (counts)					
Base	Topsmelt					Base	Topsmelt				
	# Tests	<70%	<90%	<90% & sig	>PMSD		# Tests	<70%	<90%	<90% & sig	>PMSD
NAV	10	4	6	4	4	NAV	7	0	1	0	0
SUB	10	0	4	0	0	SUB	3	0	1	0	0
NAB	7	2	3	2	2	NAB	3	1	1	1	1
NI	7	1	3	1	1	NI	2	0	0	0	0
Total	34	7	16	7	7	Total	15	1	3	1	1

Base	Mysids					Base	Mysids				
	# Tests	<70%	<90%	<90% & sig	>PMSD		# Tests	<70%	<90%	<90% & sig	>PMSD
NAV	10	5	7	6	5	NAV	8	0	1	1	0
SUB	10	2	7	4	2	SUB	3	0	3	2	1
NAB	5	3	4	4	3	NAB	1	0	0	0	0
NI	5	1	3	1	2	NI	1	0	0	0	0
Total	30	11	21	15	12	Total	13	0	4	3	1

Base	Combined					Base	Combined				
	# Tests	<70%	<90%	<90% & sig	>PMSD		# Tests	<70%	<90%	<90% & sig	>PMSD
NAV	20	9	13	10	9	NAV	15	0	2	1	0
SUB	20	2	11	4	2	SUB	6	0	4	2	1
NAB	12	5	7	6	5	NAB	4	1	1	1	1
NI	12	2	6	2	3	NI	3	0	0	0	0
Total	64	18	37	22	19	Total	28	1	7	4	2

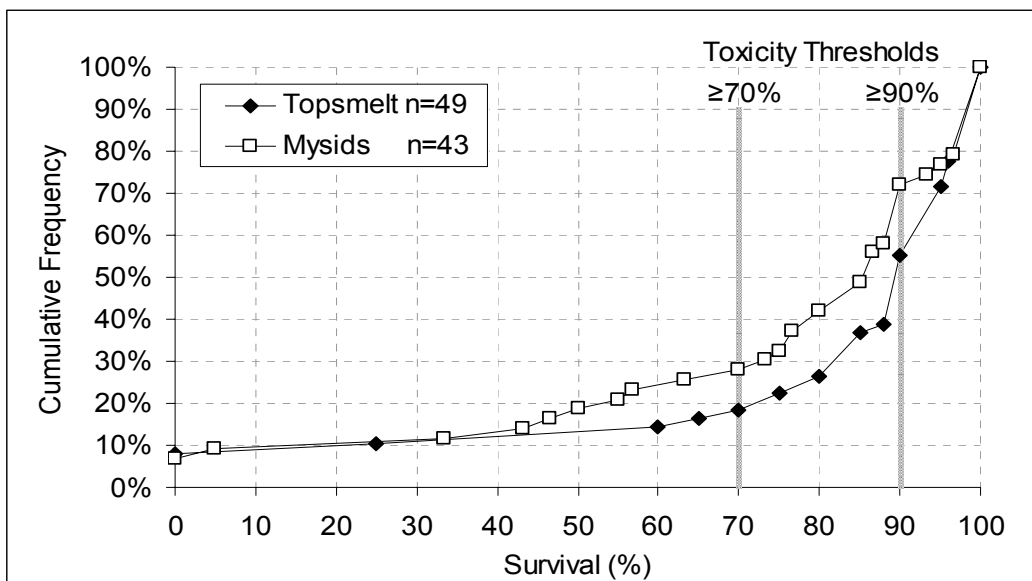


Figure 60. Mysid and topsmelt bioassay results in 100% storm water measured as percent survival in first-flush and composite storm water samples. The NPDES permit thresholds for first-flush samples are also shown.

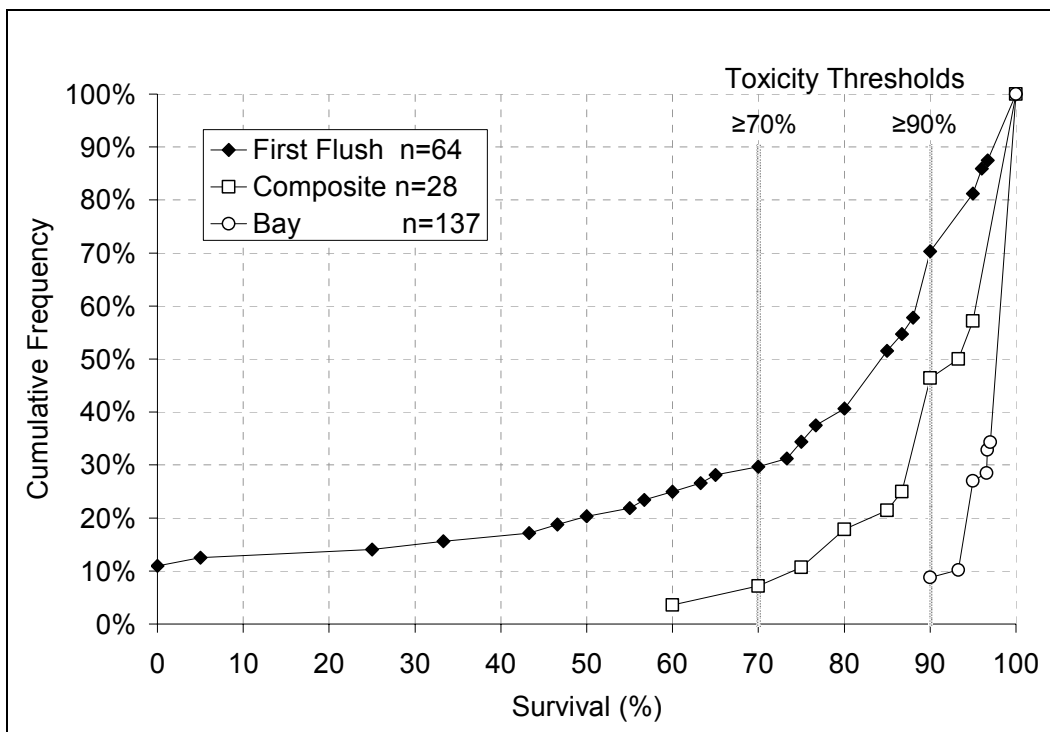


Figure 61. Combined mysid and topsmelt bioassay results in 100% storm water measured as percent survival in first-flush, composite and receiving water (Bay) samples collected from all bases. The NPDES permit thresholds for first-flush samples are also shown.

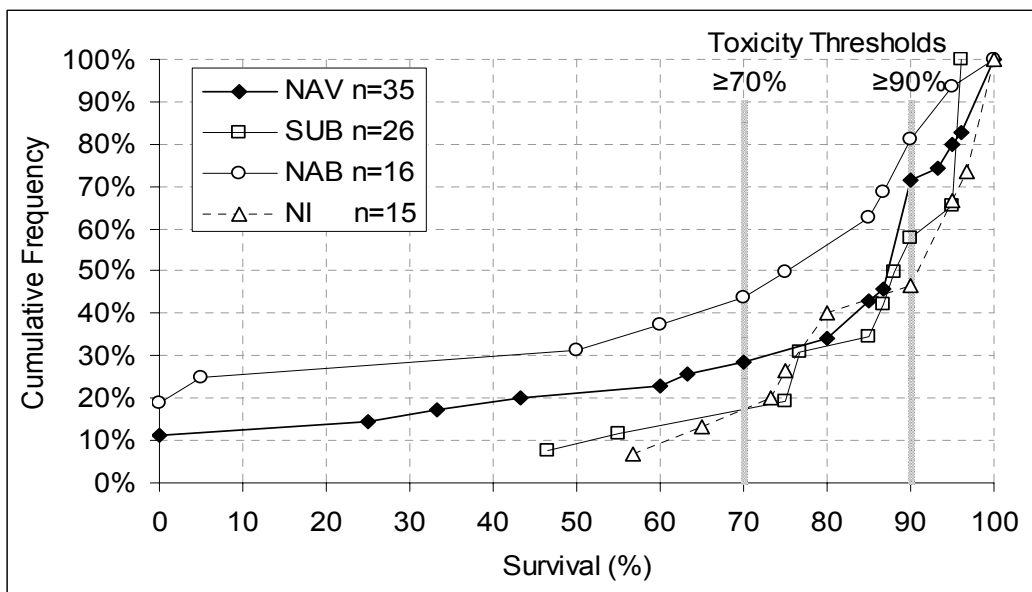


Figure 62. Combined mysid and topsmelt toxicity (as percent survival) in 100% storm water measured in first-flush and composite samples collected at the four bases Naval Station San Diego (NAV), Naval Submarine Base San Diego (SUB), Naval Amphibious Base Coronado (NAB), and Naval Air Station North Island (NI).

The EPA has spent considerable effort developing and refining toxicity-based measures for monitoring and maintaining water quality. These include development of test procedures that will provide the desired level of sensitivity in identifying adverse effects in discharges, as well as an indication of the potential for adverse effects in the receiving environment. As part of this program, the EPA has developed test procedures specifically aimed at achieving the desired level of sensitivity in terms of detecting adverse effects (e.g., the number of replicates required per test concentration) and, based on extensive studies, has quantitatively established an acceptable range of test sensitivity for each procedure. Implicit in this approach is that there must be a difference between the control and treatment; in other words, toxicity is evident only if it can be distinguished from the control.

This sensitivity is usually described as the minimum significant difference (MSD), which is defined as “the smallest difference between the control and another test treatment that can be determined as statistically significant in a given test, and the PMSD is the MSD represented as a percentage of the control response” (EPA, 2000a). By placing an upper limit (90<sup>th</sup> percentile) on the PMSD, the EPA has, in effect, taken the position that toxicity tests that fall outside of this range do not exhibit sufficient sensitivity to detect adverse effects and, therefore, must be repeated. The EPA has also placed a lower bound (10<sup>th</sup> percentile) on the PMSD, in this case trying to avoid rare situations in which the test exhibits high statistical sensitivity and can detect very small differences between the control and treatment with results that are not likely repeatable or not of biological significance. The evaluation and use of PMSD in WET testing can be found throughout the literature (Erickson and McDonald, 1995; Thursby, Heltshe, and Scott, 1997; Shukla et al., 2000; Wang, Denton, and Shukla, 2000; Phillips et al., 2001; Denton, Fox, and Faulk, 2003).

PMSD incorporates method variability specific to each test species and endpoint. PMSD data were calculated, compiled, and tabulated for each bioassay test species (Table 44). The data are also shown in Figure 63 through Figure 65 as probability distributions in which the PMSD is plotted as a cumulative frequency distribution. Shown along with these data are the PMSD results from the EPA WET variability guidance document (EPA, 2000a) as well as recent results provided by Nautilus Environmental, LLC. The EPA data were derived solely from reference toxicant data from as many as five laboratories, while the data from this study included storm water and reference toxicant tests from two laboratories. The Nautilus data included results from storm water, other effluents, and reference toxicant data. Most data were derived from dilution series tests typically having four replicates for topsmelt, three replicates for mysids, and five replicates for mussels. The EPA document did not have topsmelt data, and therefore, inland silversides, another fish survival endpoint, are shown for comparison purposes only. The mussel data from EPA included a slightly more variable endpoint of survival and development rather than just the normal development endpoint used in this study or by Nautilus.

The 10<sup>th</sup> and 90<sup>th</sup> percentile results are highlighted in the table because they are the lower and upper bounds for test method variability and indicate acceptable limits on the sensitivity of a test to detect a difference from controls (EPA, 2000a). The lower bound is established by the 10<sup>th</sup> percentile value of the distribution, meaning that this level of sensitivity will be achieved only 10% of the time, and consequently, will not be repeatable most of the time by other laboratories or even the same laboratory. Similarly, the upper bound is established by the 90<sup>th</sup> percentile value of the distribution, meaning that most laboratories will be able to identify the same sample as toxic, and repeat the result.

The study's 90<sup>th</sup> percentile PMSD for topsmelt, based on 54 test results, was 24%. The comparable value, calculated from the Nautilus data set containing 100 test results, was 26%. Because EPA did not provide topsmelt data, results for 48 inland silverside tests with a 90<sup>th</sup> percentile PMSD of 41% were used for comparison (EPA, 2000a). The study data were generally lower than the Nautilus data



(Figure 63), though both groups had a similar 90<sup>th</sup> percentile value. This agreement suggests that a sample size of 54 was sufficient to predict a 90<sup>th</sup> percentile PMSD (Phillips et al., 2001). The EPA's inland silverside endpoint data showed relatively higher method variability and a considerably higher 90<sup>th</sup> percentile value. Because PMSD is test-species-specific, this result is shown only for comparison only.

The study's 90<sup>th</sup> percentile PMSD for mysids, based on 47 test results, was 15%. The comparable value calculated from the Nautilus data set containing 100 test results was 29%. The comparable EPA value was 26% based on a sample size of 32. The study data were lower than the Nautilus and EPA results, indicating the test method variability was better than observed by the other laboratories. The lower values probably reflect the fact that all of the EPA and 50% of the Nautilus dataset for mysids were derived from reference toxicant results, while only 20% of the study dataset was composed of reference toxicant data. The bias may therefore have been a result of variability increasing with increasing toxicity that occurs with reference toxicant tests.

The study's 90<sup>th</sup> percentile PMSD for mussels, based on 48 test results, was 22%. The comparable value calculated from the Nautilus data set containing 100 test results was 26%. The comparable EPA value was 42% based on 34 test results, though as mentioned above, the endpoint used was for survival and development. These results indicate that the study method variability in the study was at least as good as or better than observed by the other laboratories.

As stated previously, establishing a quantifiable difference between the control and treatment is fundamental to the issue of identifying toxicity. This issue was addressed above when evaluating storm water toxicity results relative to the permit requirement and to individual tests that could be declared toxic on the basis of a t-test (Table 43). This table also included the number of tests that would be declared toxic using the upper bound 90<sup>th</sup> percentile PMSD, a value that 90% of laboratories would also declare as toxic. Using this criterion for identifying a toxic result, 30% (19 of 64 tests) of first-flush samples were identified as toxic compared to the 58% (37 of 64 tests) identified as failing the 90% survival requirement. The 90% survival requirement in the permit therefore classifies twice as many test results as a failure than would be declared toxic by most laboratories. A similar comparison for composite samples showed 7% (2 of 28 tests) of samples declared toxic compared with 25% (7 of 28) using the permit cutoff, a difference of a factor of four.

In summary, acute storm water toxicity was highly variable, spanning the full range of impact, from 0 to 100% survival of test organisms. The toxicity of first-flush storm water samples, representing the discharge at one moment in time, was higher than in composite samples that were representative of the entire discharge. A base-by-base evaluation showed that toxicity generally decreased in the relative order NAB>NAV>NI~SUB. The 90% survival requirement in the NPDES permit failed for 58% of first-flush samples. However, the permit requirement did not accurately identify when samples were acutely toxic or not. When using a science-based approach to WET test methods and statistical data evaluation, toxicity of first-flush storm water would have been declared toxic 30% of the time, while composite samples would have been identified as toxic 7% of the time. Using the no observable effects concentration from dilution series testing showed that a storm water fraction of less than 6% present in the receiving environment would not result in adverse impacts.

Table 44. PMSD data for individual test species and endpoints. The data shown are the number of test results, the lower (10<sup>th</sup>), median (50<sup>th</sup>), and upper (90<sup>th</sup>) percentiles of the distribution. Along with the study results are data from EPA (2000b) and recent results from the contract laboratory, Nautilus Environmental, LLC. Note that some EPA data (EPA, 2000a) are for slightly different endpoints and are included for comparison purposes only.

Topsmelt Survival PMSD			
	EPA*	Study	Nautilus
n	48	54	100
10th Percentile	7	6	9
50th Percentile	20	15	16
90th Percentile	41	24	26

\* EPA values are for Inland Silversides for comparison

Mysid Survival PMSD			
	EPA	Study	Nautilus
n	32	48	100
10th Percentile	5	4	5
50th Percentile	15	9	15
90th Percentile	26	15	29

Mussel Embryo-Larval Development PMSD			
	EPA <sup>+</sup>	Study	Nautilus
n	34	48	100
10th Percentile	7	3	3
50th Percentile	20	9	9
90th Percentile	42	22	26

<sup>+</sup> EPA values are for normal and survival endpoint

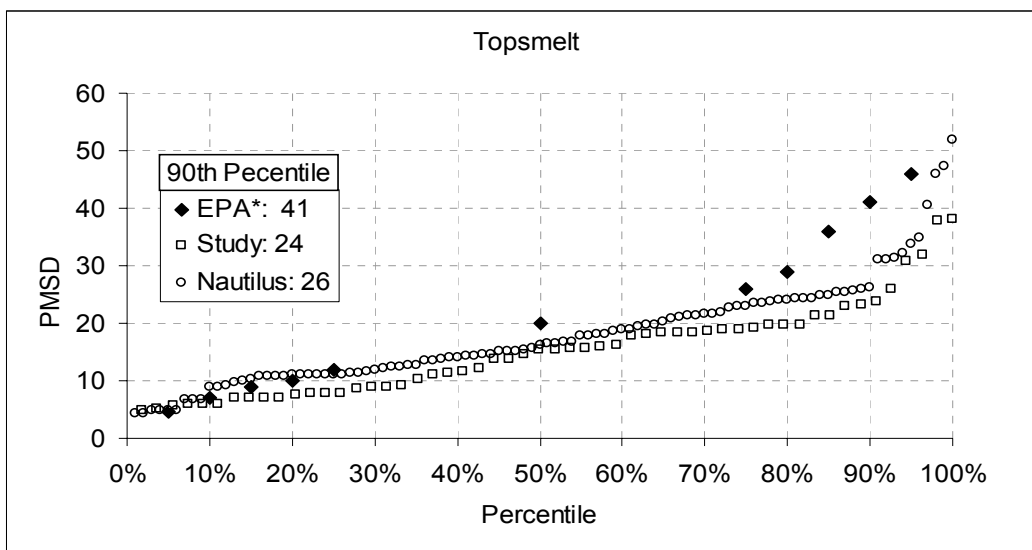


Figure 63. PMSD probability distribution for topsmelt derived from data in this study and additional data from Nautilus Environmental, LLC. EPA\* data (EPA, 2000a) for inland silversides are shown for comparison.

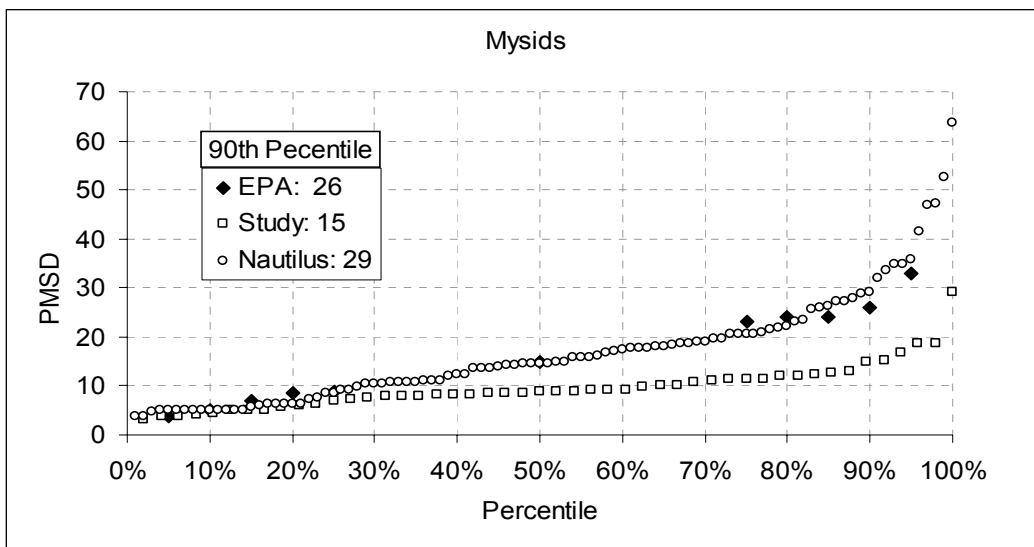


Figure 64. PMSD probability distribution for mysids derived from data in this study (EPA, 2000b) and additional data from Nautilus Environmental, LLC.

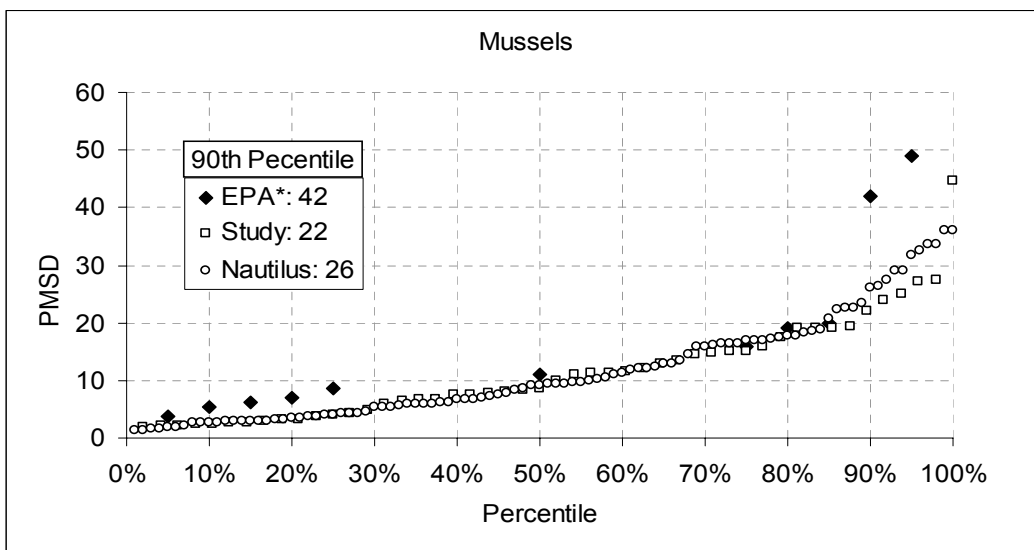


Figure 65. PMSD probability distribution for mussel embryo-larval development derived from data in this study and additional data from Nautilus Environmental, LLC. The EPA\* data (EPA, 2000a) were for a survival and development endpoint which is different than just the normal development endpoint used in the study and by Nautilus.

## 8.2 CAUSES OF TOXICITY

The causes of toxicity in storm water samples were evaluated using results of the toxicity identification evaluation as well as chemistry results. TIEs were conducted on a single first-flush storm water sample collected from 10 of the 14 drainage areas evaluated at the four bases. The limited number of samples analyzed was a direct result of the exceptionally high costs involved in conducting these tests. Additionally, of the 10 samples evaluated, only one was sufficiently toxic to all three

species tested. The TIE dataset generated, while substantial for a single project, was somewhat limited in total number of measurements. Though TIE procedures are good at identifying and confirming the basic contaminant groups such as metals, non-polar organics, and volatile compounds that cause toxicity in a sample, the ability to identify the specific contaminant(s) within these groups usually requires evaluation of sample chemistry. This step is somewhat circular, but provides the best information available for identifying the cause of toxicity. The extensive chemistry data collected as a part of the study provided a good basis for confirming results of the TIEs for the likely causes of industrial storm water toxicity at these facilities.

Results of the TIE indicated that the primary and consistent toxicants of concern to mussel embryo-larval development in all storm water samples were copper and zinc, either alone or in combination (Table 45). At Naval Submarine Base San Diego outfall 11B, the surfactant nonylphenol was identified as a partial causative agent to mussels on the basis of anecdotal information regarding its toxicity threshold. However, recently released saltwater aquatic life criteria (EPA, 2006) indicated the sample had a concentration (0.18 µg/L), which was well below the acute criterion of 7.0 µg/L, which suggests that nonylphenol likely was not the partial causative agent. This suggests that the additional cause of toxicity in the sample is still unknown.

Most mysid and topsmelt (or inland silversides) TIE baseline tests did not exhibit sufficient toxicity to perform a TIE. Four samples were evaluated for toxicity to mysids and two to topsmelt (Table 45). Two of the four mysid evaluations showed copper and or zinc as the primary toxicant of concern. The other two storm water samples collected from Naval Amphibious Base Coronado outfall 18 and at Naval Air Station North Island outfall 23A identified the surfactant MBAS as the likely causative agent. The data cited in the Nautilus TIE reports and from their own anecdotal experience suggest that MBAS surfactant levels above 1 mg/L frequently result in toxic responses. These levels were exceeded in the samples from Naval Amphibious Base Coronado outfall 18 (1.9 mg/L) and at Naval Air Station North Island outfall 23A (1.1 mg/L). The two samples that were toxic to topsmelt were also from collected from naval Amphibious Base Coronado outfall 18 and at Naval Air Station North Island outfall 23A. MBAS was identified as the likely causative agent of toxicity to topsmelt, but the analysis could not be completed nor confirmed because of the loss in sample integrity with time.

Fifty-one storm water outfall samples were collected and analyzed for chemistry. All of these samples were analyzed for total and dissolved copper and zinc, with 38 of these also run for a full suite of total and dissolved metals (this does not include metal scans performed as part of the TIEs). Organic compounds were run primarily on composite samples and chlorinated pesticides were not initially identified as CoCs, so this resulted in 37 PAH, 31 PCB, and 18 pesticide sample analyses. Analyses for surfactants were only conducted as part of the TIE analyses and were conducted only after non-polar organics were identified as causative agents. The storm water chemistry results indicated were highly variable, typical of industrial and urban storm water runoff (Burton, Pittt, and Clark, 2000; Burton and Pitt, 2002). Of the analytes measured, only copper and zinc (Figure 66 and Figure 67) were at concentrations consistently above acute WQS. One set of samples at Naval Air Station North Island also had two PAH analytes above an acute WQS. All other chemicals were measured at levels well below acute WQS or below levels known to cause acute toxicity as described earlier.

Because both copper and zinc were additive in their toxic effect, their concentration data were converted into acute toxic units (TU<sub>A</sub>) to assess their potential in explaining storm water toxicity. The TU<sub>A</sub> is a way to normalize the concentration data so that they can be placed on the same scale for comparison. TU<sub>A</sub> is calculated by dividing the dissolved metal concentration in the sample by the

average concentration of dissolved metal that causes a LC50 in reference toxicant tests conducted with the same metal. A  $TU_A$  of 1, therefore, suggests that the concentration of metal in the sample should be sufficient to cause a 50% reduction in survival. The average concentration of copper and zinc that causes a LC50 varies with species. Reference toxicant data collected during this study were used to determine a LC50 and to compute  $TU_A$  for each species. The average LC50 data from these reference tests are shown in Table 46.

Figure 68 and Figure 69 show the dose-response relationship between mysid and topsmelt survival with summed  $TU_A$  for copper and zinc. The plots are based on results for the samples containing 100% storm water only. Both plots showed a general decreasing trend in survival with increasing  $TU_A$ . The response to the combined copper and zinc dose explained about 40% ( $R^2$  of 0.4) of the variability in the data. These storm water data showed a slightly higher LC50 ( $TU_A > 1.0$ ) than was calculated for the average reference toxicant data, suggesting that storm water has a slightly reduced toxic potential than observed with laboratory water. This toxicity reduction likely occurred as a result of complexation reactions with the very high DOC (~11 mg/L) found in storm water (Rosen et al., 2005; Arnold, 2005). Though the relationship does not explain most of the variability, the combined chemicals had a stronger relationship with survival than either of the chemicals alone. None of the other chemicals showed a trend with the toxicity data.

Because of the high sensitivity of the mussel embryo-larval development test to copper and zinc, a similar dose-response plot comparing percent normal larval development with  $TU_A$ s was made using all the dilution series results rather than just the 100% storm water effluent sample. Copper and zinc concentrations in the 100% storm water sample were therefore adjusted by the amount of dilution used to produce the dilution series test concentrations. Figure 70 shows the results. The linear regression was generated only for  $TU_A$  values less than 6.2, as doses above this amount always resulted in 0% normal development. The response to the combined copper and zinc dose explained about half ( $R^2$  of 0.5) of the variability in the data. The combination of chemicals had a stronger relationship with survival than either of the chemicals alone. While these data are not the strongest dose-response relationships, none of the other chemicals showed any type of trend with the toxicity data.

A comparison of storm water chemistry data by facility showed the same relative trends as was observed for toxicity (Figure 62). The generalized order of  $NAB > NAV > SUB = NI$  that was observed for toxicity also was observed for average copper and zinc concentrations. This general trend was also seen in the organics data, even though there was no relationship between these compounds and toxicity.

In summary, the TIE and chemistry together identified copper and zinc as the primary toxicants of concern at all 10 drainage areas. Their concentrations were always above acute WQS and though individually they were not always high enough to be acutely toxic to topsmelt or mysids, they were nearly always high enough to be toxic to mussel larvae. The TIEs also identified surfactants as causative agents at three sites. While the sources of copper and zinc include some industrial activities and structural materials at these facilities, they are also derived from the ubiquitous sources that include atmospheric deposition and automobiles (Tsai, Hoenicke, Hansen, and Lee, 2000; CALTRANS, 2003; Sabine, Schiff, Lim, and Stolzenbach, 2004; Moran, 2004; Rosselot, 2005a; Rosselot 2005b). The ultimate source(s) of surfactants at these bases is not known, though they are commonly found in natural fats and oils, petroleum fractions, detergents, and some herbicides. Though the list of CoCs was based on likely contaminants to be found at these facilities, the list was not exhaustive. However, the TIEs would have identified any other contaminants causing toxicity that were not measured independently in the chemistry scans.

Table 45. Toxicity Identification Evaluation summary for first-flush storm water samples collected at each base. The table identifies the primary causative agents of toxicity to each species and endpoint for each sample.

Base	Outfall	Species/Endpoint		
		Mussel Embryo-Larval Development	Mysid Survival	Inland Silverside <sup>a</sup> or Topsmelt <sup>b</sup> Survival
NAV	9	Copper, zinc	Not toxic	Not toxic <sup>a</sup>
NAV	11	Copper, zinc	Not toxic	Not toxic <sup>a</sup>
NAV	14	Copper, zinc	Not toxic	Not toxic <sup>a</sup>
SUB	11B	Copper, surfactants	Not toxic	Not toxic <sup>a</sup>
SUB	23CE	Copper, zinc	Zinc	Not toxic <sup>a</sup>
SUB	26	Copper, zinc	Not toxic	Not toxic <sup>a</sup>
NAB	9	Copper, zinc	Copper, zinc	Not toxic <sup>b</sup>
NAB	18	Copper, zinc, surfactants	Surfactants	Surfactants <sup>b</sup>
NI	23A	Copper, zinc, surfactants	Surfactants	Surfactants <sup>b</sup>
NI	26	Not toxic	Not toxic	Not toxic <sup>b</sup>

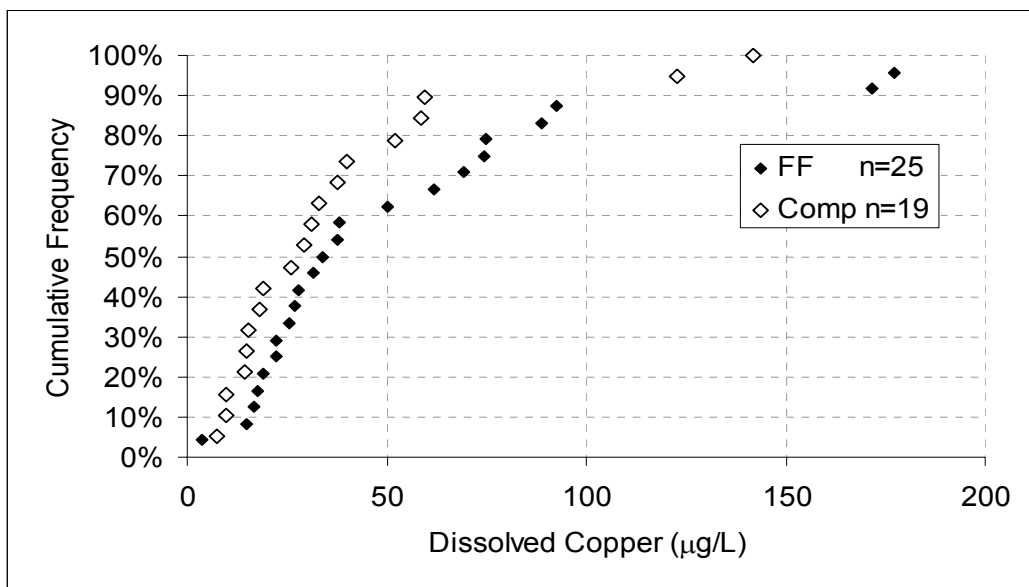


Figure 66. Cumulative frequency distribution plot of dissolved copper measured in all first-flush (FF) and composite (Comp) storm water samples.

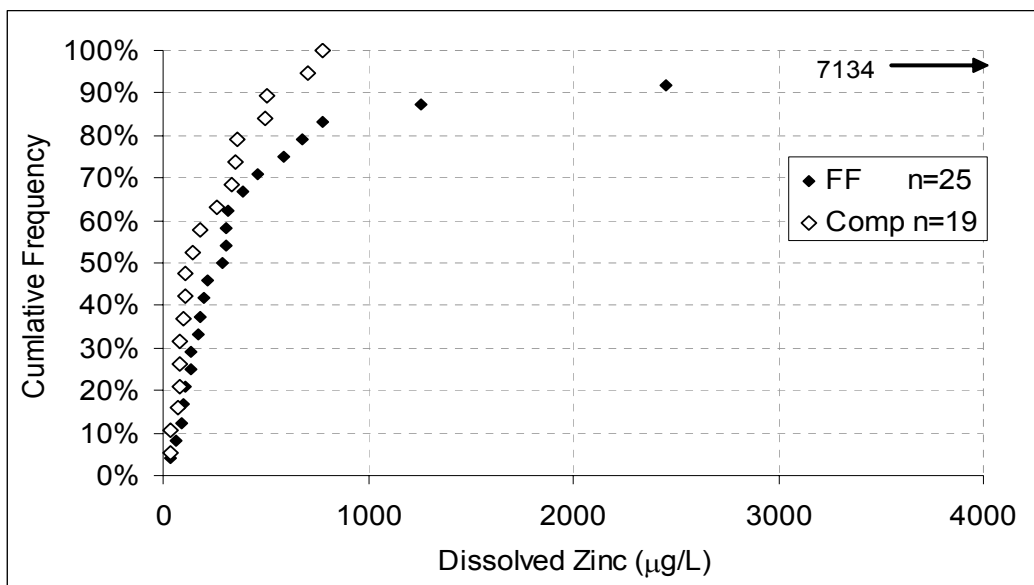


Figure 67. Cumulative frequency distribution plot of dissolved zinc measured in all first-flush (FF) and composite (Comp) storm water samples. One value was off-scale at 7134 µg/L.

Table 46. Average LC50/EC50 values from reference toxicant data collected during this study. These values were used to compute  $TU_A$ .

	Mysids	Topsmelt	Mussel Embryos
Dissolved Copper (µg/L)	233	163	9.6
Dissolved Zinc (µg/L)	647	880	160

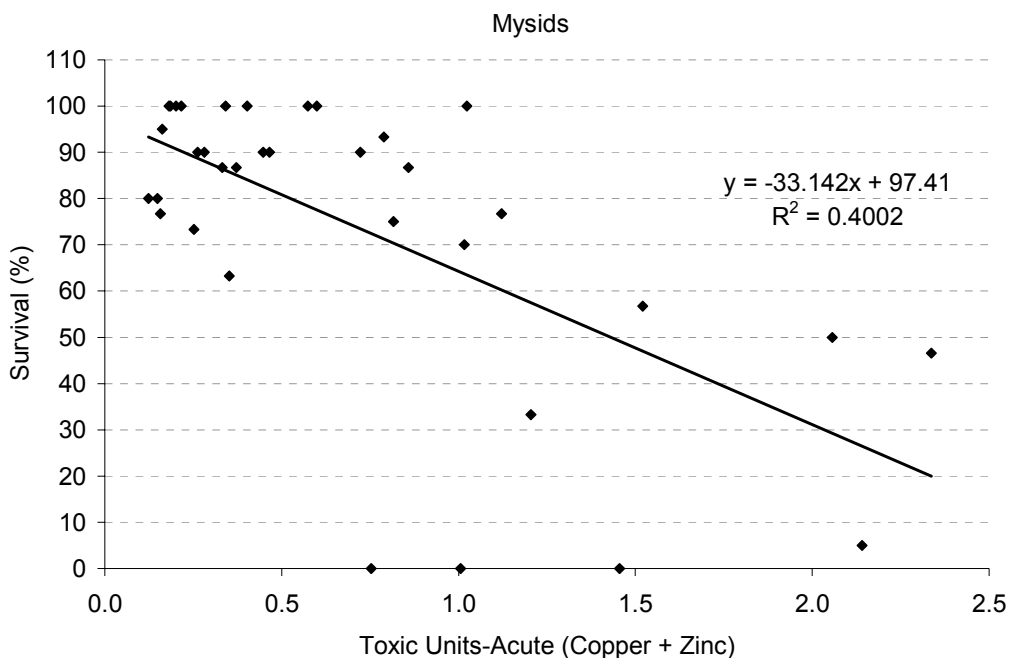


Figure 68. Mysid survival as a function of summed copper and zinc  $TU_A$ .

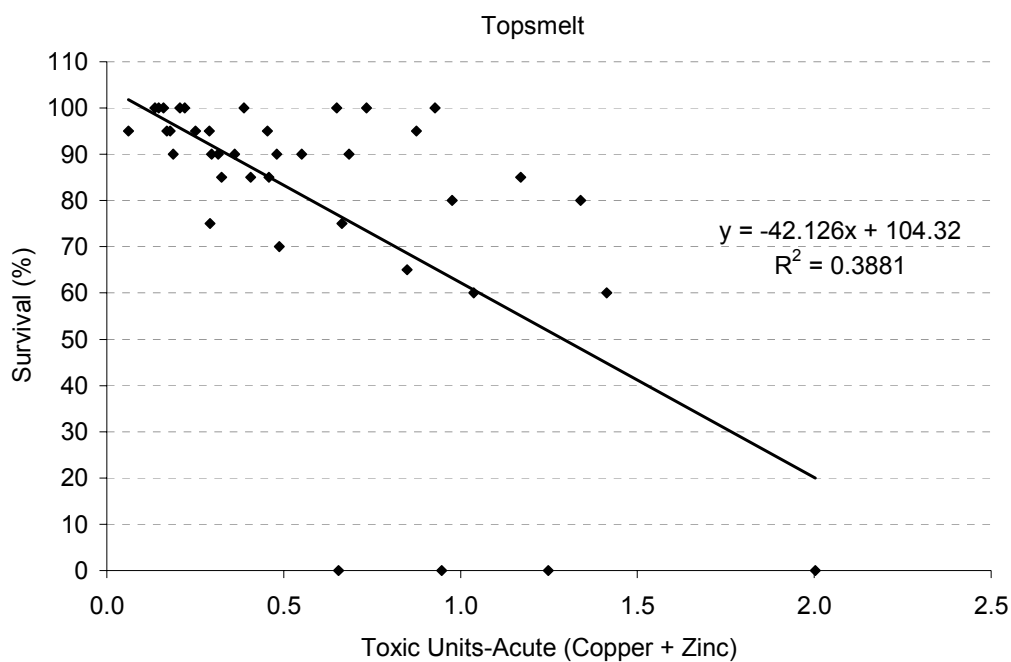


Figure 69. Topsmelt survival as a function of summed copper and zinc  $TU_A$ .

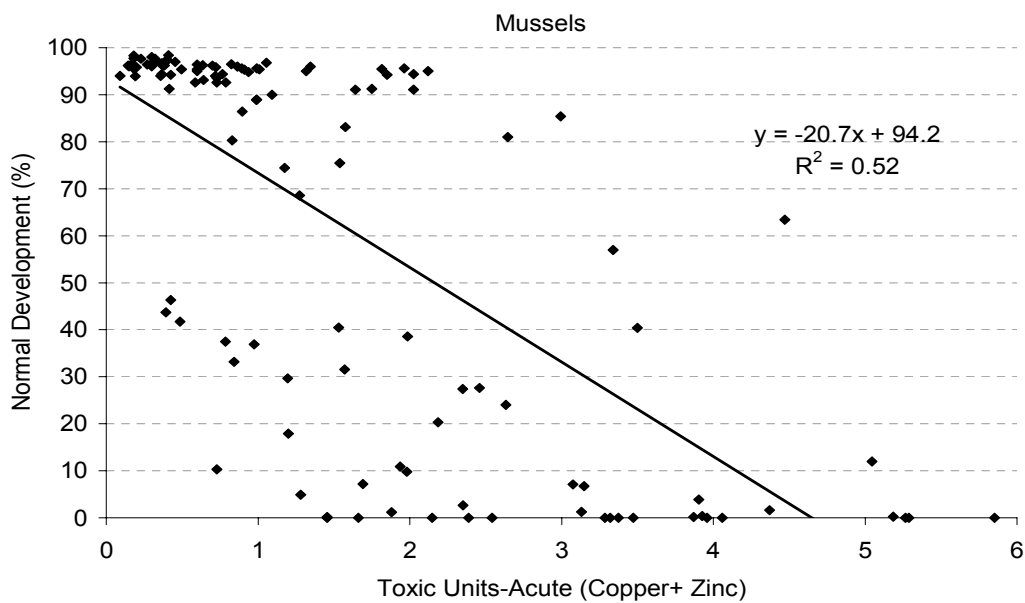


Figure 70. Normal mussel embryo-larval development as a function of summed copper and zinc  $TU_A$ . The regression was determined for data points with a  $TU_A < 6.2$ .



### 8.3 RECEIVING WATER IMPACTS

Receiving waters were evaluated for chemistry and toxicity to evaluate the magnitude of toxic response directly in the receiving water resulting from the storm water discharges. They were also evaluated for exposure conditions by mapping the spatial and temporal distribution of storm water plumes as they mixed with bay waters. These data, along with those collected on storm water, provide an ability to gauge the ability of the WET tests performed on undiluted storm water to predict impacts on receiving water quality for which they were designed.

During this study, a total of 202 individual toxicity bioassays were performed on 85 individual receiving water samples. This total includes bay water sampled before (27 samples) and during (35 samples) storm events at all locations. Sampling was also conducted after (23 samples) storm events mostly at Naval Station San Diego and Naval Submarine Base San Diego. One set of “after” samples was also collected outside one outfall at each base immediately after a storm event (SDB5). These samples captured a receiving water condition after it had rained ~6 inches during the previous 14 days, which is ~60% of normal annual rainfall, and thus represented a fairly extreme condition for accumulated sources. The vast majority (80%) of receiving water samples were collected within a few feet of the outfall discharge pipe, though as discussed previously, three stations sampled were further away from the discharge, up to 50 feet, as a result of obstructions or very shallow water when sampling by boat. There were also two stations, one at Naval Station San Diego (Bay 14A; see Figure 5) and Naval Submarine Base San Diego (26A; see Figure 10) that were purposefully sampled away from the shoreline to evaluate gradients in storm discharge.

None of the receiving water samples were toxic to topsmelt or mysids. Survival for these two species ranged from 90 to 100% and averaged 98% (Figure 71). Mussel embryo-larval normal development in receiving waters averaged 91%. Two of the mussel embryo-larval development tests showed significant toxicity (Figure 72). These two “during” samples were collected during the first-flush of the year storm event (SDB4) that had a record 183-day antecedent dry period, and thus represented an extreme discharge condition. The two samples were collected outside of Naval Station San Diego outfall 14 and Naval Amphibious Base Coronado outfall 9. Comparable receiving water samples collected outside of Naval Submarine Base San Diego outfall 11B and off Naval Air Station North Island outfall 23A during the same storm did not exhibit toxicity.

The receiving water samples from these two sites had the highest levels of copper (14 and 17 µg/L) and zinc (176 and 182 µg/L) measured in the study. These concentrations exceeded acute and chronic WQS. The associated first-flush storm water samples analyzed from the two sites also had the highest combination of copper (172 µg/L) and zinc (7134 µg/L) concentrations measured in the study. These levels were a factor of 5 to 30 times more than the average concentrations measured at those sites at all other times. Even at these high levels, the topsmelt and mysid survival data were not the lowest measured during the study. The storm water samples had dilution series NOEC values of <6.25% for mussels and 25% for topsmelt and mysids, the lowest NOEC values measured in the study. The mussel NOEC values suggest that only a small fraction of storm water was needed to cause an adverse impact in the receiving environment, a result related to the very high copper and zinc levels.

The storm water and receiving water samples collected from the other two bases (Naval Submarine Base San Diego outfall 11B and Naval Amphibious Base Coronado outfall 23A) during the first-flush of the year storm event were also the highest observed at those sites during the entire study. Receiving water dissolved copper concentrations at the two sites did exceed acute and chronic WQS, though dissolved zinc was below acute and chronic WQS. Dissolved copper in the receiving water was as high as 8 µg/L, without an associated toxic effect. The lack of toxicity at these copper

concentrations was consistent with recent data that show copper complexation with DOC as a mechanism for reducing potential toxicity (Rosen et al., 2005; Arnold, 2005). DOC levels measured in bay samples during this study as well as previously by Blake, Chadwick, Zirino, and Rivera-Durate (2004) and Rosen et al. (2005) generally ranged between 1 and 4 mg/L. These DOC concentrations should have been sufficient to effectively complex copper and reduce its toxic effect.

The fact that samples during this storm event contained the highest copper and zinc levels measured in the study at each of the four bases suggests that the historically long antecedent dry period was a major contributing factor.

Less than 1% of 202 toxicity tests conducted on receiving water samples in this study exhibited toxicity. The limited nature of the impact was primarily a result of low chemical exposure in the receiving water, but as described above, also included some level of metal complexation. The three components that characterize exposure conditions include magnitude, extent, and duration. The plume mapping surveys and the special floating bioassay study were used to characterize receiving water exposure under various discharge conditions.

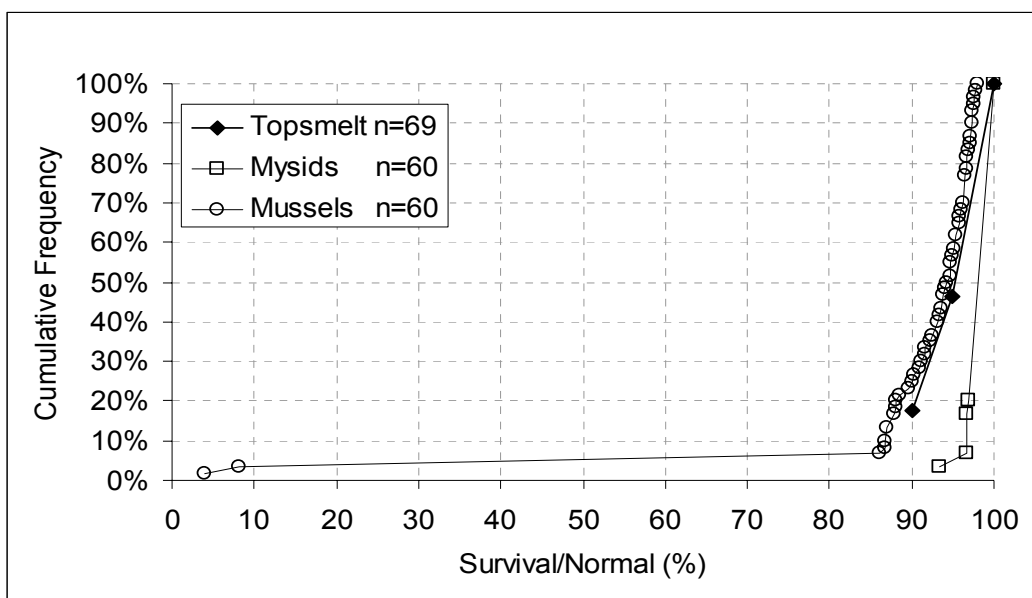


Figure 71. Topsmelt, mysid, and mussel bioassay results measured in receiving waters. The plot shows combined results for samples taken before, during, and after storm events. All results were for 100% receiving water.

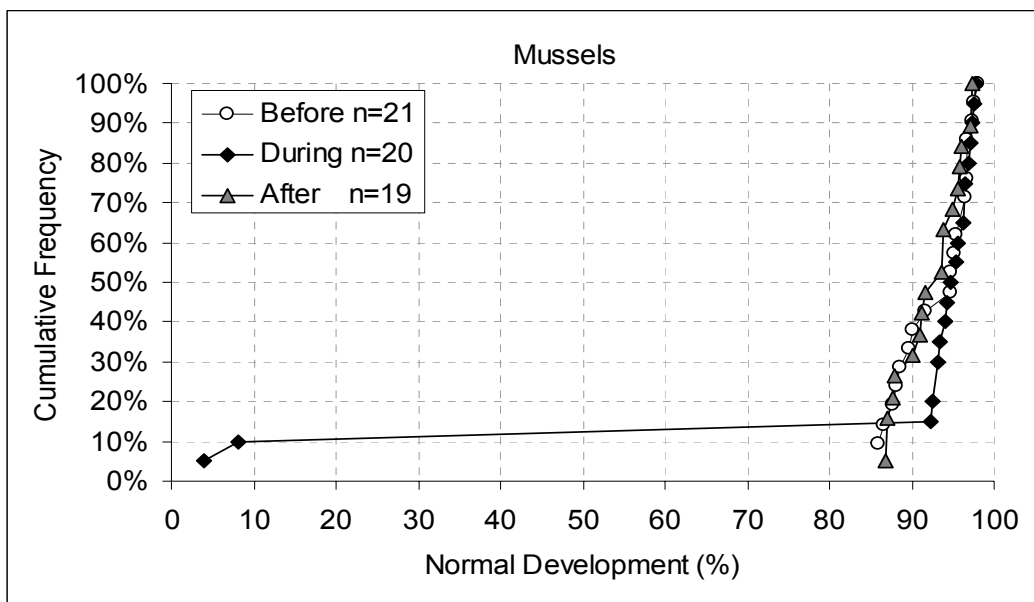


Figure 72. Mussel embryo-larval development results for receiving water samples collected before, during, and after storm water events. All results were for 100% receiving water. Two samples were significantly toxic.

The large scale mapping surveys consistently showed that storm water plumes were limited in their spatial extent, with maximum storm water signals mostly found immediately along the shoreline of each base, with a decreasing gradient that typically extended only as far as the pier heads. The plumes were also confined to the top two meters of the water column, a result of the discharges being made just above or just below the water surface, depending on tide height. The mapping data showed that plumes were highly transitory, showing changes with tide stage and relaxing back to pre-storm conditions relatively quickly, usually within 24 hours at all bases. The mapping surveys showed that exposure conditions in the receiving environment were minimal in their spatial extent, and were relatively short-lived.

The magnitude of the storm water signatures, as measured by salinity during the mapping surveys, were less than 14‰, with most typically around 5‰. The maximum storm water signatures were mostly found immediately along the shoreline and decreasing to levels of about 1‰ storm water or more out at the pier heads. A comparison of first-flush concentrations of copper and zinc with those measured in the receiving water showed that, on average, receiving water levels were reduced by a factor of 15 and 29, respectively. These calculate as a storm water fraction ranging from 3 to 6%. The salinity and chemistry data collected from the mapping surveys indicate that storm water from these facilities generated small magnitude discharges, even along the immediate shoreline.

The high-resolution monitoring conducted during the floating bioassay study showed that the magnitude of the exposure can be much larger, though considerably shorter lived than indicated by the large-scale mapping data. The salinity data during this special effort showed storm water fractions approaching 100% immediately at the point of discharge under the most intense rainfall conditions. However, these larger magnitude conditions were very short-lived, on the order of minutes to tens of minutes. Over the full 96-hour exposure period, the average storm water fraction was less than 4%. The maximum dissolved copper data measured during this survey (5.5 µg/L) exceeded its acute WQS of 4.8 µg/L, again for a time frame of tens of minutes. Again using the

reduction of copper and zinc levels measured in the first-flush storm water samples relative to the maximum levels measured in the receiving water, the maximum storm water fraction was between 4 and 20%. Like the average exposure computed using salinity, the chemistry data monitored over the full 96-hour monitoring period averaged between 4 and 6%.

In summary, storm water discharges to San Diego Bay resulted in less than 1% of 202 samples showing a toxic impact to one of the most sensitive toxicity endpoints available. The two receiving water samples that showed a toxic result were collected during the same storm event, one that represented a first-flush of the year after a historically long antecedent dry period. This exceptionally long dry condition resulted in extrema in copper and zinc levels at all four bases. At two of the bases, the amount of copper and zinc were high enough to result in receiving water concentrations above acute and chronic WQS and cause toxicity once storm water was mixed in the receiving environment. In these two cases, the associated first-flush storm water samples were toxic to topsmelt and mysids. In the other 200 cases, the data showed no receiving water toxicity, whether or not the first-flush sample was significantly toxic to topsmelt and mysids. The lack of relationship between the measurements of toxicity in first-flush samples with toxicity observed in the receiving environment was a result of limited receiving water exposure conditions. Both the mapping surveys and the special floating bioassay study clearly showed that storm water discharges from Navy facilities were limited in magnitude, minimal in their spatial extent, and very short-lived. Thus, toxicity measured in first-flush undiluted storm water overestimates the exposure conditions measured in the receiving water and thereby overestimates the potential for toxic impacts to receiving waters.



## 9. CONCLUSIONS

The goal of this study was to develop a robust dataset of storm water and receiving water toxicity that can be used to support a scientifically based acute toxicity threshold for storm water discharges from Navy facilities. The approach taken was to simultaneously measure toxicity and chemistry in storm water and receiving waters and to characterize receiving water conditions before, during, and after storm discharges. This approach allowed the magnitude and extent of storm water toxicity to be evaluated and directly related to the magnitude and extent of receiving water toxicity.

The study provided a robust high-quality dataset to evaluate industrial storm water toxicity from Navy facilities bordering San Diego Bay. The dataset was composed of 333 toxicity tests using topsmelt and mysid survival and mussel-embryo-larval development as endpoints. It included the analysis of total and dissolved metals, PAH, PCB, and chlorinated pesticides on 136 discrete storm water and receiving water samples. It also included 17 plume mapping surveys conducted before, during, and after storm events around each base as well as a special floating bioassay study to assess exposure conditions in the receiving environment. The study dataset represents the largest and most comprehensive evaluation of storm water toxicity and impacts of marine waters to date.

The study captured nearly, if not the full range, of rainfall and discharge conditions likely to occur from these facilities. The study captured discharges during drought conditions, during near-record wet conditions, and included measurements during record rainfall event and a record antecedent dry period. The drainage areas monitored had a wide range in size (0.5 to 75 acres) and contained a various industrial activities, most of which are similar at each base. Thus the study effectively characterized the bounds of variability inherent in storm water discharges.

The study established that acute storm water toxicity was highly variable, spanning the full range of impact, from 0 to 100% survival of topsmelt and mysids. This variability was likely tied to variability in contaminant levels, though the relationship between chemistry and toxicity was not very strong. The toxicity of first-flush storm water samples, representing the discharge at one moment in time, was higher than in composite samples that were representative of the entire discharge. The 90% survival requirement in the NPDES permit failed for 58% of first-flush samples and for 25% of composite samples. However, the permit requirement did not accurately identify when samples were acutely toxic or not. When using a science-based approach to WET test methods and statistical data evaluation, including t-testing and consideration of method variability, toxicity of first-flush storm water would have been declared toxic 30% (cf. 58%) of the time while composite samples would have been identified as toxic 7% (cf. 25%) of the time.

The toxicity identification evaluation and chemistry data together identified copper and zinc as the primary toxicants of concern at all 10 drainage areas evaluated. Their concentrations were always above acute WQS, and though individually they were not always high enough to be acutely toxic to either topsmelt or mysids, they were nearly always high enough to be toxic to mussel larvae. The TIEs also identified surfactants as causative agents at three sites. Though not every possible contaminant was measured directly in the study, the TIEs would have identified any other contaminants causing toxicity that were not measured independently in the chemistry scans.

Less than 1% of 202 receiving water toxicity tests exhibited toxicity. This toxicity was observed only to one of the most sensitive toxicity endpoints available. The two receiving water samples that showed a toxic result were collected during the same storm event, one that represented a first-flush of the year after a historically long antecedent dry period. In the other 200 cases, the data showed no receiving water toxicity, whether or not the associated first-flush samples were significantly toxic

to topsmelt and mysids. The lack of relationship between the measurements of toxicity in first-flush samples with toxicity observed in the receiving environment was a result of limited receiving water exposure conditions. The mapping surveys and the special floating bioassay study clearly showed that storm water discharges from Navy facilities were limited in magnitude, minimal in their spatial extent, and very short-lived. Thus, toxicity measured in first-flush undiluted storm water overestimates the exposure conditions measured in the receiving water and thereby overestimates the potential for toxic impacts.

In summary, this study provides one of the most extensive datasets on storm water runoff ever conducted, effectively characterizing the bounds of variability inherent in these types of discharges and their impacts to receiving water quality. Using multiple lines of evidence, the data showed that first-flush storm water can be acutely toxic, primarily as a result of copper and zinc concentrations in the discharge. The data also showed that the total storm discharge, represented by composite samples, was generally less toxic and had lower contaminant concentrations. Most importantly, there was no relationship between toxicity measured in storm water (end-of-pipe) and toxicity measured in the receiving water. These results show that WET testing on storm water as required in the permit cannot be used to infer toxicity in the receiving environment.

This study was conducted to support a scientifically based acute toxicity threshold for storm water discharges. To ensure that an acute toxicity threshold for storm water discharges will accurately identify and be protective of water quality impacts in the receiving environment, the proposed Navy alternative toxicity threshold should include the following:

- The use of appropriate WET test methods and data evaluation when declaring a test result as toxic
- Acknowledgment of WET method variability and the minimum significant difference that laboratory testing can provide in declaring a toxic result
- Consideration of realistic exposure conditions when using WET test to infer toxicity in the receiving water

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**SPAWAR**  
***Systems Center***  
***San Diego***

## APPENDICES for

Storm Water Toxicity Evaluation Conducted at  
Naval Station San Diego, Naval Submarine Base San Diego,  
Naval Amphibious Base Coronado,  
and Naval Air Station North Island

## FINAL REPORT

May 2006

Prepared for Commander Navy Region Southwest

by

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**Appendix A**

**Sampling Summary Table**

## **Sample ID Naming Convention:**

Base-Location-Storm Event-Sample Type

### **Bases:**

NAV-Naval Station San Diego  
SUB-Submarine Base San Diego  
NAB-Naval Amphibious Base Coronado  
NI-Naval Naval Air Station North Island

### **Locations:**

OF-outfall storm water  
PR-pier storm water  
Bay-bay receiving water

### **Storm Sampling Event:**

SDB1...SDB7, TIE etc.

### **Sample Type:**

FF-first-flush storm water  
COMP-composite storm water  
PRE-pre-storm receiving water  
DUR-during storm receiving water  
AFT-after storm receiving water

### **Examples:**

NAV-OF9-SDB1-FF:

Naval Station San Diego-Outfall 9-Storm 1-First-flush

SUB-BAY11B-SDB4-AFT:

Submarine Base San Diego-bay water outside outfall 11B-Storm 4-After

# NAV

## Naval Station San Diego

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
11/7/2002	NAV	SDB1	OF 9	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	OF 11	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	OF 14	COMP	X	X	X	X	X		X	X		
	NAV	SDB1	Bay	PRE				X			X			
	NAV	SDB1	Bay 9	PRE	X	X	X		X					
	NAV	SDB1	Bay 9	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 9	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 11	PRE	X	X	X		X					
	NAV	SDB1	Bay 11	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 11	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 14	PRE	X	X	X		X					
	NAV	SDB1	Bay 14	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 14	AFT	X	X	X	X	X		X			
	NAV	SDB1	Bay 14A	PRE	X	X	X		X					
	NAV	SDB1	Bay 14A	DUR	X	X	X	X	X		X			
	NAV	SDB1	Bay 14A	AFT	X	X	X	X	X		X			
2/24/2003	NAV	SDB2	PR 5	FF	X	X	X	X	-		X	X		
	NAV	SDB2	PR 5	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	PR 6	FF	X	X	X	X	-		X	X		
	NAV	SDB2	PR 6	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 9	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 9	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 11	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 11	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	OF 14	FF	X	X	X	X	-		X	X		
	NAV	SDB2	OF 14	COMP	X	X	X	X	-		X	X		
	NAV	SDB2	Bay 9	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 9	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 9	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 11	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 14	AFT	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	PRE	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	DUR	X	X	X	X	-		X			
	NAV	SDB2	Bay 14A	AFT	X	X	X	X	-		X			
2/18/2004	NAV	TIE1	OF 9	FF	X	X	X	T						
	NAV	TIE1	OF 11	FF	X	X	X	T						
	NAV	TIE1	OF 14	FF	X	X	X	T						
10/17/2004	NAV	SDB4	OF 14	FF	X	X	X		X					X
	ALL+	SDB4	Bay	PRE	X	X	X		X					X
	NAV	SDB4	Bay 14	DUR	X	X	X		X					X
10/26/2004	NAV	SDB45	OF 14	FF	X	X	X	X	X	X	X	X	X	
	NAV	SDB45	OF 14	COMP		X	X	X	X	X	X	X	X	
	NAV	SDB45	Bay 14	PRE	X	X	X		X	X				X
	NAV	SDB45	Bay 14	DUR1*	X	X	X		X	X				X
	NAV	SDB45	Bay 14	DUR2					X	X				X
	NAV	SDB45	Bay 14	DUR3					X	X				X
	NAV	SDB45	Bay 14	DUR4					X	X				X
	NAV	SDB45	Bay 14	AFT1					X	X				X
	NAV	SDB45	Bay 14	AFT2					X	X				X
	NAV	SDB45	Bay 14	AFT3					X	X				X
1/10/2005	NAV	SDB5	Bay 14	AFT	X	X	X							

+ Collected at SSC-SD

\* *in situ* toxicity

- Lost

T Analyzed by toxicity lab

# SUB

## Submarine Base San Diego

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
2/24/2003	SUB	SDB2	OF 11B	FF	X	X	X	X	-		X	X		
	SUB	SDB2	OF 24	FF	X	X	X	X	-		X	X		
	SUB	SDB2	OF 26	FF	X	X	X	X	-		X	X		
	SUB	SDB2	Bay 11B	PRE	X	X	X	X	-		X			
	SUB	SDB2	Bay 11B	DUR	X	X	X	X	-		X			
	SUB	SDB2	Bay 24	DUR	X	X	X	X	-		X			
	SUB	SDB2	Bay 26	DUR	X	X	X	X	-		X			
12/11/2003	SUB	SDB2A	Bay 11B	PRE	X	X	X							
	SUB	SDB2A	Bay 23CE	PRE	X	X	X							
	SUB	SDB2A	Bay 26	PRE	X	X	X							
2/2/2004	SUB	SDB3	OF 11B	FF	X	X			X	X	X			X
	SUB	SDB3	OF 11B	COMP	X	X	X	X	X	X	X	X	X	
	SUB	SDB3	OF 23 C&E	FF	X	X	X		X	X	X			X
	SUB	SDB3	OF 23 C&E	COMP	X	X	X	X	X	X	X	X	X	
	SUB	SDB3	OF 26	FF	X	X	X		X	X	X			X
	SUB	SDB3	OF 26	COMP	X	X		X	X	X	X	X	X	X
	SUB	SDB3	Bay 11B	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 11B	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 11B	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 23 C&E	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26	AFT	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	PRE	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	DUR	X	X	X		X	X	X			X
	SUB	SDB3	Bay 26A	AFT	X	X	X		X	X	X			X
2/18/2004	SUB	TIE1	OF 11B	FF	X	X	X	T						
	SUB	TIE1	OF 23 C&E	FF	X	X	X	T						
	SUB	TIE1	OF 26	FF	X	X	X	T						
2/26/2004	SUB	TIE1A	Bay 11B	AFT			X							
	SUB	TIE1A	Bay 23 C&E	AFT			X							
	SUB	TIE1A	Bay 26	AFT			X							
10/17/2004	SUB	SDB4	OF 11B	FF	X	X	X		X					X
	SUB	SDB4	Bay 11B	DUR	X	X	X		X					X
1/10/2005	SUB	SDB5	Bay 11B	AFT	X		X							

T Analyzed by toxicity lab

# NAB

## Naval Amphibious Base Coronado

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
10/17/2004	NAB	SDB4	OF 9	FF	X	X	X		X					X
	NAB	SDB4	Bay 9	DUR	X	X	X		X					X
1/10/2005	NAB	SDB5	Bay 9	AFT	X	X	X							
2/10/2005	NAB	SDB6	OF 9	FF	X	X	X		X	X	X	X	X	X
	NAB	SDB6	OF 9	COMP	X	X	X	X	X	X	X	X	X	
	NAB	SDB6	OF18	FF	X	X	X		X	X	X	X	X	X
	NAB	SDB6	OF 18	COMP				X	X	X	X	X	X	
	NAB	SDB6	Bay 9	PRE	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 9	DUR	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 18	PRE	X	X	X		X	X	X	X	X	X
	NAB	SDB6	Bay 18	DUR	X	X	X		X	X	X	X	X	X
3/19/2005	NAB	TIE2	OF 9	FF	X	X	X	T						
	NAB	TIE2	OF 18	FF	X	X	X	T						
	NAB	TIE2	Bay 9	DUR	X	X	X							
	NAB	TIE2	Bay 18	DUR	X	X	X							
4/27/2005	NAB	SDB7	OF 9	FF	X				X	X	X			X
	NAB	SDB7	OF 9	COMP	X			X	X	X	X	X	X	
	NAB	SDB7	OF 18	FF	X				X	X	X			X
	NAB	SDB7	OF 18	COMP	X			X	X	X	X	X	X	
	NAB	SDB7	Bay 9	PRE	X		X		X	X	X			X
	NAB	SDB7	Bay 9	DUR	X		X		X	X	X			X
	NAB	SDB7	Bay 18	PRE	X		X		X	X	X			X
	NAB	SDB7	Bay 18	DUR	X		X		X	X	X			X

T Analyzed by toxicity lab

# NI

## Naval Air Station North Island

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
10/17/2004	NI	SDB4	OF 23A	FF	X	X	X		X					X
	NI	SDB4	Bay 23A	DUR	X	X	X		X					X
1/10/2005	NI	SDB5	BAY 23A	AFT			X							
2/10/2005	NI	SDB6	OF 23A	FF	X	X	X		X	X	X	X	X	
	NI	SDB6	OF 26	FF	X	X	X		X	X	X	X	X	X
	NI	SDB6	OF 26	COMP	X	X	X	X	X	X	X	X	X	
	NI	SDB6	BAY 23A	PRE	X	X	X		X	X	X	X	X	X
	NI	SDB6	BAY 23A	DUR	X	X	X		X	X	X	X	X	X
	NI	SDB6	Bay 26	PRE	X	X	X		X	X	X	X	X	X
	NI	SDB6	Bay 26	DUR	X	X	X		X	X	X	X	X	X
3/19/2005	NI	TIE2	OF 23A	FF	X	X	X	T						
	NI	TIE2	OF 26	FF	X	X	X	T						
	NI	TIE2	Bay 23A	DUR	X	X	X							
	NI	TIE2	Bay 26	DUR	X	X	X							
4/27/2005	NI	SDB7	OF 23A	FF	X			X	X	X	X	X	X	
	NI	SDB7	OF 26	FF	X				X	X	X			X
	NI	SDB7	OF 26	COMP	X			X	X	X	X	X	X	
	NI	SDB7	BAY 23A	PRE	X		X		X	X	X			X
	NI	SDB7	BAY 23A	DUR	X		X		X	X	X			X
	NI	SDB7	Bay 26	PRE	X		X		X	X				X
	NI	SDB7	Bay 26	DUR	X		X		X	X	X			X

T Analyzed by toxicity lab

# Other

## Downtown Piers

Sample Dates	Base	Storm	Outfall	Sample Type	Topsmelt	Mysid	Mussel	Metals	TSS	DOC	PAH	PCB	Pest	Cu/Zn
1/10/2005	NA	SDB5	DOWNTOWN PIER	AFT	X	X	X							

## **Appendix B**

### **Toxicity Data Summary Tables**

FOR ALL TABLES “-“ means No Data.

# NAV

## OUTFALLS

### TOPSMELT (*A. affinis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
Nautilus	2/24/2003	NAV	SDB2	OF11 FF	23.30	10.0	50.0	41.71	-	-	10.53	95	0
Nautilus	2/24/2003	NAV	SDB2	PR5 FF	19.68	10.0	50.0	49.46	-	-	10.53	95	0
Nautilus	2/24/2003	NAV	SDB2	PR6 FF	30.92	50.0	100.0	>100	31.12	70.33	10.53	95	60
Nautilus	2/24/2003	NAV	SDB2	OF14 FF	31.94	100.0	>100	>100	13.44	>100	12.83	90	70
Nautilus	2/24/2003	NAV	SDB2	OF9 FF	15.44	100.0	>100	>100	16.00	>100	0.00	100	85
Nautilus <sup>a</sup>	2/18/2004	NAV	TIE1	OF9 FF	7.00	100.0	>100	>100	>100	>100	0.00	100	96
Nautilus <sup>a</sup>	2/18/2004	NAV	TIE1	OF11 FF	7.00	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus <sup>a</sup>	2/18/2004	NAV	TIE1	OF14 FF	5.00	100.0	>100	>100	>100	>100	0.00	100	100
SSC - SD	10/17/2004	NAV	SDB4	OF14 FF	19.80	50.0	100.0	73.88	42.64	55.33	0.00	100	25
SSC - SD	10/26/2004	NAV	SD45	OF14 FF	7.89	100.0	>100	>100	>100	>100	0.00	100	90
SSC - SD	11/7/2002	NAV	SDB1	OF9 Comp.	13.68	50.0	>50	>50	-	-	11.21	90	N/A
SSC - SD	11/7/2002	NAV	SDB1	OF11 Comp.	8.98	100.0	>100	>100	-	-	0.00	100	100
SSC - SD	11/7/2002	NAV	SDB1	OF14 Comp.	10.16	100.0	>100	>100	>100	>100	9.26	95	100
Nautilus	2/24/2003	NAV	SDB2	OF9 Comp	15.71	100.0	>100	>100	>100	>100	0.00	100	90
Nautilus	2/24/2003	NAV	SDB2	OF11 Comp	15.70	100.0	>100	>100	>100	>100	0.00	100	90
Nautilus	2/24/2003	NAV	SDB2	OF14 Comp	18.24	100.0	>100	>100	>100	>100	12.83	90	95
Nautilus	2/24/2003	NAV	SDB2	PR5 Comp	19.72	100.0	>100	>100	-	-	10.53	95	95
Nautilus	2/24/2003	NAV	SDB2	PR6 Comp	19.04	100.0	>100	>100	73.80	>100	10.53	95	75

<sup>a</sup>Testing conducted with inland silversides (*Menidia beryllina*) due to unavailability of topsmelt

### MYSIDS (*A. bahia*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
Nautilus	2/24/2003	NAV	SDB2	OF11 FF	-	-	-	30.0	14.0	20.0	0.00	100	0
Nautilus	2/24/2003	NAV	SDB2	PR5 FF	5.97	-	-	22.4	3.6	9.1	0.00	100	0
Nautilus	2/24/2003	NAV	SDB2	PR6 FF	11.50	50.0	100.0	84.0	50.0	63.9	0.00	100	33.3
Nautilus	2/24/2003	NAV	SDB2	OF9 FF	8.58	100.0	>100	>100	89.0	>100	0.00	100	90
Nautilus	2/24/2003	NAV	SDB2	OF14 FF	8.38	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/18/2004	NAV	TIE1	OF9 FF	5.00	100.0	>100	>100	>100	>100	8.60	95	90
Nautilus	2/18/2004	NAV	TIE1	OF11 FF	5.00	50.0	100.0	>100	80.00	>100	8.60	95	85
Nautilus	2/18/2004	NAV	TIE1	OF14 FF	10.00	100.0	>100	>100	75.00	>100	8.60	95	85
SSC - SD	10/17/2004	NAV	SDB4	OF14 FF	9.25	25	50	98.5	36.8	58.6	0.00	100	43.3
SSC - SD	10/26/2004	NAV	SD45	OF14 FF	4.20	50	100	>100	51.5	91.1	0.00	100	63.3
Nautilus	2/24/2003	NAV	SDB2	OF9 Comp	-	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/24/2003	NAV	SDB2	OF11 Comp	3.79	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/24/2003	NAV	SDB2	OF14 Comp	-	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/24/2003	NAV	SDB2	PR5 Comp	3.79	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/24/2003	NAV	SDB2	PR6 Comp	8.57	100.0	>100	>100	98.5	>100	0.00	100	90
SSC - SD	11/7/2002	NAV	SDB1	OF14 Comp	12.33	100.0	>100	>100	>100	>100	5.97	96.7	93.3
SSC - SD	11/7/2002	NAV	SDB1	OF11 Comp	3.09	100.0	>100	>100	>100	>100	0.00	100	100
SSC - SD	11/7/2002	NAV	SDB1	OF9 Comp	15.12	50.0	>50	>50	>50	>50	0.00	100	N/A
SSC - SD	10/26/2004	NAV	SD45	OF14 Comp	11.30	-	-	-	-	-	0.00	100	80



Mussel (*M. galloprovincialis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Dev	%Devel in 100%
Nautilus	2/24/2003	NAV	SDB2	OF9 FF	2.81	10.0	50.0	55.84	51.29	53.39	3.76	96.4	27.4
Nautilus	2/24/2003	NAV	SDB2	OF11 FF	5.82	10.0	50.0	51.55	50.09	50.78	2.59	95.4	0
Nautilus	2/24/2003	NAV	SDB2	OF14 FF	-	50.0	58.0	56.22	52.39	54.17	2.76	96.6	27.6
Nautilus	2/24/2003	NAV	SDB2	PR5 FF	10.26	10.0	50.0	25.10	-	-	6.72	88.6	0
Nautilus	2/24/2003	NAV	SDB2	PR6 FF	7.55	-	-	22.36	-	-	6.72	88.6	0
Nautilus	2/18/2004	NAV	TIE1	OF9 FF	22.00	25.0	50.0	38.43	27.69	31.72	4.13	81	0
Nautilus	2/18/2004	NAV	TIE1	OF11 FF	25.00	25.0	50.0	34.16	27.50	30.48	4.13	81	0
Nautilus	2/18/2004	NAV	TIE1	OF14 FF	15.00	25.0	50.0	27.43	23.56	25.32	4.13	81	0
SSC - SD	10/17/2004	NAV	SDB4	OF14 FF	6.40	<6.25	6.3	8.0	4.9	6.2	2.07	97.5	0
SSC - SD	10/26/2004	NAV	SD45	OF14 FF	-	25.0	50.0	49.1	43.4	46.0	4.17	92.6	1.2
Nautilus	2/24/2003	NAV	SDB2	OF14 Comp	2.93	65.0	>65	>65	>65	>65	2.75	96.6	94.8
Nautilus	2/24/2003	NAV	SDB2	OF9 Comp	-	61.0	>61	>61	>61	>61	-	96.4	96.8
Nautilus	2/24/2003	NAV	SDB2	PR6 Comp	3.84	50.0	58.0	53.5	51.5	52.4	-	96.6	0.4
Nautilus	2/24/2003	NAV	SDB2	PR5 Comp	-	50.0	58.0	56.8	-	-	-	88.6	38.6
Nautilus	2/24/2003	NAV	SDB2	OF11 Comp	4.05	65.0	>65	>65	>65	>65	-	95.4	91.2
SSC - SD	10/26/2004	NAV	SD45	OF14 Comp	4.06	50	61.4	>61.4	>61.4	>61.4	4.2	92.6	86.40

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC - SD	11/7/2002	NAV	SDB1	Bay 9	None	100.0	95.0	100.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 11	None	100.0	95.0	95.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 14	None	95.0	100.0	95.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 14A	None	100.0	100.0	95.0
Nautilus	2/24/2003	NAV	SDB2	Bay 11	None	95.0	90.0	95.0
Nautilus	2/24/2003	NAV	SDB2	Bay 14	None	90.0	90.0	90.0
Nautilus	2/24/2003	NAV	SDB2	Bay 9	None	100.0	95.0	90.0
Nautilus	2/24/2003	NAV	SDB2	Bay 14A	None	95.0	90.0	100.0
SSC - SD	10/17/2004	ALL/NAV	SDB4	Bay 14	None	100.0	100.0	-
SSC - SD	10/26/2004	NAV	SD45	Bay 14	None	100.0	-	-
SSC - SD	1/10/2005	NAV	SDB5	Bay 14	None	-	-	100.0

### MYSIDS (*A. bahia*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC - SD	11/7/2002	NAV	SDB1	Bay 9	None	96.6	100.0	100.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 11	None	100.0	100.0	100.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 14A	None	100.0	100.0	100.0
SSC - SD	11/7/2002	NAV	SDB1	Bay 14	None	100.0	96.6	100.0
Nautilus	2/24/2003	NAV	SDB2	Bay 9	None	100.0	100.0	100.0
Nautilus	2/24/2003	NAV	SDB2	Bay 11	None	100.0	100.0	100.0
Nautilus	2/24/2003	NAV	SDB2	Bay 14	None	100.0	100.0	100.0
Nautilus	2/24/2003	NAV	SDB2	Bay 14A	None	100.0	100.0	97.0
SSC - SD	10/17/2004	ALL/NAV	SDB4	Bay 14	None	100.0	100.0	-
SSC - SD	10/26/2004	NAV	SD45	Bay 14	None	100.0	-	-
SSC - SD	1/10/2005	NAV	SDB5	Bay 14	None	-	-	100.0

### MUSSELS (*M. galloprovincialis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Normal Development		
						PRE	DUR	AFT
Nautilus	2/28/2003	NAV	SDB2	Bay 9	None	96.4	93.4	97.4
Nautilus	2/28/2003	NAV	SDB2	Bay 11	None	95.4	96.2	97.4
Nautilus	2/28/2003	NAV	SDB2	Bay 14	None	96.6	96.4	97.2
Nautilus	2/28/2003	NAV	SDB2	Bay 14A	None	88.6	92.6	91.2
SSC-SD	10/17/2005	ALL/NAV	SDB4	Bay 14	Dur	96.8	8.2	-
SSC-SD	10/26/2005	NAV	SDB45	Bay 14	None	92.6	-	-
SSC-SD	1/10/2005	NAV	SDB5	Bay 14	None	-	-	94.9

Note: "ALL"- Pre-sample was taken off SSC-SD pier 159 and used as control for all four bases.

# SUB

## OUTFALLS

### TOPSMELT (*A. affinis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
Nautilus	2/24/2003	SUB	SDB2	OF11B FF	21.29	100.0	>100	>100	95.0	>100	10.53	90	85
Nautilus	2/24/2003	SUB	SDB2	OF24 FF	18.68	100.0	>100	>100	80.0	>100	12.83	90	75
Nautilus	2/24/2003	SUB	SDB2	OF26 FF	23.89	100.0	>100	>100	>100	>100	12.83	90	90
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E FF	9.19	100.0	>100	>100	>100	>100	0.00	100	95
SSC - SD	2/2/2004	SUB	SDB3	OF26 FF	18.49	100.0	>100	>100	>100	>100	22.22	90	95
SSC - SD	2/2/2004	SUB	SDB3	OF11B FF	11.02	100.0	>100	>100	>100	>100	10.53	95	100
Nautilus	2/18/2004	SUB	TIE1	OF11B FF	6.00	100.0	>100	>100	>100	>100	0.00	100	96
Nautilus	2/18/2004	SUB	TIE1	OF23 C&E FF	7.00	100.0	>100	>100	87.50	>100	0.00	100	88
Nautilus	2/18/2004	SUB	TIE1	OF26 FF	6.00	100.0	>100	>100	>100	>100	0.00	100	96
SSC - SD	10/17/2004	SUB	SDB4	OF11B FF	13.74	100.0	>100	>100	50	>100	0.00	100	85
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E Comp.	5.67	50.0	100.0	>100	>100	>100	0.00	100	90
SSC - SD	2/2/2004	SUB	SDB3	OF26 Comp.	25.82	100.0	>100	>100	>100	>100	22.22	90	85
SSC - SD	2/2/2004	SUB	SDB3	OF11B Comp.	5.90	100.0	>100	>100	>100	>100	10.53	100	100

### MYSIDS (*A. bahia*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
Nautilus	2/24/2003	SUB	SBD2	OF11B FF	12.13	100.0	>100	>100	84.9	>100	0.00	100	86.7
Nautilus	2/24/2003	SUB	SBD2	OF24 FF	-	100.0	>100	>100	>100	>100	0.00	100	100
Nautilus	2/24/2003	SUB	SBD2	OF26 FF	-	100.0	>100	>100	>100	>100	0.00	100	100
SSC - SD	2/2/2004	SUB	SDB3	OF11B FF	4.32	50.0	100.0	>100	71.54	>100	0.00	100	76.7
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E FF	7.46	50.0	100.0	>100	69.17	>100	5.97	96.7	76.7
SSC - SD	2/2/2004	SUB	SDB3	OF26 FF	13.04	100.0	>100	>100	>100	>100	0.00	100	90
Nautilus	2/18/2004	SUB	TIE1	OF11B FF	8.00	100.0	>100	>100	86.88	>100	9.00	95	85
Nautilus	2/18/2004	SUB	TIE1	OF23 C&E FF	11.00	50.0	100.0	>100	56.33	75.83	8.60	95	55
Nautilus	2/18/2004	SUB	TIE1	OF26 FF	7.00	100.0	>100	>100	98.33	>100	8.60	95	88
SSC - SD	10/17/2004	SUB	SDB4	OF11B FF	8.20	25	50	93.7	28.7	50.2	0.00	100	46.6
SSC - SD	2/2/2004	SUB	SDB3	OF11B Comp.	9.96	50.0	100.0	>100	57.19	>100	0.00	100	80
SSC - SD	2/2/2004	SUB	SDB3	OF26 Comp.	9.27	50.0	100.0	>100	67.49	92.34	0.00	100	70
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E Comp.	12.11	100.0	>100	>100	>100	>100	5.97	96.7	86.7

### MUSSELS (*M. galloprovincialis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Dev	%Devel in 100%
Nautilus	2/24/2003	SUB	SDB2	OF11B FF	9.18	50.0	58.0	53.9	-	-	-	86	0
Nautilus	2/24/2003	SUB	SDB2	OF24 FF	12.79	10.0	50.0	41.40	-	-	8.39	86	0.2
Nautilus	2/24/2003	SUB	SDB2	OF26 FF	12.09	10.0	50.0	33.01	-	-	8.39	86	0
SSC - SD	2/2/2004	SUB	SDB3	OF11B FF	8.49	33.0	66.0	47.50	36.82	41.54	3.17	94.8	4.4
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E FF	17.49	16.5	33.0	24.64	-	-	5.54	87.7	0
SSC - SD	2/2/2004	SUB	SDB3	OF26 FF	7.73	16.5	33.0	40.33	28.82	33.79	9.16	96.6	2.7
SSC - SD	10/17/2004	SUB	SDB4	OF11B FF	-	<6.25	6.3	9.8	6.2	7.7	2.07	97.5	0
Nautilus	2/18/2004	SUB	TIE1	OF11B FF	15.00	25.0	50.0	32.08	25.01	28.14	6.52	81	0
Nautilus	2/18/2004	SUB	TIE1	OF23 C&E FF	10.00	12.5	25.0	18.59	13.46	15.39	6.52	81	0
Nautilus	2/18/2004	SUB	TIE1	OF26 FF	11.00	12.5	25.0	15.96	12.99	14.32	6.52	81	0
SSC - SD	2/2/2004	SUB	SDB3	OF11B Comp.	12.17	33.0	66.0	49.08	-	-	3.17	94.8	10.2
SSC - SD	2/2/2004	SUB	SDB3	OF23 C&E Comp.	19.07	16.5	33.0	21.81	-	-	5.54	87.7	0

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
Nautilus	2/24/2003	SUB	SDB2	Bay 11B	None	90.0	-	100.0
Nautilus	2/24/2003	SUB	SDB2	Bay 24	None	-	-	100.0
Nautilus	2/24/2003	SUB	SDB2	Bay 26	None	-	-	95.0
SSC - SD	12/11/2003	SUB	SDB2A	Bay 23CE	None	90.0	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 11B	None	100.0	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 26	None	95.0	-	-
SSC - SD	2/2/2004	SUB	SDB3	Bay 23 C&E	None	100.0	95.0	95.0
SSC - SD	2/2/2004	SUB	SDB3	Bay 26	None	90.0	100.0	100.0
SSC - SD	2/2/2004	SUB	SDB3	Bay 26A	None	100.0	100.0	100.0
SSC - SD	2/2/2004	SUB	SDB3	Bay 11B	None	95.0	100.0	100.0
SSC - SD	10/17/2004	SUB	SDB4	Bay 11B	None	-	90.0	-
SSC - SD	1/10/2005	SUB	SDB5	Bay 11B	None	-	-	100.0

### MYSIDS (*A. bahia*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
Nautilus	2/24/2003	SUB	SDB2	Bay 11B	None	100.0	-	97.0
Nautilus	2/24/2003	SUB	SDB2	Bay 24	None	-	-	100.0
Nautilus	2/24/2003	SUB	SDB2	Bay 26	None	-	-	100.0
SSC - SD	12/11/2003	SUB	SDB2A	Bay 23CE	None	96.7	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 11B	None	93.3	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 26	None	100.0	-	-
SSC - SD	2/2/2004	SUB	SDB3	Bay 11B	None	100.0	100.0	96.7
SSC - SD	2/2/2004	SUB	SDB3	Bay 26	None	100.0	100.0	96.7
SSC - SD	2/2/2004	SUB	SDB3	Bay 26A	None	100.0	100.0	100.0
SSC - SD	2/2/2004	SUB	SDB3	Bay 23 C&E	None	96.7	100.0	100.0
SSC - SD	10/17/2004	SUB	SDB4	Bay 11B	None	-	100.0	-

### MUSSELS (*M. galloprovincialis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Normal Development		
						PRE	DUR	AFT
Nautilus	2/24/2003	SUB	SDB2	Bay 11B	None	86.0	-	86.8
Nautilus	2/24/2003	SUB	SDB2	Bay 24	None	-	-	87.8
Nautilus	2/24/2003	SUB	SDB2	Bay 26	None	-	-	91.0
SSC - SD	12/11/2003	SUB	SDB2A	Bay 23CE	None	88.1	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 11B	None	86.0	-	-
SSC - SD	12/11/2003	SUB	SDB2A	Bay 26	None	86.7	-	-
SSC - SD	2/2/2004	SUB	SDB3	Bay 11B	None	94.8	94.3	96.1
SSC - SD	2/2/2004	SUB	SDB3	Bay 23 C&E	None	87.8	94.8	95.7
SSC - SD	2/2/2004	SUB	SDB3	Bay 26A	None	95.1	94.0	93.9
SSC - SD	2/2/2004	SUB	SDB3	Bay 26	None	89.7	97.3	95.9
Nautilus	2/26/2004	SUB	TIE-Add	Bay 11B	None			87.0
Nautilus	2/26/2004	SUB	TIE-Add	Bay 23 C&E	None			88.0
Nautilus	2/26/2004	SUB	TIE-Add	Bay 26	None			87.0
SSC - SD	10/17/2004	SUB	SDB4	Bay 11B	None	-	96.9	-
SSC - SD	1/10/2005	SUB	SDB5	Bay 11B	None	-	-	91.7

# NAB

## OUTFALLS

### TOPSMELT (*A. affinis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
SSC - SD	10/17/2004	NAB	SDB4	OF9 FF	18.30	12.5	25.0	22.1	13.1	16.8	0.00	100	0
SSC - SD	2/10/2005	NAB	SDB6	OF9 FF	-	100	>100	>100	>100	>100	0.00	100	95
SSC - SD	2/10/2005	NAB	SDB6	OF18 FF	-	100	>100	>100	>100	>100	0.00	100	100
Nautilus	3/19/2005	NAB	TIE2	OF9 FF	12.50	100	>100	>100	-	>100	0.00	100	95
Nautilus	3/19/2005	NAB	TIE2	OF18 FF	12.50	25	50.0	38.2	-	32.1	0.00	100	0
SSC - SD	4/27/2005	NAB	SDB7	OF9 FF	15.50	100	>100	>100	96.8	>100	10.53	95	85
SSC - SD	4/27/2005	NAB	SDB7	OF18 FF	11.47	100.0	>100	>100	10.7	>100	0.00	100	90
SSC - SD	2/10/2005	NAB	SDB6	OF9 Comp	-	100	>100	>100	>100	>100	0.00	100	100
SSC - SD	4/27/2005	NAB	SDB7	OF9 Comp	18.44	50	100.0	>100	36.8	73.0	10.53	95	60
SSC - SD	4/27/2005	NAB	SDB7	OF18 Comp	8.69	100.0	>100	>100	>100	>100	0.00	100	90

### MYSIDS (*A. bahia*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
SSC - SD	10/17/2004	NAB	SDB4	OF9 FF	29.00	12.5	25	19.3	11.9	15.0	0.00	100	0
SSC - SD	2/10/2005	NAB	SDB6	OF9 FF	8.93	100	>100	>100	>100	>100	0.00	100	90
SSC - SD	2/10/2005	NAB	SDB6	OF18 FF	6.38	50	100	>100	83.3	>100	0.00	100	86.7
Nautilus	3/19/2005	NAB	TIE2	OF9 FF	28.90	50	100	>100	-	73.4	10.50	95	50
Nautilus	3/19/2005	NAB	TIE2	OF18 FF	14.80	25	50	42.4	-	32.7	10.50	95	5
SSC - SD	2/10/2005	NAB	SDB6	OF9 Comp	8.58	100	>100	>100	>100	>100	0.00	100	90

### MUSSELS (*M. galloprovincialis*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Dev	%Devel in 100%
SSC - SD	10/17/2004	NAB	SDB4	OF9 FF	2.59	<6.25	6.3	1.7	0.6	1.0	2.07	97.5	0
SSC - SD	2/10/2005	NAB	SDB6	OF9 FF	6.82	12.4	24.8	32.1	16.6	23.1	1.20	96.4	0
SSC - SD	2/10/2005	NAB	SDB6	OF18 FF	3.24	12.4	24.8	22.4	17.2	19.5	1.55	97.3	0
Nautilus	3/19/2005	NAB	TIE2	OF9FF	4.67	<12.5	12.5	12.5	-	11.3	4.29	95	0
Nautilus	3/19/2005	NAB	TIE2	OF18 FF	3.04	<12.5	12.5	13.7	-	12.6	4.29	95	0
SSC - SD	2/10/2005	NAB	SDB6	OF9 Comp	3.68	12.9	25.7	37.7	26.7	30.8	1.20	96.4	0

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC-SD	10/19/2004	NAB	SDB4	Bay 9	None	-	95.0	-
SSC-SD	1/10/2005	NAB	SDB5	Bay 9	None	-	-	100.0
SSC-SD	2/10/2005	NAB	SDB6	Bay 9	None	100.0	90.0	-
SSC-SD	2/10/2005	NAB	SDB6	Bay 18	None	100.0	100.0	-
Nautilus	3/19/2005	NAB	TIE2	Bay 9	None	-	100.0	-
Nautilus	3/19/2005	NAB	TIE2	Bay 18	None	-	95.0	-
SSC-SD	4/27/2005	NAB	SDB7	Bay 9	None	95.0	100.0	-
SSC-SD	4/27/2005	NAB	SDB7	Bay 18	None	100.0	95.0	-

### MYSIDS (*A. bahia*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC-SD	10/17/2005	NAB	SDB4	Bay 9	None	-	100.0	-
SSC-SD	1/10/2005	NAB	SDB5	Bay 9	None	-	-	96.7
SSC-SD	2/10/2005	NAB	SDB6	Bay 9	None	100.0	100.0	-
SSC-SD	2/10/2005	NAB	SDB6	Bay 18	None	100.0	96.7	-
Nautilus	3/19/2005	NAB	TIE2	Bay 9	None	-	100.0	-
Nautilus	3/19/2005	NAB	TIE2	Bay 18	None	-	100.0	-

### MUSSELS (*M. galloprovincialis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Normal Development		
						PRE	DUR	AFT
SSC-SD	10/17/2005	NAB	SDB4	Bay 9	Dur	-	4.0	-
SSC-SD	1/10/2005	NAB	SDB5	Bay 9	None	-	-	90.2
SSC-SD	2/10/2005	NAB	SDB6	Bay 9	None	96.4	97.7	-
SSC-SD	2/10/2005	NAB	SDB6	Bay 18	None	97.3	95.4	-
Nautilus	3/19/2005	NAB	TIE2	Bay 9	None	-	96.0	-
Nautilus	3/19/2005	NAB	TIE2	Bay 18	None	-	96.0	-
SSC-SD	4/27/2005	NAB	SDB7	Bay 9	None	94.6	93.2	-
SSC-SD	4/27/2005	NAB	SDB7	Bay 18	None	91.6	93.2	-

**NI**

## OUTFALLS

### TOPSMELT (*A. affinis*)

Laboratory	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
SSC - SD	10/17/2004	NI	SDB4	OF23A FF	15.88	100.0	>100	>100	22.5	>100	0.00	100	80
SSC - SD	2/10/2005	NI	SDB6	OF23A FF	-	100	>100	>100	>100	>100	0.00	100	90
SSC - SD	2/10/2005	NI	SDB6	OF26 FF	-	100	>100	>100	>100	>100	10.53	95	95
Nautilus	3/19/2005	NI	TIE2	OF23a FF	12.2	50	100	>100	-	86	0	100	65
Nautilus	3/19/2005	NI	TIE2	OF26 FF	10.00	100	>100	>100	-	>100	0.00	100	100
SSC - SD	4/27/2005	NI	SDB7	OF23A FF	7.93	100	>100	>100	>100	>100	0.00	100	95
SSC - SD	4/27/2005	NI	SDB7	OF26 FF	16.25	100	>100	>100	79.0	>100	12.83	90	80
SSC - SD	2/10/2005	NI	SDB6	OF26Comp	-	100	>100	>100	>100	>100	10.53	95	100
SSC - SD	4/27/2005	NI	SDB7	OF26 Comp	19.10	100	>100	>100	>100	>100	12.83	90	100

### MYSIDS (*A. bahia*)

Lab	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Survival	%Survival in 100%
SSC - SD	10/17/2004	NI	SDB4	OF23A FF	10.80	25	50	>100	30.2	57.9	0.00	100	56.7
SSC - SD	2/10/2005	NI	SDB6	OF23A FF	5.20	100	>100	>100	>100	>100	0.00	100	96.7
SSC - SD	2/10/2005	NI	SDB6	OF26 FF	7.82	50	100	>100	61.5	96.2	0.00	100	73.3
Nautilus	3/19/2005	NI	TIE2	OF23a FF	12.00	100	>100	>100	-	>100	10.50	95	75
Nautilus	3/19/2005	NI	TIE2	OF26 FF	14.80	100	>100	>100	>100	>100	10.50	95	95
SSC - SD	2/10/2005	NI	SDB6	OF26 Comp	8.29	100	>100	>100	>100	>100	0.00	100	100

### MUSSELS (*M. galloprovincialis*)

Laboratory	Sample Date	Sample Location	Survey	Sample ID	PMSD	NOEC	LOEC	LC50/EC50	LC10/EC10	LC25/EC25	Control CV%	% Control Dev	%Devel in 100%
SSC - SD	10/17/2004	NI	SDB4	OF23A FF	4.90	6.3	12.5	17.0	11.9	14.1	2.07	97.5	0
SSC - SD	2/10/2005	NI	SDB6	OF23A FF	2.02	12.4	24.8	19.3	15.0	16.9	0.85	98.2	0
SSC - SD	2/10/2005	NI	SDB6	OF26 FF	1.89	12.4	24.8	31.9	26.3	28.8	1.35	97.5	0
Nautilus	3/19/2005	NI	TIE2	OF23a FF	4.19	12.5	25	22.1	-	19.4	4.29	95	0
Nautilus	3/19/2005	NI	TIE2	OF26 FF	4.28	69	>69	>69	-	>69	4.29	93	89
SSC - SD	2/10/2005	NI	SDB6	OF26 Comp	2.64	55.7	>55.7	>55.7	>55.7	>55.7	1.35	97.5	95.5

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC-SD	10/17/2005	NI	SDB4	Bay 23A	None	-	95.0	-
SSC-SD	1/10/2005	NI	SDB5	Downtown Pier	None	-	-	100.0
SSC-SD	2/10/2005	NI	SDB6	Bay 23A	None	100.0	100.0	-
SSC-SD	2/10/2005	NI	SDB6	Bay 26	None	95.0	100.0	-
Nautilus	3/19/2005	NI	TIE2	Bay 23A	None	-	95.0	-
Nautilus	3/19/2005	NI	TIE2	Bay 26	None	-	100.0	-
SSC-SD	4/27/2005	NI	SDB7	Bay 23A	None	100.0	100.0	-
SSC-SD	4/27/2005	NI	SDB7	Bay 26	None	90.0	100.0	-

### MYSIDS (*A. bahia*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Survival		
						PRE	DUR	AFT
SSC-SD	10/17/2005	NI	SDB4	Bay 23A	None	-	100.0	-
SSC-SD	1/10/2005	NI	SDB5	Downtown Pier	None	-	-	93.3
SSC-SD	2/10/2005	NI	SDB6	Bay 23A	None	100.0	100.0	-
SSC-SD	2/10/2005	NI	SDB6	Bay 26	None	100.0	100.0	-
Nautilus	3/19/2005	NI	TIE2	Bay 23A	None	-	100.0	-
Nautilus	3/19/2005	NI	TIE2	Bay 26	None	-	95.0	-

### MUSSELS (*M. galloprovincialis*)

Laboratory	Sample Date	Location	Survey	Sample ID	Significant	% Normal Development		
						PRE	DUR	AFT
SSC-SD	10/17/2005	NI	SDB4	Bay 23A	None	-	97.6	-
SSC-SD	1/10/2005	NI	SDB5	Bay 23A	None	-	-	93.9
SSC-SD	1/10/2005	NI	SDB5	Downtown Pier	None	-	-	93.6
SSC-SD	2/10/2005	NI	SDB6	Bay 23A	None	98.0	97.1	-
SSC-SD	2/10/2005	NI	SDB6	Bay 26	None	97.5	96.4	-
Nautilus	3/19/2005	NI	TIE2	Bay 23A	None	-	96.0	-
Nautilus	3/19/2005	NI	TIE2	Bay 26	None	-	95.0	-
SSC-SD	4/27/2005	NI	SDB7	Bay 23A	None	90.0	92.3	-
SSC-SD	4/27/2005	NI	SDB7	Bay 26	None	96.8	95.7	-



# **Appendix C**

## **Toxicity Data**

#### Note regarding the organization of the tables

The following tables contain toxicity and water quality data from the laboratory toxicity tests conducted over the course of this study for both storm water effluent (Outfalls) and in the receiving environment (Bay Samples) immediately adjacent to the outfalls prior to (PRE), during (DUR), and after (AFT) each storm event. Except where otherwise noted, the PRE water samples, which were collected approximately 24 hours prior to the storm event, served as the negative control for the dilution series tests using the Outfall samples. To prevent redundancy, the PRE sample data have been grouped with the Bay Sample tables, and not the Outfall tables. Therefore, to identify the relevant negative control associated with a particular sample, it is advised that the reader refer to the Bay Sample tables. For instance, the control for outfall sample NAV-OF9-SDB1-COMP is the Bay sample NAV-Bay9-SDB1-PRE.

## **Appendix C1**

### ***NAV***

SDB1- 11/7/2002  
SDB2- 2/24/2003  
TIE1- 2/18/2004  
SDB4- 10/17/2004  
SDB45- 10/26/2004  
SDB5- 01/10/2005

# SDB1 – 11/7/2002

## OUTFALLS

TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF9-SDB1-COMP	12.5	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-OF11-SDB1-COMP	6.25	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	12.5	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	90.0	11.5	90.0	0.091	No
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-OF14-SDB1-COMP	6.25	a	5	100.0	100.0	0.0	105.3	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	12.5	a	5	100.0	95.0	10.0	100.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	25	a	5	100.0	95.0	10.0	100.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	105.3	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	105.3	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF9-SDB1-COMP	12.5	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	90.0	17.3	93.1	0.291	No
		b	7	70.0					
		c	10	100.0					
NAV-OF11-SDB1-COMP	6.25	a	9	90.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	11	100.0					
	12.5	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	12	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-OF14-SDB1-COMP	6.25	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	12.5	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
	25	a	9	90.0	90.0	10.0	90.0	0.113	No
		b	8	80.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	9	90.0					
	100	a	9	90.0	93.3	5.8	93.3	0.092	No
		b	10	100.0					
		c	9	90.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF9-SDB1-COMP	4.4	a	38.0	41.7	3.3	106.8	0.248	No
		b	42.8					
		c	44.4					
	8.8	a	36.4	36.9	3.0	94.5	0.286	No
		b	40.1					
		c	34.2					
	17.5	a	12.3	10.9	2.9	27.9	0.001	Yes
		b	12.8					
		c	7.5					
	35.0	a	0.0	0.2	0.3	0.5	0.003	Yes
		b	0.0					
		c	0.5					
	70	a	0.0	0.0	0.0	0.0	0.003	Yes
		b	0.0					
		c	0.0					
NAV-OF11-SDB1-COMP	4.6	a	53.5	46.3	6.7	102.8	0.398	No
		b	40.1					
		c	45.5					
	9.1	a	32.1	33.2	3.3	73.5	0.008	Yes
		b	36.9					
		c	30.5					
	18.3	a	6.4	7.1	1.2	15.8	0.001	Yes
		b	8.6					
		c	6.4					
	36.5	a	0.0	0.0	0.0	0.0	0.001	Yes
		b	0.0					
		c	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
	73	a	0.0	0.0	0.0	0.0	0.001	Yes
		b	0.0					
		c	0.0					
NAV-OF14-SDB1-COMP	5.1	a	42.8	43.7	0.8	89.4	0.063	No
		b	43.9					
		c	44.4					
	10.2	a	41.2	37.4	6.5	76.6	0.036	Yes
		b	41.2					
		c	30.0					
	20.4	a	32.1	31.6	1.9	64.6	0.003	Yes
		b	33.2					
		c	29.4					
	40.7	a	0.5	1.2	0.6	2.5	0.001	Yes
		b	1.6					
		c	1.6					
	81.4	a	0.0	0.0	0.0	0.0	0.001	Yes
		b	0.0					
		c	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB1

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB1-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY9-SDB1-DUR	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY9-SDB1-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY11-SDB1-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY11-SDB1-DUR	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NAV-BAY11-SDB1-AFT	100	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY14-SDB1-PRE	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY14-SDB1-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY14-SDB1-AFT	100	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14A-SDB1-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY14A-SDB1-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY14A-SDB1-AFT	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB1-PRE	100	a	9	90.0	96.7	5.8	100.0	0.500	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY9-SDB1-DUR	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY9-SDB1-AFT	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB1-PRE	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB1-DUR	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB1-AFT	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14-SDB1-PRE	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14-SDB1-DUR	100	a	10	100.0	96.7	5.8	100.0	0.500	No
		b	9	90.0					
		c	10	100.0					
NAV-BAY14-SDB1-AFT	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB1-PRE	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB1-DUR	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB1-AFT	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB1-PRE	100	a	34.2	39.0	5.1	85.9	0.081	No
		b	38.5					
		c	44.4					
NAV-BAY9-SDB1-DUR	100	a	41.7	47.1	9.3	103.5	0.401	No
		b	41.7					
		c	57.8					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB1-AFT	100	a	41.2	39.6	8.9	87.1	0.189	No
		b	47.6					
		c	29.9					
NAV-BAY11-SDB1-PRE	100	a	44.4	45.1	3.8	99.2	0.457	No
		b	41.7					
		c	49.2					
NAV-BAY11-SDB1-DUR	100	a	45.5	41.7	4.4	91.8	0.165	No
		b	42.8					
		c	36.9					
NAV-BAY11-SDB1-AFT	100	a	43.9	45.6	1.6	100.4	0.473	No
		b	47.1					
		c	46.0					
NAV-BAY14-SDB1-PRE	100	a	46.0	48.8	3.6	107.5	0.165	No
		b	47.6					
		c	52.9					
NAV-BAY14-SDB1-DUR	100	a	42.2	41.5	1.7	91.4	0.107	No
		b	42.8					
		c	39.6					
NAV-BAY14-SDB1-AFT	100	a	31.6	33.9	3.6	74.5	0.009	Yes
		b	32.1					
		c	38.0					
NAV-BAY14A-SDB1-PRE	100	a	42.8	47.1	4.6	103.5	0.333	No
		b	46.5					
		c	51.9					
NAV-BAY14A-SDB1-DUR	100	a	49.7	44.4	5.6	97.6	0.401	No
		b	38.5					
		c	44.9					
NAV-BAY14A-SDB1-AFT	100	a	49.2	46.2	3.9	101.6	0.417	No
		b	41.7					
		c	47.6					

**QA/QC SAMPLES<sup>a</sup>**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	n/a	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control 1	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	200	a	3	60.0	65.0	10.0	65.0	0.003	Yes
		b	3	60.0					
		c	4	80.0					
		d	3	60.0					
	400	a	1	20.0	20.0	16.3	20.0	0.001	Yes
		b	0	0.0					
		c	2	40.0					
		d	1	20.0					



**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	10	100.0	96.7	5.8	n/a	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control 1	n/a	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	200	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	400	a	3	30.0	33.3	5.8	34.5	0.000	Yes
		b	4	40.0					
		c	3	30.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	49.7	45.5	3.9	n/a	n/a	n/a
		b	44.4					
		c	42.2					
Brine Control	n/a	a	42.8	42.1	3.8	92.5	0.170	No
		b	38.0					
		c	45.5					
Salt Control	n/a	a	36.4	37.4	6.0	82.4	0.067	No
		b	32.1					
		c	43.9					
Copper Ref. Tox.	1.5	a	50.3	53.3	2.6	117.3	0.025	Yes <sup>c</sup>
		b	55.1					
		c	54.5					
	3.0	a	47.1	49.2	2.1	108.2	0.117	No
		b	49.2					
		c	51.3					
	6.0	a	20.3	19.8	1.9	43.5	0.001	Yes
		b	21.4					
		c	17.6					
	9.0	a	1.1	1.2	0.3	2.7	0.001	Yes
		b	1.6					
		c	1.1					
	12.0	a	0.0	0.0	0.0	0.0	0.001	Yes
		b	0.0					
		c	0.0					

**REFERENCE TOXICANT RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100.0	200.0	248.4	184.7-333.9
MYSIDS	200.0	400.0	336.4	294.1-384.7
MUSSELS	3.0	6.0	5.7	5.4-5.9

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB1

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

# WATER QUALITY

## TOPSMELT (*A. affinis*)

Sample ID	Effluent Concentration (% or µg/l Cu)	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
		0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF9-SDB1-COMP	12.5%	ND	7.8	7.8	7.8	7.8	ND	6.4	6.1	7.2	6.2	ND	19.5	19.9	18.9	19.2	ND	33.0	ND	34.0	ND
	50%	ND	7.9	7.8	7.8	7.8	ND	6.0	6.0	6.9	6.2	ND	20.2	19.9	19.3	19.4	ND	32.0	33.0	34.0	ND
NAV-OF11-SDB1-COMP	6.25%	ND	7.9	7.8	7.8	7.8	ND	6.4	6.2	6.9	6.3	ND	19.9	19.5	19.0	19.3	ND	ND	ND	34.0	ND
	12.5%	ND	7.9	7.8	7.8	7.8	ND	6.2	6.0	7.1	6.2	ND	19.9	19.3	19.1	19.1	ND	ND	ND	33.0	ND
	25%	ND	7.9	7.8	7.8	7.8	ND	6.3	6.0	6.9	6.2	ND	20.0	19.6	19.2	18.9	ND	ND	ND	34.0	ND
	50%	ND	7.9	7.8	7.8	7.8	ND	6.2	6.0	6.9	6.0	ND	20.0	19.5	19.1	19.0	ND	ND	ND	33.0	ND
	100%	ND	7.9	7.8	7.8	7.7	ND	5.6	5.7	6.7	6.0	ND	20.0	19.8	19.3	19.0	ND	32.0	32.0	32.0	ND
NAV-OF14-SDB1-COMP	6.25%	ND	7.9	7.8	7.8	7.8	ND	6.3	6.0	7.0	6.3	ND	20.1	19.4	19.0	19.2	ND	ND	ND	34.0	ND
	12.5%	ND	7.9	7.8	7.8	7.8	ND	6.2	5.9	6.9	6.1	ND	19.9	19.3	19.1	19.1	ND	ND	ND	34.0	ND
	25%	ND	7.9	7.8	7.8	7.7	ND	5.8	5.9	6.7	6.1	ND	20.2	19.3	19.0	19.2	ND	ND	ND	34.0	ND
	50%	ND	7.9	7.8	7.8	7.7	ND	6.0	6.0	6.5	6.0	ND	20.2	19.3	19.1	19.1	ND	ND	ND	34.0	ND
	100%	ND	7.9	7.8	7.8	7.7	ND	5.0	5.4	6.3	5.8	ND	20.2	19.3	19.3	19.3	ND	ND	32.0	34.0	ND
NAV-BAY9-SDB1-PRE	100%	7.9	7.9	7.9	7.8	7.8	7.3	6.5	6.9	6.9	6.3	19.9	19.4	18.3	19.0	19.3	35.0	ND	34.0	34.0	ND
NAV-BAY11-SDB1-PRE	100%	7.9	7.9	7.8	7.8	7.8	7.3	6.4	6.9	7.2	6.3	19.8	19.4	18.0	18.9	19.0	35.0	33.0	33.0	33.0	ND
NAV-BAY14-SDB1-PRE	100%	7.9	7.9	7.8	7.8	7.8	7.2	6.4	6.7	7.2	6.2	19.8	19.4	18.3	18.8	19.0	35.0	ND	ND	33.0	ND
NAV-BAY14A-SDB1-PRE	100%	7.9	7.9	7.8	7.8	7.8	7.3	6.4	7.0	7.1	6.0	19.8	19.4	18.1	18.9	19.3	35.0	ND	ND	34.0	ND
NAV-BAY9-SDB1-DUR	100%	7.9	7.8	7.9	7.8	7.8	7.2	6.4	6.8	7.2	6.4	20.0	19.4	18.8	18.7	18.9	32.0	ND	33.0	34.0	ND
NAV-BAY11-SDB1-DUR	100%	7.9	7.8	7.8	7.8	7.8	7.5	6.4	6.7	7.2	6.6	19.8	19.8	18.8	18.8	18.9	32.0	ND	ND	33.0	ND
NAV-BAY14-SDB1-DUR	100%	7.9	7.8	7.8	7.8	7.8	7.3	6.4	6.7	7.0	6.6	19.8	19.4	18.8	18.8	18.8	32.0	ND	ND	33.0	ND
NAV-BAY14A-SDB1-DUR	100%	7.9	7.8	7.8	7.8	7.8	7.3	6.5	6.7	7.3	6.6	19.8	19.3	18.8	18.8	18.9	32.0	ND	33.0	33.0	ND
NAV-BAY9-SDB1-AFT	100%	7.9	7.8	7.8	7.8	7.8	7.3	6.4	6.6	7.1	6.2	19.9	19.9	18.4	19.0	19.3	35.0	ND	ND	33.0	ND
NAV-BAY11-SDB1-AFT	100%	7.9	7.8	7.8	7.8	7.8	7.2	6.4	6.7	7.2	6.2	19.8	19.3	18.1	18.7	18.8	35.0	ND	33.0	33.0	ND
NAV-BAY14-SDB1-AFT	100%	7.9	7.8	7.8	7.8	7.8	7.2	6.4	6.7	7.3	6.4	19.8	19.4	18.3	18.8	18.8	35.0	ND	32.0	33.0	ND
NAV-BAY14A-SDB1-AFT	100%	7.9	7.8	7.8	7.8	7.8	7.2	6.4	6.7	7.2	6.2	20.2	19.4	18.3	18.8	18.8	35.0	ND	32.0	32.0	ND
Natural Seawater Control	100%	ND	ND	7.8	7.8	7.8	ND	ND	7.0	7.1	6.3	ND	ND	19.8	19.2	19.3	ND	ND	ND	33.0	ND
Salt Control	100%	ND	7.9	7.9	7.8	7.8	ND	5.8	6.7	6.8	6.3	ND	19.9	18.6	19.1	19.3	ND	32.0	33.0	33.0	ND

## MYSIDS (*A. bahia*)

Sample ID	Effluent Concentration (% or µg/l Cu)	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
		0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF9-SDB1-COMP	12.5%	ND	ND	7.8	7.7	7.7	ND	ND	5.5	6.4	5.7	ND	ND	19.8	19.6	19.6	ND	ND	ND	33.0	33.0
	50%	ND	ND	7.7	7.5	7.5	ND	ND	5.3	4.7	4.8	ND	ND	19.9	19.6	19.7	ND	ND	ND	33.0	34.0
NAV-OF11-SDB1-COMP	6.25%	ND	ND	7.7	7.7	7.7	ND	ND	5.7	6.0	5.6	ND	ND	19.5	19.8	19.8	ND	ND	ND	33.0	33.0
	12.5%	ND	ND	7.7	7.6	7.7	ND	ND	5.5	5.4	5.7	ND	ND	19.5	19.7	19.6	ND	ND	ND	33.0	33.0
	25%	ND	ND	7.7	7.7	7.7	ND	ND	5.7	5.9	5.5	ND	ND	19.6	19.8	19.7	ND	ND	ND	33.0	33.0
	50%	ND	ND	7.7	7.7	7.7	ND	ND	5.7	5.8	5.4	ND	ND	19.6	19.9	19.8	ND	ND	ND	32.0	33.0
	100%	ND	ND	7.7	7.7	7.7	ND	ND	4.8	5.8	5.3	ND	ND	19.8	20.0	20.0	ND	ND	32.0	32.0	32.0
	6.25%	ND	ND	7.8	7.7	7.7	ND	ND	5.7	6.4	6.1	ND	ND	19.2	19.8	19.5	ND	ND	ND	34.0	ND
NAV-OF14-SDB1-COMP	12.5%	ND	ND	7.7	7.7	7.7	ND	ND	5.8	6.2	6.1	ND	ND	19.3	19.8	19.8	ND	ND	ND	34.0	ND
	25%	ND	ND	7.8	7.7	7.7	ND	ND	5.7	6.1	5.8	ND	ND	19.3	19.8	19.5	ND	ND	ND	34.0	ND
	50%	ND	ND	7.8	7.7	7.7	ND	ND	5.7	5.8	5.7	ND	ND	19.4	19.8	19.5	ND	ND	ND	33.0	34.0
	100%	ND	ND	7.7	7.7	7.7	ND	ND	4.8	5.2	5.2	ND	ND	19.7	19.9	19.6	ND	ND	33.0	34.0	34.0
NAV-BAY9-SDB1-PRE	100%	7.9	ND	7.8	7.5	7.4	7.3	ND	6.0	4.4	4.6	19.9	ND	19.3	20.0	19.6	35.0	ND	34.0	33.0	ND
NAV-BAY11-SDB1-PRE	100%	7.9	ND	7.6	7.7	7.6	7.3	ND	5.7	6.5	5.7	19.8	ND	19.1	19.9	19.5	35.0	ND	ND	34.0	ND
NAV-BAY14-SDB1-PRE	100%	7.9	ND	7.7	7.7	7.7	7.2	ND	5.8	6.5	5.9	19.8	ND	19.7	19.5	19.4	35.0	ND	ND	34.0	ND
NAV-BAY14A-SDB1-PRE	100%	7.9	ND	7.7	7.7	7.7	7.3	ND	6.1	6.6	6.0	19.8	ND	19.2	19.6	19.4	35.0	ND	ND	34.0	ND
NAV-BAY9-SDB1-DUR	100%	7.9	ND	7.7	7.7	7.7	7.2	ND	5.9	6.4	6.0	20.0	ND	21.1	19.4	19.3	35.0	ND	33.0	34.0	ND
NAV-BAY11-SDB1-DUR	100%	7.9	ND	7.7	7.7	7.7	7.5	ND	5.6	6.5	5.9	19.7	ND	19.9	19.4	19.5	35.0	ND	33.0	33.0	ND
NAV-BAY14-SDB1-DUR	100%	7.9	ND	7.6	7.7	7.7	7.3	ND	5.7	6.3	6.1	19.8	ND	19.7	19.3	19.5	35.0	ND	ND	33.0	33.0
NAV-BAY14A-SDB1-DUR	100%	7.9	ND	7.7	7.7	7.7	7.3	ND	5.8	6.6	5.9	19.8	ND	19.3	19.5	19.3	35.0	ND	ND	34.0	33.0
NAV-BAY9-SDB1-AFT	100%	7.9	ND	7.7	7.7	7.7	7.3	ND	5.7	6.5	6.0	19.9	ND	19.3	19.4	19.4	35.0	ND	ND	33.0	33.0
NAV-BAY11-SDB1-AFT	100%	7.9	ND	7.6	7.7	7.7	7.2	ND	5.7	5.9	5.7	19.8	ND	19.8	19.6	19.5	35.0	ND	ND	33.0	34.0
NAV-BAY14-SDB1-AFT	100%	7.9	ND	7.8	7.5	7.5	7.2	ND	6.0	4.4	4.8	19.8	ND	19.5	19.6	19.6	35.0	ND	ND	33.0	33.0
NAV-BAY14A-SDB1-AFT	100%	7.9	ND	7.7	7.6	7.6	7.2	ND	6.0	4.9	5.1	20.2	ND	19.3	19.6	19.6	35.0	ND	ND	33.0	33.0
Natural Seawater Control	100%	ND	ND	7.8	7.7	7.7	ND	ND	6.4	6.4	6.0	ND	ND	19.8	20.0	19.9	ND	ND	ND	32.0	33.0
Salt Control	100%	ND	ND	7.9	7.8	7.8	ND	ND	6.0	5.9	5.9	ND	ND	19.3	19.9	19.9	ND	ND	33.0	33.0	33.0

ND - water quality not recorded

# SDB2 – 02/24/2003

## OUTFALLS

TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1,3</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-PR5-SDB2-FF	10	a	5	100.0	90.0	20.0	94.7	0.338	No
		b	3	60.0					
		c	5	100.0					
		d	5	100.0					
	50	a	3	60.0	65.0	10.0	68.4	0.003	Yes
		b	3	60.0					
		c	4	80.0					
		d	3	60.0					
	100	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
NAV-PR5-SDB2-COMP	10	a	3	60.0	85.0	19.1	89.5	0.201	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	90.0	11.5	94.7	0.269	No
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					
	100	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NAV-PR6-SDB2-FF	10	a	4	80.0	90.0	11.5	94.7	0.269	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	50	a	3	60.0	80.0	23.1	84.2	0.149	No
		b	3	60.0					
		c	5	100.0					
		d	5	100.0					
	100	a	2	40.0	60.0	28.3	63.2	0.042	Yes
		b	3	60.0					
		c	2	40.0					
		d	5	100.0					
NAV-PR6-SDB2-COMP	10	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	3	60.0	75.0	19.1	78.9	0.065	No
		b	4	80.0					
		c	3	60.0					
		d	5	100.0					
NAV-OF9-SDB2-FF	10	a	4	80.0	90.0	11.5	90.0	0.091	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	3	60.0	85.0	19.1	85.0	0.108	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					

TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1,3</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF9-SDB2-COMP	10	a	4	80.0	90.0	11.5	90.0	0.091	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	3	60.0	90.0	20.0	90.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-OF11-SDB2-FF	10	a	5	100.0	90.0	11.5	94.7	0.269	No
		b	4	80.0					
		c	5	100.0					
		d	4	80.0					
	50	a	1	20.0	55.0	25.2	57.9	0.021	Yes
		b	3	60.0					
		c	4	80.0					
		d	3	60.0					
	100	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
NAV-OF11-SDB2-COMP	10	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-OF14-SDB2-FF	10	a	3	60.0	80.0	16.3	88.9	0.180	No
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					
	50	a	6	100.0	80.0	16.3	88.9	0.180	No
		b	4	80.0					
		c	3	60.0					
		d	4	80.0					
	100	a	2	40.0	70.0	25.8	77.8	0.114	No
		b	4	80.0					
		c	5	100.0					
		d	3	60.0					
NAV-OF14-SDB2-COMP	10	a	5	100.0	90.0	11.5	100.0	0.500	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
	50	a	5	100.0	95.0	10.0	105.6	0.269	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	4	80.0	95.0	10.0	105.6	0.269	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-PR5-SDB2-FF	10	a	7	70.0	70.0	10.0	70.0	0.018	Yes
		b	8	80.0					
		c	6	60.0					
	50	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
	100	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
NAV-PR5-SDB2-COMP	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	9	90.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-PR6-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	90.0	10.0	90.0	0.113	No
		b	8	80.0					
		c	9	90.0					
	100	a	2	20.0	33.3	15.3	33.3	0.009	Yes
		b	5	50.0					
		c	3	30.0					
NAV-PR6-SDB2-COMP	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	9	90.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	10	100.0					
	100	a	9	90.0	90.0	10.0	90.0	0.113	No
		b	8	80.0					
		c	10	100.0					
NAV-OF9-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	9	90.0	93.3	5.8	93.3	0.092	No
		b	10	100.0					
		c	9	90.0					
	100	a	8	80.0	90.0	10.0	90.0	0.113	No
		b	10	100.0					
		c	9	90.0					
NAV-OF9-SDB2-COMP	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-OF11-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
	100	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF11-SDB2-COMP	10	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-OF14-SDB2-FF	10	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	9	90.0					
	50	a	10	100.0	93.3	11.5	93.3	0.211	No
		b	10	100.0					
		c	8	80.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-OF14-SDB2-COMP	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-PR5-SDB2-FF	10	a	96	4	96.0	95.4	2.7	107.7	0.020	Yes <sup>c</sup>
		b	91	9	91.0					
		c	97	3	97.0					
		d	95	5	95.0					
		e	98	2	98.0					
	50	a	7	93	7.0	12.0	9.2	13.5	0.000	Yes
		b	6	94	6.0					
		c	28	72	28.0					
		d	7	93	7.0					
		e	12	88	12.0					
	58	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					
NAV-PR5-SDB2-COMP	10	a	96	4	96.0	95.8	1.9	108.1	0.016	Yes <sup>c</sup>
		b	97	3	97.0					
		c	95	5	95.0					
		d	98	2	98.0					
		e	93	7	93.0					
	50	a	95	5	95.0	95.6	1.3	107.9	0.018	Yes <sup>c</sup>
		b	95	5	95.0					
		c	95	5	95.0					
		d	98	2	98.0					
		e	95	5	95.0					
	58	a	13	87	13.0	38.6	21.7	43.6	0.003	Yes
		b	38	62	38.0					
		c	67	33	67.0					
		d	23	77	23.0					
		e	52	48	52.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-PR6-SDB2-FF	10	a	96	4	96.0	94.4	4.2	106.5	0.045	Yes <sup>c</sup>
		b	95	5	95.0					
		c	97	3	97.0					
		d	97	3	97.0					
		e	87	13	87.0					
	50	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					
	58	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					
NAV-PR6-SDB2-COMP	10	a	99	1	99.0	97.2	2.2	109.7	0.008	Yes <sup>c</sup>
		b	96	4	96.0					
		c	96	4	96.0					
		d	95	5	95.0					
		e	100	0	100.0					
	50	a	99	1	99.0	95.6	3.2	107.9	0.019	Yes <sup>c</sup>
		b	98	2	98.0					
		c	94	6	94.0					
		d	96	4	96.0					
		e	91	9	91.0					
	58	a	0	100	0.0	0.4	0.5	0.5	0.000	Yes
		b	0	100	0.0					
		c	1	99	1.0					
		d	1	99	1.0					
		e	0	100	0.0					
NAV-OF9-SDB2-FF	10	a	98	2	98.0	97.4	0.9	101.0	0.141	No
		b	98	2	98.0					
		c	97	3	97.0					
		d	96	4	96.0					
		e	98	2	98.0					
	50	a	90	10	90.0	91.1	3.3	94.5	0.009	Yes <sup>c</sup>
		b	86	14	86.0					
		c	500	32	94.0					
		d	94	6	94.0					
		e	245	23	91.4					
	58	a	26	74	26.0	27.4	3.7	28.4	0.000	Yes
		b	34	66	34.0					
		c	26	74	26.0					
		d	26	74	26.0					
		e	25	75	25.0					
NAV-OF9-SDB2-COMP	10	a	96	4	96.0	96.4	1.5	100.0	0.500	No
		b	99	1	99.0					
		c	96	4	96.0					
		d	96	4	96.0					
		e	95	5	95.0					
	50	a	99	1	99.0	96.0	2.0	99.6	0.369	No
		b	246	13	95.0					
		c	97	3	97.0					
		d	95	5	95.0					
		e	94	6	94.0					
	61	a	100	0	100.0	96.8	2.3	100.4	0.380	No
		b	96	4	96.0					
		c	98	2	98.0					
		d	96	4	96.0					
		e	94	6	94.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>2</sup>	SIG DIFF FROM CONTROL?
NAV-OF11-SDB2-FF	10	a	92	8	92.0	95.0	2.6	99.6	0.389	No
		b	94	6	94.0					
		c	96	4	96.0					
		d	94	6	94.0					
		e	99	1	99.0					
	50	a	80	20	80.0	85.4	8.2	89.5	0.026	Yes
		b	94	6	94.0					
		c	74	26	74.0					
		d	230	24	90.6					
		e	229	30	88.4					
	58	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					
NAV-OF11-SDB2-COMP	10	a	98	2	98.0	96.4	1.3	101.0	0.151	No
		b	97	3	97.0					
		c	95	5	95.0					
		d	97	3	97.0					
		e	95	5	95.0					
	50	a	98	2	98.0	96.0	2.0	100.6	0.304	No
		b	95	5	95.0					
		c	93	7	93.0					
		d	97	3	97.0					
		e	97	3	97.0					
	65	a	96	4	96.0	91.2	5.4	95.6	0.079	No
		b	93	7	93.0					
		c	82	18	82.0					
		d	92	8	92.0					
		e	93	7	93.0					
NAV-OF14-SDB2-FF	10	a	94	6	94.0	94.2	2.6	97.5	0.058	No
		b	93	7	93.0					
		c	91	9	91.0					
		d	98	2	98.0					
		e	95	5	95.0					
	50	a	95	5	95.0	95.0	3.0	98.3	0.161	No
		b	98	2	98.0					
		c	96	4	96.0					
		d	90	10	90.0					
		e	96	4	96.0					
	58	a	76	24	76.0	27.6	30.3	28.6	0.004	Yes
		b	5	95	5.0					
		c	11	89	11.0					
		d	7	93	7.0					
		e	39	61	39.0					
NAV-OF14-SDB2-COMP	10	a	99	1	99.0	96.2	2.2	99.6	0.368	No
		b	96	4	96.0					
		c	97	3	97.0					
		d	96	4	96.0					
		e	93	7	93.0					
	50	a	97	3	97.0	95.8	1.3	99.2	0.184	No
		b	94	6	94.0					
		c	96	4	96.0					
		d	97	3	97.0					
		e	95	5	95.0					
	65	a	94	6	94.0	94.8	2.3	98.1	0.088	No
		b	96	4	96.0					
		c	94	6	94.0					
		d	98	2	98.0					
		e	92	8	92.0					

<sup>1</sup>Controls (QA/QC) correspond to all samples from SDB2

<sup>2</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>3</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>4</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>5</sup>Controls were Scripps filtered seawater

<sup>6</sup>NAV-BAY14A-SDB2 PRE was used as a control for NAV-PR5-SDB2-FF, NAV-PR5-SDB2-COMP, NAV-PR6-SDB2-FF, NAV-PR6-SDB2-COMP



## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB2-PRE	100	a	5	100.0	100.0	0.0	102.6	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY9-SDB2-DUR	100	a	4	80.0	95.0	10.0	82.1	0.338	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY9-SDB2-AFT	100	a	5	100.0	90.0	20.0	102.6	0.257	No
		b	5	100.0					
		c	5	100.0					
		d	3	60.0					
NAV-BAY11-SDB2-PRE	100	a	4	80.0	95.0	10.0	82.1	0.338	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY11-SDB2-DUR	100	a	5	100.0	90.0	11.5	102.6	0.149	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
NAV-BAY11-SDB2-AFT	100	a	5	100.0	95.0	10.0	102.6	0.338	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
NAV-BAY14-SDB2-PRE	100	a	5	100.0	90.0	11.5	102.6	0.149	No
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					
NAV-BAY14-SDB2-DUR	100	a	4	80.0	90.0	11.5	82.1	0.149	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
NAV-BAY14-SDB2-AFT	100	a	4	80.0	90.0	11.5	82.1	0.149	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NAV-BAY14A-SDB2-PRE	100	a	5	100.0	95.0	10.0	102.6	0.338	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NAV-BAY14A-SDB2-DUR	100	a	5	100.0	90.0	11.5	102.6	0.149	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
NAV-BAY14A-SDB2-AFT	100	a	5	100.0	100.0	0.0	102.6	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB2-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY9-SDB2-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY9-SDB2-AFT	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB2-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB2-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY11-SDB2-AFT	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14-SDB2-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14-SDB2-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14-SDB2-AFT	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB2-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB2-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
NAV-BAY14A-SDB2-AFT	100	a	9	90.0	97.0	5.8	97.0	0.211	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY9-SDB2-PRE	100	a	97	3	97.0	96.4	1.7	100.2	0.457	No
		b	95	5	95.0					
		c	95	5	95.0					
		d	99	1	99.0					
		e	96	4	96.0					
NAV-BAY9-SDB2-DUR	100	a	89	11	89.0	92.8	2.6	96.5	0.063	No
		b	93	7	93.0					
		c	96	4	96.0					
		d	94	6	94.0					
		e	92	8	92.0					
NAV-BAY9-SDB2-AFT	100	a	96	4	96.0	97.4	2.4	101.2	0.276	No
		b	98	2	98.0					
		c	100	0	100.0					
		d	94	6	94.0					
		e	99	1	99.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY11-SDB2-PRE	100	a	96	4	96.0	95.4	1.5	99.2	0.331	No
		b	97	3	97.0					
		c	93	7	93.0					
		d	95	5	95.0					
		e	96	4	96.0					
NAV-BAY11-SDB2-DUR	100	a	96	4	96.0	96.2	0.8	100.0	0.500	No
		b	95	5	95.0					
		c	97	3	97.0					
		d	96	4	96.0					
		e	97	3	97.0					
NAV-BAY11-SDB2-AFT	100	a	97	3	97.0	97.4	1.1	101.2	0.253	No
		b	97	3	97.0					
		c	99	1	99.0					
		d	96	4	96.0					
		e	98	2	98.0					
NAV-BAY14-SDB2-PRE	100	a	98	2	98.0	96.6	1.3	100.4	0.412	No
		b	95	5	95.0					
		c	98	2	98.0					
		d	96	4	96.0					
		e	96	4	96.0					
NAV-BAY14-SDB2-DUR	100	a	96	4	96.0	96.4	1.8	100.2	0.457	No
		b	99	1	99.0					
		c	94	6	94.0					
		d	97	3	97.0					
		e	96	4	96.0					
NAV-BAY14-SDB2-AFT	100	a	98	2	98.0	97.2	2.4	101.0	0.309	No
		b	98	2	98.0					
		c	98	2	98.0					
		d	93	7	93.0					
		e	99	1	99.0					
NAV-BAY14A-SDB2-PRE	100	a	89	11	89.0	88.6	5.2	92.1	0.015	Yes
		b	81	19	81.0					
		c	87	13	87.0					
		d	95	5	95.0					
		e	91	9	91.0					
NAV-BAY14A-SDB2-DUR	100	a	99	1	99.0	92.6	8.5	96.3	0.210	No
		b	98	2	98.0					
		c	93	7	93.0					
		d	95	5	95.0					
		e	78	22	78.0					
NAV-BAY14A-SDB2-AFT	100	a	97	3	97.0	91.2	5.1	94.8	0.058	No
		b	87	13	87.0					
		c	95	5	95.0					
		d	92	8	92.0					
		e	85	15	85.0					

**QA/QC SAMPLES<sup>a</sup>**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	10	100.0	97.5	97.5	n/a	n/a	n/a
		b	10	100.0					
		c	10	100.0					
		d	9	90.0					
Salt Control 1	n/a	a	10	100.0	100.0	100.0	102.6	0.196	No
		b	10	100.0					
		c	10	100.0					
		d	10	100.0					
Salt Control 2	n/a	a	8	80.0	87.5	87.5	89.7	0.015	Yes
		b	9	90.0					
		c	9	90.0					
		d	9	90.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	10	100.0	100.0	0.0	100.0	n/a	n/a
		b	10	100.0					
		c	10	100.0					
Salt Control 1	n/a	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
Salt Control 2	n/a	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	99	1	99.0	96.2	3.6	n/a	n/a	n/a
		b	97	3	97.0					
		c	92	8	92.0					
		d	100	0	100.0					
		e	93	7	93.0					
Brine Control	n/a	a	98	2	98.0	94.4	3.3	98.1	0.215	No
		b	91	9	91.0					
		c	91	9	91.0					
		d	95	5	95.0					
		e	97	3	97.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	2/25/2003	100.0	200.0	161.5	135.2-193.3
MYSIDS	2/26/2003	100.0	200.0	237.4	212.4-266.0
MUSSELS	2/27/2003	5.0	10.0	7.54	n/a

Reference Toxicant tests are within two standard deviations of Nautilus' control chart mean

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB2

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)		
		0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	96
NAV-PR5-SDB2-FF	10%	8.1	7.9	8.2	7.6	7.7	7.4	6.6	7.7	7.8	7.0	20.1	20.3	20.1	20.3	20.1	33.0	33.0	33.0
	50%	8.4	8.0	8.4	7.7	7.7	8.0	6.0	8.1	7.5	6.0	20.3	20.3	20.3	20.1	20.1	33.0	33.0	33.0
	100%	8.6	8.2	N	N	N	7.5	5.3	N	N	N	20.3	20.2	N	N	N	33.0	33.0	N
NAV-PR5-SDB2-COMP	10%	8.1	7.9	8.2	7.6	7.7	7.5	6.8	8.4	8.1	7.0	19.9	20.2	20.1	20.4	19.9	33.0	32.0	33.0
	50%	8.4	8.0	8.4	7.7	7.7	7.6	6.6	8.6	7.9	6.8	20.0	20.2	20.1	20.1	20.0	33.0	33.0	33.0
	100%	8.6	8.3	8.6	7.8	7.8	7.6	6.3	8.5	7.1	6.6	20.3	20.2	21.0	20.0	20.0	33.0	33.0	33.0
NAV-PR6-SDB2-FF	10%	8.1	7.8	8.2	7.5	7.6	7.5	6.4	7.5	7.4	6.1	19.8	20.3	19.9	20.4	20.1	33.0	33.0	33.0
	50%	8.4	7.8	8.4	7.5	7.6	8.0	5.8	8.0	5.6	5.5	20.1	20.3	20.2	20.1	20.1	33.0	33.0	33.0
	100%	8.5	7.9	8.6	7.8	7.9	8.2	4.2 <sup>A</sup>	8.5	7.9	6.6	20.7	20.2	20.7	20.1	20.1	33.0	33.0	34.0
NAV-PR6-SDB2-COMP	10%	8.1	7.9	8.2	7.5	7.7	7.5	6.6	7.5	7.6	6.6	20.7	20.2	20.2	20.1	20.0	33.0	32.0	32.0
	50%	8.4	7.7	8.4	7.6	7.7	7.8	6.4	8.2	6.8	6.6	20.1	20.1	20.3	19.9	20.0	33.0	33.0	33.0
	100%	8.6	8.2	8.6	7.7	7.8	7.9	6.0	8.5	6.0	6.3	20.1	20.0	20.9	19.9	20.0	33.0	33.0	33.0
NAV-OF9-SDB2-FF	10%	8.1	7.9	8.2	7.6	7.7	7.2	6.5	7.9	7.5	6.6	19.9	20.3	20.9	20.1	20.1	33.0	33.0	33.0
	50%	8.3	8.0	8.4	7.6	7.7	7.3	6.2	8.2	7.7	6.6	20.0	20.3	20.9	20.1	20.1	33.0	33.0	33.0
	100%	8.5	8.1	8.6	7.7	7.8	7.5	5.8	8.2	6.8	6.4	20.3	20.2	20.6	20.0	20.1	33.0	33.0	33.0
NAV-OF9-SDB2-COMP	10%	8.1	7.9	8.2	7.6	7.5	7.5	6.5	8.2	7.8	6.8	20.1	20.3	20.3	20.0	20.0	33.0	33.0	33.0
	50%	8.3	8.0	8.4	7.7	7.6	7.7	6.6	8.3	7.3	6.7	20.1	20.3	20.3	20.0	20.0	33.0	33.0	33.0
	100%	8.5	8.2	8.6	7.8	7.6	7.7	6.5	8.4	7.0	6.9	20.3	20.2	21.0	19.9	20.0	33.0	33.0	33.0
NAV-OF11-SDB2-FF	10%	8.1	7.9	8.2	7.5	7.7	7.1	6.6	7.9	7.6	6.7	20.4	20.2	20.3	20.1	20.0	33.0	33.0	32.0
	50%	8.4	8.1	8.6	7.6	7.7	7.2	6.6	8.5	5.5	6.0	20.3	20.2	20.8	19.9	20.0	33.0	33.0	32.0
	100%	8.6	8.3	N	N	N	7.4	6.0	N	N	N	20.3	20.1	N	N	N	33.0	33.0	N
NAV-OF11-SDB2-COMP	10%	8.0	7.9	8.2	7.6	7.7	7.8	6.9	8.1	7.9	6.8	19.8	20.3	20.4	20.2	20.1	33.0	33.0	33.0
	50%	8.3	8.0	8.3	7.7	7.7	7.9	6.8	8.2	8.0	6.9	19.9	20.3	20.6	20.1	20.1	34.0	34.0	34.0
	100%	8.4	8.1	8.5	7.7	7.8	7.9	6.6	8.2	6.5	6.5	20.3	20.2	21.0	20.0	20.0	35.0	35.0	35.0
NAV-OF14-SDB2-FF	10%	8.1	7.9	8.2	7.6	7.7	7.4	7.0	8.4	8.1	7.1	20.5	20.2	20.1	20.4	20.3	33.0	32.0	32.0
	50%	8.4	8.0	8.4	7.6	7.7	7.7	6.1	8.7	7.1	6.4	20.3	20.2	20.1	20.3	20.1	33.0	32.0	33.0
	100%	8.5	8.2	8.6	7.9	8.0	7.9	5.4	8.7	8.8	7.4	20.5	20.1	20.0	20.3	20.1	33.0	33.0	34.0
NAV-OF14-SDB2-COMP	10%	8.0	7.9	8.2	7.6	7.7	7.3	7.0	8.3	7.7	6.7	20.5	20.3	20.4	20.1	20.0	33.0	32.0	32.0
	50%	8.3	7.9	8.4	7.6	7.7	7.5	6.7	8.5	7.7	6.8	20.5	20.2	20.8	20.0	20.0	33.0	33.0	33.0
	100%	8.5	8.2	8.5	7.8	7.8	7.8	6.7	8.4	7.2	6.4	20.5	20.1	21.0	19.9	20.0	33.0	33.0	33.0
NAV-BAY9-SDB2-PRE	100%	8.0	7.8	8.0	7.6	7.6	8.2	6.8	8.4	8.1	6.7	19.9	20.3	20.7	20.4	20.5	33.0	33.0	32.0
NAV-BAY11-SDB2-PRE	100%	8.0	7.8	8.1	7.5	7.6	8.1	6.8	8.0	7.8	6.7	19.8	20.4	20.9	20.5	20.5	33.0	33.0	32.0
NAV-BAY14-SDB2-PRE	100%	8.0	7.9	8.1	7.5	7.5	7.8	6.5	8.3	7.4	6.4	19.9	20.5	20.2	20.6	20.5	33.0	33.0	32.0
NAV-BAY14A-SDB2-PRE	100%	8.0	7.8	8.1	7.6	7.6	8.0	6.8	8.4	7.9	6.7	19.7	20.5	20.7	20.6	20.5	33.0	33.0	32.0
NAV-BAY9-SDB2-DUR	100%	7.9	7.8	7.9	7.5	7.6	7.0	6.5	8.3	7.8	6.5	20.5	20.5	20.2	20.4	20.4	31.0	31.0	31.0
NAV-BAY11-SDB2-DUR	100%	8.0	7.8	8.1	7.5	7.6	8.2	6.4	8.5	7.7	6.6	20.1	20.4	19.7	20.4	20.4	31.0	31.0	31.0
NAV-BAY14-SDB2-DUR	100%	8.0	7.8	8.1	7.5	7.6	8.1	6.7	8.4	7.7	6.6	20.0	20.4	20.1	20.5	20.4	32.0	32.0	32.0
NAV-BAY14A-SDB2-DUR	100%	8.0	7.8	8.1	7.5	7.6	8.2	6.6	8.5	7.4	6.5	19.9	20.4	20.1	20.5	20.4	32.0	32.0	32.0
NAV-BAY9-SDB2-AFT	100%	8.0	7.8	8.1	7.5	7.6	8.1	6.8	8.5	7.8	6.8	20.1	20.5	20.1	20.4	20.4	31.0	31.0	31.0
NAV-BAY11-SDB2-AFT	100%	8.0	7.8	8.1	7.5	7.6	8.0	6.7	8.6	8.0	6.8	20.1	20.4	19.9	20.4	20.3	31.0	31.0	31.0
NAV-BAY14-SDB2-AFT	100%	8.0	7.8	8.1	7.6	7.6	8.1	6.7	8.3	8.3	6.9	20.0	20.4	20.3	20.4	20.3	32.0	32.0	32.0
NAV-BAY14A-SDB2-AFT	100%	8.0	7.8	8.1	7.5	7.6	8.1	6.7	8.4	8.1	6.7	19.7	20.5	20.0	20.4	20.3	32.0	32.0	32.0
Natural Seawater Control	100%	7.8	7.8	7.9	7.5	7.5	8.7	6.5	8.9	7.6	6.5	20.1	20.3	19.2	20.4	20.4	33.0	33.0	33.0
Salt Control	100%	7.5	8.4	8.8	7.6	7.7	7.4	5.7	7.1	6.1	6.2	21.0	20.4	20.7	20.3	20.1	33.0	33.0	33.0

MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)		
		0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	96
NAV-PR5-SDB2-FF	10%	8.1	8.1	8.1	7.9	7.9	8.1	6.3	8.3	5.8	6.0	20.5	20.4	20.1	19.7	19.3	32.0	33.0	33.0
	50%	8.5	8.1	8.3	N	N	8.4	5.0	8.6	N	N	20.8	20.3	20.3	N	N	33.0	33.0	N
	100%	8.5	8.3	8.5	N	N	8.8	4.1 <sup>A</sup>	9.5	N	N	21.0	20.3	19.0	N	N	33.0	33.0	N
NAV-PR5-SDB2-COMP	10%	8.1	8.1	8.1	7.9	7.9	8.2	6.3	8.2	5.7	5.9	20.7	20.5	20.3	20.4	20.1	32.0	32.0	32.0
	50%	8.3	8.2	8.3	8.0	8.0	8.2	5.8	8.6	5.4	5.7	20.2	20.4	20.4	20.4	20.3	33.0	33.0	33.0
	100%	8.5	8.3	8.5	8.1	8.0	8.4	5.2	9.1	5.2	5.0	20.7	20.3	20.6	20.3	20.3	33.0	33.0	33.0
NAV-PR6-SDB2-FF	10%	8.1	7.9	8.1	7.8	7.8	8.2	4.9	8.3	5.4	6.0	20.2	20.4	20.3	19.9	19.7	33.0	33.0	32.0
	50%	8.3	7.8	8.3	8.2	8.1	8.5	2.3 <sup>A</sup>	8.8	7.2	6.6	20.3	20.4	20.3	19.2	19.6	33.0	33.0	35.0
	100%	8.5	7.9	8.5	8.2	8.1	8.8	1.2 <sup>A</sup>	9.6	7.3	6.8	20.7	20.3	19.0	19.3	19.4	33.0	33.0	35.0
NAV-PR6-SDB2-COMP	10%	8.1	8.0	8.1	7.9	7.9	8.1	6.0	8.2	5.6	5.7	20.5	20.7	20.3	20.3	20.1	33.0	32.0	32.0
	50%	8.3	8.1	8.3	7.9	8.0	8.4	5.4	8.5	5.3	5.3	20.8	20.5	20.5	20.3	20.1	33.0	33.0	33.0
	100%	8.5	8.2	8.5	8.3	8.3	8.5	3.8 <sup>A</sup>	9.5	6.9	6.9	21.0	20.4	19.3	20.1	20.0	33.0	33.0	34.0
NAV-OF9-SDB2-FF	10%	8.0	8.1	8.1	7.9	7.9	7.7	6.3	7.7	6.0	5.3	20.7	20.3	20.7	19.8	20.0	33.0	33.0	32.0
	50%	8.3	8.1	8.3	8.1	8.1	7.9	5.3 <sup>A</sup>	8.2	7.1	6.7	21.0	20.3	20.8	19.7	19.6	33.0	33.0	34.0
	100%	8.5	8.2	8.4	8.2	8.1	8.6	3.5 <sup>A</sup>	9.0	7.3	6.9	21.0	20.3	20.3	19.6	19.6	33.0	33.0	35.0
NAV-OF9-SDB2-COMP	10%	8.1	8.1	8.1	8.0	8.0	7.7	6.3	8.1	5.8	5.8	19.8	20.3	19.7	20.2	19.9	33.0	33.0	33.0
	50%	8.3	8.1	8.2	8.0	8.0	8.1	5.7	8.4	5.7	5.7	19.9	20.3	20.1	20.1	19.9	33.0	33.0	33.0
	100%	8.5	8.3	8.3	8.1	8.1	8.5	5.7	9.1	5.2	5.2	20.0	20.1	19.9	20.1	20.0	33.0	33.0	33.0
NAV-OF11-SDB2-FF	10%	8.1	8.1	8.1	7.9	7.9	7.7	6.1	8.0	5.6	5.4	20.1	20.4	20.6	20.0	19.9	33.0	32.0	33.0
	50%	8.4	8.2	8.3	8.0	N	8.0	5.5	8.5	5.9	N	20.6	20.3	20.3	20.0	N	33.0	33.0	N
	100%	8.5	8.3	8.5	N	N	8.6	4.6 <sup>A</sup>	9.6	N	N	20.8	20.3	19.0	N	N	33.0	33.0	N
	10%	8.1	7.9	8.1	7.9	7.9	7.8	6.3	8.1	6.1	6.1	20.5	20.6	19.8	20.3	20.3	33.0	33.0	32.0
	50%	8.2	8.1	8.2	7.9	8.0	8.1	6.3	8.5	5.7	5.7	20.6	20.4	19.9	20.3	20.3	34.0	34.0	33.0
	100%	8.4	8.2	8.3	8.1	8.0	8.4	5.7	9.0	5.4	5.3	20.9	20.3	19.4	20.3	20.3	35.0	35.0	34.0
NAV-OF14-SDB2-FF	10%	8.1	8.1	8.1	7.8	7.9	8.2	6.2	8.7	5.7	5.7	20.4	20.4	20.1	19.9	19.9	32.0	33.0	32.0
	50%	8.3	8.1	8.3	7.9	8.0	8.4	4.7 <sup>A</sup>	8.9	6.7	6.8	20.7	20.3	20.1	19.9	19.5	33.0	33.0	34.0
	100%	8.5	8.2	8.5	8.1	8.1	8.6	3.1 <sup>A</sup>	9.7	7.1	6.8	21.0	20.3	19.0	19.7	19.4	33.0	33.0	34.0
NAV-OF14-SDB2-COMP	10%	8.1	8.0	8.0	7.9	7.9	8.1	6.3	8.0	6.0	6.2	20.5	20.6	19.9	20.4	19.9	32.0	32.0	32.0
	50%	8.3	8.1	8.2	8.0	8.0	8.2	6.3	8.8	5.7	5.7	20.7	20.5	20.0	20.4	20.3	33.0	33.0	33.0
	100%	8.5	8.3	8.4	8.1	8.1	8.4	5.7	9.4	5.2	5.6	20.7	20.4	19.7	20.3	20.3	33.0	33.0	33.0
NAV-BAY9-SDB2-PRE	100%	7.7	8.1	7.9	7.9	8.0	8.1	8.4	9.3	6.1	6.2	21.0	20.7	21.0	20.3	19.9	33.0	33.0	33.0
NAV-BAY11-SDB2-PRE	100%	7.9	8.1	7.9	7.9	7.9	8.1	8.0	9.2	6.0	6.2	21.0	20.9	21.0	20.2	20.0	32.0	33.0	32.0
NAV-BAY14-SDB2-PRE	100%	7.8	8.1	7.9	7.9	7.9	8.2	8.0	9.8	6.2	6.4	21.0	20.9	21.0	20.2	19.9	32.0	33.0	33.0
NAV-BAY14A-SDB2-PRE	100%	7.9	8.1	7.9	7.8	7.9	8.2	8.4	6.1	5.8	6.2	21.0	20.7	20.3	19.8	19.9	32.0	32.0	32.0
NAV-BAY9-SDB2-DUR	100%	8.0	8.0	8.0	7.9	7.9	8.0	6.7	10.0	6.3	6.3	21.0	20.3	19.5	20.0	19.9	31.0	31.0	31.0
NAV-BAY11-SDB2-DUR	100%	8.0	8.0	8.0	7.9	7.9	8.1	6.4	10.0	6.3	6.3	20.5	20.3	20.3	20.0	19.7	31.0	31.0	31.0
NAV-BAY14-SDB2-DUR	100%	8.0	8.0	7.9	7.9	7.9	8.1	6.6	10.0	6.3	6.1	20.8	20.1	19.5	19.9	19.7	32.0	32.0	32.0
NAV-BAY14A-SDB2-DUR	100%	8.0	8.0	8.0	7.9	7.9	7.9	6.5	9.9	6.4	6.3	21.0	20.1	19.9	19.9	19.8	32.0	32.0	32.0
NAV-BAY9-SDB2-AFT	100%	8.0	7.9	8.0	7.9	7.9	8.0	6.5	9.0	6.2	5.9	21.0	20.6	19.3	20.1	19.9	31.0	31.0	31.0
NAV-BAY11-SDB2-AFT	100%	8.0	8.0	8.0	7.9	7.9	8.0	6.6	9.0	6.2	6.0	20.4	20.4	19.9	20.1	20.0	31.0	31.0	31.0
NAV-BAY14-SDB2-AFT	100%	8.0	8.0	8.0	7.9	7.9	7.9	6.6	9.3	6.3	6.1	21.0	20.3	19.3	20.1	20.0	31.0	31.0	31.0
NAV-BAY14A-SDB2-AFT	100%	8.0	8.0	8.0	7.9	7.9	7.9	6.4	9.3	6.3	6.1	20.5	20.3	19.0	20.1	20.0	32.0	32.0	32.0
Natural Seawater Control	100%	7.9	7.9	7.9	7.9	7.9	8.0	6.7	8.9	6.5	6.1	21.0	20.3	20.8	20.1	19.9	33.0	33.0	33.0
Salt Control	100%	8.4	8.3	8.2	8.1	8.0	7.1	5.9	8.2	5.5	5.9	21.0	20.3	20.4	19.8	20.0	33.0	33.0	33.0

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	pH (SU)		D.O. (mg/l)		Temp (°C)		Salinity (‰)	
		0	48	0	48	0	48	0	48
NAV-OF9-SDB2-FF	100%	7.9	7.9	9.5	8.1	15.2	15.5	33.0	33.0
NAV-OF9-SDB2-COMP	100%	7.9	8.0	9.5	8.4	15.2	15.1	33.0	34.0
NAV-OF11-SDB2-FF	100%	7.9	8.0	9.4	8.3	15.2	15.5	33.0	33.0
NAV-OF11-SDB2-COMP	100%	7.9	8.1	9.0	8.3	15.2	15.0	32.0	34.0
NAV-OF14-SDB2-FF	100%	7.9	8.0	9.5	8.3	15.2	15.2	33.0	34.0
NAV-OF14-SDB2-COMP	100%	7.9	8.1	9.5	8.3	15.2	15.0	32.0	34.0
NAV-PR5-SDB2-COMP	100%	7.9	8.1	9.4	8.4	15.2	14.9	33.0	36.0
NAV-PR6-SDB2-COMP	100%	7.9	8.0	9.5	8.4	15.2	14.9	33.0	34.0
NAV-BAY9-SDB2-PRE	100%	8.0	7.9	9.5	8.3	15.2	14.7	32.0	33.0
NAV-BAY11-SDB2-PRE	100%	8.0	7.9	9.4	8.1	15.2	14.7	32.0	33.0
NAV-BAY14-SDB2-PRE	100%	8.0	8.0	9.2	8.3	15.2	14.6	32.0	33.0
NAV-BAY14A-SDB2-PRE	100%	8.0	8.0	9.2	8.4	15.2	14.6	32.0	33.0
NAV-BAY9-SDB2-DUR	100%	8.0	8.0	9.4	8.3	15.2	14.6	31.0	31.0
NAV-BAY11-SDB2-DUR	100%	8.0	8.0	9.5	8.4	15.2	14.6	31.0	32.0
NAV-BAY14-SDB2-DUR	100%	8.0	8.0	9.4	8.4	15.2	14.6	31.0	32.0
NAV-BAY14A-SDB2-DUR	100%	8.0	8.0	9.4	8.4	15.2	14.6	32.0	32.0
NAV-BAY9-SDB2-AFT	100%	8.0	8.0	9.4	8.3	15.2	14.8	31.0	31.0
NAV-BAY11-SDB2-AFT	100%	8.0	8.0	9.3	8.4	15.2	14.6	31.0	32.0
NAV-BAY14-SDB2-AFT	100%	8.0	8.0	9.4	8.3	15.2	14.6	31.0	32.0
NAV-BAY14A-SDB2-AFT	100%	8.0	8.0	9.3	8.3	15.2	14.6	31.0	32.0
Natural Seawater Control	100%	8.0	8.0	8.3	8.4	15.2	14.6	33.0	34.0
Brine Control	100%	7.9	8.0	7.8	8.4	15.2	14.2	33.0	34.0

N - water quality not taken due to 100% mortality in treatment

<sup>A</sup> Sample mg/L was aerated due to D.O. near 4.0 mg/L

# TIE1 – 02/18/2004

## OUTFALLS

### INLAND SILVERSIDE (*M. berylina*)

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NAV-OF9-TIE1-FF	25	100.0
	50	100.0
	100	96.0
NAV-OF11-TIE1-FF	25	100.0
	50	96.0
	100	100.0
NAV-OF14-TIE1-FF	25	100.0
	50	100.0
	100	100.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NAV-OF9-TIE1-FF	10	100.0
	50	93.0
	100	90.0
NAV-OF11-TIE1-FF	25	100.0
	50	98.0
	100	85.0
NAV-OF14-TIE1-FF	25	93.0
	50	98.0
	100	85.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
NAV-OF9-TIE1-FF	13	82.0
	25	81.0
	50	1.0
	68	0.0
NAV-OF11-TIE1-FF	13	77.0
	25	79.0
	50	0.0
	68	0.0
NAV-OF14-TIE1-FF	13	77.0
	25	61.0
	50	0.0
	68	0.0

Please refer to TIE Report August 2004 for raw data and water quality



## QA/QC SAMPLES<sup>a</sup>

### INLAND SILVERSIDE (*M. berylina*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Natural Seawater Control	n/a	100.0
Salt Control	n/a	96.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Natural Seawater Control	n/a	95.0
Salt Control	n/a	100.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN NORM DEV (%)
Natural Seawater Control	n/a	81.0
Brine Control	n/a	80.0

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
INLAND SILVERSIDE	02/26/004	100	200	137.6	129.5-146.2
MYSIDS	2/27/2004	200	400	337.1	242.4-438.7
MUSSELS	2/19/2004	5	10	10.2	9.9-10.5

Please refer to TIE Report August 2004 for raw data and water quality

# SDB4 – 10/17/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB4-FF	12.5	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	25	a	5	100	100.0	19.1	100.0	0.108	No
		b	4	100					
		c	3	100					
		d	5	100					
	50	a	5	100	80.0	28.3	80.0	0.126	No
		b	5	100					
		c	2	40					
		d	4	80					
	100	a	1	20	25.0	19.1	25.0	0.002	Yes
		b	2	40					
		c	2	40					
		d	0	0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB4-FF	12.5	a	9	90	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	10	100					
	25	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	50	a	8	80	86.7	11.5	86.7	0.211	No
		b	8	80					
		c	10	100					
	100	a	4	40	43.3	5.8	43.3	0.002	Yes
		b	4	40					
		c	5	50					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB4-FF	6.25	a	103	23	81.7	75.5	12.5	77.4	0.012	Yes
		b	123	37	76.9					
		c	143	58	71.1					
		d	142	15	90.4					
		e	105	79	57.1					
	12.5	a	29	136	17.6	7.1	6.5	7.3	0.000	Yes
		b	2	174	1.1					
		c	4	160	2.4					
		d	12	149	7.5					
		e	9	124	6.8					
	25	a	1	180	0.6	1.8	1.3	1.8	0.000	Yes
		b	3	164	1.8					
		c	7	171	3.9					
		d	2	151	1.3					
		e	2	163	1.2					
	50	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					
	62.7	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken during the storm (DUR) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB4-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
ALL-BAY-SDB4-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	-
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB4-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
ALL-BAY-SDB4-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	-
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB4-DUR	100	a	2	160	1.2	8.2	7.5	8.4	0.000	Yes
		b	12	158	7.1					
		c	33	140	19.1					
		d	20	148	11.9					
		e	3	171	1.7					
ALL-BAY-SDB4-PRE	100	a	183	3	98.4	97.5	0.9	100.0	-	-
		b	165	3	98.2					
		c	179	4	97.8					
		d	175	7	96.2					
		e	192	6	97.0					

All – Sample collected at SSC-SD

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	90.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	9	90.0	83.3	5.8	89.3	0.051	No
		b	8	80.0					
		c	8	80.0					
	400	a	2	20.0	6.7	11.5	7.1	0.001	Yes
		b	0	0.0					
		c	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	148	25	85.5	94.5	5.4	100.0	n/a	No
		b	175	5	97.2					
		c	139	10	93.3					
		d	193	4	98.0					
		e	174	3	98.3					
Brine Control	n/a	a	177	6	96.7	95.7	1.1	98.1	0.011	Yes
		b	170	10	94.4					
		c	186	6	96.9					
		d	171	8	95.5					
		e	164	9	94.8					
Copper Ref. Tox.	2.9	a	167	9	94.9	95.1	0.7	100.7	0.374	No
		b	200	11	94.8					
		c	168	10	94.4					
		d	176	8	95.7					
		e	168	7	96.0					
	4.1	a	166	3	98.2	90.3	10.0	95.6	0.308	No
		b	202	7	96.7					
		c	164	17	90.6					
		d	118	43	73.3					
		e	141	11	92.8					
	5.9	a	178	9	95.2	79.0	14.3	83.7	0.182	Yes
		b	169	20	89.4					
		c	157	36	81.3					
		d	128	60	68.1					
		e	124	79	61.1					
	8.4	a	69	106	39.4	23.7	13.7	25.1	0.017	Yes
		b	56	141	28.4					
		c	58	126	31.5					
		d	12	177	6.3					
		e	24	162	12.9					
	12.0	a	1	177	0.6	1.3	1.3	1.3	0.000	Yes
		b	5	172	2.8					
		c	5	203	2.4					
		d	1	207	0.5					
		e	0	171	0.0					
	17.2	a	3	177	1.7	0.5	0.7	0.5	0.000	Yes
		b	1	167	0.6					
		c	0	191	0.0					
		d	0	175	0.0					
		e	0	199	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	50	100	132.0	120.2-144.8
MYSIDS	200	400	265.3	232.5-302.4
MUSSELS	5.9	8.4	7.29	6.1-8.3

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a- t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF14-SDB4-FF	12.5%	a	7.9	7.8	7.6	7.6	7.6	6.6	5.6	5.2	5.3	5.5	20.2	18.3	19.6	19.2	19.4	33.7	34.1	34.4	34.4	34.5
	25%	a	7.9	7.7	7.7	7.7	7.8	6.7	6.6	6.2	6.8	7.0	19.9	18.0	19.6	19.4	19.3	33.6	34.0	34.3	34.3	34.3
	50%	a	8.0	7.7	7.7	7.8	7.8	6.6	6.7	6.2	6.5	6.5	19.4	18.3	19.4	18.9	19.3	33.2	33.5	34.3	34.3	34.6
	100%	a	8.2	7.7	7.3	7.7	7.8	6.8	6.6	3.0	6.6	7.0	18.2	18.1	19.5	19.0	18.7	32.4	32.7	33.9	33.9	34.4
NAV-BAY14-SDB4-DUR	100%	a	7.7	7.5	7.6	7.6	7.7	6.7	5.7	5.2	6.1	6.2	18.8	18.3	19.6	19.4	19.5	30.8	31.0	31.1	31.4	31.4
Scripps Control	0	a	7.8	7.8	7.7	7.8	7.7	6.9	5.9	5.5	6.0	6.0	19.1	18.3	19.7	19.0	19.5	33.8	34.0	34.0	34.3	34.3
Cu Ref. Tox.	50 µg/l	a	7.9	7.8	7.7	7.8	7.7	6.9	6.2	6.5	6.3	5.9	18.7	18.0	19.2	19.1	19.4	33.9	34.4	34.7	34.2	34.3
	100 µg/l	a	7.9	7.8	7.0	7.8	7.8	7.1	6.0	6.1	6.4	6.3	18.8	18.0	19.1	19.0	19.4	33.8	34.1	34.5	34.3	34.5
	200 µg/l	a	7.8	7.8	7.7	7.9	7.8	7.0	6.0	5.9	6.5	6.5	18.6	18.1	19.4	19.1	19.3	33.8	34.0	34.7	34.1	34.2
	400 µg/l	a	7.8	7.9	N	N	N	7.0	6.2	N	N	N	18.6	18.0	N	N	N	33.8	34.1	N	N	N
Salt Control	n/a	a	8.1	7.9	7.7	7.8	7.6	6.9	5.9	6.2	6.0	6.1	19.8	18.0	18.9	18.9	19.4	33.3	33.5	33.6	33.6	33.7

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF14-SDB4-FF	12.5%	a	7.9	7.6	7.6	7.6	7.5	6.7	4.7	4.5	4.0	4.4	19.7	18.6	19.6	19.4	19.6	34.2	34.5	34.5	34.4	34.4
	25%	a	7.9	7.7	7.8	7.7	7.9	6.7	6.7	6.5	6.2	7.1	19.5	18.6	19.4	19.3	19.3	34.0	34.3	34.3	34.3	34.6
	50%	a	8.0	7.7	7.8	7.8	7.8	6.6	6.6	6.5	6.5	6.4	19.3	18.3	19.4	19.2	19.4	33.7	34.1	34.2	34.3	34.7
	100%	a	8.2	7.7	7.8	7.7	7.9	6.7	6.8	6.4	6.0	6.6	18.5	17.7	19.1	19.1	19.3	32.9	33.3	33.4	33.8	34.2
NAV-BAY14-SDB4-DUR	100%	a	7.7	7.5	7.5	7.6	7.7	6.8	4.7	4.8	5.4	5.3	18.6	18.3	19.6	19.6	19.6	31.2	31.5	31.4	31.7	31.8
Scripps Control	0	a	7.9	7.7	7.7	7.7	7.6	6.9	4.7	5.3	5.0	4.8	18.8	18.3	19.4	19.3	19.5	34.4	34.6	34.6	34.2	34.3
Cu Ref. Tox.	25 µg/l	a	7.9	7.7	7.7	7.8	7.6	6.9	5.4	5.7	5.4	5.2	18.8	18.6	19.4	19.3	19.6	34.3	34.4	34.6	34.3	34.3
	50 µg/l	a	7.9	7.7	7.6	7.7	7.6	7.1	5.3	5.3	5.0	4.5	18.7	18.6	19.5	19.3	19.6	34.4	34.5	34.5	34.2	34.2
	100 µg/l	a	7.9	7.7	7.6	7.7	7.7	7.1	5.7	4.9	5.6	5.1	18.6	18.5	19.4	19.3	19.6	34.2	34.4	34.5	34.3	34.3
	200 µg/l	a	7.9	7.8	7.8	7.8	7.7	7.0	5.9	6.3	6.1	5.7	18.7	18.6	19.1	19.3	19.6	34.4	34.6	34.2	34.3	34.4
	400 µg/l	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2
Salt Control	n/a	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)		D.O. (mg/l)		Temp (°C)		Salinity (‰)	
			0	48	0	48	0	48	0	48
NAV-OF14-SDB4-FF	6.25%	f	7.7	7.6	7.0	6.6	15.7	15.7	33.6	33.8
	25%	f	7.7	7.6	7.0	5.8	15.5	15.7	34.0	33.9
	62.7%	f	7.7	7.3	6.9	3.3	15.6	15.7	33.6	34.0
NAV-BAY14-SDB4-DUR	100%	f	7.7	7.8	7.0	6.8	15.1	15.3	34.0	34.2
Scripps Control	0	f	7.8	7.6	6.9	6.8	15.6	15.7	34.0	34.2
Cu Ref. Tox.	2.9 µg/l	f	7.8	7.8	7.0	6.8	15.8	15.7	33.9	34.1
	8.4 µg/l	f	7.8	7.7	6.9	6.8	15.7	15.5	33.9	34.1
	24 µg/l	f	7.8	7.8	6.9	7.1	15.8	15.5	34.1	34.1
Brine Control	0	f	7.9	7.9	7.0	7.0	15.5	15.7	33.7	34.2

N - water quality not taken due to 100% mortality in treatment

# SDB45 – 10/26/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB45-FF	12.5	a	5	100	95.0	10.0	95.0	0.196	No
		b	4	80					
		c	5	100					
		d	5	100					
	25	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	50	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	100	a	4	80	90.0	11.5	90.0	0.091	No
		b	5	100					
		c	5	100					
		d	4	80					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB45-FF	12.5	a	9	90	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	10	100					
	25	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	50	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	100	a	7	70	63.3	5.8	63.3	0.004	Yes
		b	6	60					
		c	6	60					
NAV-OF14-SDB45-COMP	100	a	7	70	80.0	10.0	80.0	0.037	Yes
		b	9	90					
		c	8	80					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB45-FF	6.25	a	172	13	93.0	93.9	3.0	101.4	0.244	No
		b	172	16	91.5					
		c	158	14	91.9					
		d	181	11	94.3					
		e	186	2	98.9					
	12.5	a	185	10	94.9	96.2	1.1	103.9	0.020	Yes <sup>c</sup>
		b	184	4	97.9					
		c	155	6	96.3					
		d	149	7	95.5					
		e	193	7	96.5					
	25	a	158	11	93.5	94.4	1.5	102.0	0.122	No
		b	169	9	94.9					
		c	159	12	93.0					
		d	180	12	93.8					
		e	181	6	96.8					
	50	a	135	25	84.4	40.4	27.2	43.7	0.006	Yes
		b	25	133	15.8					
		c	61	114	34.9					
		d	39	144	21.3					
		e	71	84	45.8					
	61.4	a	5	142	3.4	1.2	1.4	1.2	0.000	Yes
		b	2	170	1.2					
		c	2	165	1.2					
		d	0	147	0.0					
		e	0	167	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-OF14-SDB45-COMP	6.25	a	200	10	95.2	94.0	2.1	101.6	0.186	No
		b	173	9	95.1					
		c	202	8	96.2					
		d	158	13	92.4					
		e	158	15	91.3					
	12.5	a	187	11	94.4	95.6	1.5	103.2	0.039	Yes <sup>c</sup>
		b	169	11	93.9					
		c	183	4	97.9					
		d	186	8	95.9					
		e	182	8	95.8					
	25	a	170	5	97.1	94.3	2.1	101.9	0.144	No
		b	152	9	94.4					
		c	157	14	91.8					
		d	169	8	95.5					
		e	170	13	92.9					
	50	a	162	7	95.9	93.6	2.7	101.1	0.285	No
		b	145	7	95.4					
		c	147	17	89.6					
		d	151	8	95.0					
		e	163	14	92.1					
	61.4	a	122	21	85.3	86.4	1.1	93.3	0.003	Yes
		b	132	21	86.3					
		c	137	21	86.7					
		d	147	20	88.0					
		e	113	19	85.6					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB45

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB45-PRE	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB45-PRE	100	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB45-PRE	100.0	a	206	12	94.5	92.6	2.8	100.0	n/a	n/a
		b	149	16	90.3					
		c	168	13	92.8					
		d	142	17	89.3					
		e	165	7	95.9					



## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100	90.0	11.5	90.0	0.091	No
		b	4	80					
		c	5	100					
		d	4	80					
	100	a	4	80	60.0	16.3	60.0	0.008	Yes
		b	2	40					
		c	3	60					
		d	3	60					
	200	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	0	0					
	400	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	0	0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	10	100.0	100.0	0.0	100.0	n/a	n/a
		b	10	100.0					
		c	10	100.0					
Salt Control	n/a	a	9	90.0	80.0	26.5	80.0	0.160	No
		b	10	100.0					
		c	5	50.0					
Copper Ref. Tox.	25	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	50	a	10	100	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	9	90					
	100	a	10	100	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	9	90					
	200	a	9	90	83.3	11.5	83.3	0.065	No
		b	7	70					
		c	9	90					
	400	a	1	10	6.7	5.8	6.7	0.001	Yes
		b	1	10					
		c	0	0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	148	25	85.5	94.5	5.4	100.0	n/a	No
		b	175	5	97.2					
		c	139	10	93.3					
		d	193	4	98.0					
		e	174	3	98.3					
Brine Control	n/a	a	177	6	96.7	95.7	1.1	98.1	0.011	Yes
		b	170	10	94.4					
		c	186	6	96.9					
		d	171	8	95.5					
		e	164	9	94.8					
Copper Ref. Tox.	2.9	a	167	9	94.9	95.1	0.7	100.7	0.374	No
		b	200	11	94.8					
		c	168	10	94.4					
		d	176	8	95.7					
		e	168	7	96.0					
	4.1	a	166	3	98.2	90.3	10.0	95.6	0.308	No
		b	202	7	96.7					
		c	164	17	90.6					
		d	118	43	73.3					
		e	141	11	92.8					
	5.9	a	178	9	95.2	79.0	14.3	83.7	0.182	Yes
		b	169	20	89.4					
		c	157	36	81.3					
		d	128	60	68.1					
		e	124	79	61.1					
	8.4	a	69	106	39.4	23.7	13.7	25.1	0.017	Yes
		b	56	141	28.4					
		c	58	126	31.5					
		d	12	177	6.3					
		e	24	162	12.9					
	12.0	a	1	177	0.6	1.3	1.3	1.3	0.000	Yes
		b	5	172	2.8					
		c	5	203	2.4					
		d	1	207	0.5					
		e	0	171	0.0					
	17.2	a	3	177	1.7	0.5	0.7	0.5	0.000	Yes
		b	1	167	0.6					
		c	0	191	0.0					
		d	0	175	0.0					
		e	0	199	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	50	100.0	97.7	80.6-118.1
MYSIDS	100	200.0	287.0	237.0-314.4
MUSSELS <sup>d</sup>	5.9	8.4	7.3	6.1-8.3

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB45

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>d</sup>Copper reference toxicant test performed on 10/17/2004

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF14-SDB45-FF	12.5%	a	8.0	7.8	7.7	7.7	7.7	6.6	7.0	6.4	6.3	5.9	18.4	18.9	19.1	19.0	19.1	33.8	33.9	34.3	34.3	34.6
	25%	a	8.2	7.9	7.7	7.6	7.7	6.8	7.1	6.4	6.2	6.0	18.3	18.0	19.1	18.9	19.1	33.8	34.0	34.4	34.3	34.6
	50%	a	8.5	8.1	7.8	7.8	7.7	6.7	6.5	6.5	5.8	5.5	18.3	18.9	19.1	19.0	19.1	33.8	34.0	34.2	34.3	34.4
	100%	a	8.8	8.3	8.1	8.1	7.9	6.6	5.6	5.6	4.5	4.5	18.4	19.0	19.3	19.3	19.3	34.0	34.0	34.1	34.5	34.5
NAV-BAY14-SDB45-PRE	100%	a	7.8	7.7	7.7	7.6	7.6	6.8	6.9	6.6	6.0	5.7	18.4	19.1	18.8	19.1	19.2	33.7	33.9	34.2	34.1	34.0
Scripps Cu Ref. Tox.	50 µg/l	a	7.9	7.8	7.7	7.7	7.6	6.4	7.1	6.8	6.6	6.0	18.3	19.3	18.9	19.2	19.1	33.9	34.0	34.4	34.1	34.0
	100 µg/l	a	7.9	7.7	7.7	7.7	7.7	6.6	7.0	6.6	6.7	6.3	18.3	19.1	18.9	19.0	19.4	33.9	34.0	34.4	34.3	34.7
	200 µg/l	a	7.9	7.7	7.7	N	N	6.6	7.0	6.9	N	N	18.3	19.2	19.0	N	N	33.9	33.9	34.1	N	N
	400 µg/l	a	7.8	7.8	7.7	N	N	6.7	7.0	7.1	N	N	18.3	19.1	19.1	N	N	33.9	34.0	34.5	N	N
Salt Control	n/a	a	8.0	7.6	7.6	7.8	7.7	6.2	7.0	6.8	6.3	6.2	19.0	19.1	18.6	18.9	19.0	33.3	33.6	34.1	33.9	34.3

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAV-OF14-SDB45-FF	12.5%	a	8.0	8.0	7.7	7.6	7.6	6.9	6.1	5.5	4.4	4.4	18.6	19.3	18.8	19.1	19.3	33.6	33.8	34.2	34.0	34.1
	25%	a	8.2	8.0	7.7	7.9	7.7	6.8	6.6	5.2	6.3	5.8	18.6	19.3	19.0	19.2	18.8	33.8	33.7	34.0	34.1	34.4
	50%	a	8.6	8.2	8.0	7.8	7.8	7.0	5.3	4.5	2.5	7.1	18.6	19.4	19.0	19.2	18.9	33.7	33.8	33.9	34.1	34.4
	100%	a	9.1	8.6	8.3	8.3	ND	7.0	5.0	4.7	4.0	6.7	18.6	19.4	19.0	19.1	19.1	33.9	33.9	34.1	34.5	34.7
NAV-OF14-SDB45-COMP	100%	a	ND	8.6	8.3	8.5	8.3	ND	6.1	5.1	5.2	4.6	ND	19.3	18.9	19.1	19.3	ND	32.6	32.7	34.4	34.5
NAV-BAY14-SDB45-PRE	100%	a	7.8	7.7	7.5	7.4	7.9	6.8	6.2	5.6	3.7	7.0	18.8	19.4	19.0	19.1	19.0	33.6	33.6	33.8	33.9	34.4
Scripps Control	0	a	7.9	7.7	7.6	7.5	7.8	6.7	6.4	5.3	5.2	5.7	19.0	19.3	18.9	19.1	18.9	33.8	33.9	34.0	34.1	34.4
Scripps Cu Ref. Tox.	25 µg/l	a	7.9	7.8	7.6	7.6	7.7	6.8	7.2	6.7	5.9	5.2	18.5	19.4	19.0	19.1	19.5	33.9	33.9	34.2	33.8	34.0
	50 µg/l	a	7.9	7.7	7.6	7.6	7.5	6.6	6.8	6.4	4.5	4.0	18.8	19.4	19.0	19.1	19.5	33.9	33.9	34.0	34.0	34.1
	100 µg/l	a	7.9	7.7	7.6	7.6	7.6	6.7	6.3	6.4	5.2	4.9	18.8	19.3	19.0	19.1	19.4	33.9	33.9	34.2	34.0	34.1
	200 µg/l	a	7.9	7.7	7.6	7.7	7.7	6.7	6.7	6.7	6.1	5.4	18.8	19.3	18.9	19.1	19.4	33.9	34.0	34.2	34.1	34.2
	400 µg/l	a	7.9	7.8	7.6	7.7	7.7	6.6	6.8	7.1	6.5	6.0	18.6	19.3	19.0	19.3	19.6	33.9	34.0	34.1	34.0	34.2
Salt Control	n/a	a	8.0	7.9	7.7	7.9	7.7	6.0	6.6	5.5	5.2	5.5	19.4	19.4	19.0	19.1	18.8	33.2	33.2	33.4	33.6	34.1

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			D.O. (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NAV-OF14-SDB45-FF	6.25%	f	7.8	7.8	7.8	6.8	7.6	7.6	17.1	17.2	16.5	33.7	33.7	33.6
	12.5%	f	7.8	7.8	7.8	7.1	7.9	7.6	17.2	17.5	16.5	33.6	33.4	33.5
	25%	f	7.8	7.9	7.7	7.1	6.9	7.5	16.7	17.0	16.4	33.9	33.8	34.0
	50.00%	f	7.9	7.8	7.7	7.0	6.6	7.7	17.2	17.5	16.4	34.0	34.1	34.4
	61.4%	f	8.0	7.9	7.7	7.1	6.6	7.2	16.9	17.2	16.5	33.9	33.7	34.0
NAV-OF14-SDB45-COMP	6%	f	7.8	7.8	7.8	7.0	7.2	7.7	17.1	17.7	16.4	33.6	33.5	33.5
	12.50%	f	7.8	7.8	7.8	7.0	6.7	6.7	17.7	18.0	16.5	33.6	33.7	34.0
	25.0%	f	7.8	7.8	7.8	7.2	6.4	6.4	17.1	17.1	16.5	33.6	33.6	33.7
	50%	f	7.9	7.8	7.8	7.1	7.0	7.5	17.3	17.7	16.6	33.7	33.8	34.0
	61.4%	f	7.9	7.8	7.8	7.4	7.5	7.5	17.5	17.3	16.6	33.9	33.7	33.9
NAV-BAY14-SDB45-PRE	100%	f	7.9	7.8	7.8	6.9	6.9	7.6	ND	18.3	16.3	ND	33.7	33.9
Scripps Control	0	f	7.8	ND	7.6	6.9	ND	6.8	15.6	ND	15.7	34.0	ND	34.2
Cu Ref. Tox.	2.9 µg/l	f	7.8	ND	7.8	7.0	ND	6.8	15.8	ND	15.7	33.9	ND	34.1
	8.4 µg/l	f	7.8	ND	7.7	6.9	ND	6.8	15.7	ND	15.5	33.9	ND	34.1
	24 µg/l	f	7.8	ND	7.8	6.9	ND	7.1	15.8	ND	15.5	34.1	ND	34.1
Brine Control	0	f	7.9	ND	7.9	7.0	ND	7.0	15.5	ND	15.7	33.7	ND	34.2

N - water quality not taken due to 100% mortality in treatment

ND - water quality not recorded

# SDB5 – 01/10/2005

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB	100	a	5	100.0	100	0.0	100	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB5-AFT	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAV-BAY14-SDB5-AFT	100	a	162	8	95.3	94.9	2.0	105.3	0.004	Yes <sup>c</sup>
		b	156	14	91.8					
		c	149	6	96.1					
		d	166	10	94.3					
		e	168	5	97.1					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	(% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100	100.0	0.0	100.0	n/a	n/a
		b	5	100					
		c	5	100					
		d	5	100					
Copper Ref. Tox.	25	a	5	100.0	100	0.0	100	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	95	10.0	95	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90	11.5	90	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	1	20.0	15	10.0	15	0.000	Yes
		b	1	20.0					
		c	1	20.0					
		d	0	0.0					
	400	a	0	0.0	0	0.0	0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Copper Ref. Tox.	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	11	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	8	80.0	90.0	10.0	96.4	0.325	No
		b	9	90.0					
		c	10	100.0					
	400	a	2	20.0	26.7	11.5	28.6	0.002	Yes
		b	2	20.0					
		c	4	40.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	ABNORMA	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	No
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	138.54	114.4-167.8
MYSIDS	200	400	324.9	276.2-379.8
MUSSELS <sup>d</sup>	4.1	5.9	6.0	5.9-6.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB5

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>d</sup>Copper reference toxicant test performed on 02/10/2005

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## **Appendix C2**

### ***SUB***

SDB2- 2/24/2003  
SDB2A- 12/11/2003  
SDB3- 10/17/2004  
TIE1- 2/18/2004  
TIE1A- 2/26/2004  
SDB4- 10/26/2004  
SDB5- 01/10/2005

## SDB2 – 02/24/2003

### OUTFALLS

#### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB2-FF	10	a	5	100.0	100.0	0.0	111.1	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	90.0	11.5	100.0	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	100	a	3	60.0	85.0	19.1	94.4	0.337	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
SUB-OF24-SDB2-FF	10	a	4	80.0	90.0	11.5	100.0	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	90.0	11.5	100.0	0.500	No
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					
	100	a	4	80.0	80.0	0.0	88.9	0.091	No
		b	4	80.0					
		c	4	80.0					
		d	4	80.0					
SUB-OF26-SDB2-FF	25	a	5	100.0	85.0	19.1	94.4	0.337	No
		b	3	60.0					
		c	5	100.0					
		d	4	80.0					
	50	a	4	80.0	90.0	11.5	100.0	0.500	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	100.0	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					

#### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	9	90.0					
	100	a	7	70.0	86.7	15.3	86.7	0.135	No
		b	10	100.0					
		c	9	90.0					



**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF24-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
SUB-OF26-SDB2-FF	10	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB2-FF	10.00	a	93	7	93.0	96.2	2.6	111.9	0.015	Yes <sup>c</sup>
		b	97	3	97.0					
		c	96	4	96.0					
		d	100	0	100.0					
		e	95	5	95.0					
	50.0	a	93	7	93.0	94.2	1.9	109.5	0.030	Yes <sup>c</sup>
		b	95	5	95.0					
		c	92	8	92.0					
		d	97	3	97.0					
		e	94	6	94.0					
	58	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					
SUB-OF24-SDB2-FF	10	a	93	7	93.0	95.6	2.3	111.2	0.018	Yes <sup>c</sup>
		b	94	6	94.0					
		c	98	2	98.0					
		d	95	5	95.0					
		e	98	2	98.0					
	50	a	84	16	84.0	63.4	15.1	73.7	0.012	Yes
		b	44	56	44.0					
		c	71	29	71.0					
		d	56	44	56.0					
		e	62	38	62.0					
	58	a	0	100	0.0	0.2	0.4	0.2	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	1	99	1.0					
		e	0	100	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF26-SDB2-FF	10	a	93	7	93.0	96.2	2.6	111.9	0.015	Yes <sup>c</sup>
		b	100	0	100.0					
		c	95	5	95.0					
		d	96	4	96.0					
		e	97	3	97.0					
	50	a	36	64	36.0	40.4	11.7	47.0	0.000	Yes
		b	38	62	38.0					
		c	35	65	35.0					
		d	32	68	32.0					
		e	61	39	61.0					
	58	a	0	100	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	100	0.0					
		c	0	100	0.0					
		d	0	100	0.0					
		e	0	100	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB2

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2-PRE	100	a	4	80.0	90.0	11.5	92.3	0.149	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
SUB-BAY11B-SDB2-AFT	100	a	5	100.0	100.0	0.0	102.6	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY24-SDB2-AFT	100	a	5	100.0	100.0	0.0	102.6	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAV-BAY26-SDB2-AFT	100	a	4	80.0	95.0	10.0	97.4	0.338	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2-PRE	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY11B-SDB2-AFT	100	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
SUB-BAY24-SDB2-AFT	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26-SDB2-AFT	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2-PRE	100	a	89	11	89.0	86.0	7.1	89.4	0.015	Yes
		b	83	17	83.0					
		c	93	7	93.0					
		d	75	25	75.0					
		e	90	10	90.0					
SUB-BAY11B-SDB2-AFT	100	a	94	6	94.0	86.8	7.3	90.2	0.021	Yes
		b	93	7	93.0					
		c	77	23	77.0					
		d	88	12	88.0					
		e	82	18	82.0					
SUB-BAY24-SDB2-AFT	100	a	78	22	78.0	87.8	9.7	91.3	0.064	No
		b	96	4	96.0					
		c	91	9	91.0					
		d	77	23	77.0					
		e	97	3	97.0					
SUB-BAY26-SDB2-AFT	100	a	88	12	88.0	91.0	4.2	94.6	0.035	Yes
		b	88	12	88.0					
		c	88	12	88.0					
		d	97	3	97.0					
		e	94	6	94.0					

**QA/QC SAMPLES<sup>a</sup>**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	10	100.0	97.5	5.0	n/a	n/a	n/a
		b	10	100.0					
		c	10	100.0					
		d	9	90.0					
Salt Control 2	n/a	a	8	80.0	87.5	5.0	89.7	0.015	Yes
		b	9	90.0					
		c	9	90.0					
		d	9	90.0					
Salt Control 3	n/a	a	10	100.0	95.0	5.8	97.4	0.269	No
		b	10	100.0					
		c	9	90.0					
		d	9	90.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	10	100.0	100.0	0.0	100.0	n/a	n/a
		b	10	100.0					
		c	10	100.0					
Salt Control 1	n/a	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
Salt Control 2	n/a	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Natural Seawater Control	n/a	a	99	1	99.0	96.2	3.6	n/a	n/a	n/a
		b	97	3	97.0					
		c	92	8	92.0					
		d	100	0	100.0					
		e	93	7	93.0					
Brine Control	n/a	a	98	2	98.0	94.4	3.3	98.1	0.215	No
		b	91	9	91.0					
		c	91	9	91.0					
		d	95	5	95.0					
		e	97	3	97.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100.0	200.0	161.5	135.2-193.3
MYSIDS	100.0	200.0	237.4	212.4-266.0
MUSSELS	5.0	100.0	7.5	n/a

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB2

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## SDB2A – 12/11/2003

### BAY SAMPLES

#### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2A-PRE	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY23C&E-SDB2A-PRE	100	a	4	80.0	90.0	11.5	94.7	0.269	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY26-SDB2A-PRE	100	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					

#### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2A-PRE	100	a	9	90.0	93.3	5.8	96.6	0.259	No
		b	9	90.0					
		c	10	100.0					
SUB-BAY23C&E-SDB2A-PRE	100	a	10	100.0	96.7	5.8	100.0	0.500	No
		b	9	90.0					
		c	10	100.0					
SUB-BAY26-SDB2A-PRE	100	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					

#### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB2A-PRE	100	a	94.8	86.0	7.0	95.0	0.146	No
		b	77.8					
		c	85.6					
		d	86.0					
SUB-BAY23C&E-SDB2A-PRE	100	a	90.2	88.1	2.3	97.3	0.087	No
		b	86.0					
		c	90.0					
		d	86.1					
SUB-BAY26-SDB2A-PRE	100	a	89.2	86.7	3.2	95.7	0.051	No
		b	84.9					
		c	83.1					
		d	89.6					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	10	100.0	95.0	10.0	n/a	n/a	n/a
		b	10	100.0					
		c	8	80.0					
		d	10	100.0					
Copper Ref. Tox.	50	a	4	80.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	90.0	11.5	90.0	0.282	No
		b	5	100.0					
		c	2	40.0					
		d	5	100.0					
	200	a	2	40.0	0.0	0.0	0.0	0.048	Yes
		b	4	80.0					
		c	0	0.0					
		d	4	80.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	1	20.0					
		d	0	0.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	10	100.0	96.7	5.8	n/a	n/a	n/a
		b	10	100.0					
		c	9	90.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	96.7	5.8	100.0	0.500	No
		b	10	100.0					
		c	9	90.0					
	200	a	9	90.0	93.3	5.8	96.6	0.259	No
		b	9	90.0					
		c	10	100.0					
	400	a	0	0.0	3.3	5.8	3.4	0.000	Yes
		b	1	10.0					
		c	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	87.8	90.6	2.2	n/a	n/a	n/a
		b	93.0					
		c	90.1					
		d	91.4					
Copper Ref. Tox.	2.9	a	88.0	92.0	2.7	101.6	0.220	No
		b	94.0					
		c	93.0					
		d	93.0					
	4.1	a	91.4	91.5	4.2	101.0	0.355	No
		b	86.0					
		c	92.4					
		d	96.2					
	5.9	a	70.5	71.9	1.1	79.4	0.000	Yes
		b	72.2					
		c	71.8					
		d	73.2					
	8.4	a	10.9	10.2	4.6	11.3	0.000	Yes
		b	16.0					
		c	8.9					
		d	5.0					
	12.0	a	2.0	2.0	0.8	2.2	0.000	Yes
		b	2.0					
		c	3.0					
		d	1.0					
	17.2	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	197.0	146-246
MYSIDS	200	400	277	241-316
MUSSELS	4.1	5.9	6.83	5.9-7.6

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB2A

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

# SDB3 – 02/02/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB3-FF	12.5	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	25	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-OF11B-SDB3-COMP	12.5	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-OF23C&E-SDB3-FF	12.5	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-OF23C&E-SDB3-COMP	12.5	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					



**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB3-FF	12.5	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.500	No
		b	10	100.0					
		c	9	90.0					
	100	a	7	70.0	80.0	10.0	80.0	0.041	Yes
		b	8	80.0					
		c	9	90.0					
SUB-OF11B-SDB3-COMP	12.5	a	10	100.0	100.0	0.0	100.0	NT	
		b	10	100.0					
	50	a	9	90.0	90.0	0.0	90.0	NT	
		b	9	90.0					
	100	a	7	70.0	80.0	14.1	80.0	NT	
		b	9	90.0					
SUB-OF23C&E-SDB3-FF	12.5	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	100.0	0.500	No
		b	9	90.0					
		c	10	100.0					
	100	a	8	80.0	76.7	5.8	79.3	0.007	Yes
		b	7	70.0					
		c	8	80.0					
SUB-OF23C&E-SDB3-COMP	12.5	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	100.0	0.0	103.4	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	100.0	0.500	No
		b	9	90.0					
		c	10	100.0					
	100	a	10	100.0	86.7	11.5	89.7	0.137	No
		b	8	80.0					
		c	8	80.0					
SUB-OF26-SDB3-FF	12.5	a	10	100.0	93.3	11.5	93.3	0.211	No
		b	8	80.0					
		c	10	100.0					
	25	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	9	100.0					
	100	a	10	100.0	90.0	10.0	90.0	0.113	No
		b	8	80.0					
		c	9	90.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF26-SDB3-COMP	12.5	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	9	90.0					
	100	a	8	80.0	70.0	17.3	75.8	0.048	Yes
		b	5	50.0					
		c	8	80.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB3-FF	8.25	a	97.4	96.3	1.9	101.6	0.253	No
		b	93.6					
		c	96.5					
		d	97.8					
	16.5	a	96.1	97.7	2.1	103.0	0.122	No
		b	95.7					
		c	99.5					
		d	99.4					
	33.0	a	94.7	93.2	1.7	98.3	0.227	No
		b	91.4					
		c	92.1					
		d	94.4					
	66.0	a	0.0	4.9	4.0	5.2	0.000	Yes
		b	7.3					
		c	9.0					
		d	3.3					
SUB-OF11B-SDB3-COMP	8.25	a	93.8	96.1	1.7	101.3	0.279	No
		b	95.8					
		c	97.2					
		d	97.6					
	16.5	a	99.4	98.0	1.2	103.3	0.101	No
		b	97.6					
		c	96.7					
		d	98.2					
	33.0	a	97.5	95.4	2.2	100.6	0.396	No
		b	92.4					
		c	96.2					
		d	95.6					
	66.0	a	13.0	17.9	10.3	18.9	0.000	Yes
		b	13.7					
		c	33.3					
		d	11.7					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF23C&E-SDB3-FF	8.25	a	95.2	95.4	2.4	108.7	0.010	Yes <sup>c</sup>
		b	93.2					
		c	98.7					
		d	94.3					
	16.5	a	94.2	88.9	10.9	101.3	0.425	No
		b	91.5					
		c	97.1					
		d	72.9					
	33.0	a	17.2	9.8	5.5	11.1	0.000	Yes
		b	10.5					
		c	7.1					
		d	4.3					
	66.0	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					
SUB-OF23C&E-SDB3-COMP	8.25	a	93.4	91.2	7.8	103.9	0.229	No
		b	97.5					
		c	94.1					
		d	79.9					
	16.5	a	87.0	80.3	11.1	91.4	0.137	No
		b	75.7					
		c	91.4					
		d	66.9					
	33.0	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					
	66.0	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					
SUB-OF26-SDB3-FF	8.25	a	96.3	96.4	0.3	101.4	0.130	No
		b	96.8					
		c	96.3					
		d	-					
	16.5	a	90.7	92.6	3.5	97.3	0.130	No
		b	96.5					
		c	94.4					
		d	88.8					
	33.0	a	83.8	74.5	12.9	78.3	0.024	Yes
		b	79.4					
		c	79.5					
		d	55.3					
	66.0	a	7.3	2.6	3.1	2.8	0.000	Yes
		b	0.7					
		c	2.0					
		d	0.6					

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB3

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

NT-No statistical test due to difference in replication

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

Notes:

1) 23CE Pr did not possess normal development for any replicate. This was not a toxic sample, however, because both outfall samples associated with this site had high normal development at the lower concentrations, which used this receiving water sample as the diluent. Scripps natural seawater controls served as the controls for outfall 23CE for data analysis.

2) OF26 Comp was accidentally salted up instead of adjusted with brine. Embryos did not develop properly in the salt control (as expected, which is why these tests are conducted with hypersaline brine), so this data was not tabulated.

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB3-PRE	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY11B-SDB3-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY11B-SDB3-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY23C&E-SDB3-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY23C&E-SDB3-DUR	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY23C&E-SDB3-AFT	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY26-SDB3-PRE	100	a	5	100.0	90.0	20.0	90.0	0.196	No
		b	5	100.0					
		c	3	60.0					
		d	5	100.0					
SUB-BAY26-SDB3-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY26-SDB3-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY26A-SDB3-PRE	100	a	5	100.0	90.0	20.0	90.0	0.196	No
		b	5	100.0					
		c	3	60.0					
		d	5	100.0					
SUB-BAY26A-SDB3-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
SUB-BAY26A-SDB3-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB3-PRE	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY11B-SDB3-DUR	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY11B-SDB3-AFT	100	a	10	100.0	96.7	5.8	96.7	0.500	No
		b	10	100.0					
		c	9	90.0					
SUB-BAY23C&E-SDB3-PRE	100	a	10	100.0	96.7	5.8	96.7	0.500	No
		b	10	100.0					
		c	9	90.0					
SUB-BAY23C&E-SDB3-DUR	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY23C&E-SDB3-AFT	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26-SDB3-PRE	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26-SDB3-DUR	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26-SDB3-AFT	100	a	10	100.0	96.7	5.8	96.7	0.500	No
		b	10	100.0					
		c	9	90.0					
SUB-BAY26A-SDB3-PRE	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26A-SDB3-DUR	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
SUB-BAY26A-SDB3-AFT	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB3-PRE	100	a	92.4	94.8	3.0	108.0	0.021	Yes <sup>c</sup>
		b	98.2					
		c	93.9					
		d	-					
SUB-BAY11B-SDB3-DUR	100	a	94.4	94.3	0.6	107.4	0.026	Yes <sup>c</sup>
		b	94.0					
		c	95.1					
		d	93.7					
SUB-BAY11B-SDB3-AFT	100	a	95.5	96.1	1.8	109.5	0.009	Yes <sup>c</sup>
		b	97.8					
		c	93.8					
		d	97.4					
SUB-BAY23C&E-SDB3-PRE	100	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					
SUB-BAY23C&E-SDB3-DUR	100	a	95.3	94.8	0.5	108.0	0.024	Yes <sup>c</sup>
		b	94.1					
		c	94.7					
		d	94.9					
SUB-BAY23C&E-SDB3-AFT	100	a	93.2	95.7	2.2	109.1	0.009	Yes <sup>c</sup>
		b	98.1					
		c	97.0					
		d	94.6					
SUB-BAY26-SDB3-PRE	100	a	80.0	89.6	7.6	102.1	0.336	No
		b	87.7					
		c	93.5					
		d	97.4					
SUB-BAY26-SDB3-DUR	100	a	96.0	97.3	1.9	110.9	0.006	Yes <sup>c</sup>
		b	99.4					
		c	95.5					
		d	98.4					
SUB-BAY26-SDB3-AFT	100	a	93.5	95.9	1.8	109.2	0.010	Yes <sup>c</sup>
		b	95.5					
		c	97.6					
		d	96.9					
SUB-BAY26A-SDB3-PRE	100	a	95.7	95.1	1.9	108.4	0.013	Yes <sup>c</sup>
		b	97.3					
		c	92.8					
		d	94.8					
SUB-BAY26A-SDB3-DUR	100	a	92.5	94.0	1.6	107.1	0.021	Yes <sup>c</sup>
		b	93.4					
		c	96.2					
		d	94.0					
SUB-BAY26A-SDB3-AFT	100	a	92.4	93.9	2.3	107.0	0.020	Yes <sup>c</sup>
		b	94.2					
		c	97.0					
		d	92.1					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	n/a	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	200	a	5	100.0	50.0	34.6	50.0	0.032	Yes
		b	2	40.0					
		c	1	20.0					
		d	2	40.0					
	400	a	0	0.0	10.0	11.5	10.0	0.000	Yes
		b	1	20.0					
		c	1	20.0					
		d	0	0.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	10	100.0	96.7	5.8	n/a	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control	n/a	a	9	90.0	93.3	5.8	96.6	0.259	No
		b	10	100.0					
		c	9	90.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	107.1	0.211	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	96.7	5.8	96.7	0.500	No
		b	10	100.0					
		c	9	90.0					
	200	a	9	90.0	83.3	5.8	86.2	0.024	Yes
		b	8	80.0					
		c	8	80.0					
	400	a	2	20.0	30.0	10.0	36.0	0.001	Yes
		b	4	40.0					
		c	3	30.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	90.8	87.8	2.8	n/a	n/a	n/a
		b	85.1					
		c	87.4					
		d	-					
Brine Control	n/a	a	92.4	93.9	2.3	107.0	0.020	Yes <sup>c</sup>
		b	94.2					
		c	97.0					
		d	92.1					
Copper Ref. Tox.	2.9	a	70.7	76.2	6.8	86.8	0.018	Yes
		b	77.6					
		c	85.3					
		d	71.1					
	4.1	a	61.4	58.1	2.2	66.2	0.000	Yes
		b	57.6					
		c	57.0					
		d	56.4					
	5.9	a	11.0	19.2	10.3	21.9	0.000	Yes
		b	28.7					
		c	27.7					
		d	9.7					
	8.4	a	3.7	6.9	3.9	7.9	0.000	Yes
		b	4.1					
		c	12.2					
		d	7.7					
	12.0	a	1.2	1.5	1.4	1.7	0.000	Yes
		b	0.0					
		c	3.4					
		d	1.3					
	17.2	a	0.0	0.0	0.0	0.0	0.000	Yes
		b	0.0					
		c	0.0					
		d	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	218.0	181-264
MYSIDS	100	200	315	264-393
MUSSELS	2.9	4.1	4.60	4.1-5.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB3

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**Notes:**

- 23CE Pr did not possess normal development for any replicate. This was not a toxic sample, however, because both outfall samples associated with this site had high normal development at the lower concentrations, which used this receiving water sample as the diluent. Scripps natural seawater controls served as the controls for outfall 23CE for data analysis.
- OF26 Comp was accidentally salted up instead of adjusted with brine. Embryos did not develop properly in the salt control (as expected, which is why these tests are conducted with hypersaline brine), so this data was not tabulated.



## WATER QUALITY

### TOPSMELT (*A. affinis*)

Sample ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)	Dissolved Oxygen (mg/l)	Temp. (°C)	Salinity (‰)
SUB-OF11B-SDB3-FF	12.5%	a	7.62-7.98	5.8-6.9	19.1-21.1	34-35
	50%	a	7.52-8.0	5.4-6.9	19.1-21.6	33-35
	100%	a	7.59-8.01	5.5-7.8	19.1-21.6	32-34
SUB-OF11B-SDB3-COMP	12.5%	a	7.67-7.81	6.0-6.2	19.3-21.4	34-35
	50%	a	7.68-8.48	5.9-7.3	19.3-21.4	34-36
	100%	a	7.74-8.76	5.3-7.2	19.3-21.2	35-37
SUB-OF23C&E-SDB3-FF	12.5%	a	7.6-7.9	5.5-6.5	19.3-21.5	33-35
	50%	a	7.5-7.9	5.8-6.6	19.3-21.4	33-35
	100%	a	7.4-8.0	4.7-6.4	19.3-21.4	33-34
SUB-OF23C&E-SDB3-COMP	12.5%	a	7.6-7.9	6.2-7.1	19.3-21.5	33-36
	50%	a	7.6-7.9	5.7-7.1	19.3-21.5	32-35
	100%	a	7.5-8.0	5.5-7.0	19.3-21.5	32-35
SUB-OF26-SDB3-FF	12.5%	a	7.62-7.74	6.0-6.8	19.3-21.4	33-36
	50%	a	7.6-7.73	6.1-6.8	19.3-21.4	32-35
	100%	a	7.52-8.03	5.4-6.2	19.3-21.3	32-36
SUB-OF26-SDB3-COMP	12.5%	a	7.63-7.69	6.1-6.8	19.3-21.4	34-36
	50%	a	7.56-7.7	5.9-6.6	19.3-21.4	34-36
	100%	a	7.48-7.7	5.2-6.1	19.3-21.3	35-37
SUB-BAY11B-SDB3-PRE	100%	a	7.61-7.92	5.8-7.0	19.3-21.4	33-35
SUB-BAY11B-SDB3-DUR	100%	a	7.6-7.8	5.8-7.1	19.0-21.2	33-37
SUB-BAY11B-SDB3-AFT	100%	a	7.6-7.9	6.2-7.1	19.0-20.9	33-36
SUB-BAY23C&E-SDB3-PRE	100%	a	7.67-7.91	6.2-7.0	19.3-21.4	33-35
SUB-BAY23C&E-SDB3-DUR	100%	a	7.6-7.8	6.0-7.3	18.8-21.1	33-35
SUB-BAY23C&E-SDB3-AFT	100%	a	7.6-7.7	6.1-7.0	19.0-21.0	33-36
SUB-BAY26-SDB3-PRE	100%	a	7.52-7.91	5.5-6.7	19.3-21.3	33-36
SUB-BAY26-SDB3-DUR	100%	a	7.6-9	5.7-7.1	19.1-21.3	34-36
SUB-BAY26-SDB3-AFT	100%	a	7.6-7.9	5.7-7.1	19.1-21.1	34-36
SUB-BAY26A-SDB3-PRE	100%	a	7.7-7.9	6.1-7.1	19.3-21.5	33-35
SUB-BAY26A-SDB3-DUR	100%	a	7.7-7.9	5.9-6.9	19.3-21.5	33-34
SUB-BAY26A-SDB3-AFT	100%	a	7.7-7.9	6.1-6.9	19.3-21.3	33-36
Scripps Control	0	a	7.6-7.8	6.2-7.2	18.9-20.5	34-36
Cu Ref Tox	100 µg/l	a	7.6-7.9	6.0-7.3	19.0-20.8	34-35
	400 µg/l	a	7.6-7.8	5.9-7.1	18.9-20.7	34-37

### MYSIDS (*A. bahia*)

Sample ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)	Dissolved Oxygen (mg/l)	Temp. (°C)	Salinity (‰)
SUB-OF11B-SDB3-FF	100%	a	7.5-7.9	4.1-6.4	19.0-20.4	32-34
SUB-OF11B-SDB3-COMP	100%	a	7.8-8.7	4.4-7.4	18.9-20.4	35-37
SUB-OF23C&E-SDB3-FF	100%	a	7.6-8.0	4.5-6.6	18.8-20.7	33-35
SUB-OF23C&E-SDB3-COMP	100%	a	7.4-8.0	4.1-7.5	18.8-20.8	36-37
SUB-OF26-SDB3-FF	100%	a	7.4-7.9	4.3-6.3	18.8-20.8	33-34
SUB-OF26-SDB3-COMP	100%	a	7.4-8.0	4.6-6.9	18.6-20.5	34-35
SUB-BAY11B-SDB3-PRE	100%	a	7.5-7.9	4.7-7.1	19.0-20.5	34-36
SUB-BAY11B-SDB3-DUR	100%	a	7.5-7.7	5.7-6.6	18.9-20.2	34-35
SUB-BAY11B-SDB3-AFT	100%	a	7.4-7.8	5.3-6.6	18.8-20.4	34-35
SUB-BAY23C&E-SDB3-PRE	100%	a	7.5-8.0	4.9-7.0	18.9-22.1	35-36
SUB-BAY23C&E-SDB3-DUR	100%	a	7.6-7.7	6.0-6.3	18.9-20.3	34-36
SUB-BAY23C&E-SDB3-AFT	100%	a	7.6-7.7	6.0-6.3	18.8-20.2	34-35
SUB-BAY26-SDB3-PRE	100%	a	7.6-7.9	5.1-7.1	19.0-20.8	35-36
SUB-BAY26-SDB3-DUR	100%	a	7.6-7.7	6.0-6.6	18.9-20.8	34-35
SUB-BAY26-SDB3-AFT	100%	a	7.7	7	18.8	35
SUB-BAY26A-SDB3-PRE	100%	a	7.70-7.72	5.8-6.9	18.7-19.0	34-35
SUB-BAY26A-SDB3-DUR	100%	a	7.63-7.67	5.3-6.2	18.8-19.0	34
SUB-BAY26A-SDB3-AFT	100%	a	7.61-7.69	6.2-6.7	18.9-20.8	34-35
Scripps Control	0	a	7.7-8.0	5.1-6.2	18.9-19.9	34-37
Cu Ref Tox	100 µg/l	a	7.6-7.9	5.8-7.0	19.0-20.4	34-35
	400 µg/l	a	7.6-7.9	6.1-7.0	18.8-20.5	35
Salt Control	0	a	7.6-7.9	5.9-7.0	19.0-20.2	35

**OUTFALLS****INLAND SILVERSIDE (*M. berylina*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
SUB-OF11B-TIE1-FF	25	100.0
	50	100.0
	100	96.0
SUB-OF23C&E-TIE1-FF	25	100.0
	50	96.0
	100	100.0
SUB-OF26-TIE1-FF	25	100.0
	50	100.0
	100	100.0

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
SUB-OF11B-TIE1-FF	25	98.0
	50	100.0
	100	85.0
SUB-OF23C&E-TIE1-FF	25	93.0
	50	93.0
	100	55.0
SUB-OF26-TIE1-FF	25	95.0
	50	95.0
	100	58.0

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
SUB-OF11B-TIE1-FF	13	81.0
	25	69.0
	50	1.0
	68	0.0
SUB-OF23C&E-TIE1-FF	13	73.0
	25	0.0
	50	0.0
	68	0.0
SUB-OF26-TIE1-FF	13	70.0
	25	0.0
	50	0.0
	68	0.0

Please refer to TIE Report August 2004 for raw data and water quality

## QA/QC SAMPLES<sup>a</sup>

### INLAND SILVERSIDE (*M. berylina*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Natural Seawater Control	n/a	100.0
Salt Control	n/a	96.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Natural Seawater Control	n/a	95.0
Salt Control	n/a	98.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN NORM DEV (%)
Natural Seawater Control	n/a	81.0
Brine Control	n/a	75.0

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
INLAND SILVERSIDE	2/26/004	100	200	137.6	129.5-146.2
MYSIDS	2/27/2004	200	400	337.1	242.4-438.7
MUSSELS	2/19/2004	5	10	10.2	9.9-10.5

Please refer to TIE Report August 2004 for raw data and water quality

<sup>a</sup>Controls (QA/QC) correspond to all samples from TIE1

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## TIE1A – 02/26/2004

### BAY SAMPLES

#### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
SUB-BAY11B-TIE1A-AFT	100	87.0
SUB-BAY23C&E-TIE1A-AFT	100	88.0
SUB-BAY26-TIE1A-AFT	100	87.0

### QA/QC SAMPLES<sup>a</sup>

#### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN NORM DEV (%)
Natural Seawater Control	n/a	89.0

### SUMMARY RESULTS- QA/QC

#### COPPER REFERENCE TOXICANT TEST

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
MUSSELS	2/19/2004	5	10	10.2	9.9-10.5

Please refer to TIE Report August 2004 for raw data and water quality

### WATER QUALITY

#### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	pH (SU)	D.O. (mg/L)	Temp <sup>1</sup> (°C)	Salinity (‰)
SUB-BAY11B-TIE1A-AFT	100.0%	7.9	6.0	10.9	33.5
SUB-BAY23C&E-TIE1A-AFT	100.0%	8.1	8.3	12.4	33.4
SUB-BAY26-TIE1A-AFT	100.0%	8.2	7.9	13.8	33.1

<sup>1</sup> Temperature upon arrival

# SDB4 – 10/17/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB4-FF	12.5	a	5	100.0	95.0	10.0	95.0	0.338	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	100.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	90.0	11.5	90.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	100	a	5	100.0	85.0	19.1	85.0	0.365	No
		b	5	100.0					
		c	4	80.0					
		d	3	60.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB4-FF	12.5	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
	25	a	9	90.0	93.3	5.8	93.3	0.092	No
		b	10	100.0					
		c	9	90.0					
	50	a	7	70.0	73.3	5.8	73.3	0.008	Yes
		b	7	70.0					
		c	8	80.0					
	100	a	6	60.0	46.7	11.5	46.7	0.008	Yes
		b	4	40.0					
		c	4	40.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-OF11B-SDB4-FF	6.25	a	170	12	93.4	90.0	2.8	92.3	0.001	Yes
		b	157	13	92.4					
		c	161	25	86.6					
		d	144	17	89.4					
		e	143	19	88.3					
	12.5	a	19	120	13.7	20.3	13.7	20.8	0.000	Yes
		b	25	164	13.2					
		c	17	162	9.5					
		d	44	158	21.8					
		e	59	77	43.4					
	25	a	3	180	1.6	1.6	1.0	1.7	0.000	Yes
		b	5	176	2.8					
		c	0	180	0.0					
		d	3	176	1.7					
		e	3	148	2.0					
	50	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					
	61.4	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB4-DUR	100	a	5	100.0	90.0	20.0	90.0	0.196	No
		b	5	100.0					
		c	3	60.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB4-DUR	100	a	10	100.0	100.0	0.0	100.0	N/A	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEV (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB4-DUR	100	a	181	4	97.8	96.9	1.3	99.4	0.2105	No
		b	156	5	96.9					
		c	161	9	94.7					
		d	164	5	97.0					
		e	146	3	98.0					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	90.0	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	9	90.0	83.3	5.8	89.3	0.051	No
		b	8	80.0					
		c	8	80.0					
	400	a	2	20.0	6.7	11.5	7.1	0.001	Yes
		b	0	0.0					
		c	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	148	25	85.5	94.5	5.4	100.0	n/a	n/a
		b	175	5	97.2					
		c	139	10	93.3					
		d	193	4	98.0					
		e	174	3	98.3					
Brine Control	n/a	a	177	6	96.7	95.7	1.1	98.1	0.3233	No
		b	170	10	94.4					
		c	186	6	96.9					
		d	171	8	95.5					
		e	164	9	94.8					
Copper Ref. Tox.	2.9	a	167	9	94.9	95.1	0.7	100.7	0.397	No
		b	200	11	94.8					
		c	168	10	94.4					
		d	176	8	95.7					
		e	168	7	96.0					
	4.1	a	166	3	98.2	90.3	10.0	95.6	0.221	No
		b	202	7	96.7					
		c	164	17	90.6					
		d	118	43	73.3					
		e	141	11	92.8					
	5.9	a	178	9	95.2	79.0	14.3	83.7	0.036	Yes
		b	169	20	89.4					
		c	157	36	81.3					
		d	128	60	68.1					
		e	124	79	61.1					
	8.4	a	69	106	39.4	23.7	13.7	25.1	0.000	Yes
		b	56	141	28.4					
		c	58	126	31.5					
		d	12	177	6.3					
		e	24	162	12.9					
	12.0	a	1	177	0.6	1.3	1.3	1.3	0.000	Yes
		b	5	172	2.8					
		c	5	203	2.4					
		d	1	207	0.5					
		e	0	171	0.0					
	17.2	a	3	177	1.7	0.5	0.7	0.5	0.000	Yes
		b	1	167	0.6					
		c	0	191	0.0					
		d	0	175	0.0					
		e	0	199	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	50	100	132.0	120.2-144.8
MYSIDS	200	400	265.3	232.5-302.4
MUSSELS	5.9	8.4	7.29	6.1-8.3

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater



## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
SUB-OF11B-SDB4-FF	12.5%	a	7.9	7.6	7.5	7.9	8.0	6.8	5.0	4.9	6.8	7.0	19.6	18.6	19.8	18.3	18.9	33.9	34.1	34.1	34.6	35.9
	25%	a	8.0	7.6	7.8	7.7	7.9	6.7	6.4	6.5	6.4	7.0	19.5	18.6	19.4	19.2	19.3	33.8	34.0	34.2	34.2	34.4
	50%	a	8.2	7.6	7.6	7.8	7.9	6.7	6.6	6.3	6.8	6.8	19.2	18.8	19.4	18.4	18.9	33.6	33.9	33.9	35.3	36.6
	100%	a	8.5	7.6	7.7	7.7	7.6	7.0	6.2	6.6	6.6	6.2	18.8	18.3	19.2	18.8	19.2	33.1	33.5	33.8	34.3	34.6
SUB-BAY11B-SDB4-DUR	100%	a	7.6	7.5	7.6	7.6	7.6	6.6	5.7	5.0	5.5	5.3	18.3	18.4	19.6	19.3	19.4	32.7	32.8	32.8	33.1	33.1
Scripps Control	0	a	7.8	7.8	7.7	7.8	7.7	6.9	5.9	5.5	6.0	6.0	19.1	18.3	19.7	19.0	19.5	33.8	34.0	34.0	34.3	34.3
Scripps Cu Ref. Tox.	50 µg/l	a	7.9	7.8	7.7	7.8	7.7	6.9	6.2	6.5	6.3	5.9	18.7	18.0	19.2	19.1	19.4	33.9	34.4	34.7	34.2	34.3
	100 µg/l	a	7.9	7.8	7.0	7.8	7.8	7.1	6.0	6.1	6.4	6.3	18.8	18.0	19.1	19.0	19.4	33.8	34.1	34.5	34.3	34.5
	200 µg/l	a	7.8	7.8	7.7	7.9	7.8	7.0	6.0	5.9	6.5	6.5	18.6	18.1	19.4	19.1	19.3	33.8	34.0	34.7	34.1	34.2
	400 µg/l	a	7.8	7.9	N	N	N	7.0	6.2	N	N	N	18.6	18.0	N	N	N	33.8	34.1	N	N	N
Salt Control	n/a	a	8.1	7.9	7.7	7.8	7.6	6.9	5.9	6.2	6.0	6.1	19.8	18.0	18.9	18.9	19.4	33.3	33.5	33.6	33.6	33.7

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
SUB-OF11B-SDB4-FF	12.5%	a	7.9	7.5	7.9	7.9	7.9	6.7	3.3	6.9	6.5	7.0	19.4	18.8	19.1	19.0	19.1	34.2	34.4	34.7	34.6	34.8
	25%	a	8.0	7.6	7.8	7.7	7.7	6.7	6.4	6.5	6.5	6.7	19.4	18.7	19.3	19.3	19.3	34.2	34.3	34.3	34.3	34.8
	50%	a	8.2	7.6	7.7	7.8	7.8	6.7	6.3	6.5	6.5	6.8	19.0	18.9	19.3	19.2	19.2	34.0	34.1	34.1	34.3	34.8
	100%	a	8.5	7.3	7.6	7.7	7.7	6.9	2.7	6.0	6.6	6.5	18.8	18.6	19.3	19.3	19.3	33.5	33.7	33.8	34.2	34.5
SUB-BAY11B-SDB4-DUR	100%	a	7.6	7.6	7.6	7.5	7.5	6.6	5.3	5.0	4.7	4.8	18.3	18.3	19.6	19.6	19.6	33.1	33.3	33.3	33.2	33.3
Scripps Control	0	a	7.9	7.7	7.7	7.7	7.6	6.9	4.7	5.3	5.0	4.8	18.8	18.3	19.4	19.3	19.5	34.4	34.6	34.6	34.2	34.3
Scripps Cu Ref. Tox.	25 µg/l	a	7.9	7.7	7.7	7.8	7.6	6.9	5.4	5.7	5.4	5.2	18.8	18.6	19.4	19.3	19.6	34.3	34.4	34.6	34.3	34.3
	50 µg/l	a	7.9	7.7	7.6	7.7	7.6	7.1	5.3	5.3	5.0	4.5	18.7	18.6	19.5	19.3	19.6	34.4	34.5	34.5	34.2	34.2
	100 µg/l	a	7.9	7.7	7.6	7.7	7.7	7.1	5.7	4.9	5.6	5.1	18.6	18.5	19.4	19.3	19.6	34.2	34.4	34.5	34.3	34.3
	200 µg/l	a	7.9	7.8	7.8	7.8	7.7	7.0	5.9	6.3	6.1	5.7	18.7	18.6	19.1	19.3	19.6	34.4	34.6	34.2	34.3	34.4
	400 µg/l	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2
Salt Control	n/a	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)		D.O. (mg/l)		Temp (°C)		Salinity (‰)	
			0	48	0	48	0	48	0	48
SUB-OF11B-SDB4-FF	6.25%	f	7.7	7.8	6.9	6.4	15.1	15.7	33.5	34.1
	25%	f	7.6	7.7	6.8	5.9	15.1	15.6	34.3	34.1
	61.4%	f	7.6	7.2	7.0	3.4	15.5	15.7	34.1	34.4
SUB-BAY11B-SDB4-DUR	100%	f	7.7	7.8	7.0	7.0	15.2	15.1	32.6	32.9
Scripps Control	0	f	7.8	7.6	6.9	6.8	15.6	15.7	34.0	34.2
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.8	7.8	7.0	6.8	15.8	15.7	33.9	34.1
	8.4 µg/l	f	7.8	7.7	6.9	6.8	15.7	15.5	33.9	34.1
	24 µg/l	f	7.8	7.8	6.9	7.1	15.8	15.5	34.1	34.1
Brine Control	0	f	7.9	7.9	7.0	7.0	15.5	15.7	33.7	34.2

N - water quality not taken due to 100% mortality in treatment

# SDB5 – 01/10/2005

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB5-AFT	100	a	5	100.0	100	0.0	100	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
SUB-BAY11B-SDB5-AFT	100	a	162	8	95.3	94.9	2.0	105.3	0.004	Yes <sup>c</sup>
		b	156	14	91.8					
		c	149	6	96.1					
		d	166	10	94.3					
		e	168	5	97.1					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	25	a	5	100.0	100	0.0	100	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	95	10.0	95	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90	11.5	90	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	1	20.0	15	10.0	15	0.000	Yes
		b	1	20.0					
		c	1	20.0					
		d	0	0.0					
	400	a	0	0.0	0	0.0	0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	No
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	138.54	114.4-167.8
MUSSELS <sup>d</sup>	4.1	5.9	6.0	5.9-6.1

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB5

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>d</sup>Copper reference toxicant test performed on 02/10/2005

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
SUB-BAY11B-SDB5-AFT	100%	a	7.9	7.8	7.6	7.8	7.7	7.4	6.5	6.4	6.6	6.4	18.6	19.0	19.8	19.8	18.0	32.8	31.3	31.3	31.3	31.7
Scripps Control	0	a	7.9	7.8	7.5	7.7	7.6	7.2	6.7	6.5	6.5	6.3	19.3	19.9	19.8	19.7	18.6	31.9	31.1	29.0	29.1	29.2

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			Dissolved Oxygen (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
SUB-BAY11B-SDB5-AFT	100%	f	7.8	7.8	7.9	7.4	7.7	7.5	17.1	15.8	16.1	30.9	30.7	30.7
Scripps Control	0	f	7.8	7.8	7.8	6.9	7.9	7.5	17.0	16.0	16.3	28.4	28.3	28.4

## **Appendix C3**

### ***NAB***

SDB4- 10/17/2004

SDB5- 01/10/2005

SDB6- 2/10/2005

TIE2- 3/18/2005

SDB7- 4/27/2005

# SDB4 – 10/17/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB4-FF	12.5	a	5	100	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	5	100					
		d	4	80					
	25	a	2	40	30.0	25.8	30.0	0.006	Yes
		b	0	0					
		c	3	60					
		d	1	20					
	50	a	0	0	5.0	10.0	5.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	1	20					
	100	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	0	0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB4-FF	12.5	a	7	70	86.7	15.3	86.7	0.135	No
		b	10	100					
		c	9	90					
	25	a	1	10	26.7	28.9	26.7	0.024	Yes
		b	6	60					
		c	1	10					
	50	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					
	100	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB4-FF	6.25	a	1	169	0.6	3.8	2.5	3.9	0.000	Yes
		b	9	182	4.7					
		c	13	162	7.4					
		d	6	171	3.4					
		e	6	186	3.1					
	12.5	a	3	180	1.6	0.4	0.7	0.4	0.000	Yes
		b	0	187	0.0					
		c	0	182	0.0					
		d	0	189	0.0					
		e	1	184	0.5					
	25	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					
	50	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					
	63.5	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB4-DUR	100	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB4-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB4-DUR	100	a	6	207	2.8	4.0	1.9	4.1	0.0000	Yes
		b	10	185	5.1					
		c	10	162	5.8					
		d	7	139	4.8					
		e	2	150	1.3					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	90.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	9	90.0	83.3	5.8	89.3	0.051	No
		b	8	80.0					
		c	8	80.0					
	400	a	2	20.0	6.7	11.5	7.1	0.001	Yes
		b	0	0.0					
		c	0	0.0					



**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	148	25	85.5	94.5	5.4	100.0	n/a	No
		b	175	5	97.2					
		c	139	10	93.3					
		d	193	4	98.0					
		e	174	3	98.3					
Brine Control	n/a	a	177	6	96.7	95.7	1.1	98.1	0.011	Yes
		b	170	10	94.4					
		c	186	6	96.9					
		d	171	8	95.5					
		e	164	9	94.8					
Copper Ref. Tox.	2.9	a	167	9	94.9	95.1	0.7	100.7	0.374	No
		b	200	11	94.8					
		c	168	10	94.4					
		d	176	8	95.7					
		e	168	7	96.0					
	4.1	a	166	3	98.2	90.3	10.0	95.6	0.308	No
		b	202	7	96.7					
		c	164	17	90.6					
		d	118	43	73.3					
		e	141	11	92.8					
	5.9	a	178	9	95.2	79.0	14.3	83.7	0.182	No
		b	169	20	89.4					
		c	157	36	81.3					
		d	128	60	68.1					
		e	124	79	61.1					
	8.4	a	69	106	39.4	23.7	13.7	25.1	0.017	Yes
		b	56	141	28.4					
		c	58	126	31.5					
		d	12	177	6.3					
		e	24	162	12.9					
	12.0	a	1	177	0.6	1.3	1.3	1.3	0.000	Yes
		b	5	172	2.8					
		c	5	203	2.4					
		d	1	207	0.5					
		e	0	171	0.0					
	17.2	a	3	177	1.7	0.5	0.7	0.5	0.000	Yes
		b	1	167	0.6					
		c	0	191	0.0					
		d	0	175	0.0					
		e	0	199	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	50	100	132.0	120.2-144.8
MYSIDS	200	400	265.3	232.5-302.4
MUSSELS	5.9	8.4	7.29	6.1-8.3

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-OF9-SDB4-FF	12.5%	a	7.8	7.5	7.5	7.5	7.6	6.7	4.6	5.7	5.2	5.8	19.9	18.3	19.2	19.3	19.4	33.9	34.2	34.3	34.4	34.6
	25%	a	7.8	7.5	7.8	7.7	7.8	6.7	6.0	6.5	6.7	6.8	19.9	18.3	19.2	19.2	19.4	33.5	33.8	34.1	34.4	34.7
	50%	a	7.9	7.6	7.8	7.8	7.8	6.7	6.4	6.8	6.7	6.7	19.3	18.2	19.1	19.0	19.4	33.3	33.5	33.6	34.1	34.2
	100%	a	8.0	7.6	7.5	N	N	7.1	6.6	6.0	N	N	18.3	18.0	19.1	N	N	32.6	32.8	33.1	N	N
NAB-BAY9-SDB4-DUR	100%	a	7.7	7.6	7.5	7.7	7.7	6.9	5.7	5.6	NT	5.9	18.4	18.3	19.3	19.4	19.4	34.0	34.2	34.2	34.6	34.6
Scripps Control	0	a	7.8	7.8	7.7	7.8	7.7	6.9	5.9	5.5	6.0	6.0	19.1	18.3	19.7	19.0	19.5	33.8	34.0	34.0	34.3	34.3
Scripps Cu Ref. Tox.	50 µg/l	a	7.9	7.8	7.7	7.8	7.7	6.9	6.2	6.5	6.3	5.9	18.7	18.0	19.2	19.1	19.4	33.9	34.4	34.7	34.2	34.3
	100 µg/l	a	7.9	7.8	7.0	7.8	7.8	7.1	6.0	6.1	6.4	6.3	18.8	18.0	19.1	19.0	19.4	33.8	34.1	34.5	34.3	34.5
	200 µg/l	a	7.8	7.8	7.7	7.9	7.8	7.0	6.0	5.9	6.5	6.5	18.6	18.1	19.4	19.1	19.3	33.8	34.0	34.7	34.1	34.2
	400 µg/l	a	7.8	7.9	N	N	N	7.0	6.2	N	N	N	18.6	18.0	N	N	N	33.8	34.1	N	N	N
Salt Control	n/a	a	8.1	7.9	7.7	7.8	7.6	6.9	5.9	6.2	6.0	6.1	19.8	18.0	18.9	18.9	19.4	33.3	33.5	33.6	33.6	33.7

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-OF9-SDB4-FF	12.5%	a	7.8	7.4	7.7	7.9	7.9	6.7	3.3	6.5	7.0	7.2	19.6	18.3	19.4	19.3	19.3	34.3	34.4	34.4	34.8	35.3
	25%	a	7.8	7.6	7.8	7.8	7.9	6.8	6.5	6.6	6.9	6.9	19.5	18.5	19.1	19.3	19.4	34.1	34.3	34.5	34.4	34.6
	50%	a	7.9	7.5	7.7	7.6	7.9	7.0	6.1	6.6	6.6	6.6	19.0	18.8	19.1	19.1	19.1	33.7	33.9	33.9	34.0	34.6
	100%	a	8.0	7.5	7.4	7.7	7.9	7.1	5.9	6.0	6.9	6.9	18.6	18.6	19.0	18.4	19.2	33.0	33.1	32.9	34.4	35.2
NAB-BAY9-SDB4-DUR	100%	a	7.7	7.6	7.6	7.6	7.6	6.8	5.2	5.6	5.7	5.1	18.4	18.3	19.3	19.5	19.6	34.6	34.7	34.7	34.6	34.8
Scripps Control	0	a	7.9	7.7	7.7	7.7	7.6	6.9	4.7	5.3	5.0	4.8	18.8	18.3	19.4	19.3	19.5	34.4	34.6	34.6	34.2	34.3
Scripps Cu Ref. Tox.	25 µg/l	a	7.9	7.7	7.7	7.8	7.6	6.9	5.4	5.7	5.4	5.2	18.8	18.6	19.4	19.3	19.6	34.3	34.4	34.6	34.3	34.3
	50 µg/l	a	7.9	7.7	7.6	7.7	7.6	7.1	5.3	5.3	5.0	4.5	18.7	18.6	19.5	19.3	19.6	34.4	34.5	34.5	34.2	34.2
	100 µg/l	a	7.9	7.7	7.6	7.7	7.7	7.1	5.7	4.9	5.6	5.1	18.6	18.5	19.4	19.3	19.6	34.2	34.4	34.5	34.3	34.3
	200 µg/l	a	7.9	7.8	7.8	7.8	7.7	7.0	5.9	6.3	6.1	5.7	18.7	18.6	19.1	19.3	19.6	34.4	34.6	34.2	34.3	34.4
	400 µg/l	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2
Salt Control	n/a	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)		D.O. (mg/l)		Temp (°C)		Salinity (‰)	
			0	48	0	48	0	48	0	48
NAB-OF9-SDB4-FF	6.25%	f	7.7	7.7	7.0	6.6	15.7	15.4	33.9	34.1
	25%	f	7.6	7.5	7.0	4.3	15.5	15.4	34.0	34.0
	63.5%	f	7.4	7.1	7.0	1.9	15.7	15.4	33.4	34.0
NAB-BAY9-SDB4-DUR	100%	f	7.7	7.9	6.8	7.2	15.5	15.1	34.1	34.4
Scripps Control	0	f	7.8	7.6	6.9	6.8	15.6	15.7	34.0	34.2
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.8	7.8	7.0	6.8	15.8	15.7	33.9	34.1
	8.4 µg/l	f	7.8	7.7	6.9	6.8	15.7	15.5	33.9	34.1
	24 µg/l	f	7.8	7.8	6.9	7.1	15.8	15.5	34.1	34.1
Brine Control	0	f	7.9	7.9	7.0	7.0	15.5	15.7	33.7	34.2

N - water quality not taken due to 100% mortality in treatment

# SDB5– 01/10/2005

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB5-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB5-AFT	100	a	9	90.0	96.7	5.8	103.6	0.259	No
		b	10	100.0					
		c	10	100.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB5-AFT	100	a	107	19	84.9	90.2	4.3	100.1	0.478	No
		b	156	15	91.2					
		c	164	9	94.8					
		d	150	23	86.7					
		e	145	10	93.5					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100	100.0	0.0	100.0	n/a	n/a
		b	5	100					
		c	5	100					
		d	5	100					
Copper Ref. Tox.	25	a	5	100.0	100	0.0	100	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	95	10.0	95	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90	11.5	90	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	1	20.0	15	10.0	15	0.000	Yes
		b	1	20.0					
		c	1	20.0					
		d	0	0.0					
	400	a	0	0.0	0	0.0	0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Copper Ref. Tox.	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	11	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	8	80.0	90.0	10.0	96.4	0.325	No
		b	9	90.0					
		c	10	100.0					
	400	a	2	20.0	26.7	11.5	28.6	0.002	Yes
		b	2	20.0					
		c	4	40.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	No
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100.0	200.0	138.5	114.4-167.8
MYSIDS	200.0	400.0	324.9	276.2-379.8
MUSSELS <sup>d</sup>	4.1	5.9	6.0	5.9-6.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB5

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>d</sup>Copper reference toxicant test performed on 02/10/2005

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-BAY9-SDB5-AFT	100%	a	7.9	7.8	7.6	7.8	7.7	7.5	6.4	6.3	6.1	6.4	19.1	18.8	19.7	19.7	18.0	33.3	31.0	30.7	30.9	31.5
Scripps Control	0	a	7.9	7.8	7.5	7.7	7.6	7.2	6.7	6.5	6.5	6.3	19.3	19.9	19.8	19.7	18.6	31.9	31.1	29.0	29.1	29.2

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-BAY9-SDB5-AFT	100%	a	7.9	7.8	7.6	7.7	7.6	7.5	6.2	4.8	5.4	5.5	19.3	18.8	19.7	19.7	18.3	33.2	31.1	30.8	31.0	31.2
Scripps Control	0	a	7.9	7.8	7.5	7.7	7.5	7.3	5.9	5.4	6.2	5.3	18.9	19.1	19.8	19.6	18.2	31.8	30.7	30.2	30.9	31.3

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			Dissolved Oxygen (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NAB-BAY9-SDB5-AFT	100%	f	7.7	7.8	7.8	7.3	7.7	7.5	17.1	16.0	16.0	28.8	28.7	28.9
Scripps Control	0	f	7.8	7.8	7.8	6.9	7.9	7.5	17.0	16.0	16.3	28.4	28.3	28.4

# SDB6- 02/10/2005

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB6-FF	12.5	a	4	80	90.0	11.5	90.0	0.091	No
		b	4	80					
		c	5	100					
		d	5	100					
	25	a	5	100	95.0	10.0	95.0	0.196	No
		b	4	80					
		c	5	100					
		d	5	100					
	50	a	5	100	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	4	80					
		d	5	100					
	100	a	4	80	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	5	100					
		d	5	100					
NAB-OF9-SDB6-COMP	12.5	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	50	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
NAB-OF18-SDB6-FF	12.5	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	25	a	5	100	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	5	100					
		d	4	80					
	50	a	5	100	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	5	100					
		d	4	80					
	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB6-FF	12.5	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	25	a	10	100	96.7	5.8	96.7	0.211	No
		b	9	90					
		c	10	100					
	50	a	10	100	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	9	90					
	100	a	8	80	90.0	10.0	90.0	0.113	No
		b	9	90					
		c	10	100					
NAB-OF9-SDB6-COMP	12.5	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	50	a	10	100	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	9	90					
	100	a	10	100	90.0	10.0	90.0	0.113	No
		b	9	90					
		c	8	80					
NAB-OF18-SDB6-FF	12.5	a	10	100	100.0	0.0	100.0	n/a	No
		b	10	100					
		c	10	100					
	25	a	10	100	96.7	5.8	96.7	0.211	No
		b	10	100					
		c	9	90					
	50	a	10	100	96.7	5.8	96.7	0.211	No
		b	9	90					
		c	10	100					
	100	a	9	90	86.7	5.8	86.7	0.029	Yes
		b	8	80					
		c	9	90					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB6-FF	6.2	a	180	8	96	96.9	0.8	100.5	0.217	No
		b	227	5	98					
		c	201	7	97					
		d	234	6	98					
		e	220	7	97					
	12.4	a	235	7	97	96.3	1.4	99.9	0.441	No
		b	207	13	94					
		c	202	7	97					
		d	186	8	96					
		e	209	5	98					
	24.8	a	-	-	-	68.6	17.1	71.1	0.053	No
		b	-	-	-					
		c	152	72	68					
		d	124	115	52					
		e	172	28	86					
	49.5	a	0	236	0	0.0	0.0	0.0	0.000	Yes
		b	0	209	0					
		c	0	206	0					
		d	0	213	0					
		e	0	230	0					



**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB6-COMP	6.4	a	220	8	96	98.4	1.2	102.0	0.016	Yes <sup>c</sup>
		b	215	2	99					
		c	196	2	99.0					
		d	217	5	97.7					
		e	211	1	99.5					
	12.9	a	209	2	99.1	96.5	1.9	100.1	0.471	No
		b	218	14	94.0					
		c	225	7	97.0					
		d	199	6	97.1					
		e	163	8	95.3					
	25.7	a	192	23	89.3	91.1	4.8	94.5	0.034	Yes
		b	215	14	93.9					
		c	197	39	83.5					
		d	211	13	94.2					
		e	215	12	94.7					
	51.4	a	0	228	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	217	0.0					
		c	0	236	0.0					
		d	0	210	0.0					
		e	0	217	0.0					
NAB-OF18-SDB6-FF	6.2	a	187	8	95.9	96.0	1.8	98.7	0.138	No
		b	215	3	98.6					
		c	207	10	95.4					
		d	221	15	93.6					
		e	231	8	96.7					
	12.4	a	215	7	96.8	96.4	1.9	99.1	0.224	No
		b	238	2	99.2					
		c	185	12	93.9					
		d	246	10	96.1					
		e	220	9	96.1					
	24.8	a	66	138	32.4	29.7	6.4	30.5	0.000	Yes
		b	57	156	26.8					
		c	57	102	35.8					
		d	47	190	19.8					
		e	85	168	33.6					
	49.5	a	0	243	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	222	0.0					
		c	0	228	0.0					
		d	0	240	0.0					
		e	0	221	0.0					

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB6

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB6-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY18-SDB6-PRE	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY9-SDB6-DUR	100	a	4	80.0	90.0	11.5	90.0	0.091	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY18-SDB6-DUR	100	a	5	100.0	100.0	0.0	100.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	6	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB6-PRE	100	a	10	100.0	100.0	0.0	107.1	n/a	No
		b	10	100.0					
		c	10	100.0					
NAB-BAY18-SDB6-PRE	100	a	10	100.0	100.0	0.0	107.1	n/a	No
		b	10	100.0					
		c	10	100.0					
NAB-BAY9-SDB6-DUR	100	a	10	100.0	100.0	0.0	107.1	n/a	No
		b	10	100.0					
		c	10	100.0					
NAB-BAY18-SDB6-DUR	100	a	10	100.0	96.7	5.8	103.6	0.343	No
		b	10	100.0					
		c	9	90.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB6-PRE	100	a	215	10	95.6	96.4	1.2	98.0	0.0470	No
		b	197	7	96.6					
		c	191	7	96.5					
		d	219	11	95.2					
		e	219	4	98.2					
NAB-BAY18-SDB6-PRE	100	a	164	9	94.8	97.3	1.5	98.9	0.3135	No
		b	218	7	96.9					
		c	213	4	98.2					
		d	243	4	98.4					
		e	216	4	98.2					
NAB-BAY9-SDB6-DUR	100	a	213	4	98.2	97.7	1.3	100.0	0.0670	Yes <sup>c</sup>
		b	208	6	97.2					
		c	200	2	99.0					
		d	207	3	98.6					
		e	221	10	95.7					
NAB-BAY18-SDB6-DUR	100	a	212	13	94.2	95.4	1.5	97.6	0.0384	Yes
		b	188	5	97.4					
		c	187	12	94.0					
		d	245	13	95.0					
		e	209	8	96.3					

**QA/QC SAMPLES<sup>a</sup>**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	70.0	47.6	70.0	0.148	No
		b	0	0.0					
		c	5	100.0					
		d	4	80.0					
	200	a	1	20.0	10.0	11.5	10.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	1	20.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	8	80.0	93.3	11.5	100.0	n/a	n/a
		b	10	100.0					
		c	11	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.211	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	100	a	10	100.0	100.0	0.0	107.1	0.371	No
		b	10	100.0					
		c	10	100.0					
	200	a	10	100.0	96.7	5.8	103.6	0.500	No
		b	10	100.0					
		c	9	90.0					
	400	a	3	30.0	33.3	5.8	35.7	0.005	Yes
		b	3	30.0					
		c	4	40.0					
	800	a	0	0.0	0.0	0.0	0.0	0.004	Yes
		b	0	0.0					
		c	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	No
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	123.5	103.3-147.5
MYSIDS	200	400	352.5	326.3-387.7
MUSSELS	4.1	5.9	6.0	5.9-6.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB6

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-OF9-SDB6-FF	12.5%	a	7.6	7.7	7.7	7.6	7.6	7.0	7.2	6.6	6.4	6.3	18.8	18.8	19.6	19.6	20.2	32.9	32.8	32.6	33.3	33.4
	25%	a	7.6	7.7	7.7	7.6	7.6	7.3	7.2	6.5	6.3	6.7	18.9	18.7	19.6	19.4	20.0	33.0	33.0	33.1	33.6	34.0
	50%	a	7.6	7.6	7.7	7.6	7.6	7.3	6.7	6.3	5.7	6.2	19.4	18.8	19.6	19.6	20.2	32.8	32.9	33.0	33.4	33.4
	100%	a	7.8	7.7	7.7	7.6	7.6	7.4	6.0	5.9	5.3	5.3	19.1	18.8	19.6	19.6	20.2	33.3	33.2	33.1	33.6	33.6
NAB-OF9-SDB6-COMP	12.5%	a	7.6	7.7	7.7	7.6	7.6	7.0	7.3	6.8	6.9	6.7	18.7	18.3	19.0	19.6	19.5	33.0	33.2	34.1	32.8	33.5
	25%	a	7.6	7.7	7.6	7.6	7.6	7.0	7.3	6.8	7.1	6.8	18.6	18.3	19.0	19.6	19.5	33.0	33.2	33.1	32.8	33.5
	50%	a	7.7	7.7	7.6	7.6	7.6	7.3	7.1	6.6	6.8	6.9	18.7	18.3	19.2	19.4	19.5	32.6	32.7	32.8	32.5	33.4
	100%	a	7.8	7.7	7.7	7.6	7.6	7.6	6.9	6.5	6.5	6.7	19.0	18.3	19.4	19.3	19.5	32.4	32.8	32.9	32.9	33.1
NAB-OF18-SDB6-FF	12.5%	a	7.6	7.6	7.6	7.6	7.6	7.1	7.0	6.5	6.8	6.6	18.8	18.0	19.4	19.4	19.8	32.9	32.9	32.9	33.1	33.7
	50%	a	7.6	7.6	7.6	7.5	7.5	7.1	6.6	6.1	5.7	6.1	18.8	18.6	19.4	19.6	20.0	32.8	32.8	32.9	33.1	33.2
	100%	a	7.7	7.7	7.7	7.5	7.5	7.9	6.0	5.5	5.3	5.9	18.9	18.6	19.4	19.5	19.9	32.7	32.6	32.9	33.0	33.1
NAB-BAY9-SDB6-PRE	100%	a	7.6	7.7	7.7	7.6	7.6	6.8	7.4	6.4	7.2	6.7	18.9	18.8	19.6	19.4	20.0	33.0	33.2	33.0	34.0	34.3
NAB-BAY18-SDB6-PRE	100%	a	7.6	7.6	7.7	7.6	7.6	6.9	7.5	6.7	7.4	7.0	18.6	18.2	19.0	19.6	19.4	32.7	32.8	32.9	33.6	34.1
NAB-BAY9-SDB6-DUR	100%	a	7.6	7.6	7.7	7.6	7.6	7.6	7.2	6.7	7.1	7.0	19.9	18.3	19.0	19.5	19.5	31.7	32.0	32.0	31.5	32.0
NAB-BAY18-SDB6-DUR	100%	a	7.6	7.6	7.6	7.6	7.6	7.6	7.2	6.4	7.0	6.6	19.6	18.7	19.5	19.3	19.9	33.1	33.2	33.0	33.2	33.8
Scripps Control	0	a	7.6	7.7	7.7	7.6	7.6	7.8	7.7	7.2	7.4	7.2	18.8	18.2	19.0	19.3	19.1	32.0	32.6	33.5	32.1	33.5
Scripps Cu Ref. Tox.	50 µg/l	a	7.6	7.7	7.7	7.6	7.6	6.8	7.3	7.2	7.4	7.1	18.5	18.7	19.3	19.3	19.4	32.2	32.9	33.1	31.7	32.4
	100 µg/l	a	7.6	7.7	7.6	7.6	7.6	6.9	7.7	7.2	6.9	7.1	18.6	18.5	19.0	19.6	19.5	32.5	32.9	33.1	31.9	32.4
	200 µg/l	a	7.6	7.7	7.6	7.7	7.7	6.9	7.8	7.2	7.9	7.0	18.6	18.1	19.3	19.4	19.4	32.1	32.9	33.0	32.5	32.6
	400 µg/l	a	7.6	7.7	7.6	N	N	6.9	7.9	7.1	N	N	18.6	18.1	19.1	N	N	32.1	32.9	33.0	N	N
Salt Control	n/a	a	7.6	7.7	7.4	7.3	7.3	5.9	7.1	6.9	7.2	6.9	18.8	18.3	19.0	19.4	19.5	31.6	32.7	33.1	32.0	32.7

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-OF9-SDB6-FF	12.5%	a	7.5	7.6	7.5	7.5	7.5	7.0	7.5	5.1	5.5	5.2	18.9	18.5	19.4	19.5	19.4	32.9	32.9	32.6	33.2	33.3
	25%	a	7.6	7.6	7.6	7.5	7.5	7.4	7.3	5.1	5.8	5.7	19.0	18.5	19.5	19.4	19.2	32.9	32.9	32.9	33.5	33.5
	50%	a	7.7	7.6	7.6	7.5	7.5	7.4	6.3	5.0	5.3	5.5	19.0	18.6	19.5	19.4	19.3	33.1	32.7	32.6	33.4	33.3
	100%	a	7.8	7.6	7.6	7.6	7.6	7.7	5.9	4.9	5.0	4.8	19.3	18.6	19.4	19.5	19.3	32.9	33.3	33.3	33.5	33.6
NAB-OF9-SDB6-COMP	12.5%	a	7.7	7.7	7.6	7.5	7.6	7.1	7.0	5.4	6.3	6.1	19.2	18.7	19.5	19.5	19.4	32.4	32.8	32.7	32.9	33.2
	25%	a	7.8	7.7	7.6	7.6	7.6	7.3	6.5	5.2	6.1	6.1	18.8	18.8	19.5	19.5	19.4	32.8	33.0	32.9	32.9	33.3
	50%	a	7.8	7.7	7.6	7.6	7.6	7.4	6.3	5.0	6.0	6.1	19.3	18.8	19.5	19.5	19.3	32.4	32.5	32.6	33.4	33.1
	100%	a	7.9	7.7	7.6	7.6	7.6	7.6	5.3	4.6	5.4	5.5	19.9	18.8	19.5	19.6	19.4	32.3	32.3	32.4	32.5	32.6
NAB-OF18-SDB6-FF	12.5%	a	7.6	7.7	7.5	7.5	7.6	7.3	7.2	5.1	5.0	5.5	18.8	18.6	19.6	19.5	19.3	32.7	33.0	32.9	33.1	33.2
	50%	a	7.7	7.6	7.5	7.4	7.5	7.5	5.6	5.0	4.6	4.6	18.8	18.6	19.6	19.5	19.3	32.6	32.8	32.8	33.1	33.1
	100%	a	7.8	7.6	7.5	7.5	7.5	8.0	5.3	4.3	4.5	4.3	19.1	18.6	19.6	19.5	19.3	32.5	32.8	32.5	33.0	33.0
NAB-BAY9-SDB6-PRE	100%	a	7.5	7.7	7.5	7.5	7.5	7.3	7.0	5.0	5.9	6.7	19.1	18.6	19.6	19.6	19.4	32.6	33.0	32.6	33.4	34.0
NAB-BAY18-SDB6-PRE	100%	a	7.7	7.7	7.6	7.6	7.6	6.8	7.2	5.5	6.4	5.6	18.8	18.6	19.7	19.4	19.6	31.7	33.3	33.0	32.9	33.4
NAB-BAY9-SDB6-DUR	100%	a	7.5	7.6	7.5	7.5	ND	7.4	7.1	5.0	6.1	ND	18.9	18.6	19.6	19.5	ND	30.7	30.5	30.7	30.3	ND
NAB-BAY18-SDB6-DUR	100%	a	7.5	7.6	7.5	7.6	7.6	7.8	6.8	5.4	6.8	6.4	20.0	18.6	19.7	19.5	19.4	31.3	31.8	32.7	32.8	32.4
Scripps Control	0	a	7.7	7.7	7.6	7.6	7.6	6.8	7.3	5.4	6.1	6.4	19.3	18.8	19.8	19.8	18.9	32.1	32.1	32.3	31.9	32.1
Scripps Cu Ref. Tox.	100 µg/l	a	7.6	7.6	7.5	7.6	7.5	6.9	7.2	5.1	6.1	5.8	19.3	18.8	19.7	19.8	19.6	32.2	32.2	32.6	32.1	32.2
	200 µg/l	a	7.6	7.6	7.6	7.6	7.6	7.0	7.2	5.0	6.5	6.4	19.1	18.7	19.7	19.8	19.5	32.4	32.3	32.6	32.1	32.1
	400 µg/l	a	7.6	7.7	7.6	7.6	7.6	7.0	7.3	5.4	7.0	6.9	19.0	18.8	19.7	19.6	19.4	32.1	32.1	32.6	32.2	32.2
	800 µg/l	a	7.6	7.6	7.6	7.2	7.7	7.1	7.6	6.0	6.2	6.9	19.0	18.8	19.6	19.8	19.4	32.3	32.0	32.6	32.2	32.2
Salt Control	n/a	a	7.6	7.4	7.3	7.7	7.2	5.8	6.6	4.7	7.6	6.4	19.3	18.8	19.8	19.6	19.6	31.8	31.9	32.2	32.2	32.7

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			Dissolved Oxygen (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NAB-OF9-SDB6-FF	6.2%	f	7.7	7.8	7.8	8.1	7.1	7.1	15.1	15.7	15.3	32.7	32.2	32.6
	12.4%	f	7.8	7.8	7.8	8.0	7.1	7.4	15.2	15.7	15.3	32.4	32.1	32.0
	24.8%	f	7.8	7.8	7.8	8.1	7.2	7.4	15.0	15.7	15.3	31.5	31.8	32.0
	49.5%	f	7.9	7.8	7.8	8.0	7.2	7.3	15.1	15.7	15.3	32.3	31.9	31.5
NAB-OF9-SDB6-COMP	6.2%	f	7.8	7.7	7.8	8.0	7.0	7.0	15.2	15.6	15.6	32.9	32.2	32.2
	12.4%	f	7.8	7.7	7.8	7.4	7.1	7.0	15.2	15.8	15.6	32.6	32.3	32.3
	24.8%	f	7.8	7.7	7.8	7.7	7.1	7.0	15.1	15.8	15.4	32.8	32.4	32.4
	49.5%	f	7.8	7.8	7.8	7.8	7.2	7.0	15.0	15.5	15.4	32.2	32.0	32.0
NAB-OF18-SDB6-FF	6.4%	f	7.8	7.8	7.8	8.1	7.2	7.6	16.2	15.8	15.5	32.2	31.4	32.1
	12.9%	f	7.8	7.8	7.8	8.2	7.1	7.7	16.2	15.9	15.6	32.0	31.1	32.1
	25.7%	f	7.8	7.8	7.8	8.1	7.1	7.6	16.2	15.8	15.5	31.7	31.0	31.6
	51.4%	f	7.9	7.7	7.8	8.1	7.0	7.4	16.0	16.0	15.4	31.1	30.8	30.8
NAB-BAY9-SDB6-PRE	100%	f	7.8	7.7	7.8	7.9	7.1	7.3	15.2	15.6	15.3	32.5	32.2	32.4
NAB-BAY18-SDB6-PRE	100%	f	7.7	7.7	7.8	8.1	7.1	7.0	15.1	15.7	15.5	32.5	32.0	32.1
NAB-BAY9-SDB6-DUR	100%	f	7.8	7.8	7.8	8.1	7.0	7.1	16.3	15.7	15.6	29.8	29.7	30.5
NAB-BAY18-SDB6-DUR	100%	f	7.9	7.8	7.8	7.8	6.8	7.2	16.2	16.0	15.6	32.1	32.0	32.4
Scripps Control	0	f	7.9	7.7	7.7	7.5	6.8	7.6	15.1	15.8	15.3	28.2	28.0	27.8
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.9	7.7	7.8	7.7	6.9	7.7	15.0	15.7	15.4	29.0	28.5	28.4
	4.1 µg/l	f	7.9	7.8	7.8	7.8	6.9	7.6	15.1	15.8	15.3	28.3	28.1	28.0
	5.9 µg/l	f	7.9	7.8	7.8	8.1	6.8	7.8	15.0	15.8	15.3	27.6	27.9	28.4
	8.4 µg/l	f	7.9	7.7	7.7	7.9	6.9	7.8	15.0	15.9	15.4	28.0	28.0	28.2
	12 µg/l	f	7.9	7.8	7.7	8.0	7.0	7.5	15.3	16.0	15.3	28.3	28.1	28.3
	17.2 µg/l	f	7.9	7.8	7.7	8.0	7.2	7.2	15.0	15.8	15.3	28.0	28.1	28.4
Brine Control 1	n/a	f	8.0	7.8	7.8	7.4	7.2	7.3	16.3	16.0	15.8	32.6	32.3	32.1
Brine Control 2	n/a	f	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

N - water quality not taken due to 100% mortality in treatment

ND - water quality not recorded

**OUTFALLS****TOPSMELT (*A. affinis*)**

<b>SAMPLE ID</b>	<b>CONC (%)</b>	<b>MEAN SURVIVAL (%)</b>
NAB-OF9-TIE2-FF	25	95.0
	50	100.0
	100	95.0
NAB-OF18-TIE2-FF	25	95.0
	50	15.0
	100	0.0

**MYSIDS (*A. bahia*)**

<b>SAMPLE ID</b>	<b>CONC (%)</b>	<b>MEAN SURVIVAL (%)</b>
NAB-OF9-TIE2-FF	25	95.0
	50	90.0
	100	50.0
NAB-OF18-TIE2-FF	25	95.0
	50	20.0
	100	5.0

**MUSSELS (*M. galloprovincialis*)**

<b>SAMPLE ID</b>	<b>CONC (%)</b>	<b>MEAN NORM DEV (%)</b>
NAB-OF9-TIE2-FF	12.5	57.0
	25	0.0
	50	0.0
	61	0.0
NAB-OF18-TIE2-FF	12.5	81.0
	25	0.0
	57	0.0

Please refer to TIE 2 Report for raw data and water quality

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NAB-BAY9-TIE2-DUR	100	100.0
NAB-BAY18-TIE2-DUR	100	95.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NAB-BAY9-TIE2-DUR	100	100.0
NAB-BAY18-TIE2-DUR	100	100.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
NAB-BAY9-TIE2-DUR	100	96.0
NAB-BAY18-TIE2-DUR	100	96.0

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Scripps Control	n/a	100.0
Salt Control	n/a	100.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Natural Seawater	n/a	100.0
Salt Control	n/a	95.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN NORM DEV (%)
Natural Seawater	n/a	96.0
Brine Control	n/a	95.0

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	4/6/2005	50	100	101.8	86.1-120.5
MYSIDS	5/19/2005	214.4	326	271.5	236.1-305.75
MUSSELS	3/19/2005	10	20.0	13.04	12.8-13.3

Reference Toxicant tests are within two standard deviations of Nautilus' control chart mean  
Please refer to TIE II Report for raw data and water quality



# SDB7- 04/27/2005

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-OF9-SDB7-FF	12.5	a	4	80.0	90.0	11.5	94.7	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	6	100.0					
	50	a	6	100.0	95.0	10.0	100.0	0.312	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	4	80.0	85.0	10.0	89.5	0.104	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
NAB-OF9-SDB7-COMP	12.5	a	5	100.0	90.8	10.7	95.6	0.500	No
		b	4	80.0					
		c	5	100.0					
		d	5	83.3					
	50	a	4	66.7	81.7	13.7	86.0	0.104	No
		b	4	80.0					
		c	5	100.0					
		d	4	80.0					
	100	a	3	60.0	60.0	16.3	63.2	0.007	Yes
		b	4	80.0					
		c	3	60.0					
		d	2	40.0					
NAB-OF18-SDB7-FF	12.5	a	4	80.0	85.0	10.0	85.0	0.029	Yes
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
	50	a	5	100.0	90.0	11.5	90.0	0.091	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					
	100	a	5	100.0	90.0	11.5	90.0	0.091	No
		b	4	80.0					
		c	5	100.0					
		d	4	80.0					
NAB-OF18-SDB7-COMP	12.5	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	90.0	11.5	90.0	0.091	No
		b	5	100.0					
		c	4	80.0					
		d	4	80.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB7

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB7-PRE	100	a	4	80.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY18-SDB7-PRE	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY9-SDB7-DUR	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NAB-BAY18-SDB7-DUR	100	a	4	80.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NAB-BAY9-SDB7-PRE	100	a	137	8	94.5	94.6	1.0	102.7	0.064	No
		b	115	7	94.3					
		c	133	9	93.7					
		d	134	5	96.4					
		e	135	8	94.4					
NAB-BAY18-SDB7-PRE	100	a	133	16	89.3	91.6	3.6	99.4	0.395	No
		b	116	15	88.5					
		c	138	7	95.2					
		d	138	6	95.8					
		e	129	16	89.0					
NAB-BAY9-SDB7-DUR	100	a	136	9	93.8	93.2	2.1	101.2	0.248	No
		b	125	13	90.6					
		c	128	11	92.1					
		d	122	5	96.1					
		e	117	8	93.6					
NAB-BAY18-SDB7-DUR	100	a	112	18	86.2	92.3	3.6	100.2	0.470	No
		b	136	9	93.8					
		c	139	10	93.3					
		d	128	10	92.8					
		e	124	6	95.4					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	95.0	10.0	n/a	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	3	60.0	85.0	19.1	89.5	0.201	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	75.0	19.1	78.9	0.065	No
		b	3	60.0					
		c	4	80.0					
		d	3	60.0					
	200	a	2	40.0	70.0	34.6	73.7	0.124	No
		b	5	100.0					
		c	5	100.0					
		d	2	40.0					
	400	a	0	0.0	25.0	25.2	26.3	0.004	Yes
		b	3	60.0					
		c	1	20.0					
		d	1	20.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	153	12	92.7	92.1	2.4	100.0	n/a	n/a
		b	154	20	88.5					
		c	137	9	93.8					
		d	99	7	93.4					
Copper Ref. Tox.	2.9	a	120	18	87.0	82.7	8.5	89.8	0.034	Yes
		b	131	17	88.5					
		c	95	37	72.0					
		d	130	13	90.9					
		e	101	33	75.4					
	4.1	a	95	81	54.0	54.7	10.4	59.3	0.000	Yes
		b	87	50	63.5					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	0	131	0.0	2.3	3.2	2.5	0.000	Yes
		b	4	165	2.4					
		c	9	106	7.8					
		d	2	149	1.3					
		e	0	147	0.0					
	8.4	a	0	131	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	135	0.0					
		c	0	151	0.0					
		d	0	154	0.0					
		e	0	137	0.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	200.0	400.0	268.2	160.3-506.5
MUSSELS	2.9	4.1	4.3	3.78-4.69

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB7

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NAB-OF9-SDB7-FF	12.5%	a	7.9	7.8	7.7	7.8	7.7	7.4	6.8	6.6	7.2	7.1	18.9	18.6	19.3	19.0	19.1	33.1	33.3	33.3	33.6	33.6
	25%	a	8.0	7.8	7.7	7.8	7.7	7.9	6.5	6.4	7.0	7.0	18.8	18.6	19.3	19.0	19.1	32.9	32.9	32.9	33.2	33.1
	100%	a	8.1	7.9	7.7	7.8	7.7	7.9	6.2	6.5	6.4	6.4	18.6	18.5	19.3	18.9	19.0	32.1	32.2	32.2	32.3	33.4
NAB-OF9-SDB7-COMP	12.5%	a	7.8	7.8	7.7	7.8	7.6	7.6	6.3	6.1	6.6	6.1	19.2	18.3	19.4	18.6	19.3	33.4	33.3	33.3	33.2	33.7
	25%	a	7.9	7.8	7.6	7.7	7.7	7.8	5.5	5.8	7.0	6.6	18.6	18.3	19.4	18.6	19.2	33.1	33.0	33.1	33.2	33.3
	100%	a	8.1	7.9	7.7	7.8	7.8	8.2	5.6	6.0	6.3	6.6	18.2	18.3	19.4	18.3	19.2	32.5	32.6	32.8	32.9	33.0
NAB-OF18-SDB7-FF	12.5%	a	7.8	7.8	7.6	7.8	7.7	7.5	6.2	6.1	6.8	6.8	19.0	18.5	19.5	18.7	19.0	33.1	33.2	33.0	33.3	33.4
	50%	a	8.0	7.8	7.6	7.8	7.7	7.7	6.3	6.3	6.8	6.5	18.8	18.5	19.4	18.6	18.9	32.8	32.9	32.7	33.1	33.1
	100%	a	8.1	7.9	7.7	7.6	7.6	7.8	5.7	5.7	5.7	6.2	18.6	18.4	19.3	18.6	18.9	32.2	32.2	32.1	32.2	32.3
NAB-OF18-SDB7-COMP	12.5%	a	7.8	7.7	7.7	7.8	7.7	7.8	6.7	6.4	7.2	7.1	18.6	18.0	19.3	18.0	18.8	33.4	33.5	33.3	33.8	34.0
	50%	a	7.8	7.7	7.6	7.7	7.7	7.8	6.6	6.3	6.9	7.2	18.9	18.0	19.3	18.1	18.8	32.8	32.9	32.9	33.1	33.3
	100%	a	7.9	7.7	7.5	7.7	7.7	8.0	5.6	5.8	6.1	6.6	18.6	18.1	19.3	18.2	18.8	32.2	32.2	32.2	32.3	32.3
NAB-BAY9-SDB7-PRE	100%	a	7.8	7.8	7.7	7.8	7.8	7.4	6.9	6.3	7.3	6.8	19.0	18.6	19.3	18.8	19.3	33.6	33.7	33.9	33.9	33.8
NAB-BAY18-SDB7-PRE	100%	a	7.8	7.8	7.7	7.8	7.7	7.3	6.6	6.4	7.3	6.3	19.1	18.4	19.4	18.8	19.3	33.5	33.7	33.9	33.7	33.7
NAB-BAY9-SDB7-DUR	100%	a	7.7	7.6	7.7	7.7	7.7	7.3	7.0	6.4	7.3	6.2	18.6	18.3	19.3	18.6	19.1	32.2	32.2	32.3	32.2	32.2
NAB-BAY18-SDB7-DUR	100%	a	7.7	7.7	7.7	7.8	7.8	7.5	7.0	6.7	7.5	7.1	18.4	18.3	19.4	18.6	19.0	32.9	33.0	33.0	33.1	33.0
Scripps Control	0	a	7.8	7.8	7.6	7.8	7.7	7.7	6.9	6.6	7.5	7.2	18.6	18.3	19.3	18.3	19.1	31.6	31.5	31.7	31.7	31.9
Scripps Cu Ref. Tox.	50 µg/l	a	7.8	7.8	7.6	7.8	7.8	7.8	7.0	6.7	7.7	7.4	18.8	18.3	19.3	18.3	19.0	31.5	31.5	31.6	31.6	31.6
	100 µg/l	a	7.8	7.8	7.6	7.8	7.8	7.7	7.0	6.6	7.7	7.6	18.8	18.3	19.3	18.4	19.1	31.5	31.5	31.6	31.5	31.6
	200 µg/l	a	7.8	7.8	7.6	7.8	7.7	7.7	7.1	6.6	7.9	7.4	18.8	18.2	19.1	18.4	19.0	31.5	31.6	31.8	31.9	31.6
	400 µg/l	a	7.9	7.8	7.7	7.8	7.7	7.7	7.2	7.1	7.9	7.3	18.8	18.3	19.1	18.6	19.0	31.5	31.6	31.8	31.8	31.6
Salt Control	n/a	a	7.9	7.7	7.5	7.6	7.5	7.4	6.1	6.4	7.0	6.6	19.4	18.3	19.2	18.6	19.0	31.4	31.5	31.6	31.4	31.5

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			Dissolved Oxygen (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NAB-BAY9-SDB7-PRE	100%	f	7.8	7.8	7.8	7.5	8.4	8.2	16.0	15.1	14.9	33.8	33.8	33.8
NAB-BAY18-SDB7-PRE	100%	f	7.8	7.8	7.8	7.9	8.5	8.4	16.0	15.3	15.1	29.7	30.0	30.2
NAB-BAY9-SDB7-DUR	100%	f	7.8	7.8	7.8	7.9	8.4	8.3	16.0	15.0	14.8	29.7	29.9	30.2
NAB-BAY18-SDB7-DUR	100%	f	7.9	7.8	7.8	7.8	8.5	8.6	16.0	15.1	15.0	29.6	29.6	29.7
Scripps Control	0	f	8.1	8.0	7.7	7.5	8.2	8.2	16.0	15.5	15.2	29.4	29.3	29.0
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.9	7.9	7.9	7.2	8.3	8.5	15.8	15.2	15.0	29.5	29.6	29.7
	4.1 µg/l	f	7.8	7.8	7.7	7.9	8.4	8.4	15.8	15.2	15.3	29.5	29.6	29.7
	5.9 µg/l	f	7.8	7.8	7.7	7.8	8.3	8.4	15.9	15.2	15.4	29.5	29.6	29.6
	8.4 µg/l	f	7.8	7.8	7.7	7.9	8.6	8.2	15.9	15.2	15.2	29.6	29.5	29.6
	12 µg/l	f	7.8	7.8	7.7	7.9	8.5	8.3	15.8	15.0	15.1	29.6	29.5	29.6
	17.2 µg/l	f	7.8	7.8	7.8	7.7	8.2	8.5	15.8	15.0	15.1	29.6	29.6	29.7

## Appendix C4

***NI***

SDB4- 10/17/2004  
SDB5- 01/10/2005  
SDB6- 2/10/2005  
TIE2- 3/19/2005  
SDB7- 4/17/2005

# SDB4 – 10/17/2004

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB4-FF	12.5	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	85.0	19.1	85.0	0.108	No
		b	4	80.0					
		c	3	60.0					
		d	5	100.0					
	50	a	5	100.0	90.0	11.5	90.0	0.091	No
		b	4	80.0					
		c	5	100.0					
		d	4	80.0					
	100	a	3	60.0	80.0	16.3	80.0	0.046	Yes
		b	4	80.0					
		c	4	80.0					
		d	5	100.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB4-FF	12.5	a	9	90.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	96.7	5.8	96.7	0.211	No
		b	9	90.0					
		c	10	100.0					
	50	a	8	80.0	76.7	17.3	76.7	0.048	Yes
		b	9	90.0					
		c	6	60.0					
	100	a	6	60.0	56.7	5.8	56.7	0.003	Yes
		b	5	50.0					
		c	6	60.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB4-FF	6.25	a	164	7	95.9	92.6	3.6	95.0	0.018	Yes
		b	164	13	92.7					
		c	168	6	96.6					
		d	137	17	89.0					
		e	145	18	89.0					
	12.5	a	121	41	74.7	83.2	7.3	85.3	0.006	Yes
		b	169	20	89.4					
		c	163	32	83.6					
		d	175	17	91.1					
		e	157	47	77.0					
	25	a	5	161	3.0	6.7	5.6	6.9	0.000	Yes
		b	1	170	0.6					
		c	10	146	6.4					
		d	13	140	8.5					
		e	27	152	15.1					
	50	a	1	200	0.5	0.3	0.5	0.3	0.000	Yes
		b	0	126	0.0					
		c	2	187	1.1					
		d	0	149	0.0					
		e	0	145	0.0					
	61.4	a	0	196	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	196	0.0					
		c	0	196	0.0					
		d	0	196	0.0					
		e	0	196	0.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB4-DUR	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB4-DUR	100	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB4-DUR	100	a	167	5	97.1	97.6	0.5	100.1	0.3966	No
		b	162	3	98.2					
		c	187	4	97.9					
		d	167	5	97.1					
		e	188	4	97.9					



# QA/QC SAMPLES<sup>a</sup>

## TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	90.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

## MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	100.0	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	107.1	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	9	90.0	83.3	5.8	89.3	0.051	No
		b	8	80.0					
		c	8	80.0					
	400	a	2	20.0	6.7	11.5	7.1	0.001	Yes
		b	0	0.0					
		c	0	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	148	25	85.5	94.5	5.4	100.0	n/a	No
		b	175	5	97.2					
		c	139	10	93.3					
		d	193	4	98.0					
		e	174	3	98.3					
Brine Control	n/a	a	177	6	96.7	95.7	1.1	98.1	0.323	No
		b	170	10	94.4					
		c	186	6	96.9					
		d	171	8	95.5					
		e	164	9	94.8					
Copper Ref. Tox.	2.9	a	167	9	94.9	95.1	0.7	100.7	0.397	No
		b	200	11	94.8					
		c	168	10	94.4					
		d	176	8	95.7					
		e	168	7	96.0					
	4.1	a	166	3	98.2	90.3	10.0	95.6	0.221	No
		b	202	7	96.7					
		c	164	17	90.6					
		d	118	43	73.3					
		e	141	11	92.8					
	5.9	a	178	9	95.2	79.0	14.3	83.7	0.036	Yes
		b	169	20	89.4					
		c	157	36	81.3					
		d	128	60	68.1					
		e	124	79	61.1					
	8.4	a	69	106	39.4	23.7	13.7	25.1	0.000	Yes
		b	56	141	28.4					
		c	58	126	31.5					
		d	12	177	6.3					
		e	24	162	12.9					
	12.0	a	1	177	0.6	1.3	1.3	1.3	0.000	Yes
		b	5	172	2.8					
		c	5	203	2.4					
		d	1	207	0.5					
		e	0	171	0.0					
	17.2	a	3	177	1.7	0.5	0.7	0.5	0.000	Yes
		b	1	167	0.6					
		c	0	191	0.0					
		d	0	175	0.0					
		e	0	199	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	50	100	132.0	120.2-144.8
MYSIDS	200	400	265.3	232.5-302.4
MUSSELS	5.9	8.4	7.29	6.1-8.3

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB4

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-OF23A-SDB4-FF	12.5%	a	7.9	7.7	7.6	7.7	7.6	6.8	5.2	5.1	5.2	6.0	19.9	18.3	19.3	19.3	19.6	33.9	34.2	34.3	34.3	34.2
	25%	a	8.1	7.8	7.8	7.8	7.9	6.8	6.6	7.0	7.0	7.0	19.7	18.2	19.6	19.3	19.3	33.7	34.0	34.2	34.3	34.5
	50%	a	8.3	7.8	7.8	7.8	7.9	7.1	6.8	6.9	6.6	7.0	19.1	17.7	18.9	18.8	18.9	33.6	33.9	34.2	34.2	34.7
	100%	a	8.7	7.6	7.8	7.7	7.7	7.4	6.0	6.4	6.5	6.3	18.4	18.3	19.3	19.0	19.0	33.2	33.4	33.5	33.7	33.9
NI-BAY23A-SDB4-DUR	100%	a	7.7	7.6	7.7	7.6	7.7	7.4	6.0	5.4	6.3	6.1	18.5	18.3	19.4	19.3	19.5	33.9	34.2	34.3	34.4	34.5
Scripps Control	0	a	7.8	7.8	7.7	7.8	7.7	6.9	5.9	5.5	6.0	6.0	19.1	18.3	19.7	19.0	19.5	33.8	34.0	34.0	34.3	34.3
Scripps Cu Ref. Tox.	50 µg/l	a	7.9	7.8	7.7	7.8	7.7	6.9	6.2	6.5	6.3	5.9	18.7	18.0	19.2	19.1	19.4	33.9	34.4	34.7	34.2	34.3
	100 µg/l	a	7.9	7.8	7.0	7.8	7.8	7.1	6.0	6.1	6.4	6.3	18.8	18.0	19.1	19.0	19.4	33.8	34.1	34.5	34.3	34.5
	200 µg/l	a	7.8	7.8	7.7	7.9	7.8	7.0	6.0	5.9	6.5	6.5	18.6	18.1	19.4	19.1	19.3	33.8	34.0	34.7	34.1	34.2
	400 µg/l	a	7.8	7.9	N	N	N	7.0	6.2	N	N	N	18.6	18.0	N	N	N	33.8	34.1	N	N	N
Salt Control	n/a	a	8.1	7.9	7.7	7.8	7.6	6.9	5.9	6.2	6.0	6.1	19.8	18.0	18.9	18.9	19.4	33.3	33.5	33.6	33.6	33.7

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-OF23A-SDB4-FF	12.5%	a	7.9	7.7	7.8	7.8	7.9	6.7	3.9	6.9	6.8	6.9	19.3	18.3	19.5	19.1	19.3	34.3	34.5	34.5	34.5	34.6
	25%	a	8.1	7.6	7.7	7.9	7.9	6.8	6.2	6.5	7.0	7.1	19.2	18.8	19.6	19.3	19.4	34.4	34.5	34.5	34.5	34.6
	50%	a	8.3	7.6	7.8	7.7	7.9	7.0	6.6	6.9	6.0	6.7	18.8	18.8	19.3	19.1	19.3	34.1	34.2	34.4	34.1	34.2
	100%	a	8.7	7.7	7.8	7.8	7.9	7.1	6.3	6.7	6.5	6.6	18.3	18.0	19.5	19.1	19.4	33.6	34.2	34.4	34.0	34.5
NI-BAY23A-SDB4-DUR	100%	a	7.8	7.7	7.6	7.7	7.7	7.2	5.6	5.3	5.9	6.4	18.6	18.3	19.7	19.5	19.7	34.3	34.5	34.5	34.4	34.6
Scripps Control	0	a	7.9	7.7	7.7	7.7	7.6	6.9	4.7	5.3	5.0	4.8	18.8	18.3	19.4	19.3	19.5	34.4	34.6	34.6	34.2	34.3
Scripps Cu Ref. Tox.	25 µg/l	a	7.9	7.7	7.7	7.8	7.6	6.9	5.4	5.7	5.4	5.2	18.8	18.6	19.4	19.3	19.6	34.3	34.4	34.6	34.3	34.3
	50 µg/l	a	7.9	7.7	7.6	7.7	7.6	7.1	5.3	5.3	5.0	4.5	18.7	18.6	19.5	19.3	19.6	34.4	34.5	34.5	34.2	34.2
	100 µg/l	a	7.9	7.7	7.6	7.7	7.7	7.1	5.7	4.9	5.6	5.1	18.6	18.5	19.4	19.3	19.6	34.2	34.4	34.5	34.3	34.3
	200 µg/l	a	7.9	7.8	7.8	7.8	7.7	7.0	5.9	6.3	6.1	5.7	18.7	18.6	19.1	19.3	19.6	34.4	34.6	34.2	34.3	34.4
	400 µg/l	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2
Salt Control	n/a	a	7.9	7.8	7.6	7.9	7.8	7.0	6.1	5.5	6.4	6.1	18.7	18.6	19.4	19.3	19.6	34.3	34.5	34.6	34.2	34.2

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)		D.O. (mg/l)		Temp (°C)		Salinity (‰)	
			0	48	0	48	0	48	0	48
NI-OF23A-SDB4-FF	6.25%	f	7.7	7.6	7.0	6.6	15.7	15.7	33.6	33.8
	25%	f	7.7	7.6	7.0	5.8	15.5	15.7	34.0	33.9
	61.4%	f	7.7	7.3	6.9	3.3	15.6	15.7	33.6	34.0
NI-BAY23A-SDB4-DUR	100%	f	7.7	7.8	7.0	6.8	15.1	15.3	34.0	34.2
Scripps Control	0	f	7.8	7.6	6.9	6.8	15.6	15.7	34.0	34.2
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.8	7.8	7.0	6.8	15.8	15.7	33.9	34.1
	8.4 µg/l	f	7.8	7.7	6.9	6.8	15.7	15.5	33.9	34.1
	24 µg/l	f	7.8	7.8	6.9	7.1	15.8	15.5	34.1	34.1
Brine Control	0	f	7.9	7.9	7.0	7.0	15.5	15.7	33.7	34.2

N - water quality not taken due to 100% mortality in treatment

# SDB5 – 01/10/2005

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-DOWNTOWN PIER-SDB5-AFT	100	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-DOWNTOWN PIER-SDB5-AFT	100	a	10	100.0	93.3	5.8		n/a	No
		b	9	90.0					
		c	9	90.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB5-AFT	100	a	184	14	92.9	93.9	1.1	104.2	0.007	Yes
		b	144	7	95.4					
		c	116	9	92.8					
		d	178	11	94.2					
		e	164	10	94.3					
NI-DOWNTOWN PIER-SDB5-AFT	100	a	150	8	94.9	93.6	1.6	103.9	0.012	Yes
		b	170	11	93.9					
		c	139	7	95.2					
		d	144	11	92.9					
		e	155	15	91.2					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	25	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	90.0	11.5	94.7	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	200	a	1	20.0	15.0	10.0	16.7	0.000	Yes
		b	1	20.0					
		c	1	20.0					
		d	0	0.0					
	400	a	0	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	0.0					
		c	0	0.0					
		d	0	0.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	9	90.0	93.3	5.8	n/a	n/a	n/a
		b	9	90.0					
		c	10	100.0					
Copper Ref. Tox.	25	a	9	90.0	93.3	5.8	100.0	0.500	No
		b	9	90.0					
		c	10	100.0					
	50	a	10	100.0	103.3	5.8	110.7	0.051	No
		b	10	100.0					
		c	11	110.0					
	100	a	10	100.0	100.0	0.0	96.8	0.092	No
		b	10	100.0					
		c	10	100.0					
	200	a	8	80.0	90.0	10.0	90.0	0.325	No
		b	9	90.0					
		c	10	100.0					
	400	a	2	20.0	26.7	11.5	29.6	0.002	Yes
		b	2	20.0					
		c	4	40.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	No
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100	200	138.5	114.4-167.8
MYSIDS	200	400	324.9	276.2-379.8
MUSSELS <sup>d</sup>	4.1	5.9	6.0	5.9-6.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB5

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

<sup>d</sup>Copper reference toxicant test performed on 02/10/2005

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-DOWNTOWN PIER-SDB5-AFT	100%	a	7.9	7.8	7.5	7.7	7.6	7.2	6.7	6.5	6.5	6.3	19.3	19.9	19.8	19.7	18.6	31.9	31.1	29.0	29.1	29.2
Scripps Control	n/a	a	7.9	7.8	7.6	7.8	7.7	7.5	6.2	6.4	6.1	6.3	19.0	18.8	19.7	19.8	18.2	32.7	30.9	30.7	30.7	30.9

### MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-DOWNTOWN PIER-SDB5-AFT	100%	a	8.0	7.8	7.6	7.8	7.7	7.6	6.1	5.0	5.8	5.4	18.9	18.8	19.6	19.6	18.3	33.1	31.1	30.8	30.8	31.0
Scripps Control	n/a	a	7.9	7.8	7.5	7.7	7.5	7.3	5.9	5.4	6.2	5.3	18.9	19.1	19.8	19.6	18.2	31.8	30.7	30.2	30.9	31.3

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			D.O. (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NI-OF23A-SDB5-AFT	100%	f	7.8	7.8	7.9	7.5	7.8	7.5	17.0	15.8	16.3	30.2	30.1	29.9
NI-DOWNTOWN PIER-SDB5-AFT	100%	f	7.8	7.8	7.7	7.4	7.7	7.4	17.0	16.3	16.3	27.0	26.7	26.7
Scripps Control	n/a	f	7.8	7.8	7.8	6.9	7.9	7.5	17.0	16.0	16.3	28.4	28.3	28.4

# SDB6 – 02/10/2005

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB6-FF	12.5	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	90.0	20.0	90.0	0.196	No
		b	5	100.0					
		c	3	60.0					
		d	5	100.0					
NI-OF26-SDB6-FF	12.5	a	4	80.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	25	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
	100	a	5	100.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NI-OF26-SDB6-COMP	12.5	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	4	80.0	95.0	10.0	100.0	0.500	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB6-FF	12.5	a	10	100.0	93.3	5.8	93.3	0.092	No
		b	9	90.0					
		c	9	90.0					
	25	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	n/a	No
		b	10	100.0					
		c	10	100.0					
	100	a	9	90.0	96.7	5.8	96.7	0.211	No
		b	10	100.0					
		c	10	100.0					



**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF26-SDB6-FF	12.5	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
	25	a	10	100.0	93.3	5.8	93.3	0.051	No
		b	9	90.0					
		c	9	90.0					
	50	a	10	100.0	96.7	5.8	96.7	0.115	No
		b	9	90.0					
		c	10	100.0					
	100	a	8	80.0	73.3	11.5	73.3	0.014	Yes
		b	8	80.0					
		c	6	60.0					
NI-OF26-SDB6-COMP	12.5	a	10	100.0	93.3	11.5	93.3	0.137	No
		b	8	80.0					
		c	10	100.0					
	50	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					
	100	a	10	100.0	100.0	0.0	100.0	0.211	No
		b	10	100.0					
		c	10	100.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEV (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB6-FF	6.2	a	219	5	97.8	98.3	1.5	100.3	0.346	No
		b	244	1	99.6					
		c	215	9	96.0					
		d	230	2	99.1					
		e	229	2	99.1					
	12.4	a	210	6	97.2	96.7	1.0	98.7	0.034	Yes
		b	212	10	95.5					
		c	201	6	97.1					
		d	198	4	98.0					
		e	208	9	95.9					
	24.8	a	28	198	12.4	10.3	2.9	10.5	0.000	Yes
		b	22	208	9.6					
		c	15	199	7.0					
		d	34	206	14.2					
		e	21	226	8.5					
	49.5	a	0	221	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	203	0.0					
		c	0	219	0.0					
		d	0	219	0.0					
		e	0	235	0.0					
NI-OF26-SDB6-FF	6.2	a	207	4	98.1	97.7	0.7	100.3	0.358	No
		b	209	6	97.2					
		c	190	4	97.9					
		d	238	8	96.7					
		e	201	3	98.5					
	12.4	a	185	6	96.9	96.5	1.4	99.1	0.163	No
		b	214	13	94.3					
		c	229	8	96.6					
		d	212	7	96.8					
		e	215	4	98.2					
	24.8	a	172	22	88.7	92.6	2.5	95.0	0.004	Yes
		b	185	10	94.9					
		c	200	16	92.6					
		d	201	17	92.2					
		e	196	11	94.7					
	49.5	a	1	144	0.7	0.1	0.3	0.1	0.000	Yes
		b	0	218	0.0					
		c	0	231	0.0					
		d	0	222	0.0					
		e	0	215	0.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF26-SDB6-COMP	7.0	a	238	8	96.7	97.7	1.2	100.2	0.398	No
		b	216	7	96.9					
		c	203	2	99.0					
		d	191	2	99.0					
		e	207	7	96.7					
	13.9	a	215	9	96.0	97.0	1.4	99.6	0.319	No
		b	213	5	97.7					
		c	228	2	99.1					
		d	196	8	96.1					
		e	207	8	96.3					
	27.9	a	237	13	94.8	95.8	2.1	98.3	0.095	No
		b	202	6	97.1					
		c	218	14	94.0					
		d	181	2	98.9					
		e	218	13	94.4					
	55.7	a	198	14	93.4	95.5	1.8	97.9	0.042	Yes
		b	212	8	96.4					
		c	201	8	96.2					
		d	201	5	97.6					
		e	210	14	93.8					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB6

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

**BAY SAMPLES**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB6-PRE	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
NI-BAY26-SDB6-PRE	100	a	4	80	95.0	10.0	95.0	0.196	No
		b	5	100					
		c	5	100					
		d	5	100					
NI-OF23A-SDB6-DUR	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
NI-BAY26-SDB6-DUR	100	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB6-PRE	100	a	10	100	100.0	0.0	107.1	n/a	No
		b	10	100					
		c	10	100					
NI-BAY26-SDB6-PRE	100	a	10	100	100.0	0.0	107.1	n/a	No
		b	11	100					
		c	10	100					
NI-OF23A-SDB6-DUR	100	a	10	100	100.0	0.0	107.1	n/a	No
		b	10	100					
		c	10	100					
NI-BAY26-SDB6-DUR	100	a	10	100	100.0	0.0	107.1	n/a	No
		b	10	100					
		c	10	100					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB6-PRE	100.0	a	221	4	98.2	98.0	0.8	99.6	0.294	No
		b	203	5	97.6					
		c	214	4	98.2					
		d	188	6	96.9					
		e	234	2	99.2					
NI-BAY26-SDB6-PRE	100	a	213	3	98.6	97.5	1.3	99.0	0.377	No
		b	234	6	97.5					
		c	211	3	98.6					
		d	203	6	97.1					
		e	208	10	95.4					
NI-OF23A-SDB6-DUR	100	a	207	4	98.1	97.1	1.5	99.4	0.130	No
		b	154	3	98.1					
		c	193	6	97.0					
		d	205	5	97.6					
		e	193	11	94.6					
NI-BAY26-SDB6-DUR	100	a	218	9	96.0	96.4	0.8	98.6	0.079	No
		b	219	8	96.5					
		c	233	8	96.7					
		d	221	11	95.3					
		e	183	5	97.3					

**QA/QC SAMPLES<sup>a</sup>**
**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
Copper Ref. Tox.	50	a	5	100	100.0	0.0	100.0	n/a	No
		b	5	100					
		c	5	100					
		d	5	100					
	100	a	5	100	70.0	47.6	70.0	0.148	No
		b	0	0					
		c	5	100					
		d	4	80					
	200	a	1	20	10.0	11.5	10.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	1	20					
	400	a	0	0	0.0	0.0	0.0	0.000	Yes
		b	0	0					
		c	0	0					
		d	0	0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	8	80.0	93.3	11.5	100.0	n/a	n/a
		b	10	100.0					
		c	11	100.0					
Salt Control	n/a	a	10	100.0	100.0	0.0	107.1	0.211	No
		b	10	100.0					
		c	10	100.0					

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Copper Ref. Tox.	100	a	10	100	100.0	0.0	107.1	0.371	No
		b	10	100					
		c	10	100					
	200	a	10	100	96.7	5.8	103.6	0.500	No
		b	10	100					
		c	9	90					
	400	a	3	30	33.3	5.8	35.7	0.005	Yes
		b	3	30					
		c	4	40					
	800	a	0	0	0.0	0.0	0.0	0.004	Yes
		b	0	0					
		c	0	0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	ABNORMA	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	160	4	97.6	97.7	1.0	100.0	n/a	n/a
		b	222	4	98.2					
		c	236	6	97.5					
		d	233	9	96.3					
		e	257	3	98.8					
Brine Control 1	n/a	a	204	3	98.6	98.4	0.8	100.7	0.119	No
		b	211	5	97.7					
		c	201	5	97.6					
		d	226	1	99.6					
		e	221	3	98.7					
Brine Control 2	n/a	a	189	3	98.4	97.8	1.1	100.1	0.440	No
		b	231	10	95.9					
		c	210	4	98.1					
		d	190	4	97.9					
		e	210	3	98.6					
Copper Ref. Tox.	2.9	a	231	5	97.9	98.6	0.7	101.0	0.057	No
		b	207	4	98.1					
		c	214	1	99.5					
		d	201	3	98.5					
		e	228	2	99.1					
	4.1	a	214	8	96.4	56.4	39.6	57.7	0.040	Yes
		b	205	21	90.7					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	125	101	55.3	49.3	10.8	50.5	0.000	Yes
		b	125	94	57.1					
		c	132	106	55.5					
		d	114	125	47.7					
		e	64	142	31.1					
	8.4	a	23	187	11.0	10.1	5.2	10.3	0.000	Yes
		b	24	173	12.2					
		c	4	210	1.9					
		d	32	170	15.8					
		e	21	200	9.5					
	12.0	a	0	195	0.0	0.3	0.2	0.3	0.000	Yes
		b	1	246	0.4					
		c	1	221	0.5					
		d	1	218	0.5					
		e	0	219	0.0					
	17.2	a	0	210	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	187	0.0					
		c	0	178	0.0					
		d	0	215	0.0					
		e	0	198	0.0					

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	100.0	200.0	123.5	103.3-147.5
MYSIDS	200.0	400.0	352.5	326.3-387.7
MUSSELS	4.1	5.9	6.0	5.9-6.1

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB6

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

# WATER QUALITY

## TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-OF23A-SDB6-FF	12.5%	a	7.6	7.7	7.7	7.7	7.4	7.0	7.3	6.5	6.1	5.5	19.5	18.6	19.6	19.6	20.0	33.4	33.4	33.4	33.6	33.8
	25%	a	7.6	7.7	7.7	7.6	7.5	7.0	7.4	6.5	6.5	6.3	19.2	18.6	19.6	19.7	20.0	33.4	33.4	33.4	34.0	34.1
	50%	a	7.7	7.7	7.7	7.6	7.5	7.2	7.0	6.4	6.2	6.1	18.9	18.7	19.6	19.6	20.1	33.4	33.4	33.5	33.9	34.0
	100%	a	7.7	7.7	7.7	7.6	7.6	7.5	6.9	6.5	6.3	6.5	18.8	18.7	19.5	19.5	19.9	33.0	33.2	33.2	34.1	34.4
NI-OF26-SDB6-FF	12.5%	a	7.6	7.7	7.7	7.6	7.5	7.1	7.4	6.5	6.7	6.5	18.9	18.8	19.6	19.5	19.9	33.3	33.3	33.0	33.6	33.7
	25%	a	7.6	7.7	7.7	7.6	7.6	7.3	7.4	6.5	6.7	6.7	18.9	18.4	19.5	19.4	19.9	33.2	33.3	33.3	33.6	33.8
	50%	a	7.6	7.6	7.7	7.6	7.6	7.2	7.0	6.5	6.4	6.9	19.0	18.5	19.6	19.3	19.8	32.9	32.9	32.9	33.5	33.8
	100%	a	7.8	7.7	7.6	7.6	7.6	7.5	6.9	6.4	6.0	6.4	19.1	18.4	19.5	19.4	19.8	32.9	32.8	32.9	33.1	33.3
NI-OF26-SDB6-COMP	12.5%	a	7.7	7.7	7.7	7.6	7.6	7.3	7.3	6.5	6.3	6.6	18.8	18.4	19.6	19.5	19.7	32.9	32.9	33.0	33.7	33.8
	50%	a	7.6	7.7	7.7	7.6	7.6	7.3	7.3	6.5	6.4	6.7	18.8	18.4	19.6	19.5	19.8	33.1	32.9	33.1	33.4	33.5
	100%	a	7.8	7.7	7.6	7.6	7.6	7.8	7.3	6.7	6.7	6.8	18.9	18.3	19.5	19.0	19.6	33.2	33.1	33.6	34.1	34.8
	100%	a	7.6	7.7	7.7	7.6	7.5	6.8	7.4	6.6	7.3	5.8	19.1	18.7	19.6	19.4	20.0	33.5	33.5	33.3	33.5	34.1
NI-BAY26-SDB6-PRE	100%	a	7.6	7.7	7.7	7.6	7.6	7.2	7.2	6.6	7.3	6.4	18.9	18.8	19.6	19.3	19.9	33.0	33.3	33.3	33.3	33.8
NI-OF23A-SDB6-DUR	100%	a	7.6	7.6	7.7	7.6	7.5	7.3	7.6	6.7	7.2	6.3	19.7	18.8	19.5	19.4	19.9	32.9	32.9	33.0	33.2	33.7
NI-BAY26-SDB6-DUR	100%	a	7.6	7.7	7.7	7.5	7.5	7.3	7.2	6.5	7.0	6.6	18.8	18.8	19.7	19.6	20.3	30.7	30.8	30.4	31.2	31.2
Scripps Control	0	a	7.6	7.7	7.7	7.6	7.6	7.8	7.7	7.2	7.4	7.2	18.8	18.2	19.0	19.3	19.1	32.0	32.6	33.5	32.1	33.5
Scripps Cu Ref. Tox.	50 µg/l	a	7.6	7.7	7.7	7.6	7.6	6.8	7.3	7.2	7.4	7.1	18.5	18.7	19.3	19.3	19.4	32.2	32.9	33.1	31.7	32.4
	100 µg/l	a	7.6	7.7	7.6	7.6	7.6	6.9	7.7	7.2	6.9	7.1	18.6	18.5	19.0	19.6	19.5	32.5	32.9	33.1	31.9	32.4
	200 µg/l	a	7.6	7.7	7.6	7.7	7.7	6.9	7.8	7.2	7.9	7.0	18.6	18.1	19.3	19.4	19.4	32.1	32.9	33.0	32.5	32.6
	400 µg/l	a	7.6	7.7	7.6	N	N	6.9	7.9	7.1	N	N	18.6	18.1	19.1	N	N	32.1	32.9	33.0	N	N
Salt Control	n/a	a	7.6	7.7	7.4	7.3	7.3	5.9	7.1	6.9	7.2	6.9	18.8	18.3	19.0	19.4	19.5	31.6	32.7	33.1	32.0	32.7

## MYSIDS (*A. bahia*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-OF23A-SDB6-FF	12.5%	a	7.7	7.6	7.4	7.5	7.5	7.0	6.7	5.0	6.0	5.2	20.3	18.6	19.5	19.4	19.3	33.2	33.4	33.1	33.5	33.7
	25%	a	7.7	7.5	7.4	7.5	7.5	6.9	5.6	4.4	5.3	5.0	19.9	18.8	19.5	19.4	19.4	33.1	33.4	33.3	33.7	33.8
	50%	a	7.8	7.6	7.6	7.5	7.5	7.3	6.7	5.0	5.5	5.3	19.1	18.8	19.5	19.5	19.4	33.0	33.4	33.3	33.7	33.7
	100%	a	7.9	7.7	7.5	7.6	7.6	7.7	6.3	4.7	4.8	5.2	18.6	18.8	19.5	19.6	19.3	33.0	33.4	33.3	33.6	33.6
NI-OF26-SDB6-FF	12.5%	a	7.7	7.6	7.5	7.5	7.5	7.0	6.9	5.0	5.5	5.7	19.2	18.6	19.4	19.6	19.3	32.3	33.1	33.0	33.4	33.6
	25%	a	7.7	7.6	7.5	7.5	7.6	7.4	6.5	4.9	5.4	5.8	19.4	18.6	19.4	19.6	19.4	32.6	32.9	32.9	33.4	33.5
	50%	a	7.8	7.7	7.5	7.5	7.5	7.6	6.2	4.8	4.8	5.2	19.5	18.7	19.4	19.7	19.4	32.6	32.7	32.7	33.1	33.2
	100%	a	7.9	7.7	7.5	7.6	7.6	7.2	5.8	4.9	5.2	5.2	19.8	18.7	19.4	19.4	19.3	31.7	32.7	32.6	32.8	33.0
NI-OF26-SDB6-COMP	12.5%	a	7.7	7.7	7.6	7.5	7.5	7.3	6.9	5.0	5.9	5.8	18.9	18.7	19.7	19.6	19.4	32.9	33.0	33.0	33.8	33.5
	50%	a	7.7	7.7	7.6	7.5	7.6	7.4	6.4	4.8	5.5	5.2	18.8	18.4	19.7	19.5	19.3	32.9	33.0	33.1	33.3	33.4
	100%	a	7.8	7.7	7.6	7.6	7.5	7.8	6.2	4.4	4.9	5.1	19.2	18.6	19.7	19.6	19.4	33.0	33.2	33.1	33.1	33.4
NI-OF23A-SDB6-PRE	100%	a	7.7	7.7	7.6	7.5	7.5	6.7	7.3	5.5	5.9	4.4	20.2	18.7	19.6	19.4	19.6	33.1	33.7	33.4	33.8	34.2
NI-BAY26-SDB6-PRE	100%	a	7.7	7.6	7.5	7.5	7.6	7.1	6.8	5.3	6.2	6.0	19.3	18.6	19.6	19.6	19.4	33.1	33.4	33.3	33.8	33.8
NI-OF23A-SDB6-DUR	100%	a	7.5	7.7	7.5	7.5	7.6	7.4	7.0	5.7	6.3	5.4	19.8	18.8	19.5	19.5	19.3	32.6	33.0	33.0	33.8	33.5
NI-BAY26-SDB6-DUR	100%	a	7.6	7.7	7.6	7.6	7.6	7.9	6.9	4.7	5.5	5.5	19.9	18.6	19.7	19.7	19.4	32.6	32.9	32.9	33.3	33.4
Scripps Control	0	a	7.7	7.7	7.6	7.6	7.6	6.8	7.3	5.4	6.1	6.4	19.3	18.8	19.8	19.8	18.9	32.1	32.1	32.3	31.9	32.1
Scripps Cu Ref. Tox.	100 µg/l	a	7.6	7.6	7.5	7.6	7.5	6.9	7.2	5.1	6.1	5.8	19.3	18.8	19.7	19.8	19.6	32.2	32.2	32.6	32.1	32.2
	200 µg/l	a	7.6	7.6	7.6	7.6	7.6	7.0	7.2	5.0	6.5	6.4	19.1	18.7	19.7	19.8	19.5	32.4	32.3	32.6	32.1	32.1
	400 µg/l	a	7.6	7.7	7.6	7.6	7.6	7.0	7.3	5.4	7.0	6.9	19.0	18.8	19.7	19.6	19.4	32.1	32.1	32.6	32.2	32.2
	800 µg/l	a	7.6	7.6	7.6	7.2	7.7	7.1	7.6	6.0	6.2	6.9	19.0	18.8	19.6	19.8	19.4	32.3	32.0	32.6	32.2	32.2
Salt Control	n/a	a	7.6	7.4	7.3	7.7	7.2	5.8	6.6	4.7	7.6	6.4	19.3	18.8	19.8	19.6	19.6	31.8	31.9	32.2	32.2	32.7

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			D.O. (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NI-OF23A-SDB6-FF	6.2%	f	7.8	7.8	7.8	8.0	6.9	7.5	15.2	15.8	15.5	32.5	32.6	32.5
	12.4%	f	7.8	7.8	7.8	8.0	7.0	7.7	16.2	15.8	15.4	32.9	32.0	32.6
	24.8%	f	7.8	7.8	7.8	7.8	7.0	7.6	16.2	15.7	15.4	31.6	31.7	32.9
	49.5%	f	7.8	7.8	7.8	8.0	7.0	7.7	16.3	15.8	15.5	31.5	31.5	32.0
NI-OF26-SDB6-FF	6.2%	f	7.8	7.8	7.8	7.8	7.2	7.5	15.0	15.8	15.4	32.7	32.6	32.4
	12.4%	f	7.8	7.8	7.8	7.9	7.2	7.7	15.0	15.9	15.4	31.5	32.5	32.3
	24.8%	f	7.8	7.8	7.8	8.0	7.1	7.6	15.1	15.8	15.4	32.5	32.1	31.9
	49.5%	f	7.8	7.8	7.8	7.9	7.2	7.7	15.0	15.7	15.5	32.4	31.9	31.9
NI-OF26-SDB6-COMP	7.0%	f	7.8	7.8	7.8	8.2	7.1	7.5	16.3	15.9	15.7	32.4	32.6	33.0
	13.9%	f	7.9	7.8	7.8	8.2	7.1	7.6	16.2	15.9	15.7	32.7	32.5	32.5
	27.9%	f	7.9	7.7	7.8	8.2	7.1	7.3	16.2	16.0	15.6	32.2	31.9	32.3
	55.7%	f	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NI-OF23A-SDB6-PRE	100%	f	7.8	7.8	7.8	7.8	6.9	7.5	15.3	15.8	15.5	33.2	32.9	32.5
NI-BAY26-SDB6-PRE	100%	f	7.8	7.8	7.8	7.7	7.1	7.6	15.3	15.8	15.4	32.4	32.9	32.5
NI-OF23A-SDB6-DUR	100%	f	7.8	7.8	7.8	8.3	7.2	7.4	16.3	15.8	15.5	31.6	31.5	31.7
NI-BAY26-SDB6-DUR	100%	f	7.8	7.8	7.8	8.1	6.8	7.6	16.3	15.7	15.6	31.2	31.2	31.2
Scripps Control	0	f	7.9	7.7	7.7	7.5	6.8	7.6	15.1	15.8	15.3	28.2	28.0	27.8
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.9	7.7	7.8	7.7	6.9	7.7	15.0	15.7	15.4	29.0	28.5	28.4
	4.1 µg/l	f	7.9	7.8	7.8	7.8	6.9	7.6	15.1	15.8	15.3	28.3	28.1	28.0
	5.9 µg/l	f	7.9	7.8	7.8	8.1	6.8	7.8	15.0	15.8	15.3	27.6	27.9	28.4
	8.4 µg/l	f	7.9	7.7	7.7	7.9	6.9	7.8	15.0	15.9	15.4	28.0	28.0	28.2
	12 µg/l	f	7.9	7.8	7.7	8.0	7.0	7.5	15.3	16.0	15.3	28.3	28.1	28.3
	17.2 µg/l	f	7.9	7.8	7.7	8.0	7.2	7.2	15.0	15.8	15.3	28.0	28.1	28.4
Brine Control 1	n/a	f	8.0	7.8	7.8	7.4	7.2	7.3	16.3	16.0	15.8	32.6	32.3	32.1
Brine Control 2	n/a	f	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

N - water quality not taken due to 100% mortality in treatment

ND - water quality not recorded

**OUTFALLS****TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NI-OF23A-TIE2-FF	25	100.0
	50	95.0
	100	65.0
NI-OF26-TIE2-FF	25	95.0
	50	100.0
	100	100.0

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NI-OF23A-TIE2-FF	25	100.0
	50	100.0
	100	65.0
NI-OF26-TIE2-FF	25	95.0
	50	100.0
	100	95.0

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
NI-OF23A-TIE2-FF	12.50	95.0
	25	24.0
	50	0.0
	57	0.0
NI-OF26-TIE2-FF	12.50	96.0
	25	94.0
	50	94.0
	69	89.0

**BAY SAMPLES****TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NI-BAY23A-TIE2-DUR	100	95.0
NI-BAY26-TIE2-DUR	100	100.0

**MYSIDS (*A. bahia*)**

SAMPLE ID	CONC (%)	MEAN SURVIVAL (%)
NI-BAY23A-TIE2-DUR	100	100.0
NI-BAY26-TIE2-DUR	100	95.0

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (%)	MEAN NORM DEV (%)
NI-BAY23A-TIE2-DUR	100	96.0
NI-BAY26-TIE2-DUR	100	95.0



## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Scripps Control	n/a	100.0
Salt Control	n/a	100.0

### MYSIDS (*A. bahia*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN SURVIVAL (%)
Scripps Control	n/a	100.0
Salt Control	n/a	95.0

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (% or µg/l Cu)	MEAN NORM DEV (%)
Natural Seawater	n/a	96.0
Brine Control	n/a	95.0

Please refer to TIE II Report for raw data and water quality

<sup>a</sup>Controls (QA/QC) correspond to all samples from TIE2

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup> p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## SUMMARY RESULTS- QA/QC

### COPPER REFERENCE TOXICANT TEST

SPECIES	DATE	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	4/6/2005	50	100	101.8	86.1-120.5
MYSIDS	5/19/2005	214.4	326	271.5	236.1-305.75
MUSSELS	3/19/2005	10	20.0	13.04	12.8-13.3

Reference Toxicant tests are within two standard deviations of Nautilus' control chart mean

# SDB7 – 04/27/2005

## OUTFALLS

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>1</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB7-FF	12.5	a	5	100.0	100.0	0.0	100.0	n/a	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	4	80.0					
		d	5	100.0					
	100	a	4	80.0	95.0	10.0	95.0	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NI-OF26-SDB7-FF	12.5	a	5	100.0	100.0	0.0	111.1	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	100.0	0.0	111.1	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	100	a	4	80.0	80.0	16.3	88.9	0.180	No
		b	5	100.0					
		c	3	60.0					
		d	4	80.0					
NI-OF26-SDB7-COMP	12.5	a	5	100.0	100.0	0.0	111.1	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
	50	a	5	100.0	90.0	20.0	100.0	0.500	No
		b	5	100.0					
		c	3	60.0					
		d	5	100.0					
	100	a	5	100.0	100.0	0.0	111.1	0.091	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB7

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control  
n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## BAY SAMPLES

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (%)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-BAY23A-SDB7-PRE	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NI-BAY26-SDB7-PRE	100	a	4	80.0	90.0	11.5	94.7	0.269	No
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
NI-OF23A-SDB7-DUR	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					
NI-BAY26-SDB7-DUR	100	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

### MUSSELS (*M. galloprovincialis*)

SAMPLE ID	CONC (%)	REP.	# NORMAL	# ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
NI-OF23A-SDB7-PRE	100.0	a	128	16	88.9	90.0	2.8	97.7	0.135	No
		b	106	17	86.2					
		c	148	17	89.7					
		d	122	11	91.7					
		e	116	8	93.5					
NI-BAY26-SDB7-PRE	100	a	133	2	98.5	96.8	2.1	105.0	0.012	Yes <sup>c</sup>
		b	124	2	98.4					
		c	128	4	97.0					
		d	112	4	96.6					
		e	126	9	93.3					
NI-OF23A-SDB7-DUR	100	a	117	17	87.3	91.8	3.2	99.7	0.443	No
		b	130	13	90.9					
		c	136	12	91.9					
		d	150	11	93.2					
		e	141	6	95.9					
NI-BAY26-SDB7-DUR	100	a	130	8	94.2	95.7	2.7	103.9	0.0393	Yes <sup>c</sup>
		b	139	3	97.9					
		c	142	1	99.3					
		d	98	7	93.3					
		e	104	7	93.7					

## QA/QC SAMPLES<sup>a</sup>

### TOPSMELT (*A. affinis*)

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	5	100.0	95.0	10.0	n/a	n/a	n/a
		b	5	100.0					
		c	5	100.0					
		d	4	80.0					
Salt Control	n/a	a	5	100.0	100.0	0.0	105.3	0.196	No
		b	5	100.0					
		c	5	100.0					
		d	5	100.0					

**TOPSMELT (*A. affinis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP	SURVIVAL (#)	SURVIVAL (%)	MEAN SURVIVAL (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Copper Ref. Tox.	50	a	3	60.0	85.0	19.1	89.5	0.201	No
		b	4	80.0					
		c	5	100.0					
		d	5	100.0					
	100	a	5	100.0	75.0	19.1	78.9	0.065	No
		b	3	60.0					
		c	4	80.0					
		d	3	60.0					
	200	a	2	40.0	70.0	34.6	73.7	0.124	No
		b	5	100.0					
		c	5	100.0					
		d	2	40.0					
	400	a	0	0.0	25.0	25.2	26.3	0.004	Yes
		b	3	60.0					
		c	1	20.0					
		d	1	20.0					

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	CONC (% or µg/l Cu)	REP.	# NORMAL	ABNORMAL	NORM DEVEL (%)	MEAN NORM DEV (%)	STD DEV	% of CONTROL <sup>2</sup>	P-VALUE <sup>b</sup>	SIG DIFF FROM CONTROL?
Scripps Control	n/a	a	153	12	92.7	92.1	2.4	100.0	n/a	n/a
		b	154	20	88.5					
		c	137	9	93.8					
		d	99	7	93.4					
Copper Ref. Tox.	2.9	a	120	18	87.0	82.7	8.5	89.8	0.034	Yes
		b	131	17	88.5					
		c	95	37	72.0					
		d	130	13	90.9					
		e	101	33	75.4					
	4.1	a	95	81	54.0	54.7	10.4	59.3	0.000	Yes
		b	87	50	63.5					
		c	-	-	-					
		d	-	-	-					
		e	-	-	-					
	5.9	a	0	131	0.0	2.3	3.2	2.5	0.000	Yes
		b	4	165	2.4					
		c	9	106	7.8					
		d	2	149	1.3					
		e	0	147	0.0					
	8.4	a	0	131	0.0	0.0	0.0	0.0	0.000	Yes
		b	0	135	0.0					
		c	0	151	0.0					
		d	0	154	0.0					
		e	0	137	0.0					

**SUMMARY RESULTS- QA/QC**
**COPPER REFERENCE TOXICANT TEST**

SPECIES	NOEC (µg/l)	LOEC (µg/l)	EC50 (µg/l)	95% C.L. (µg/l)
TOPSMELT	200	400.0	268.18	160.3-506.5
MUSSELS	2.9	4.1	4.30	3.78-4.69

Dash indicates no data (replicate was spilled or organisms not added)

<sup>a</sup>Controls (QA/QC) correspond to all samples from SDB7

<sup>b</sup>Student's t-test with a one tailed distribution and two sample unequal variance

<sup>c</sup>p-value is significant because treatment had a significantly greater proportion normal compared to the control

n/a - t-test not used since control and treatment have same percentage survival

<sup>1</sup>Controls were the Bay water samples taken prior to storm (PRE) with comparable sample ID

<sup>2</sup>Controls were Scripps filtered seawater

## WATER QUALITY

### TOPSMELT (*A. affinis*)

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep	pH (SU)					Dissolved Oxygen (mg/l)					Temperature (°C)					Salinity (‰)				
			0	24	48	72	96	0	24	48	72	96	0	24	48	72	96	0	24	48	72	96
NI-OF23A-SDB7-FF	12.5%	a	7.7	7.7	7.6	7.7	7.7	7.5	6.8	6.4	7.3	6.8	18.8	18.6	19.3	18.6	19.1	33.6	33.8	33.9	34.1	34.2
	50%	a	7.7	7.7	7.6	7.7	7.6	7.7	6.4	6.5	7.4	6.4	18.6	18.6	19.4	18.8	19.2	34.0	34.2	34.1	34.3	34.3
	100%	a	7.8	7.7	7.6	7.6	7.6	8.1	6.3	6.5	7.2	7.0	18.2	18.6	19.4	18.8	19.1	34.4	34.4	34.5	34.6	34.8
NI-OF26-SDB7-FF	12.5%	a	7.7	7.7	7.6	7.7	7.7	7.5	6.3	6.1	7.2	6.7	18.8	18.3	19.4	18.6	19.2	33.1	33.3	33.4	33.6	33.6
	50%	a	7.7	7.6	7.5	7.6	7.6	7.5	5.5	5.6	6.1	6.1	18.6	18.4	19.4	18.6	19.3	32.7	32.8	32.8	33.1	33.1
	100%	a	7.8	7.5	7.5	7.5	7.6	7.8	4.8	5.0	5.7	5.6	18.1	18.6	19.4	18.7	19.3	31.6	31.8	31.9	32.0	32.1
NI-OF26-SDB7-COMP	12.5%	a	7.8	7.7	7.6	7.7	7.7	7.6	6.4	6.3	7.0	6.6	19.3	18.2	19.3	18.3	19.1	33.4	33.3	33.4	33.3	33.6
	50%	a	7.9	7.7	7.6	7.7	7.7	7.8	6.3	6.0	7.0	6.8	19.1	18.1	19.3	18.2	18.9	32.8	32.8	32.9	33.1	33.3
	100%	a	8.0	7.8	7.6	7.7	7.6	8.1	5.9	6.0	6.6	6.5	18.6	18.0	19.1	18.1	18.8	32.0	32.2	32.5	32.5	32.7
NI-OF23A-SDB7-PRE	100%	a	7.7	7.7	7.7	7.7	7.8	7.5	6.7	6.3	7.4	6.5	19.0	18.6	19.4	18.7	19.3	33.7	33.9	33.9	34.1	33.9
NI-BAY26-SDB7-PRE	100%	a	7.7	7.7	7.7	7.7	7.8	7.3	6.6	6.5	7.2	6.5	19.3	18.3	19.3	18.4	19.3	33.2	33.8	33.9	34.1	34.0
NI-OF23A-SDB7-DUR	100%	a	7.7	7.7	7.7	7.7	7.6	7.3	6.6	6.4	7.3	5.8	18.4	18.3	19.3	18.6	19.0	33.4	33.4	33.4	33.2	33.1
NI-BAY26-SDB7-DUR	100%	a	7.7	7.5	7.7	7.8	7.7	7.5	6.9	6.6	7.3	6.1	18.4	18.3	19.3	18.6	19.1	33.5	33.5	33.5	33.4	33.4
Scripps Control	0	a	7.8	7.8	7.6	7.8	7.7	7.7	6.9	6.6	7.5	7.2	18.6	18.3	19.3	18.3	19.1	31.6	31.5	31.7	31.7	31.9
Scripps Cu Ref. Tox.	50 µg/l	a	7.8	7.8	7.6	7.8	7.8	7.8	7.0	6.7	7.7	7.4	18.8	18.3	19.3	18.3	19.0	31.5	31.5	31.6	31.6	31.6
	100 µg/l	a	7.8	7.8	7.6	7.8	7.8	7.7	7.0	6.6	7.7	7.6	18.8	18.3	19.3	18.4	19.1	31.5	31.5	31.6	31.5	31.6
	200 µg/l	a	7.8	7.8	7.6	7.8	7.7	7.7	7.1	6.6	7.9	7.4	18.8	18.2	19.1	18.4	19.0	31.5	31.6	31.8	31.9	31.6
	400 µg/l	a	7.9	7.8	7.7	7.8	7.7	7.7	7.2	7.1	7.9	7.3	18.8	18.3	19.1	18.6	19.0	31.5	31.6	31.8	31.8	31.6
Salt Control	n/a	a	7.9	7.7	7.5	7.6	7.5	7.4	6.1	6.4	7.0	6.6	19.4	18.3	19.2	18.6	19.0	31.4	31.5	31.6	31.4	31.5

**MUSSELS (*M. galloprovincialis*)**

SAMPLE ID	Effluent Concentration (% or µg/l Cu)	Rep.	pH (SU)			D.O. (mg/l)			Temperature (°C)			Salinity (‰)		
			0	24	48	0	24	48	0	24	48	0	24	48
NI-OF23A-SDB7-PRE	100%	f	7.7	7.8	7.7	7.8	8.6	8.4	16.0	15.3	15.1	33.9	33.9	33.8
NI-BAY26-SDB7-PRE	100%	f	7.7	7.8	7.7	8.0	8.4	8.3	16.0	15.2	15.6	33.6	33.3	33.0
NI-OF23A-SDB7-DUR	100%	f	7.7	7.8	7.8	7.9	8.7	8.5	16.0	15.2	14.9	33.5	33.5	33.5
NI-BAY26-SDB7-DUR	100%	f	7.7	7.8	7.8	8.0	8.3	8.4	16.0	15.3	15.0	33.7	33.4	33.3
Scripps Control	0	f	8.1	8.0	7.7	7.5	8.2	8.2	16.0	15.5	15.2	29.4	29.3	29.0
Scripps Cu Ref. Tox.	2.9 µg/l	f	7.9	7.9	7.9	7.2	8.3	8.5	15.8	15.2	15.0	29.5	29.6	29.7
	4.1 µg/l	f	7.8	7.8	7.7	7.9	8.4	8.4	15.8	15.2	15.3	29.5	29.6	29.7
	5.9 µg/l	f	7.8	7.8	7.7	7.8	8.3	8.4	15.9	15.2	15.4	29.5	29.6	29.6
	8.4 µg/l	f	7.8	7.8	7.7	7.9	8.6	8.2	15.9	15.2	15.2	29.6	29.5	29.6
	12 µg/l	f	7.8	7.8	7.7	7.9	8.5	8.3	15.8	15.0	15.1	29.6	29.5	29.6
	17.2 µg/l	f	7.8	7.8	7.8	7.7	8.2	8.5	15.8	15.0	15.1	29.6	29.6	29.7

## **Appendix D**

### **Chemistry**

### Table of Data Qualifiers

Flag	Application
<b>B</b>	Analyte concentration found in the sample at a concentration <5x the level found in the procedural blank
<b>D</b>	Dilution Run. Initial run outside linear range of instrument
<b>E</b>	Estimate, result is greater than the highest concentration level in the calibration
<b>H</b>	Surrogate diluted out. Used when surrogate recovery is affected by excessive dilution of the sample extract
<b>J</b>	Analyte detected below the sample-specific Reporting Limit (RL)
<b>ME</b>	Significant matrix Interference – Estimated value
<b>MI</b>	Significant Matrix Interference – value could not be determined or estimated
<b>n</b>	Quality Control (QC) value is outside the accuracy or precision Data Quality Objective (DQO), but meets the contingency criteria
<b>N</b>	Quality Control (QC) value is outside the accuracy or precision Data Quality Objective (DQO)
<b>NA</b>	Not applicable
<b>T</b>	Holding Time (HT) exceeded
<b>U</b>	Analyte not detected at 3:1 signal:noise ratio. The sample-specific method detection limit (MDL) reported

### Table of Acronyms

Acronym	Definition
<b>CVAF</b>	Cold Vapor Atomic Fluorescence
<b>FIAS</b>	Field Injection Atomic Spectroscopy
<b>GFAA</b>	Graphite Furnace-Atomic Absorption
<b>ICP-MS</b>	Inductively Coupled Plasma – Mass Spectrometry
<b>ICP-OES</b>	Inductively Coupled Plasma – Optical Emission Spectrometry
<b>LCS</b>	Laboratory Control Sample
<b>MB</b>	Matrix Blank
<b>MSL</b>	Battelle/Marine Sciences Laboratory
<b>NS</b>	Not Spiked
<b>NS&amp;T</b>	National Standards and Trends
<b>OPR</b>	On-going Precision and Recovery
<b>PB</b>	Procedural Blank
<b>PD</b>	Percent Difference
<b>RIS</b>	Recovery Internal Standard
<b>RPD</b>	Relative Percent Difference
<b>SRM</b>	Standard Reference Material



## **Appendix D1**

### **NAV**

**SDB1- 11/7/2002**  
**SDB2- 2/24/2003**  
**SDB4- 10/17/2004**  
**SDB45- 10/26/2004**

# SDB1-11/7/2002

## METALS

MSL			Ag		Cu		Pb		Hg		Zn
CHEMISTRY CODE	CLIENT CODE	PARAMETER	(µg/L)		(µg/L)		(µg/L)		(µg/L)		(µg/L)
1919-1	NAV-OF9-SDB1-COMP (T)	Total metals	0.215		123		23.5		0.0441		969
1919-13	NAV-OF9-SDB1-COMP (D)	Dissolved metals	0.0113	J	59.6		0.437		0.00676		776
1919-2	NAV-OF11-SDB1-DUR (T)	Total metals	0.100	J	136		6.50		0.266		407
1919-14	NAV-OF11-SDB1-DUR (D)	Dissolved metals	0.0250	J	58.8		0.536		0.0116		499
1919-3 R1	NAV-OF14-SDB1-DUR (T)	Total metals	0.0688	J	75.7		8.93		0.0732		573
1919-3 R2	NAV-OF14-SDB1-DUR (T)	Total metals	--		--		--		0.0732		--
1919-3 MEAN	NAV-OF14-SDB1-DUR (T)	Total metals	--		--		--		0.0732		--
1919-15	NAV-OF14-SDB1-DUR (D)	Dissolved metals	0.0125	J	51.9		0.602		0.0123		366
1919-4 R1	NAV-BAY9-SDB1-PRE (T)	Total metals	0.0225	J	4.53		0.235		0.00358		9.06
1919-4 R2	NAV-BAY9-SDB1-PRE (T)	Total metals	0.0275	J	4.50		0.223		--		9.42
1919-4 MEAN	NAV-BAY9-SDB1-PRE (T)	Total metals	0.0250	J	4.52		0.229		--		9.24
1919-16	NAV-BAY9-SDB1-DUR (D)	Dissolved metals	0.0225	J	3.42		0.0749	J	0.00457		8.55
1919-5	NAV-BAY9-SDB1-DUR (T)	Total metals	0.0163	J	4.91		0.200		0.00292		10.4
1919-17	NAV-BAY9-SDB1-DUR (D)	Dissolved metals	0.0175	J	3.52		0.0897	J	0.00457		10.7
1919-9	NAV-BAY9-SDB1-AFT (T)	Total metals	0.0188	J	4.79		0.151		0.00244		10.4
1919-21	NAV-BAY9-SDB1-AFT (D)	Dissolved metals	0.0175	J	4.10		0.0771	J	0.00322		10.8
1919-6	NAV-BAY11-SDB1-DUR (T)	Total metals	0.0163	J	4.72		0.219		0.00329		10.1
1919-18	NAV-BAY11-SDB1-DUR (D)	Dissolved metals	0.0301	J	3.55		0.0716	J	0.00459		10.9
1919-10	NAV-BAY11-SDB1-AFT (T)	Total metals	0.0238	J	4.59		0.140		0.00197		9.91
1919-22	NAV-BAY11-SDB1-AFT (D)	Dissolved metals	0.0163	J	3.52		0.0794	J	0.00284		10.3
1919-7	NAV-BAY14-SDB1-DUR (T)	Total metals	0.0200	J	5.21		0.217		0.00279		11.3
1919-19	NAV-BAY14-SDB1-DUR (D)	Dissolved metals	0.0213	J	3.66		0.0733	J	0.00403		10.1
1919-11 R1	NAV-BAY14-SDB1-AFT (T)	Total metals	0.0225	J	4.86		0.169		0.00214		10.3
1919-11 R2	NAV-BAY14-SDB1-AFT (T)	Total metals	--		--		--		0.00205		--
1919-11 MEAN	NAV-BAY14-SDB1-AFT (T)	Total metals	--		--		--		0.00210		--
1919-23	NAV-BAY14-SDB1-AFT (D)	Dissolved metals	0.0188	J	3.97		0.0847	J	0.00387		10.2
1919-8 R1	NAV-BAY14A-SDB1-DUR (T)	Total metals	0.0225	J	4.69		0.208		0.00228		10.2
1919-8 R2	NAV-BAY14A-SDB1-DUR (T)	Total metals	0.0213	J	4.69		0.201		--		8.90
1919-8 MEAN	NAV-BAY14A-SDB1-DUR (T)	Total metals	0.0219	J	4.69		0.205		--		9.55
1919-20	NAV-BAY14A-SDB1-DUR (D)	Dissolved metals	0.0188	J	3.59		0.0889	J	0.00331		9.28
1919-12	NAV-BAY14A-SDB1-AFT (T)	Total metals	0.0238	J	5.08		0.162		0.00174		10.4
1919-24	NAV-BAY14A-SDB1-AFT (D)	Dissolved metals	0.0125	J	3.93		0.0722	J	0.00328		9.76

## METALS QA/QC

**PROJECT:** Contaminant Analyses of Storm water and San Diego Bay Seawater  
**PARAMETER:** Metals  
**LABORATORY:** Battelle Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Seawater

**SAMPLE CUSTODY AND PROCESSING:** Twenty-four seawater samples (12 total and 12 dissolved) for metals analysis were received on 11/13/02. All samples were received in good condition (i.e., all sample containers were intact). Dissolved metals were received in polyethylene containers, which are not suitable for Hg analysis. The client was informed of the potentially compromised dissolved Hg data.

Samples were assigned a Battelle Central File (CF) identification number (1919) and were entered into Battelle's log-in system.

The following lists information on sample receipt and processing activities:

Lab Sample IDs:	1907-1 through -24
Description:	Seawater/seawater samples
Collection dates	11/07/02, 11/09/02, 11/10/02
Laboratory arrival date	11/13/02
Cooler temperature on arrival	12.5°C <sup>(1)</sup>
CVAA analysis (Hg)	12/03/02, 12/04/02
Fe-Pd preconcentration	12/18/02
ICP-MS analysis (Cu, Pb, Zn)	12/30/02, 01/17/03 reruns
GFAA analysis (Ag)	12/31/02, 01/02/03

<sup>(1)</sup> Cooler temperature outside the acceptable range of 4±2°C, however samples were not compromised as they were already acidified, see note on Log-in Checklist.

### DATA QUALITY OBJECTIVES:

Analyte	Analytical Method	Range of Recovery	Relative Precision	SRM Accuracy	Project Reporting Limits (µg/L) <sup>a</sup>	Achieved Detection Limits (µg/L) <sup>b</sup>
Ag	GFAA	75-125%	±20%	±20%	0.1	0.01
Cu	ICP-MS	75-125%	±20%	±20%	0.1	0.028
Hg	CVAF	75-125%	±20%	±20%	0.001	0.00016
Pb	ICP-MS	75-125%	±20%	±20%	0.1	0.0059
Zn	ICP-MS	75-125%	±20%	±20%	0.1	0.11

(a) Extracted from the statement of work

(b) Achieved MDLs from Fe/Pd seawater MDL, Ag from GFAA report, Hg from 2002 MDL Study

**METHODS:** Five metals were analyzed: silver (Ag), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn).

Samples were preconcentrated using iron (Fe) and palladium (Pd) according to Battelle SOP MSL-I-025, *Methods of Sample Preconcentration*, which is derived from EPA Method 1640. Samples were then submitted for analysis for Cu, Pb and Zn by inductively coupled plasma-mass spectrometry (ICP-MS) following Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP-MS*, derived from EPA Method 1638. Six samples identified as OF9-SDB1, OF11-SDB1, OF14-SDB1, both dissolved and total fractions, were analyzed at a ten fold dilution directly by ICP-MS for Cu and Zn, as the preconcentrated samples were outside the calibration range of the instrument.

These results are reported.

**METHODS:**

Ag was analyzed in the Fe-Pd preconcentrate by graphite furnace atomic absorption (GFAA) following Battelle SOP MSL-I-029, *Determination of Metals in Aqueous and Digestate Samples by GFAA*, derived from EPA Method 200.9.

Hg was analyzed directly (with no preconcentration step) using cold-vapor atomic fluorescence (CVAf) spectroscopy according to Battelle SOP MSL-I-013, *Total Mercury in Aqueous Samples by CVAf*, which directly follows EPA Method 1631.

All results were reported in units of µg/L. Data are not blank corrected.

**HOLDING TIMES:**

The recommended holding times for metals analyses are 28 days from sample collection for Hg analysis and 6 months for analysis of all other metals. All samples were analyzed within their respective holding times.

**DETECTION LIMITS:**

Laboratory-achieved detection limits reported are from the Fe/Pd seawater MDL for Cu, Pb and Zn; GFAA daily analysis for Ag; and the 2002 MDL Study for Hg. MDLs were less than target reporting limits for all metals. The data are flagged by the following criteria:

- U Analyte not detected above the laboratory achieved MDL, which is reported
- J Analyte detected above the MDL, but below the reporting limit
- # Data quality precision or accuracy outside the criteria of ±20% or recoveries outside criteria of ±25%

**METHOD BLANKS:**

Three method blanks were analyzed for all metals. Blank concentrations for all metals were below or less than three times the project reporting limits. Data were not blank corrected.

**LABORATORY  
CONTROL SAMPLE  
ACCURACY:**

Four blank spike (LCS) samples were analyzed with the set of water samples. Recoveries were reported for samples spiked at approximately 0.005 µg/L for Hg and 10 µg/L for Ag, Cu, Pb, and Zn in the preconcentrated samples. LCS samples analyzed with the reanalysis of Cu and Zn by direct ICP-MS were spiked at 3.2 µg/L for Cu and 29.4 µg/L for Zn. LCS recoveries ranged from 82% to 118% and were within the QC acceptance criteria of 75% to 125% for all metals.

**MATRIX SPIKE  
ACCURACY:**

Two samples were selected as a matrix spike sample for each analyte. Recoveries were reported for samples spiked at approximately 0.02 µg/L Hg and 10 µg/L for Ag, Cu, Pb, and Zn. Matrix spike recoveries ranged from 77% to 104% and were within QC acceptance criteria of 75%-125% recovery for all metals, except one replicate for Zn (64%). Acceptable accuracy for Zn analysis is demonstrated in the three alternate MS samples.

**REPLICATE  
PRECISION:**

Replicate precision was assessed by duplicate sample analysis and expressed as the relative percent deviation (RPD) of replicate results. RPDs ranged from 0% to 20% and were within the QC acceptance criteria of 20% for all metals.

**STANDARD  
REFERENCE  
MATERIAL  
ACCURACY:**

Three SRMs were analyzed with this set of samples. CASS-4, SLRS-3 and 1640 were analyzed for ICP-MS metals and SRM 1641d was analyzed for Hg. SRM accuracy was expressed as the percent difference (PD) between the measured and certified or laboratory consensus value within the certified range.

The SRM CASS-4 is a nearshore seawater reference material, which is not certified for Ag or Hg. The certified values for CASS-4 are generally less than five times the laboratory achieved detection limit, therefore not a useful indicator of data set accuracy. However, CASS-4 was analyzed with this set because a alternate seawater SRM is not available. Laboratory consensus values were determined as CASS-4 is certified at concentrations near the detection limit. Laboratory consensus values were determined from multiple analyses of CASS-4 conducted over the past year. The target QC acceptance criterion is 20% PD, which was achieved from either end of the certified or consensus value range for all metals, except Pb (153%, 33%) and one replicate of Zn (182%). Acceptable analysis accuracy for Pb and Zn is demonstrated in the four alternate SRM recoveries.

The SRM SLRS-3 is a riparian reference material, which is not certified for Ag or Hg. The percent differences ranged from 1% to 18% and were within the QC acceptance criteria of 20% for all certified metals.

SRM 1640 and 1641 are freshwater reference materials used as instrument check samples. Data accuracy for mercury is evaluated in SRM 1641. SRM percent differences ranged from 0% to 14% and were within QC acceptance criteria of 20% (PD) for all metals.

## METALS QA/QC (CONT.)

MSL			Ag		Cu		Pb		Hg		Zn	
CHEMISTRY CODE	CLIENT CODE	PARAMETER	(µg/L)		(µg/L)		(µg/L)		(µg/L)		(µg/L)	
DETECTION LIMITS												
Project Reporting Limit			0.1		0.1		0.1		0.001		0.1	
Laboratory Achieved MDL <sup>(1)</sup>			0.010		0.028		0.0059		0.00016		0.11	
METHOD BLANKS												
blkr1			0.010	U	0.127		0.0429	J	0.000594	J	0.174	
blkr2			0.010	U	0.131		0.0248	J	0.000299	J	0.137	
blank trm r1 (reruns)					0.028	U					0.11	U
Mean			0.010	U	0.0953	J	0.0339	J	0.000446	J	0.140	
LABORATORY CONTROL SAMPLE (LCS) ACCURACY												
OPR120202run1 (Hg)	LCS R1		9.02		9.31		8.46		0.00523		10.1	
OPR120202run2 (Hg)	LCS R2		9.24		9.18		8.23		0.00532		9.87	
OPR120203run1 (Hg)	LCS R3 (reruns)		--		3.56		--		0.00593		32.3	
OPR120203run2 (Hg)	LCS R4 (reruns)		--		3.51		--		0.00590		32.4	
OPR120202run1 (Hg)	LCS R1	% Rec (10 or Hg 0.005 ppb)	90%		92%		84%		98%		99%	
OPR120202run2 (Hg)	LCS R2	% Rec (10 or Hg 0.005 ppb)	92%		90%		82%		100%		97%	
OPR120203run1 (Hg)	LCS R3 (reruns)	% Rec (3.2 Cu, 29.4 Zn or Hg 0.005 ppb)			110%				118%		110%	
OPR120203run2 (Hg)	LCS R4 (reruns)	% Rec (3.2 Cu, 29.4 Zn or Hg 0.005 ppb)			106%				112%		110%	
MATRIX SPIKE ACCURACY												
1919-4	NAV-BAY9-SDB1-PRE	Total metals	0.0225	J	4.53		0.235		0.00358		9.06	
1919-4 MS			NS		NS		NS		0.0210		NS	
1919-4 MSD			NS		NS		NS		0.0203		NS	
1919-4 MS		% Rec (0.017ppb)							102%			
1919-4 MSD		% Rec (0.017ppb)							98%			
1919-5	NAV-BAY9-SDB1-DUR	Total metals	0.0163	J	4.91		0.200		NS		10.4	
1919-5 MS			9.81		13.8		8.22		NS		18.8	
1919-5 MSD			10.35		14.4		8.46		NS		19	
1919-5 MS		% Rec (10ppb)	98%		89%		80%				84%	
1919-5 MSD		% Rec (10ppb)	103%		95%		83%				86%	
1919-7	NAV-BAY14-SDB1-DUR	Total metals	0.0200	J	5.21		0.217		0.00279		11.3	
1919-7 MS			NS		NS		NS		0.0198		NS	
1919-7 MSD			NS		NS		NS		0.0209		NS	
1919-7 MS		% Rec (0.018ppb)							97%			
1919-7 MSD		% Rec (0.018ppb)							100%			
1919-8	NAV-BAY14A-SDB1-DUR	Total metals	0.0225	J	4.69		0.208		0.00228		10.2	
1919-8 MS			NS		NS		NS		0.0217		NS	
1919-8 MSD			NS		NS		NS		0.0203		NS	
1919-8 MS		% Rec (0.018ppb)							105%			
1919-8 MSD		% Rec (0.018ppb)							102%			
1919-11	NAV-BAY14-SDB1-AFT	Total metals	0.0225	J	4.86		0.169		NS		10.3	
1919-11 MS			9.46		13		7.85		NS		18.9	
1919-11 MSD			10.4		13.9		8.28		NS		16.7	
1919-11 MS		% Rec (10ppb)	94%		81%		77%				86%	
1919-11 MSD		% Rec (10ppb)	104%		90%		81%				64%	#
REPLICATE PRECISION												
1919-3 R1	NAV-OF14-SDB1-DUR (T)	Total metals	0.0688	J	73.6		8.93		0.0732		588	
1919-3 R2	NAV-OF14-SDB1-DUR (T)	Total metals	--		--		--		0.0732		--	
1919-3 MEAN	NAV-OF14-SDB1-DUR (T)	Total metals	--		--		--		0.0732		--	
		RPD							0%			
1919-4r1	NAV-BAY9-SDB1-PRE	Total metals	0.0225	J	4.53		0.235				9.06	
1919-4r2	NAV-BAY9-SDB1-PRE	Total metals	0.0275	J	4.5		0.223				9.42	
1919-4 MEAN	NAV-BAY-SDB1-PRE	Total metals	0.0250	J	4.515		0.229				9.24	
		RPD	20%		1%		5%				4%	
1919-8r1	NAV-BAY14A-SDB1-DUR	Total metals	0.0225	J	4.69		0.208				10.2	
1919-8r2	NAV-BAY14A-SDB1-DUR	Total metals	0.0213	J	4.69		0.201				8.90	
1919-8 MEAN	NAV-BAY14A-SDB1-DUR	Total metals	0.0219	J	4.69		0.205				9.55	
		RPD	6%		0%		3%				14%	
1919-11 R1	NAV-BAY14-SDB1-AFT	Total metals	0.0225	J	4.86		0.169		0.00214		10.3	
1919-11 R2	NAV-BAY14-SDB1-AFT	Total metals	--		--		--		0.00205		--	
1919-11 MEAN	NAV-BAY14-SDB1-AFT	Total metals	--		--		--		0.00210		--	

## METALS QA/QC (CONT.)

MSL			Ag		Cu		Pb		Hg		Zn	
CHEMISTRY CODE	CLIENT CODE	PARAMETER	(µg/L)		(µg/L)		(µg/L)		(µg/L)		(µg/L)	
<b>STANDARD REFERENCE MATERIAL ACCURACY</b>												
cass4r1			--		0.692		0.0541	J	--		1.16	
cass4r2			--		0.676		0.0285	J	--		0.526	
		SRM Certified or <i>Laboratory Consensus</i> Value	NC		0.592		0.0214	J	NC		0.412	
		Range			±0.055		±0.01				±0.055	
PD CASS-4 r1					17%		153%	#			182%	#
PD CASS-4 r2					14%		33%	#			13%	
slrs3r1			--		1.36		0.0747	J	--		1.20	
slrs3r2			--		1.38		0.0691	J	--		1.23	
		SRM Certified Value	NC		1.35		0.068		NC		1.04	
		Range			±0.07		±0.007				±0.09	
PD SLRS3 r1					1%		10%				15%	
PD SLRS3 r2					2%		2%				18%	
1640Direct R1 or 1641 R1 for Hg			--		86.5		26.8		1624		60.7	
1640Direct R2 or 1641 R2 for Hg			--		76.6		24.0		1603		56.5	
1640 TRM			--		86.0		--		--		53.0	
certified value			--		85.2		27.9		1590		53.2	
Range			--						±40			
PD 1640 Direct R1					2%		4%		2%		14%	
PD 1640 Direct R2					10%		14%		1%		6%	
PD 1640 TRM					1%						0%	

(1)= Fe/Pd MDL Study, Ag from Graphite Furnace report, and Hg from 2002 MDL Study; NC = Analyte not certified; NS= Analyte not spike; # = Data quality outside the accuracy criteria of ±20% or precision/MS recovery criteria of ±25%; U= Analyte not detected above the laboratory achieved MDL, which is reported; J = Analyte detected above the MDL, but below the reporting limit.

# PAHs

CLIENT SAMPLE ID	NAV-OF9-SDB1-COMP	NAV-OF11-SDB1-COMP	NAV-OF14-SDB1-COMP	NAV-BAY9-SDB1-PRE	NAV-BAY9-SDB1-DUR	NAV-BAY9-SDB1-AFT	NAV-BAY11-SDB1-DUR	NAV-BAY11-SDB1-AFT	NAV-BAY14-SDB1-DUR	NAV-BAY14-SDB1-AFT	NAV-BAY14A-SDB1-DUR	NAV-BAY14A-SDB1-AFT
Battelle Sample ID	V9897	V9898	V9899	V9900	V9901	V9905	V9902	V9906	V9903	V9907	V9904	V9908
Battelle Batch ID	02-634	02-634	02-634	02-634	02-634	02-634	02-634	02-634	02-634	02-634	02-634	02-634
Associated Blank	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB	AB383PB
QC Type	N	N	N	N	N	N	N	N	N	N	N	N
Data File	A0409.D	A0412.D	A0413.D	A0414.D	A0416.D	A0420.D	A0417.D	A0421.D	A0418.D	A0422.D	A0419.D	A0423.D
Extraction Date	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02	11/14/02
Acquired Date	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02	11/26/02
Matrix	Water	Water	Water	Water	Water	Water	Water	Water	Water	Water	Water	Water
Sample Size	1 L	2.64 L	2.63 L	2.65 L	2.64 L	2.62 L	2.63 L	2.62 L	2.64 L	2.65 L	2.64 L	2.64 L
Dilution Factor	1.667	1.667	1.667	1.667	2	1.667	1.667	1.667	1.667	1.667	1.667	1.667
PIV	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL	1 mL
Min Reporting Limit	16.7	6.31	6.34	6.29	7.58	6.36	6.34	6.36	6.31	6.29	6.31	6.31
Amount Units	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
Naphthalene	11.70 J	5.47 J	5.84 J	2.07 J	17.10	1.58 J	1.58 J	1.98 J	1.09 J	2.39 J	1.90 J	1.43 J
C1-Naphthalenes	7.61 J	2.76 J	4.11 J	3.34 J	27.00	0.51 U	1.69 J	0.51 U	1.64 J	2.97 J	0.50 U	0.50 U
C2-Naphthalenes	1.33 U	0.50 U	0.50 U	0.50 U	43.50	0.51 U	0.50 U	0.51 U	0.50 U	0.50 U	0.50 U	0.50 U
C3-Naphthalenes	1.33 U	0.50 U	0.50 U	0.50 U	19.00	0.51 U	0.50 U	0.51 U	0.50 U	0.50 U	0.50 U	0.50 U
C4-Naphthalenes	1.33 U	0.50 U	0.50 U	0.50 U	5.66 J	0.51 U	0.50 U	0.51 U	0.50 U	0.50 U	0.50 U	0.50 U
Biphenyl	0.83 U	0.32 U	1.54 J	0.31 U	4.13 J	0.32 U	0.32 U	0.32 U	0.32 U	0.31 U	0.32 U	0.32 U
Acenaphthylene	3.70 J	1.27 J	0.80 J	0.76 J	2.10 J	0.32 U	0.31 U	0.32 U	0.31 U	0.31 U	0.31 U	0.31 U
Acenaphthene	1.07 U	4.41 J	3.76 J	5.44 J	5.55 J	4.92 J	7.39	5.46 J	5.03 J	5.09 J	3.76 J	4.57 J
Fluorene	5.51 J	2.41 J	2.54 J	2.18 J	4.07 J	1.78 J	2.68 J	2.58 J	2.02 J	4.00 J	1.24 J	1.41 J
C1-Fluorenes	0.98 U	0.37 U	0.37 U	0.37 U	3.60 J	0.37 U	0.37 U	0.37 U	0.37 U	4.21 J	0.37 U	0.37 U
C2-Fluorenes	0.98 U	0.37 U	0.37 U	0.37 U	0.45 U	0.37 U	0.37 U	0.37 U	0.37 U	16.70	0.37 U	0.37 U
C3-Fluorenes	0.98 U	0.37 U	0.37 U	0.37 U	0.45 U	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U
Phenanthrene	56.20	10.30	16.20	2.39 J	7.50 J	1.36 J	4.48 J	3.91 J	3.55 J	19.80	1.40 J	1.86 J
Anthracene	3.08 J	1.98 J	2.37 J	0.26 U	3.07 J	0.76 J	1.11 J	2.04 J	1.16 J	2.92 J	1.19 J	0.64 J
C1-Phenanthrenes/Anthracenes	36.20	11.80	19.00	0.26 U	5.76 J	0.27 U	3.49 J	0.27 U	6.03 J	20.50	0.26 U	0.26 U
C2-Phenanthrenes/Anthracenes	105.00	35.80	56.10	0.26 U	0.32 U	0.27 U	0.26 U	0.27 U	26.50	48.80	0.26 U	0.26 U
C3-Phenanthrenes/Anthracenes	89.90	16.30	40.70	0.26 U	0.32 U	0.27 U	0.26 U	0.27 U	23.20	32.20	0.26 U	0.26 U
Dibenzothiophene	24.80	14.00	19.00	0.35 U	1.18 J	0.35 U	0.82 J	0.35 U	0.69 J	2.18 J	0.35 U	0.35 U
C1-Dibenzothiophenes	64.20	33.40	42.70	0.35 U	5.55 J	0.35 U	0.35 U	0.35 U	5.86 J	14.20	0.35 U	0.35 U
C2-Dibenzothiophenes	104.00	40.70	57.80	0.35 U	0.42 U	0.35 U	0.35 U	0.35 U	8.19	28.90	0.35 U	0.35 U
C3-Dibenzothiophenes	113.00	29.30	55.80	0.35 U	0.42 U	0.35 U	0.35 U	0.35 U	13.20	32.70	0.35 U	0.35 U
Fluoranthene	99.30	13.50	26.00	9.17	18.00	11.00	17.50	15.20	12.60	53.50	10.10	9.38
Pyrene	129.00	17.00	33.90	4.66 J	9.91	5.85 J	9.61	8.25	10.90	152.00	5.44 J	4.33 J
C1-Fluoranthenes/Pyrenes	52.30	10.70	22.80	0.36 U	8.47	0.37 U	4.93 J	0.37 U	13.20	8.88	0.36 U	0.36 U
C2-Fluoranthenes/Pyrenes	73.30	14.60	26.20	0.36 U	0.43 U	0.37 U	0.36 U	0.37 U	19.70	9.50	0.36 U	0.36 U
C3-Fluoranthenes/Pyrenes	84.30	12.10	27.60	0.36 U	0.43 U	0.37 U	0.36 U	0.37 U	14.40	6.95	0.36 U	0.36 U
Benzo(a)anthracene	22.90	2.71 J	6.75	0.52 U	2.93 J	0.53 U	1.85 J	1.36 J	1.94 J	0.52 U	0.53 U	1.52 J
Chrysene	81.60	10.40	25.60	0.28 U	4.57 J	0.28 U	1.86 J	2.03 J	3.88 J	2.50 J	1.28 J	2.08 J
C1-Chrysenes	68.10	11.00	21.20	0.28 U	0.33 U	0.28 U	0.28 U	0.28 U	7.07	0.28 U	0.28 U	0.28 U
C2-Chrysenes	118.00	0.28 U	34.60	0.28 U	0.33 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U
C3-Chrysenes	0.73 U	0.28 U	0.28 U	0.28 U	0.33 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U
C4-Chrysenes	0.73 U	0.28 U	0.28 U	0.28 U	0.33 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U	0.28 U
Benzo(b)fluoranthene	56.70	5.00 J	18.10	0.32 U	0.39 U	0.33 U	0.33 U	0.33 U	0.33 U	0.32 U	0.33 U	0.33 U
Benzo(k)fluoranthene	42.20	3.41 J	8.22	0.33 U	0.39 U	0.33 U	0.33 U	0.33 U	0.33 U	0.33 U	0.33 U	0.33 U
Benzo(e)pyrene	63.90	6.61	18.80	0.34 U	0.41 U	0.35 U	0.34 U	0.35 U	0.34 U	0.34 U	0.34 U	0.34 U
Benzo(a)pyrene	52.90	4.16 J	9.28	0.49 U	0.59 U	0.50 U	0.49 U	0.50 U	0.49 U	0.49 U	0.49 U	0.49 U
Perylene	26.70	0.53 U	3.53 J	0.53 U	0.63 U	0.53 U	0.53 U	0.53 U	0.53 U	0.53 U	0.53 U	0.53 U
Indeno(1,2,3-c,d)pyrene	64.60	4.00 J	8.96	0.69 U	0.83 U	0.70 U	0.69 U	0.70 U	0.69 U	0.69 U	0.69 U	0.69 U
Dibenz(a,h)anthracene	10.60 J	0.79 U	0.79 U	0.79 U	0.95 U	0.80 U	0.79 U	0.80 U	0.79 U	0.79 U	0.79 U	0.79 U
Benzo(g,h,i)perylene	91.80	6.20 J	17.50	0.43 U	0.51 U	0.43 U	0.43 U	0.43 U	0.43 U	5.02 J	0.43 U	0.43 U
Total Priority Pollutant PAHs	731.79	92.22	185.82	26.67	74.80	27.25	48.06	42.81	42.17	247.22	26.31	27.22
Total PAH	1763.10	331.29	637.30	30.01	198.65	27.25	58.99	42.81	181.85	475.91	26.31	27.22



## PAHs (CONT.)

CLIENT SAMPLE ID	NAV- OF9- SDB1- COMP	NAV- OF11- SDB1- COMP	NAV- OF14- SDB1- COMP	NAV- BAY9- SDB1-PRE	NAV- BAY9- SDB1- DUR	NAV- BAY9- SDB1-AFT	NAV- BAY11- SDB1- DUR	NAV- BAY11- SDB1-AFT	NAV- BAY14- SDB1- DUR	NAV- BAY14- SDB1-AFT	NAV- BAY14A- SDB1- DUR	NAV- BAY14A- SDB1-AFT
<i>Surrogate Recoveries (%)</i>												
Naphthalene-d8	56	60	56	56	52	57	60	56	47	52	61	54
Phenanthrene-d10	71	71	59	62	60	65	66	67	57	65	64	63
Chrysene-d12	81	77	66	72	73	77	79	83	72	73	78	74

## PAHs QA/QC

**PROJECT:** Contamination Analysis of Stormwater and San Diego Seawater  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Waters  
**SAMPLE CUSTODY:** Water samples were collected between November 7 – 10, 2002, shipped on November 12, 2002, and received at Battelle Duxbury on November 13, 2002. All samples were received in good condition. The cooler temperature on arrival was 0.8°C. Samples were stored refrigerated until processing.

## QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	Procedural Blank	LCS/MS Recovery	MS/MSD Relative Precision	Achieved Detection Limit (ng/L)
PAH	General NS&T	40-120% Recovery	Less than 5X MDL	40-120% Recovery  (for at least 80% of analytes; analyte conc. in MS must be >10x background)	►30% RPD  (analyte conc. in MS must be >10x background)	PAH  Naphthalene ~ 17.0 Other PAHs ~0.5

**METHOD:** Water samples were extracted for PAHs following general NS&T methodologies. A volume of ~2 L of sample was extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated and processed through alumina column and HPLC/GPC. The extract was concentrated, fortified with RIS and submitted for GC/MS analysis. Water extracts were analyzed directly using gas chromatography/mass spectrometry (GC/MS) following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Water samples for PAH were stored refrigerated until extraction. There is a 7-day holding time associated with these samples.

Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
02-634	11/14/02	11/26/02 -11/26/02

**BLANKS:** A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.

**02-634** – The blank was void of contamination.

**Comments** – None.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of PAH analytes were calculated to measure data quality in terms of accuracy.

**02-634** – All PAHs were recovered within the laboratory control limits specified by the method (40 – 120%) ranging from 58 – 82% recovery.

**Comments** – None.

**MATRIX SPIKES:**

A matrix spike (MS) sample was prepared with each analytical batch. The percent recoveries of PAH analytes were calculated to measure data quality in terms of accuracy.

**02-634** – All PAHs were recovered within the laboratory control limits specified by the method (40 – 120%) and ranged from 61 – 89% recovery for the matrix spike. All PAHs were recovered within the laboratory control limits specified by the method (40 – 120%) and ranged from 59 – 86% recovery for the matrix spike duplicate.

**Comments** – None.

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including Naphthalene-d8, Phenanthrene-d10, and Chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**02-634** – Surrogate recovery for all PAH surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery).

**Comments** – None.

**REPLICATES:**

Replicate samples for waters were prepared with each analytical batch as an MS and MSD. The RPD between replicate analyses for PAH analytes is calculated to measure data quality in terms of precision.

**02-634** – All PAH analytes were recovered within the laboratory control limits specified by the method (<30%) and ranged from 0 – 6.6 % RPD.

**Comments** – None.

# PAHs QA/QC (CONT.)

CLIENT SAMPLE ID	LAB CONTROL SAMPLE			MATRIX SPIKE- NAV-OF9-SDB1- COMP		MATRIX SPIKE DUPLICATE- NAV- OF9-SDB1-COMP		PROCEDURAL BLANK	
Battelle Sample ID	AB384LCS			V9897MS		V9897MSD		AB383PB	
Battelle Batch ID	02-634			02-634		02-634		02-634	
Associated Blank	AB383PB			AB383PB		AB383PB		NA	
QC Type	LCS			MS		MSD		PB	
Data File	A0408.D			A0410.D		A0411.D		A0407.D	
Extraction Date	14-Nov-02			11/14/02		11/14/02		14-Nov-02	
Acquired Date	26-Nov-02			11/26/02		11/26/02		26-Nov-02	
Matrix	Water			Water		Water		Water	
Sample Size	2 L			0.81 L		0.81 L		2 L	
Dilution Factor	1.667			1.667		1.667		1.667	
PIV	1 mL			1 mL		1 mL		1 mL	
Min Reporting Limit	8.34			20.6		20.6		8.34	
Amount Units	ng/L		Rec% Q	ng/L		ng/L		ng/L	
Naphthalene	291.00		58	763.00		744.00		0.66	U
C1-Naphthalenes	0.66	U	NA	950.00		942.00		0.66	U
C2-Naphthalenes	0.66	U	NA	1.64	U	1.64	U	0.66	U
C3-Naphthalenes	0.66	U	NA	1.64	U	1.64	U	0.66	U
C4-Naphthalenes	0.66	U	NA	1.64	U	1.64	U	0.66	U
Biphenyl	313.00		62	833.00		833.00		0.42	U
Acenaphthylene	309.00		62	854.00		828.00		0.41	U
Acenaphthene	321.00		64	885.00		863.00		0.54	U
Fluorene	332.00		66	962.00		925.00		0.49	U
C1-Fluorenes	0.49	U	NA	1.21	U	1.21	U	0.49	U
C2-Fluorenes	0.49	U	NA	1.21	U	1.21	U	0.49	U
C3-Fluorenes	0.49	U	NA	1.21	U	1.21	U	0.49	U
Phenanthrene	370.00		74	1090.00		1060.00		0.38	U
Anthracene	330.00		66	948.00		909.00		0.35	U
C1-Phenanthrenes/Anthracenes	0.35	U	NA	70.00		56.00		0.35	U
C2-Phenanthrenes/Anthracenes	0.35	U	NA	140.00		141.00		0.35	U
C3-Phenanthrenes/Anthracenes	0.35	U	NA	132.00		122.00		0.35	U
Dibenzothiophene	3.84	J	NA	43.00		38.80		0.46	U
C1-Dibenzothiophenes	0.46	U	NA	86.90		78.00		0.46	U
C2-Dibenzothiophenes	0.46	U	NA	131.00		118.00		0.46	U
C3-Dibenzothiophenes	0.46	U	NA	131.00		120.00		0.46	U
Fluoranthene	399.00		80	1160.00		1120.00		0.44	U
Pyrene	397.00		79	1180.00		1150.00		0.48	U
C1-Fluoranthenes/Pyrenes	0.48	U	NA	64.60		72.10		0.48	U
C2-Fluoranthenes/Pyrenes	0.48	U	NA	98.80		105.00		0.48	U
C3-Fluoranthenes/Pyrenes	0.48	U	NA	97.90		100.00		0.48	U
Benzo(a)anthracene	399.00		80	1070.00		1050.00		0.69	U
Chrysene	392.00		78	1120.00		1090.00		0.37	U
C1-Chrysenes	0.37	U	NA	88.30		90.60		0.37	U
C2-Chrysenes	0.37	U	NA	151.00		153.00		0.37	U
C3-Chrysenes	0.37	U	NA	0.90	U	0.90	U	0.37	U
C4-Chrysenes	0.37	U	NA	0.90	U	0.90	U	0.37	U
Benzo(b)fluoranthene	404.00		81	1120.00		1060.00		0.43	U
Benzo(k)fluoranthene	423.00		85	1100.00		1100.00		0.43	U
Benzo(e)pyrene	369.00		75	1020.00		969.00		0.45	U
Benzo(a)pyrene	380.00		76	1010.00		965.00		0.65	U
Perylene	343.00		69	972.00		920.00		0.70	U
Indeno(1,2,3-c,d)pyrene	394.00		79	1060.00		1020.00		0.91	U
Dibenz(a,h)anthracene	412.00		82	1110.00		1050.00		1.04	U
Benzo(g,h,i)perylene	313.00		63	905.00		853.00		0.57	U
Total Priority Pollutant PAHs				16337.00		15787.00			
<b>Surrogate Recoveries (%)</b>									
Naphthalene-d8	61			60		61		61	
Phenanthrene-d10	66			77		73		66	
Chrysene-d12	79			85		82		81	

# PCBs

CLIENT SAMPLE ID:	NAV-OF9-SDB1-COMP		NAV-OF11-SDB1-COMP		NAV-OF14-SDB1-COMP	
Battelle Sample ID:	V9897		V9898		V9899	
Client Description:	Seawater/ Stormwater		Seawater/ Stormwater		Seawater/ Stormwater	
Battelle Batch ID:	02-634		02-634		02-634	
Sample Volume (L):	1.000		2.640		2.630	
Units:	ng/L		ng/L		ng/L	
CI2 08	2.197		0.100	U	0.100	U
CI3 18	0.100	U	0.100	U	0.100	U
CI3 28	0.969		0.100	U	0.100	U
CI4 44	1.484		0.100	U	0.243	
CI4 49	2.929		0.100	U	0.100	U
CI4 52	2.274		0.100	U	0.100	U
CI4 66	0.812		0.100	U	0.100	U
CI5 77	0.100	U	0.100	U	0.100	U
CI5 87	1.110		0.195		0.376	
CI5 101	1.880		0.517		0.624	
CI5 105	0.600		0.272		0.296	
CI5 118	1.617		0.473		0.383	
CI6 126	0.100	U	0.100	U	0.100	U
CI6 128	1.010		0.155		0.348	
CI6 138	3.824		0.568		1.472	
CI6 153	3.627		0.514		1.625	
CI6 156	0.100	U	0.100	U	0.100	U
CI7 169	0.100	U	0.100	U	0.100	U
CI7 170	1.285		0.100	U	0.264	
CI7 180	3.166		0.212		1.026	
CI7 183	1.317		0.147		0.344	
CI7 184	0.100	U	0.100	U	0.100	U
CI7 187	1.382		0.096	J	0.636	
CI8 195	0.432		0.058	J	0.139	
CI9 206	0.182		0.047	J	0.120	
CI10 209	1.472		0.100	U	0.100	U
Total PCB	33.568		3.253		7.896	
<i>Surrogate Recoveries:</i>						
CI3(34)	84		84		69	
CI5(112)	87		82		70	

## PCBs QA/QC

**PROJECT:** Contamination Analysis of Stormwater and San Diego Seawater  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Waters  
**SAMPLE CUSTODY:** Water samples were collected between November 7 – 10, 2002, shipped on November 12, 2002, and received at Battelle Duxbury on November 13, 2002. All samples were received in good condition. The cooler temperature on arrival was 0.8 C. Samples were stored refrigerated until processing.

### QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	Procedural Blank	LCS/MS Recovery	MS/MSD Relative Precision	Achieved Detection Limit (ng/L)						
PCB	General NS&T	40-120% Recovery	Less than 5X MDL	40-120% Recovery  (for at least 80% of analytes; analyte conc. in MS must be >10x background)	►30% RPD  (analyte conc. in MS must be >10x background)	PCB  ~ 0.1						
METHOD:	Water samples were extracted for PCBs following general NS&T methodologies. A volume of ~2 L of sample was extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated and processed through alumina column and HPLC/GPC. The extract was concentrated, fortified with RIS, solvent exchanged, and submitted for GC/ECD analysis. Water extracts were analyzed directly using gas chromatography/electron capture detector (GC/ECD) following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.											
HOLDING TIMES:	<p>Water samples for PCB were stored refrigerated until extraction. There is a 7-day holding time associated with these samples.</p> <p>Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection.</p> <table><tr><td>Batch</td><td>Extraction Date</td><td>Analysis Date</td></tr><tr><td>02-634</td><td>11/14/02</td><td>12/11/02 -1/7/03</td></tr></table> <p>The original instrumental runs of the procedural blank in December yielded a cross-contamination of the procedural blank due to a calibration standard run just prior to the procedural blank. Archive extracts of the blank and samples were run in January (outside the 40 day extract holding time), and the blank was void of contamination. This data is reported. Therefore the extract analysis was outside the 40-day holding time for extracts. The QC data is acceptable so there is no impact on the reported data.</p>						Batch	Extraction Date	Analysis Date	02-634	11/14/02	12/11/02 -1/7/03
Batch	Extraction Date	Analysis Date										
02-634	11/14/02	12/11/02 -1/7/03										
BLANKS:	<p>A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.</p> <p><b>02-634</b> – No analytes were detected in the blank.</p>											
LABORATORY CONTROL	<p><b>Comments</b> – None.</p> <p>A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of PCB analytes were calculated to measure data quality in terms of accuracy.</p>											

**SAMPLE:**

**02-634** – All PCBs were recovered within the laboratory control limits specified by the method (40 – 120 and ranged from 51 – 108% recovery).

**MATRIX SPIKES:**

**Comments** – None.

A matrix spike (MS) sample was prepared with each analytical batch. The percent recoveries of PCB analytes were calculated to measure data quality in terms of accuracy.

**02-634** – All PCBs were recovered within the laboratory control limits specified by the method (40 – 120%) and ranged from 58 – 115% recovery for the matrix spike. All PCBs were recovered within the laboratory control limits specified by the method (40 – 120%) and ranged from 56 – 105% recovery for the matrix spike duplicate.

**SURROGATES:**

**Comments** – None.

Two surrogate compounds were added prior to extraction, including PCB34 and PCB112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**02-634** – Surrogate recovery for all PCB surrogate compounds was within the laboratory control limits specified by the method (40 – 120% recovery).

**REPLICATES:**

**Comments** – None.

Replicate samples for waters were prepared with each analytical batch as an MS and MSD. The RPD between replicate analyses for PCB analytes is calculated to measure data quality in terms of precision.

**02-634** – All PCB analytes were recovered within the laboratory control limits specified by the method (<30%) and ranged from 0 – 5 % RPD.

**Comments** – None.

# PCBs QA/QC (CONT.)

CLIENT SAMPLE ID:	LAB CONTROL SAMPLE			MATRIX SPIKE-NAV-OF9-SDB1-COMP			MATRIX SPIKE DUPLICATE-NAV-OF9-SDB1-COMP					PROCEDURAL BLANK	
Battelle Sample ID:	AB384LCS			V9897MS			V9897MSD					AB383PB	
Client Description:	NA			Seawater/ Stormwater			Seawater/ Stormwater					NA	
Battelle Batch ID:	02-634			02-634			02-634					02-634	
Sample Volume (L):	NA			0.810			0.810					2.000	
Units:	ng	% Recovery		ng/L	% Recovery		ng/L	% Recovery	% RPD			ng/L	
CI2 08	32.495	108		38.940	99		38.761	99	0			0.100	U
CI3 18	15.448	51		21.597	58		20.784	56	4			0.100	U
CI3 28	21.306	71		32.103	84		30.401	79	6			0.100	U
CI4 44	23.283	78		33.239	86		31.348	81	6			0.100	U
CI4 49	22.610	75		35.044	86		33.163	81	6			0.100	U
CI4 52	23.756	79		34.663	87		32.879	83	6			0.100	U
CI4 66	22.233	74		32.694	86		30.833	81	6			0.100	U
CI5 77	29.721	99		42.657	115		39.109	105	9			0.100	U
CI5 87	26.402	88		36.435	95		36.024	94	1			0.100	U
CI5 101	23.748	79		33.167	84		32.124	82	3			0.100	U
CI5 105	24.910	83		34.939	93		34.363	91	2			0.100	U
CI5 118	25.245	84		33.772	87		32.764	84	3			0.100	U
CI6 126	23.713	79		35.130	95		34.350	93	2			0.100	U
CI6 128	25.318	84		34.923	92		33.682	88	4			0.100	U
CI6 138	25.607	85		36.596	88		36.781	89	1			0.100	U
CI6 153	25.238	84		38.724	95		37.542	92	3			0.100	U
CI6 156	NS	NA		NS	NA		NS	NA	NA			0.100	U
CI7 169	26.460	88		36.201	97		35.542	96	2			0.100	U
CI7 170	25.218	84		35.203	91		34.149	89	3			0.100	U
CI7 180	25.032	83		40.609	101		41.735	104	3			0.100	U
CI7 183	25.920	86		36.061	94		34.618	90	4			0.100	U
CI7 184	28.021	93		35.550	96		36.625	98	3			0.100	U
CI7 187	25.135	84		34.984	91		34.066	88	3			0.100	U
CI8 195	23.998	80		32.706	87		32.072	85	2			0.100	U
CI9 206	17.842	59		24.040	64		22.982	62	5			0.100	U
CI10 209	22.546	75		30.938	80		29.570	76	5			0.100	U
Total PCB	611.206	NA		860.915	NA		836.266	NA	NA			0.000	
Surrogate Recoveries:													
CI3(34)	70			80			57					75	
CI5(112)	82			88			85					83	



## TSS

SAMPLE LABEL	TSS (mg/L)
NAV-OF9-SDB1-COMP	170.267
NAV-OF11-SDB1-COMP	122.600
NAV-OF14-SDB1-COMP	126.800
NAV-BAY-PRE	0.72
NAV-BAY9-SDB1-PRE	1.44
NAV-BAY9-SDB1-DUR	0.72
NAV-BAY9-SDB1-AFT	0.65
NAV-BAY11-SDB1-PRE	1.38
NAV-BAY11-SDB1-DUR	1.00
NAV-BAY11-SDB1-AFT	0.52
NAV-BAY14-SDB1-PRE	0.85
NAV-BAY14-SDB1-DUR	1.21
NAV-BAY14-SDB1-AFT	0.65
NAV-BAY14A-SDB1-PRE	1.18
NAV-BAY14A-SDB1-DUR	0.93
NAV-BAY14A-SDB1-AFT	0.67

## SDB2- 2/24/2003

### METALS

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)
1979-7		NAV-PR5-SDB2-FF (T)	0.192 J	320	1.49	5.49	3.33	84.7	515	0.00555 J	22.4	7.72	20.5	0.671	0.715	521
1979-22		NAV-PR5-SDB2-FF (D)	0.0150 J	39.6 J	1.23	4.97	1.30	69.4	22.9	0.00273 J	14.4	5.22	11.8	0.367	0.0859 J	458
1979-9		NAV-PR5-SDB2-COMP (T)	0.247 J	1025	1.78	2.27	7.19	104	1417	0.0213	31.5	11.2	23.4	0.102 J	1.13	391
1979-24		NAV-PR5-SDB2-COMP (D)	0.00809 J	15.1 J	1.18	0.303	1.12	14.2	17.6	0.00219 J	5.94	1.88	0.533	0.247	0.0603 J	80.8
1979-8		NAV-PR6-SDB2-FF (T)	0.0522 J	179	1.66	1.37	4.24	183	426	0.0188	84.2	17.2	4.06	1.08	0.205 J	314
1979-23		NAV-PR6-SDB2-FF (D)	0.0266 J	30.4 J	1.41	1.23	3.58	177	161	0.0133	81.5	17.2	0.879	1.33	0.289 J	288
1979-10		NAV-PR6-SDB2-COMP (T)	0.132 J	722	1.36	1.12	6.67	66.2	1149	0.0189	32.9	7.33	14.6	0.161 J	0.816	249
1979-25		NAV-PR6-SDB2-COMP (D)	0.0119 J	32.2 J	1.04	0.265	1.69	33.0	27.5	0.00412 J	14.1	4.11	0.281	0.257	0.101 J	78.2

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)
1979-1		NAV-OF9-SDB2-FF (T)	0.168 J	1840	1.58	0.987	6.56	54.2	2390	0.0173	92.6	12.5	22.7	0.187 J	1.00	433
1979-16		NAV-OF9-SDB2-FF (D)	0.0203 J	16.6 J	0.695	0.388	1.22	25.8	18.5	0.00367 J	28.7	6.95	0.369	0.132 J	0.165 J	218
1979-4		NAV-OF9-SDB2-COMP (T)	0.185 J	1050	1.42	0.659	8.56	36.1	1610	0.0151	50.0	7.93	15.9	0.0660 J	1.12	233
1979-19		NAV-OF9-SDB2-COMP (D)	0.010 U	8.25 J	0.820	0.386	2.32	9.88	62.1	0.00186 J	11.8	2.83	0.156	0.0352 U	0.266 J	112
1979-2		NAV-OF11-SDB2-FF (T)	0.175 J	1690	1.18	1.23	5.55	68.4	2250	0.0508	75.8	9.32	22.4	0.169 J	0.924	555
1979-17		NAV-OF11-SDB2-FF (D)	0.0293 J	18.0 J	0.366 J	0.756	0.803 J	33.9	31.2	0.00605 J	34.9	5.27	0.541	0.0927 J	0.122 J	393
1979-5		NAV-OF11-SDB2-COMP (T)	0.107 J	777	1.33	0.776	4.70	46.9	1390	0.0541	55.5	4.48	14.1	0.108 J	0.872	298
1979-20		NAV-OF11-SDB2-COMP (D)	0.0130 J	18.7 J	0.814	0.669	1.20	15.1	68.7	0.00314 J	25.1	2.21	0.247	0.0703 J	0.227 J	179
1979-11		NAV-BAY11-SDB2-DUR (T)	0.0293 J	74.9	1.15	0.105	1.96	4.73	129	0.00216 J	10.7	2.06	0.428	0.0435 J	0.201 J	23.5
1979-26		NAV-BAY11-SDB2-DUR (D)	0.010 U	13.7 J	1.13	0.100	0.219 J	3.16	88.5	0.000973 J	9.01	1.17	0.0789	0.0352 U	0.228 J	21.6
1979-3		NAV-OF14-SDB2-FF (T)	0.229 J	2640	2.92	2.59	13.7	72.6	3940	0.0536	131	15.7	43.8	0.149 J	1.44	797
1979-18		NAV-OF14-SDB2-FF (D)	0.0267 J	10.5 J	0.781	0.983	0.804 J	22.1	18.6	0.00374 J	31.5	5.78	0.916	0.0873 J	0.0945 J	310
1979-6		NAV-OF14-SDB2-COMP (T)	0.0680 J	1270	2.02	0.673	7.24	28.9	1870	0.0314	56.5	5.34	15.0	0.0352 U	0.945	200
1979-21		NAV-OF14-SDB2-COMP (D)	0.010 U	39.9 J	1.24	0.533	1.73	7.23	70.8	0.00177 J	15.9	1.80	0.330	0.0352 U	0.124 J	110
1979-12		NAV-BAY14-SDB2-DUR (T)	0.0324 J	107	1.17	0.109	1.75	5.01	152	0.00229 J	12.5	1.93	0.623	0.0539 J	0.253 J	24.7
1979-27		NAV-BAY14-SDB2-DUR (D)	0.0111 J	2.32 J	1.11	0.106	0.242 J	3.53	125	0.00102 J	10.0	1.21	0.137	0.0640 J	0.235 J	24.9

## METALS (CONT.)

MSL			GFAA		ICP-MS		ICP-MS		CVAF		ICP-MS	
CHEMISTRY CODE	CLIENT CODE	PARAMETER	Ag ( µg/L)		Cu ( µg/L)		Pb ( µg/L)		Hg ( µg/L)		Zn ( µg/L)	
1919-25	NAV-BAY9-SDB2-PRE (T)	Total metals	0.0254	J	5.70		0.0828	J	0.00102		11.8	
1919-39	NAV-BAY9-SDB2-PRE (D)	Dissolved metals	0.0227	J	3.89		0.0541	J	0.0130		5.23	
1919-29	NAV-BAY9-SDB2-DUR (T)	Total metals	0.0581	J	6.13		0.0602	J	0.00904		12.7	
1919-43	NAV-BAY9-SDB2-DUR (D)	Dissolved metals	0.0138	J	3.92		0.0592	J	0.00134		3.09	
1919-31 r1	NAV-BAY9-SDB2-AFT (T)	Total metals	0.0241	J	5.00		0.0988	J	0.000979	J	16.0	
1919-31 r2	NAV-BAY9-SDB2-AFT (T)	Total metals	--		--		0.0892	J	0.00123		15.0	
1919-45	NAV-BAY9-SDB2-AFT (D)	Dissolved metals	0.0226	J	4.25		0.100		0.000876	J	14.8	
1919-26	NAV-BAY11-SDB2-PRE (T)	Total metals	0.0310	J	5.82		0.516		0.00210		16.5	
1919-40	NAV-BAY11-SDB2-PRE (D)	Dissolved metals	0.0329	J	3.74		0.318		0.00129		14.9	
1919-32	NAV-BAY11-SDB2-AFT (T)	Total metals	0.0151	J	5.10		0.151		--		12.5	
1919-46	NAV-BAY11-SDB2-AFT(D)	Dissolved metals	0.0303	J	4.13		0.629		0.00227		20.5	
1919-27	NAV-BAY14-SDB2-PRE (T)	Total metals	0.0368	J	4.86		0.0541	J	0.00139		18.2	
1919-41	NAV-BAY14-SDB2-PRE (D)	Dissolved metals	0.0246	J	3.87		0.0772	J	0.000830	J	15.2	
1919-33	NAV-BAY14-SDB2-AFT (T)	Total metals	0.0196	J	5.24		0.110		0.00101		4.82	
1919-47	NAV-BAY14-SDB2-AFT (D)	Dissolved metals	0.0240	J	4.24		0.106		--		4.79	
1919-28 r1	NAV-BAY14A-SDB2-PRE (T)	Total metals	0.0235	J	4.97		0.159		0.00158		10.6	
1919-28 r2	NAV-BAY14A-SDB2-PRE (T)	Total metals	0.0283	J	5.00		0.116		0.00115		2.83	
1919-42	NAV-BAY14A-SDB2-PRE (D)	Dissolved metals	0.0312	J	4.31		0.558		0.0101		14.2	
1919-30	NAV-BAY14A-SDB2-DUR (T)	Total metals	0.0280	J	5.89		0.293		0.00166		14.9	
1919-44	NAV-BAY14A-SDB2-DUR (D)	Dissolved metals	0.0178	J	3.80		0.290		0.00134		13.8	
1919-34	NAV-BAY14A-SDB2-AFT (T)	Total metals	0.0201	J	4.95		--		0.00129		--	
1919-48	NAV-BAY14A-SDB2-AFT (D)	Dissolved metals	0.0186	J	3.95		0.293		0.00176		15.8	

## METALS QA/QC

**PROJECT:** SPAWARS Task 11, San Diego Bay Stormwater  
**PARAMETER:** Metals  
**LABORATORY:** Battelle Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Seawater and Freshwater

**SAMPLE CUSTODY AND PROCESSING:** Eighteen seawater and twelve freshwater samples were received in on 03/03/03. All samples were received in good condition (i.e., all sample containers were intact). Samples were assigned a Battelle Central File (CF) identification number (1979) and were entered into Battelle's sample tracking system.

The following lists information on sample receipt and processing activities:

<b>Chemistry Lab ID</b>	1979-1 through -30
<b>Collection dates</b>	02/25/03
<b>Laboratory arrival dates</b>	03/03/03
<b>Cooler temperatures, on arrival</b>	NA – Samples arrived preserved
<b>Fe/Pd Preconcentration (seawater)</b>	03/14/03
<b>FIAS (As – seawater)</b>	03/14/03
<b>FIAS (Se – seawater)</b>	03/17/03
<b>GFAA (Ag – seawater)</b>	03/20/03
<b>CVAA analyses (Hg)</b>	03/13/03, 03/14/03, 03/18/03
<b>ICP-MS analyses:</b>	
<b>Fe/Pd Seawater</b> (Cd, Cr, Cu, Ni, Pb)	03/18/03
<b>Direct Seawater</b> (Al, Fe, Mn, Sn, Zn)	03/27/03
<b>Freshwater</b> (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, Zn)	03/24/03
<b>Rerun Freshwater</b> (Al, Fe)	04/11/03

### QA/QC DATA QUALITY OBJECTIVES:

Analyte	Analytical Method Seawater	Analytical Method Freshwater	Range of Recovery	SRM Accuracy	Relative Precision	Detection Limits (µg/L)		
						Target MDL <sup>(1)</sup>	Achieved MDL Seawater <sup>(2)</sup>	Achieved MDL Freshwater <sup>(2)</sup>
Silver	GFAA	ICP-MS	50-150%	≤20%	≤50%	0.50	0.010	0.0038
Aluminum	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	50.0	0.823	0.823
Arsenic	FIAS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.0275	0.0087
Cadmium	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.0094	0.0008
Chromium	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	1.00	1.00	0.024
Copper	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.05	0.0029
Iron	ICP-MS	ICP-MS	50-150%	≤20%	≤50%	10.0	0.983	0.983
Mercury	CVAA	CVAA	50-150%	≤25%	≤30%	0.01	0.00014	0.00014
Manganese	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.50	0.003
Nickel	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.05	0.0114
Lead	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.0035	0.0044
Selenium	FIAS	ICP-MS	50-150%	≤20%	≤30%	0.20	0.0352	0.0991
Tin	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.0024	0.0024
Zinc	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.50	0.0493

(1) As stated in the Statement of Work for Chemical Analysis of Marine and Estuarine Samples 15 May 2001.

(2) Reported from the 2003 MDL study.

**METHODS:**

Battelle MSL analyzed both seawater and freshwater samples for fourteen metals: silver (Ag), aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn) and zinc (Zn). The samples were submitted for analyses by four analytical methods: GFAA, ICP-MS, FIAS and CVAA.

Seawater samples were preconcentrated using iron (Fe) and palladium (Pd) in accordance with the Battelle SOP MSL-I-025, *Methods of Sample Preconcentration*, which is derived from EPA Method 1640. The sample preconcentration was submitted for analysis by ICP-MS and GFAA.

Seawater samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) in accordance with Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP-MS*. This method is based on two EPA Methods: 200.8 and 1638. Analytes reported from the preconcentrated seawater samples include: Cd, Cr, Cu, Ni, and Pb. Analytes reported from the direct analysis of the seawater samples include: Al, Fe, Mn, Sn, and Zn. Freshwater samples were analyzed directly by ICP-MS for all analytes, except Hg.

Ag was analyzed in the Fe-Pd preconcentrate by graphite furnace atomic absorption (GFAA) following Battelle SOP MSL-I-029, *Determination of Metals in Aqueous and Digestate Samples by GFAA*, which is derived from EPA Method 200.9.

Seawater samples were analyzed by hydride generation flow injection atomic spectroscopy (FIAS) for As and Se according to Battelle SOP MSL-I-030 *Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS*.

Seawater and freshwater samples were analyzed by cold-vapor atomic fluorescence spectroscopy (CVAF) for Hg according to Battelle SOP MSL-I-013, *Total Mercury in Aqueous Samples by CVAF*, which is derived from EPA Method 1631.

All results are reported in units of µg/L.

**HOLDING TIMES:**

The holding times for metals analyses are 90 days from sample collection for Hg analysis, and 6 months from sample collection for analysis of all other metals. The holding times for all metals were achieved.

**DETECTION LIMITS:**

Target detection limits (TDL) were achieved for all analytes. Achieved method detection limits are reported from the 2003 MDL study. Sample concentrations were evaluated and flagged to the following criteria:

- U Analyte not detected at or above the detection limit, MDL reported
- J Analyte detected above MDL, but below TDL
- \* Duplicate out of QC criteria
- e SRM recovery out of QC criteria
- w Spike recovery out of QC criteria due to inappropriate spiking level
- # Continuing calibration recovered outside of acceptable method criteria

**NOTE ON Hg QA/QC SAMPLES:**

Seawater and freshwater samples were analyzed concurrently for Hg. The QC samples are reported in both the seawater and freshwater tables.

<b>METHOD BLANKS:</b>	<p><b>Seawater:</b> A minimum of one method blank was analyzed with each analysis batch. Metals concentrations in the method blanks were below the TDL, with the exception of one method blank for Ni and Cu. All sample concentrations for Ni and Cu are greater than five times the detected blank. No corrective action was required. The data were not blank-corrected.</p> <p><b>Freshwater:</b> A minimum of one method blank was analyzed with each analysis batch. All metals concentrations in the method blanks were below the TDL. The data were not blank-corrected.</p>
<b>BLANK SPIKE or OPR ACCURACY:</b>	<p><b>Seawater:</b> A minimum of one blank spike or on-going precision and recovery (OPR) sample was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.005 µg/L for Hg; 5 µg/L for As and Se; and 10 µg/L for Ag, Cd, Cr, Cu, Ni, and Pb. BS recoveries among all metals analyzed ranged from 82% to 107% and were within the QC acceptance criteria of 50% to 150% for all metals.</p> <p><b>Freshwater:</b> A minimum of one blank spike or on-going precision and recovery (OPR) sample was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.005 µg/L for Hg; 10 µg/L for Cr, Mn, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, and Pb; and 100 µg/L for Al and Fe. BS recoveries among all metals analyzed ranged from 91% to 119% and were within the QC acceptance criteria of 50% to 150% for all metals.</p>
<b>MATRIX SPIKE ACCURACY:</b>	<p><b>Seawater:</b> A minimum of one matrix spike was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.01 µg/L for Hg; 5 µg/L for As and Se; 10 µg/L for Cr, Ni, Cu, Ag, Cd, Sn, and Pb; and 100 µg/L for Al, Fe, Mn and Zn. Matrix spike recoveries among all metals analyzed ranged from 83% to 117% and were within the QC acceptance criteria of 50% to 150% for all metals, with the exception of one MS for Al (240%) and two replicates for Fe (0%, 220%). Low recoveries for the matrix spikes are due to an inappropriate spiking level relative to the native sample concentration. Spiking levels were less than 10% of the native sample concentration, therefore not appropriate for evaluating matrix spike accuracy. Acceptable MS accuracy for Al and Fe was demonstrated in the alternate matrix spike samples.</p> <p><b>Freshwater:</b> A minimum of one matrix spike was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.01 µg/L for Hg; 10 µg/L for Cr, Mn, Ni, Cu, As, Se, Ag, Cd, Sn, and Pb; and 100 µg/L for Al, Fe and Zn. Matrix spike recoveries among all metals analyzed ranged from 94% to 118% and were within the QC acceptance criteria of 50% to 150% for all metals.</p>
<b>REPLICATE PRECISION:</b>	<p>Analytical precision for each analysis batch was evaluated by the analysis of laboratory duplicates and expressed as the relative percent deviation (RPD) of duplicate results.</p> <p><b>Seawater:</b> A minimum of one set of laboratory duplicates was analyzed with each analysis batch. Precision for all metals, except Fe, ranged from 0% to 18% RPD and were within the QC limits of <math>\leq 30\%</math>. RPD values for Fe were 9% and 32% and were within the QC limits of <math>\leq 50\%</math>.</p> <p><b>Freshwater:</b> A minimum of one set of laboratory duplicates was analyzed with each analysis batch. Precision for all metals ranged from 1% to 19% RPD and</p>

**STANDARD  
REFERENCE  
MATERIAL  
ACCURACY:**

were within the QC limits of  $\leq 30\%$ .

Accuracy of recovery of SRM analytes was expressed as the percent difference (PD) between the measured and certified SRM concentrations. The target QC criterion is  $\leq 20\%$  PD.

**Seawater:** Standard reference material analyzed for seawater samples include: SRM 1640, SRM CASS-4, and SRM 1641 for Hg. The SRM 1640 is not certified for Sn and the certified value for Fe is not at a level appropriate for data quality evaluation. Percent differences for SRM 1640 and SRM 1641 ranged from 0% to 17% and were within the QC criterion.

The SRM CASS-4 is a low-level seawater reference material. Analytes of interest certified in CASS-4 are less than 10 times the laboratory achieved MDL for all metals except Cu. Currently, there is not seawater SRM certified at a practical quantification level for all analytes of interest. The SRM CASS-4 was analyzed with the preconcentrated seawater samples, and applies only to the metals obtained from this method (Ag, Cr, Ni, Cu, Cd, Pb). Percent differences for analytes within the QC criteria for CASS-4 include As (9%) and Cd (15%). The required preconcentration procedure for low level seawater samples includes the addition of chelating agents to induce precipitation of metals under specific conditions. Subsequently, reagents added to the samples should be of the purest quality to result in zero addition of metals to the samples. The current reagents available contain traces of Cr, Cu and Ni. Correcting CASS-4 results for reagent contributions provide PD values within the QC criterion for Cr (9%), Ni (2%), and Cu (1%). Since CASS-4 is not certified for Ag or Hg and is not certified at practical levels for a majority of the analytes of interest, the alternate SRM (1640 or 1641, respectively) should be used to evaluate the accuracy of this data set. The data were not blank corrected, as the sample concentrations are greater than five times the detected blank for these analytes.

**Freshwater:** Standard reference material analyzed for freshwater samples include: SRM 1640, SLRS-3 for Fe, and SRM 1641 for Hg. The SRM 1640 is not certified for Sn and the certified value for Fe is not at a level appropriate for data quality evaluation. Percent differences for all SRMs ranged from 0% to 19% and were within the QC acceptance criterion for all metals, with the following exceptions. One replicate of 1640 for Se (28%) and one replicate of 1640 for Zn (21%). In both cases, an alternate replicate of SRM 1640 was analyzed within the batch, which demonstrated acceptable accuracy for Se (0% PD) and Zn (3% PD).

## METALS QA/QC (CONT.)

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)
<b>METHOD BLANK</b>																
Method Blank		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
1979-blk TRM r1		ICP-MS	0.0038 U	NA	0.0087 U	0.0008 U	0.245 J	0.0029 U	NA	NA	0.003 U	0.0114 U	0.0044 U	0.0991 U	0.0185 J	0.0493 U
1979-blk TRM r2		ICP-MS	0.0038 U	NA	0.00929 J	0.0008 U	0.321 J	0.0029 U	NA	NA	0.003 U	0.0114 U	0.0044 U	0.0991 U	0.00810 J	0.0493 U
1979- dissolved Blank		ICP-MS	0.00463 J	0.823 U	0.0087 U	0.0039 J	0.024 U	0.0029 U	0.983 U	NA	0.003 U	0.0259 J	0.0044 U	0.0991 U	0.0103 J	0.0493 U
Blank trm r1		ICP-MS (Al, Fe)	NA	0.823 U	NA	NA	NA	NA	0.983 U	NA	NA	NA	NA	NA	NA	NA
<b>METHOD DETECTION LIMIT <sup>1</sup></b>			<b>0.0038</b>	<b>0.823</b>	<b>0.0087</b>	<b>0.0008</b>	<b>0.024</b>	<b>0.0029</b>	<b>0.983</b>	<b>0.00014</b>	<b>0.003</b>	<b>0.0114</b>	<b>0.0044</b>	<b>0.0991</b>	<b>0.0024</b>	<b>0.0493</b>
Project Target Detection Limit			0.50	50.0	0.50	0.05	1.00	0.05	10.0	0.01	0.5	0.5	0.05	0.20	0.50	0.50
<b>STANDARD REFERENCE MATERIAL</b>																
1979-1640 TRM		ICP-MS	7.49	58.2	28.3	23.1	41.5	87.8	NA	NA	132	29.2	27.7	21.9	1.54	54.9
1640 Direct		ICP-MS	7.63	53.7	30.8	25.3	40.4	89.9	NA	NA	127	29.2	27.6	28.2	1.56	64.4
1640 TRM		ICP-MS (Al, Fe)	NA	50.6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1640		certified value	7.6	52.0	26.7	22.8	38.6	85.2	34.3	NC	122	27.4	27.9	22.0	NC	53.2
1640		range	±0.25	±1.5	±0.73	±0.96	±1.6	±1.2	±1.6	NC	±1.1	±0.8	±0.14	±0.51	NC	±1.1
		% difference	2%	12%	6%	1%	8%	3%	NA	NA	9%	7%	1%	0%	NA	3%
		% difference	0%	3%	15%	11%	5%	6%	NA	NA	9%	7%	1%	28%	NA	21%
		% difference	NA	3%	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SLRS-3 (Fe)		ICP-MS	NA	NA	NA	NA	NA	NA	119	NA	NA	NA	NA	NA	NA	NA
SLRS-3 (Fe)		ICP-MS (Al, Fe)	NA	NA	NA	NA	NA	NA	92.2	NA	NA	NA	NA	NA	NA	NA
		certified value	NA	NA	NA	NA	NA	NA	100	NA	NA	NA	NA	NA	NA	NA
		range	NA	NA	NA	NA	NA	NA	±2	NA	NA	NA	NA	NA	NA	NA
		% difference	NA	NA	NA	NA	NA	NA	19%	NA	NA	NA	NA	NA	NA	NA
		% difference	NA	NA	NA	NA	NA	NA	8%	NA	NA	NA	NA	NA	NA	NA
1641d031203		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	1565	NA	NA	NA	NA	NA	NA
1641d031303		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	1466	NA	NA	NA	NA	NA	NA
1641d031703		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	1573	NA	NA	NA	NA	NA	NA
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	1590	NC	NC	NC	NC	NC	NC
1641d		range	NC	NC	NC	NC	NC	NC	NC	±4.00	NC	NC	NC	NC	NC	NC
		% difference	NA	NA	NA	NA	NA	NA	NA	2%	NA	NA	NA	NA	NA	NA
		% difference	NA	NA	NA	NA	NA	NA	NA	8%	NA	NA	NA	NA	NA	NA
		% difference	NA	NA	NA	NA	NA	NA	NA	1%	NA	NA	NA	NA	NA	NA
<b>ICV,CCV RESULTS</b>																
ICV		ICP-MS or Hg 1	102%	102%	103%	100%	103%	102%	104%	93%	103%	103%	101%	104%	101%	102%
CCV		ICP-MS or Hg 1	103%	113%	107%	102%	109%	105%	110%	100%	110%	106%	100%	104%	102%	107%
CCV		ICP-MS or Hg 1	104%	113%	105%	102%	108%	106%	115%	98%	109%	106%	98%	104%	102%	105%
CCV		ICP-MS or Hg 1	103%	113%	105%	100%	108%	106%	113%	101%	109%	106%	98%	104%	101%	105%
CCV		ICP-MS or Hg 1	101%	114%	104%	100%	108%	103%	111%	94%	108%	104%	98%	101%	100%	105%
ICV		ICP-MS (Al, Fe) or Hg 2	NA	97%	NA	NA	NA	NA	92%	94%	NA	NA	NA	NA	NA	NA
CCV		ICP-MS (Al, Fe) or Hg 2	NA	101%	NA	NA	NA	NA	96%	92%	NA	NA	NA	NA	NA	NA
CCV		ICP-MS (Al, Fe) or Hg 2	NA	NA	NA	NA	NA	NA	NA	94%	NA	NA	NA	NA	NA	NA
CCV		ICP-MS (Al, Fe) or Hg 2	NA	NA	NA	NA	NA	NA	NA	97%	NA	NA	NA	NA	NA	NA
ICV		Hg 3	NA	NA	NA	NA	NA	NA	NA	100%	NA	NA	NA	NA	NA	NA
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	101%	NA	NA	NA	NA	NA	NA
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	103%	NA	NA	NA	NA	NA	NA
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	98%	NA	NA	NA	NA	NA	NA



## METALS QA/QC (CONT.)

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)	
BLANK SPIKE RESULTS																	
		Amount Spiked	10	100	10	10	10	10	100	0.00497	10	10	10	10	10	10	
1979-blk TRM r1 or BLANK031203			0.0038 U	0.823 U	0.0087 U	0.0008 U	0.245 J	0.0029 U	36.7	0.000419 J	0.003 U	0.0114 U	0.0044 U	0.0991 U	0.0185 J	0.0493 U	
1979-blk spike r1 or OPR031203run1			10.6	114	9.40	9.96	12.1	10.9	149	0.00569	11.7	11	10.8	9.56	11.6	10.2	
		Amount Recovered	10.6	114	9.40	9.96	11.9	10.9	112	0.00527	7-Nov	11	10.8	9.56	11.6	10.2	
		Percent Recovery	106%	114%	94%	100%	119%	109%	112%	106%	117%	110%	108%	96%	116%	102%	
		Amount Spiked	10	100	10	10	10	10	100	0.00497	10	10	10	10	10	10	
1979-blk TRM r2 or BLANK031203			0.0038 U	0.823 U	0.00929 J	0.0008 U	0.321 J	0.0029 U	36.5	0.000419 J	0.003 U	0.0114 U	0.0044 U	0.0991 U	0.00810 J	0.0493 U	
1979-blk spike r2 or OPR031203run2			10.7	113	9.30	9.89	12.1	10.9	150	0.00545	11.8	11	10.6	9.05	11.7	9.76	
		Amount Recovered	10.7	113	9.29	9.89	11.8	10.9	114	0.00503	11.8	11	10.6	9.05	11.7	9.76	
		Percent Recovery	107%	113%	93%	99%	118%	109%	114%	101%	118%	110%	106%	91%	117%	98%	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS	
BLANK031303										0.000172 J							
OPR031303run1										0.00490 J							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00473			NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	97%			NA	NA	NA	NA	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS	
BLANK031303										0.000172 J							
OPR031303run2										0.00502							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00485	NA	NA	NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	100%	NA	NA	NA	NA	NA	NA	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00491	NS	NS	NS	NS	NS	NS	
BLANK031403										0.000202 J							
OPR031403run1										0.00528							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00508	NA	NA	NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	103%	NA	NA	NA	NA	NA	NA	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00491	NS	NS	NS	NS	NS	NS	
BLANK031403										0.000202 J							
OPR031403run2										0.00547							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00527	NA	NA	NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	107%	NA	NA	NA	NA	NA	NA	
MATRIX SPIKE RESULTS																	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0161	NS	NS	NS	NS	NS	NS	
1979-15		NAV-OF24-SDB2-FF								0.00679 J							
		MS								0.0223							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.0155	NA	NA	NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	96%	NA	NA	NA	NA	NA	NA	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0157	NS	NS	NS	NS	NS	NS	
1979-15		NAV-OF24-SDB2-FF								0.00679 J							
		MSD								0.0215							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.0147	NA	NA	NA	NA	NA	NA	
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	94%	NS	NS	NA	NA	NA	NA	
		Amount Spiked	10	100	10	10	10	10	100	NS	10	10	10	10	10	100	
1979-24		NAV-PR5-SDB2-Comp	0.00809 J	15.1	1.18	0.303	1.12	14.2	17.6		5.94	1.88	0.533	0.247	0.0603 J	80.8	
		MS		131	11.4	10.7	12.6	24.3	130		17.3	12.8	10.5	11.0	11.6	185	
		Amount Recovered	10.6	116	10.2	10.4	11.5	10.1	112	NA	11.4	10.9	10.0	10.8	11.5	104	
		Percent Recovery	106%	116%	102%	104%	115%	101%	112%	NA	114%	109%	100%	108%	115%	104%	
		Amount Spiked	10	100	10	10	10	10	100	NS	10	10	10	10	10	100	
1979-24		NAV-PR5-SDB2-Comp	0.00809 J	15.1	1.18	0.303	1.12	14.2	17.6		5.94	1.88	0.533	0.247	0.0603 J	80.8	
		MSD		129	11.7	10.8	12.7	24.5	132		17.3	12.9	10.9	11.1	11.9	184	
		Amount Recovered	10.7	114	10.5	10.5	11.6	10.3	114	NA	11.4	11	10.4	10.9	11.8	103	
		Percent Recovery	107%	114%	105%	105%	116%	103%	114%	NA	114%	110%	104%	109%	118%	103%	
REPLICATE RESULTS																	
1979-23		NAV-PR6-SDB2-FF	0.0266	30.4	1.41	1.23	3.58	177	161	0.0133	81.5	17.2	0.879	1.33	0.289 J	288	
1979-23	2	NAV-PR6-SDB2-FF	NA	NA	NA	NA	NA	NA	NA	0.0132	NA	NA	NA	NA	NA	NA	
		% difference	NA	NA	NA	NA	NA	NA	NA	1%	NA	NA	NA	NA	NA	NA	
1979-24		NAV-PR5-SDB2-Comp	0.00809	15.1	1.18	0.303	1.12	14.2	17.6	0.00219 J	5.94	2	0.533	0.247	0.0603 J	80.8	
1979-24	2	NAV-PR5-SDB2-Comp	0.00670	14.8	1.10	0.295	1.14	13.6	16.2	NA	5.88	1.91	0.502	0.0991 U	0.0688 J	79.7	
		% difference	19%	2%	7%	3%	2%	4%	8%	NA	1%	2%	6%	NA	13%	1%	

1= Seawater MDLs reported from the 2003 MDL Study; U= Analyte not detected at or above detection limit, MDL reported; NC = SRM not certified; NA= Not analyzed or applicable; B = Sample results are less than 5x the blank; J= Analyste detected bove the MDL, but below the TDL; e= SRM recovery out of QC criteria; w= Spike recovery out of QC criteria due to inappropriate spiking level; # = continuing calibration recovered outside of acceptable method criteria.

# METALS QA/QC (CONT.)

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)
<b>METHOD BLANK</b>																
blk TRM r1		ICP-MS Direct	NA	0.823 U	NA	NA	NA	NA	0.983 U	NA	0.003 U	NA	NA	NA	0.00578 J	0.5 U
blk TRM r2		ICP-MS Direct	NA	0.823 U	NA	NA	NA	NA	0.983 U	NA	0.003 U	NA	NA	NA	0.00754 J	0.5 U
1979-blk		Fe/Pd ICP-MS or GFAA-Ag	0.0174 J	NA	NA	0.0094 U	0.0913 J	0.151	NA	NA	NA	0.105	0.0203 J	NA	NA	NA
Method Blank		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
BLANK		FIAS - As	NA	NA	0.0275 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BLANK		FIAS - Se	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.0352 U	NA	NA
<b>METHOD DETECTION LIMIT<sup>1</sup></b>			<b>0.010</b>	<b>0.823</b>	<b>0.0275</b>	<b>0.0094</b>	<b>0.0218</b>	<b>0.0540</b>	<b>0.983</b>	<b>0.00014</b>	<b>0.003</b>	<b>0.0286</b>	<b>0.0035</b>	<b>0.0352</b>	<b>0.0024</b>	<b>0.5</b>
Project Target Detection Limit			0.50	50.0	0.50	0.05	1.00	0.05	10.0	0.01	0.50	0.05	0.05	0.20	0.50	0.50
<b>STANDARD REFERENCE MATERIAL</b>																
1640 Direct		ICP-MS Direct	NA	51.8	NA	NA	NA	NA	N/A	NA	123	NA	NA	NA	1.58	62.3
1640 TRM		ICP-MS Direct	NA	48.8	NA	NA	NA	NA	N/A	NA	117	NA	NA	NA	1.52	50.6
1640 Direct		Fe/Pd ICP-MS or GFAA-Ag	6.96	NA	NA	24.7	39.4	87.2	N/A	NA	NA	28.2	28.0	NA	NA	NA
1640 Direct		Fe/Pd ICP-MS or GFAA-Ag	NA	NA	NA	24.5	37.1	83.0	N/A	NA	NA	26.7	27.3	NA	NA	NA
1641 Direct		FIAS- Se	NA	NA	NA	NA	NA	NA	N/A	NA	NA	NA	NA	21.0	NA	NA
1640		certified value	7.6	52.0	26.7	22.8	38.6	85.2	34.3	NC	122	27.4	27.9	22.0	NC	53.2
1640		range	±0.25	±1.5	±0.73	±0.96	±1.6	±1.2	±1.6	NC	±1.1	±0.8	±0.14	±0.51	NC	±1.1
		% difference	NA	0%	NA	NA	NA	NA	N/A	NA	1%	NA	NA	NA	NA	17%
		% difference	NA	6%	NA	NA	NA	NA	N/A	NA	4%	NA	NA	NA	NA	5%
			9%	NA	NA	8%	2%	2%	N/A	NA	3%	0%	NA	NA	NA	NA
			NA	NA	NA	8%	4%	3%	N/A	NA	3%	2%	NA	NA	NA	NA
			NA	NA	NA	NA	NA	NA	N/A	NA	NA	NA	4%	NA	NA	NA
1979-cass4		Fe/Pd ICP-MS or GFAA-Ag	0.0369	N/A	N/A	0.0299	0.222	0.749	N/A	N/A	N/A	0.425	0.0265	N/A	N/A	N/A
CASS-4		FIAS - As	N/A	N/A	1.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
CASS-4		certified value	NC	NC	1.11	0.026	0.144	0.592	0.71	N/A	2.78	0.314	0.0098	NC	NC	0.381
CASS-4		range	NC	NC	±0.16	±0.003	±0.029	±0.055	±0.058	N/A	±0.19	±0.030	±0.0036	NC	NC	±0.057
		% difference	N/A	N/A	N/A	15%	54% e	27% e	N/A	N/A	N/A	35% e	170% e	N/A	N/A	N/A
		% difference	N/A	N/A	9%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1641d031203		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1565	N/A	N/A	N/A	N/A	N/A	N/A
1641d031303		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1466	N/A	N/A	N/A	N/A	N/A	N/A
1641d031703		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1573	N/A	N/A	N/A	N/A	N/A	N/A
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	1590	NC	NC	NC	NC	NC	NC
1641d		range	NC	NC	NC	NC	NC	NC	NC	±4.00	NC	NC	NC	NC	NC	NC
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2%	N/A	N/A	N/A	N/A	N/A	N/A
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	8%	N/A	N/A	N/A	N/A	N/A	N/A
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1%	N/A	N/A	N/A	N/A	N/A	N/A
<b>ICV,CCV RESULTS</b>																
ICV		ICP-MS Direct or Hg		101%					109%	93%	104%				108%	105%
CCV		ICP-MS Direct or Hg		98%					99%	100%	105%				104%	105%
CCV		ICP-MS Direct or Hg		106%					113%	98%	104%				105%	107%
CCV		ICP-MS Direct or Hg		101%					101%	101%	104%				101%	100%
CCV		ICP-MS Direct or Hg		107%					112%	94%	100%				101%	98%
ICV		Fe/Pd ICP-MS or Hg	102%			102%	103%	102%		94%		102%	100%			
CCV		Fe/Pd ICP-MS or Hg	104%			100%	99%	98%		92%		97%	102%			
CCV		Fe/Pd ICP-MS or Hg	101%			101%	98%	96%		94%		97%	105%			
CCV		Fe/Pd ICP-MS or Hg	101%			100%	98%	96%		97%		96%	102%			
CCV		Fe/Pd ICP-MS	N/A			99%	96%	95%		NA		94%	100%			
ICV		FIAS-As or Hg			103%					100%						
CCV		FIAS-As or Hg			100%					101%						
CCV		FIAS-As or Hg			98%					103%						
CCV		FIAS-As or Hg			99%					98%						
ICV		FIAS-Se												104%		
CCV		FIAS-Se												100%		
CCV		FIAS-Se												99%		
CCV		FIAS-Se												95%		

## METALS QA/QC (CONT.)

MSL Code	Instrument	Rep	Sponsor I.D.	GFAA Ag (µg/L)	ICP-MS Al (µg/L)	FIAS As (µg/L)	ICP-MS Cd (µg/L)	ICP-MS Cr (µg/L)	ICP-MS Cu (µg/L)	ICP-MS Fe (µg/L)	CVAF Hg (µg/L)	ICP-MS Mn (µg/L)	ICP-MS Ni (µg/L)	ICP-MS Pb (µg/L)	FIAS Se (µg/L)	ICP-MS Sn (µg/L)	ICP-MS Zn (µg/L)
BLANK SPIKE RESULTS																	
	Amount Spiked			10	NS	NS	10	10	10	NS	0.00497	NS	10	10	NS	NS	NS
1979-SB Blix or BLANK031203			0.0246 U				0.0721	0.180 J	0.488		0.000419 J		0.475	0.0279 U			
1979-SB LCS or OPR031303un1				9.30			6.94	9.64	9.21		0.00569		9.19	8.26			
	Amount Recovered			9.28	N/A	N/A	8.94	9.36	8.72	N/A	0.00527	N/A	8.72	8.23	N/A	N/A	N/A
	Percent Recovery			92%	N/A	N/A	89%	94%	87%	N/A	106%	N/A	87%	82%	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.00497	NS	NS	NS	NS	NS	NS
BLANK031203											0.000419 J						
OPR031303un2											0.00545						
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00503	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	101%	N/A	N/A	N/A	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS
BLANK031303											0.000172						
OPR031303un1											0.00460						
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00473	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	97%	N/A	N/A	N/A	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS
BLANK031303											0.000172						
OPR031303un2											0.00502						
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00485	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	100%	N/A	N/A	N/A	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.00491	NS	NS	NS	NS	NS	NS
BLANK (FIAS As) or Blank031403 (Hg)											0.000202 J						
LCS or OPR031403un1							5.14				0.00528						
	Amount Recovered			N/A	N/A	5.14	N/A	N/A	N/A	N/A	0.00508	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	100%	N/A	N/A	N/A	N/A	100%	N/A	N/A	N/A	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.00491	NS	NS	NS	5.0	NS	NS
BLANK (FIAS Se) or Blank031403 (Hg)											0.000202 J				0.0352 U		
LCS or OPR031403un2											0.00547				4.92		
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00527	N/A	N/A	N/A	4.92	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	107%	N/A	N/A	N/A	98%	N/A	N/A
	Amount Spiked			NS	100	NS	NS	NS	NS	100	NS	NS	NS	NS	NS	10	100
1979-1	NAV-OF9-SDB2-FF			1840						2390							
	MSD			2080						2610							
	Amount Recovered			N/A	240	N/A	N/A	N/A	N/A	220	N/A	96.4	N/A	N/A	N/A	8.70	107%
	Percent Recovery			N/A	240%	N/A	N/A	N/A	N/A	220%	N/A	96%	N/A	N/A	N/A	87%	107%
	Amount Spiked			NS	100	NS	NS	NS	NS	100	NS	100	NS	NS	NS	10	100
1979-16	NAV-OF9-SDB2-FF			16.6		0.696				NS		NS	NS	NS	5.0	10	100
	MS			119	5.38					104		138			0.132 J	0.165 J	218
	Amount Recovered			N/A	102	4.68	N/A	N/A	N/A	85.5	N/A	109	N/A	N/A	4.67	10.4	117%
	Percent Recovery			N/A	102%	90%	N/A	N/A	N/A	96%	N/A	109%	N/A	N/A	97%	104%	117%
	Amount Spiked			NS	100	NS	NS	NS	NS	100	NS	100	NS	NS	NS	10	100
1979-16	NAV-OF9-SDB2-FF			16.6						18.5		28.7					
	MSD			125						102		138				0.165 J	218
	Amount Recovered			N/A	108	N/A	N/A	N/A	N/A	83.5	N/A	104	N/A	N/A	10.5	328	
	Percent Recovery			N/A	108%	N/A	N/A	N/A	N/A	84%	N/A	104%	N/A	N/A	N/A	103%	110%
1979-18	NAV-OF14-SDB2-FF			0.0267 J		0.983	0.804	22.1				5.78		0.916			
	MS			9.46		8.46	30.3					14.6		8.47			
	Amount Recovered			9.87	N/A	8.48	8.66	8.20	N/A	N/A	N/A	104		8.55	N/A	N/A	N/A
	Percent Recovery			99%	N/A	85%	87%	82%	N/A	N/A	N/A	88%		86%	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.0158	NS	NS	NS	NS	NS	NS
1979-12	NAV-BAY14-SDB2-D										0.00239 J						
	MS										0.0188						
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0165	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	104%	N/A	N/A	N/A	N/A	N/A	N/A
	Amount Spiked			NS	NS	NS	NS	NS	NS	NS	0.0154	NS	NS	NS	NS	NS	NS
1979-12	NAV-BAY14-SDB2-D										0.00239 J						
	MSD										0.01620						
	Amount Recovered			N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0159	N/A	N/A	N/A	N/A	N/A	N/A
	Percent Recovery			N/A	N/A	N/A	N/A	N/A	N/A	N/A	100%	N/A	N/A	N/A	N/A	N/A	N/A

## METALS QA/QC (CONT.)

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Se (µg/L)	Sn (µg/L)	Zn (µg/L)
REPLICATE RESULTS																
1979-1		NAV-OF9-SDB2-FF	0.168 J	1840	1.58	0.987	6.56	54.2	2390	0.0173	92.6	12.5	22.7	0.187 J	1.00	433
1979-1	2	NAV-OF9-SDB2-FF	NA	1790	NA	NA	NA	NA	2180	0.0174	87.8	NA	NA	NA	1.02	422
		% difference	NA	3%	NA	NA	NA	NA	9%	1%	5%	NA	NA	NA	2%	3%
1979-12		NAV-BAY14-SDB2-D	0.0324 J	107	1.17	0.109	1.75	5.01	152	0.00230 J	12.5	1.93	0.623	0.0539 J	0.253 J	24.7
1979-12	2	NAV-BAY14-SDB2-D	0.0388 J	NA	1.20	0.113	1.74	4.99	NA	NA	NA	1.94	0.602	0.0352 U	NA	NA
		% difference	18%	NA	3%	4%	1%	0%	NA	NA	NA	1%	3%	NA	NA	NA
1979-16		NAV-OF9-SDB2-FF	0.0203 J	16.6 J	0.695	0.388	1.22	25.8	18.5	0.00367 J	28.7	6.95	0.369	0.132 J	0.165 J	218
1979-16	2	NAV-OF9-SDB2-FF	NA	16.4 J	NA	NA	NA	NA	25.5	NA	29.9	NA	NA	NA	0.149 J	229
		% difference	NA	1%	NA	NA	NA	NA	32%	NA	4%	NA	NA	NA	10%	5%

1= Seawater MDLs reported from the 2003 MDL Study; U= Analyte not detected at or above detection limit, MDL reported; NC = SRM not certified; NA= Not analyzed or applicable; B = Sample results are less than 5x the blank; J= Analyte detected above the MDL, but below the TDL; e= SRM recovery out of QC criteria; w= Spike recovery out of QC criteria due to inappropriate spiking level; # = continuing calibration recovered outside of acceptable method criteria.

## METALS QA/QC (CONT.)

MSL	CLIENT CODE	PARAMETER	GFAA Ag ( µg/L)	ICP-MS Cu ( µg/L)	ICP-MS Pb ( µg/L)	CVAL Hg ( µg/L)	ICP-MS Zn ( µg/L)
<b>DETECTION LIMITS</b>							
Project Reporting Limit			0.1	0.1	0.1	0.001	0.1
Laboratory Achieved MDL			0.0128	0.026	0.0055	0.00016	0.11
<b>METHOD BLANKS</b>							
Blank (1)			0.0140	0.317	0.0231	0.000367	0.232
Blank (2)			0.0252	0.254	0.0186	0.000419	0.271
		Mean	0.0196	0.286	0.0209	0.000393	0.282
<b>LABORATORY CONTROL SAMPLE (LCS) ACCURACY</b>							
Blank (1)	SB Blank (1)		0.0136	0.626	0.0243	0.000367	1.73
OPR030603run1 (Hg)	SB LCS R1		9.30	10.4	8.67	0.00529	11.6
		Amount Recovered	9.29	9.77	8.65	0.00493	9.87
		Percent Recovery	NS	NS	NS	NS	NS
		Amount Spiked	NS	NS	NS	0.00487	NS
Blank (1)						0.000367	
OPR030603run2 (Hg)						0.00542	
		Amount Recovered	NA	NA	NA	0.00506	NA
		Percent Recovery	NA	NA	104%	104%	NA
		Amount Spiked	10	10	10	0.00492	10
Blank (2)	SB Blank (2)		0.0155	0.647	0.0284	0.000419	1.07
OPR031203run1 (Hg)	SB LCS R2		9.26	10.1	8.28	0.00569	11.3
		Amount Recovered	9.24	9.45	8.25	0.00527	10.2
		Percent Recovery	92%	95%	83%	106%	102%
		Amount Spiked	NS	NS	NS	0.00491	NS
Blank (2)						0.000419	
OPR031203run2 (Hg)						0.00549	
		Amount Recovered	NA	NA	NA	0.00503	NA
		Percent Recovery	NA	NA	NA	101%	NA
<b>MATRIX SPIKE ACCURACY</b>							
1919-27	NAV-BAY14-SDB2-PRE	Total metals	0.0368	4.86	0.158	--	13.1
1919-27 MS			9.09	14.2	8.66	--	21.1
1919-27 MSD			9.23	14.4	8.73	--	21.4
		% Rec (10ppb)	91%	93%	85%	--	80%
		% Rec (10ppb)	92%	96%	86%	--	84%
1919-37	NAV-BAY11B-SDB2-AFT	Total metals	0.0128U	2.84	0.558	--	14.2
1919-37 MS			9.55	12.3	9.08	--	22.7
1919-37 MSD			9.25	12.3	8.90	--	22.7
		% Rec (10ppb)	95%	95%	85%	--	85%
		% Rec (10ppb)	92%	95%	83%	--	85%
1919-38 r1	NAV-BAY26-SDB2-AFT	Total metals	--	--	--	0.00101	--
1919-38 MS			--	--	--	0.0117	--
1919-38 MSD			--	--	--	0.0125	--
		% Rec (0.0102ppb)	--	--	--	105%	--
		% Rec (0.0108ppb)	--	--	--	106%	--
<b>REPLICATE PRECISION</b>							
1919-28 r1	NAV-BAY14A-SDB2-PRE	Total metals	0.0235J	4.97	0.153	0.00131	13.1
1919-28 r2	NAV-BAY14A-SDB2-PRE	Total metals	0.0283J	5.00	0.151	--	12.5
		MEAN	0.0259	4.99	0.152	--	12.6
		RPD	19%	1%	1%	--	5%
1919-31 r1	NAV-BAY9-SDB2-AFT	Total metals	0.0241J	5.00	0.318	0.00129	14.9
1919-31 r2	NAV-BAY9-SDB2-AFT	Total metals	--	--	--	0.00129	--
		MEAN	--	--	--	0.00125	--
		RPD	--	--	--	0%	--
1919-38 r1	NAV-BAY26-SDB2-AFT	Total metals	0.0183J	1.55	0.110	0.00101	4.82
1919-38 r2	NAV-BAY26-SDB2-AFT	Total metals	0.0191J	1.54	0.106	--	4.79
		MEAN	0.0187J	1.55	0.108	--	4.81
		RPD	4%	1%	4%	--	1%
<b>STANDARD REFERENCE MATERIAL ACCURACY</b>							
CASS-4 r1			NA	0.871	0.0234	--	0.888
CASS-4 r2			NA	0.824	0.0223	--	0.700
		Laboratory Consensus Values	NC	0.883	0.0214J	NC	0.412
		Range	--	+0.080	+0.01	--	+0.05
		PD CASS-4 R1	NA	26%#	9%	--	116%#
		PD CASS-4 R2	NA	19%	4%	--	13%
1640 Direct R1	Freshwater SRM		7.31	92.0	27.2	1550	66.7
1640 Direct R2	Freshwater SRM		7.68	89.8	28.8	1570	64.3
		certified value	7.62	85.2	27.9	1590	53.2
		Range	± 0.25	± 1.2	± 0.14	±40	± 1.1
		PD 1640 Direct R1	4%	8%	3%	3%	25%
		PD 1640 Direct R2	1%	5%	3%	1%	21%

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# PAHs

CLIENT SAMPLE ID	NAV- PR5-SDB2-FF	NAV- PR5-SDB2- COMP	NAV- PR6-SDB2-FF	NAV- PR6-SDB2- COMP	
Battelle Sample ID	U7089	U7091	U7090	U7092	
Battelle Batch ID	03-0203	03-0203	03-0203	03-0203	
Data File	A1884.D	A1886.D	A1885.D	A1887.D	
Extraction Date	03/04/03	03/04/03	03/04/03	03/04/03	
Acquired Date	03/20/03	03/20/03	03/20/03	03/20/03	
Matrix	Water	Water	Water	Water	
Sample Size (L)	2.62	2.64	2.66	2.66	
Dilution Factor	1.667	1.667	1.667	1.667	
PIV (mL)	0.3	0.3	0.3	0.3	
Min Reporting Limit	0.95	0.95	0.94	0.94	
Amount Units	ng/L	ng/L	ng/L	ng/L	
Naphthalene	6.33 B	545.51	7.70	10.74	
C1-Naphthalenes	4.17	2246.10	6.50	8.58	
C2-Naphthalenes	5.15	1886.51	9.47	13.41	
C3-Naphthalenes	4.38	784.87	8.81	6.71	
C4-Naphthalenes	0.51 U	301.05	0.50 U	0.50 U	
2-Methylnaphthalene	3.62	2088.87	4.74	8.10	
1-Methylnaphthalene	2.60	1449.34	4.68	5.34	
2,6-Dimethylnaphthalene	1.27	860.28	1.50	2.66	
2,3,5-Trimethylnaphthalene	0.82 J	150.84	0.72 J	1.20	
Biphenyl	2.18	472.71	7.14	4.17	
Acenaphthylene	1.25	15.67	1.05	2.69	
Acenaphthene	2.42	29.29	1.94	1.67	
Fluorene	3.27	94.48	2.90	3.50	
C1-Fluorenes	1.95 B	108.44	4.84	4.77	
C2-Fluorenes	10.13 B	63.38	59.86	24.62	
C3-Fluorenes	14.05 B	81.06	24.82 B	62.85	
Phenanthrene	29.86	54.65	15.88 B	34.46	
Anthracene	1.79 B	4.14	1.00 B	2.72	
C1-Phenanthrenes/Anthracenes	21.63 B	49.05	10.27 B	28.98 B	
C2-Phenanthrenes/Anthracenes	56.76 B	59.66 B	22.81 B	49.46 B	
C3-Phenanthrenes/Anthracenes	54.90 B	44.74 B	11.21 B	38.07 B	
C4-Phenanthrenes/Anthracenes	24.81 B	15.45 B	0.28 U	14.00 B	
1-Methylphenanthrene	5.84 B	12.86	3.65 B	8.78	
Dibenzothiophene	7.87	11.22	19.20	9.80	
C1-Dibenzothiophenes	14.21	19.15	30.88	20.81	
C2-Dibenzothiophenes	49.50 B	41.42 B	59.11 B	64.18 B	
C3-Dibenzothiophenes	48.76 B	39.87 B	37.56 B	52.76 B	
Fluoranthene	29.72	48.56	9.44 B	34.66	
Pyrene	31.48 B	56.25	8.35 B	38.24 B	
C1-Fluoranthenes/Pyrenes	34.42 B	24.86 B	9.16 B	21.00 B	
C2-Fluoranthenes/Pyrenes	27.19 B	26.14 B	7.14 B	26.09 B	
C3-Fluoranthenes/Pyrenes	17.20 B	24.23 B	5.11 B	25.04 B	
Benzo(a)anthracene	3.58	12.42	0.75 J	4.00	
Chrysene	21.51	30.86	4.84	30.12	
C1-Chrysenes	14.05 B	23.82	4.46 B	20.74	
C2-Chrysenes	17.70 B	33.07 B	0.28 U	27.39 B	
C3-Chrysenes	13.41 B	31.09 B	0.28 U	27.34 B	
C4-Chrysenes	0.28 U	0.28 U	0.28 U	0.28 U	
Benzo(b)fluoranthene	10.84	18.72	2.12	10.57	
Benzo(k)fluoranthene	7.08	13.96	1.21	6.19	
Benzo(e)pyrene	10.01	16.44	1.93 B	10.36	
Benzo(a)pyrene	4.99	11.68	0.72 J	4.32	
Perylene	1.48	3.60	0.53 U	1.86	
Indeno(1,2,3-cd)pyrene	6.91	12.53	1.13 B	6.08	
Dibenz(a,h)anthracene	1.23	2.44	0.78 U	1.17	
Benzo(g,h,i)perylene	15.16	25.43	2.48	13.59	
Total Priority Pollutant PAHs	177.42	976.59	61.51	204.72	
Naphthalene-d8	60	64	63	60	
Phenanthrene-d10	75	76	76	79	
Chrysene-d12	81	85	80	91	

# PAHs (CONT.)

CLIENT SAMPLE ID	NAV-BAY9-SDB2-PRE		NAV-BAY9-SDB2-DUR		NAV-BAY9-SDB2-AFT		NAV-BAY11-SDB2-PRE		NAV-BAY11-SDB2-DUR		NAV-BAY11-SDB2-AFT		NAV-BAY14-SDB2-PRE	
Battelle Sample ID	U7067		U7071		U7075		U7068		U7072		U7076		U7069	
Battelle Batch ID	03-0200		03-0200		03-0200		03-0200		03-0200		03-0200		03-0200	
Data File	A1850.D		A1857.D		A1861B.D		A1854.D		A1858.D		A1863.D		A1855.D	
Extraction Date	03/03/03		03/03/03		03/03/03		03/03/03		03/03/03		03/03/03		03/03/03	
Acquired Date	03/18/03		03/18/03		03/18/03		03/18/03		03/18/03		03/18/03		03/18/03	
Matrix	Water		Water		Water		Water		Water		Water		Water	
Sample Size (L)	1.3		2.64		2.65		2.64		2.66		2.64		2.62	
Dilution Factor	1.667		1.667		1.667		1.667		1.667		1.667		1.667	
PIV (mL)	0.3		0.3		0.3		0.3		0.3		0.3		0.3	
Min Reporting Limit	1.92		0.95		0.94		0.95		0.94		0.95		0.95	
Amount Units	ng/L		ng/L		ng/L		ng/L		ng/L		ng/L		ng/L	
Naphthalene	3.89	B	1.74	B	1.48	B	1.43	B	1.36	B	1.26	B	1.26	B
C1-Naphthalenes	2.45	B	0.91	JB	0.66	JB	1.27	B	0.70	JB	0.75	JB	0.73	JB
C2-Naphthalenes	1.02	U	2.90		0.50	U	0.50	U	0.50	U	2.46		2.18	
C3-Naphthalenes	1.02	U	2.10		1.62		0.50	U	0.50	U	2.15		1.41	
C4-Naphthalenes	1.02	U	0.50	U	0.50	U	0.50	U	0.50	U	0.50	U	0.51	U
2-Methylnaphthalene	2.00	B	0.83	JB	0.61	JB	1.12	B	0.64	JB	0.77	JB	0.67	JB
1-Methylnaphthalene	1.69	JB	0.57	JB	0.35	JB	0.94	JB	0.31	JB	0.55	JB	0.32	JB
2,6-Dimethylnaphthalene	0.73	U	0.70	J	0.36	U	0.93	J	0.36	U	1.03		0.78	J
2,3,5-Trimethylnaphthalene	0.77	U	0.78	J	0.38	U	1.37		0.37	U	0.64	J	0.48	J
Biphenyl	0.60	J	0.89	J	0.31	U	0.79	J	0.31	U	0.57	J	0.41	J
Acenaphthylene	1.37	J	0.89	J	0.65	J	1.74		0.63	J	1.04		0.66	J
Acenaphthene	6.51		6.44		3.08		4.74		4.91		10.63		3.13	
Fluorene	2.63		2.70		1.03		2.03		1.84		3.98		0.90	J
C1-Fluorenes	0.75	U	1.38		1.22		0.37	U	0.37	U	1.79		0.99	
C2-Fluorenes	0.75	U	0.37	U	0.37	U	0.37	U	0.37	U	2.71		0.37	U
C3-Fluorenes	0.75	U	0.37	U	0.37	U	0.37	U	0.37	U	0.37	U	0.37	U
Phenanthrene	2.74		7.01		1.11	B	1.87		3.32		5.05		0.89	JB
Anthracene	1.27	J	1.93		1.08		2.00		1.60		2.23		0.83	J
C1-Phenanthrenes/Anthracenes	0.58	U	4.31		2.31		0.28	U	2.98		4.02		0.29	U
C2-Phenanthrenes/Anthracenes	0.58	U	3.18		1.79		0.28	U	1.81		2.51		0.29	U
C3-Phenanthrenes/Anthracenes	0.58	U	3.52		1.48		0.28	U	1.97		1.76		0.29	U
C4-Phenanthrenes/Anthracenes	0.58	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U	0.29	U
1-Methylphenanthrene	0.67	U	1.02		0.47	J	1.39		0.57	J	0.81	J	0.33	U
Dibenzothiophene	0.90	J	1.52		0.69	J	1.62		0.78	J	1.23		0.36	J
C1-Dibenzothiophenes	0.71	U	1.96		0.89	J	0.35	U	0.83	J	1.03		0.35	U
C2-Dibenzothiophenes	0.71	U	3.64		1.99		0.35	U	1.91		2.57		0.35	U
C3-Dibenzothiophenes	0.71	U	3.23		1.15		0.35	U	1.33		1.12		0.35	U
Fluoranthene	10.18		20.21		10.58		10.30		13.99		25.73		6.95	
Pyrene	4.90		13.05		5.34		5.41		8.43		14.77		3.31	
C1-Fluoranthenes/Pyrenes	0.68	U	4.93		2.23		1.70		3.50		5.70		1.70	
C2-Fluoranthenes/Pyrenes	0.68	U	3.42		0.33	U	0.33	U	1.91		1.76		0.34	U
C3-Fluoranthenes/Pyrenes	0.68	U	2.92		0.33	U	0.33	U	0.33	U	0.33	U	0.34	U
Benzo(a)anthracene	1.07	U	2.63		0.75	J	1.62		1.28		3.30		0.34	J
Chrysene	0.56	U	5.87		1.60		2.14		2.34		4.52		0.78	J
C1-Chrysenes	0.56	U	3.33		0.28	U	0.28	U	1.60		1.79		0.28	U
C2-Chrysenes	0.56	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
C3-Chrysenes	0.56	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
C4-Chrysenes	0.56	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
Benzo(b)fluoranthene	0.66	U	3.49		1.15		2.56		1.93		2.73		0.33	U
Benzo(k)fluoranthene	0.67	U	2.44		1.08		1.91		1.45		2.48		0.33	U
Benzo(e)pyrene	0.70	U	3.04		1.06		2.08		1.27		1.62		0.88	J
Benzo(a)pyrene	1.00	U	2.19		0.74	J	1.85		1.15		1.92		0.50	U
Perylene	1.07	U	0.67	J	0.53	U	1.51		0.53	U	0.53	U	0.53	U
Indeno(1,2,3-cd)pyrene	0.82	JB	2.10	B	0.66	JB	2.13	B	0.85	JB	0.81	JB	0.35	JB
Dibenz(a,h)anthracene	1.60	U	0.58	J	0.79	U	1.21		0.78	U	0.79	U	0.80	U
Benzo(g,h,i)perylene	2.31	B	2.63	B	0.92	JB	2.49	B	1.22	B	1.10	B	0.66	JB
Total Priority Pollutant PAHs	36.62		75.89		31.26		45.41		46.29		81.56		20.07	
Naphthalene-d8	65		53		54		62		54		63		70	
Phenanthrene-d10	82		72		70		73		71		72		74	
Chrysene-d12	92		87		86		83		76		88		79	

# PAHs (CONT.)

CLIENT SAMPLE ID	NAV-BAY14-SDB2-DUR		NAV-BAY14-SDB2-AFT		NAV-BAY14A-SDB2-PRE		NAV-BAY14A-SDB2-DUR		NAV-BAY14A-SDB2-AFT	
Battelle Sample ID	U7073		U7077		U7070		U7074		U7078	
Battelle Batch ID	03-0200		03-0200		03-0200		03-0200		03-0200	
Data File	A1861.D		A1864.D		A1856.D		A1861A.D		A1866.D	
Extraction Date	03/03/03		03/03/03		03/03/03		03/03/03		03/03/03	
Acquired Date	03/18/03		03/19/03		03/18/03		03/18/03		03/19/03	
Matrix	Water		Water		Water		Water		Water	
Sample Size (L)	2.65		2.66		2.64		2.66		2.64	
Dilution Factor	1.667		1.667		1.667		1.667		1.667	
PIV (mL)	0.3		0.3		0.3		0.3		0.3	
Min Reporting Limit	0.94		0.94		0.95		0.94		0.95	
Amount Units	ng/L		ng/L		ng/L		ng/L		ng/L	
Naphthalene	1.30	B	1.18	B	1.38	B	1.27	B	1.31	B
C1-Naphthalenes	0.76	JB	0.57	JB	0.76	JB	0.70	JB	0.64	JB
C2-Naphthalenes	0.50	U	0.50	U	1.45		0.50	U	0.50	U
C3-Naphthalenes	1.55		1.08		1.11		1.13		1.50	
C4-Naphthalenes	0.50	U	0.50	U	0.50	U	0.50	U	0.50	U
2-Methylnaphthalene	0.60	JB	0.48	JB	0.73	JB	0.60	JB	0.65	JB
1-Methylnaphthalene	0.46	JB	0.27	JB	0.42	JB	0.34	JB	0.30	JB
2,6-Dimethylnaphthalene	0.36	U	0.36	U	0.73	J	0.36	U	0.36	U
2,3,5-Trimethylnaphthalene	0.38	U	0.37	U	0.38	U	0.37	U	0.38	U
Biphenyl	0.25	J	0.24	J	0.28	J	0.31	U	0.34	J
Acenaphthylene	0.54	J	0.49	J	0.54	J	0.41	J	0.64	J
Acenaphthene	2.46		2.36		2.53		2.45		3.99	
Fluorene	0.82	J	0.85	J	0.78	J	0.70	J	1.28	
C1-Fluorenes	0.37	U	0.37	U	0.37	U	1.03		1.12	
C2-Fluorenes	0.37	U	0.37	U	0.37	U	0.37	U	0.37	U
C3-Fluorenes	0.37	U	0.37	U	0.37	U	0.37	U	0.37	U
Phenanthrene	2.16		1.18	B	0.79	JB	1.54	B	1.37	B
Anthracene	1.09		0.78	J	0.68	J	1.22		1.09	
C1-Phenanthrenes/Anthracenes	2.93		2.14		1.41		2.08		2.49	
C2-Phenanthrenes/Anthracenes	2.31		1.85		0.28	U	1.45		2.30	
C3-Phenanthrenes/Anthracenes	1.85		0.28	U	0.28	U	2.01		1.59	
C4-Phenanthrenes/Anthracenes	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
1-Methylphenanthrene	0.60	J	0.48	J	0.39	J	0.43	J	0.54	J
Dibenzothiophene	0.88	J	0.60	J	0.44	J	0.72	J	0.68	J
C1-Dibenzothiophenes	1.48		0.72	J	0.35	U	1.13		0.78	J
C2-Dibenzothiophenes	2.81		1.81		0.35	U	1.62		1.74	
C3-Dibenzothiophenes	1.86		0.35	U	0.35	U	1.13		1.45	
Fluoranthene	12.93		10.43		7.22		10.95		11.65	
Pyrene	8.05		5.43		3.11		6.32		5.89	
C1-Fluoranthenes/Pyrenes	4.06		2.58		1.26		3.47		2.48	
C2-Fluoranthenes/Pyrenes	1.98		0.33	U	0.33	U	0.33	U	0.33	U
C3-Fluoranthenes/Pyrenes	0.33	U	0.33	U	0.33	U	0.33	U	0.33	U
Benzo(a)anthracene	1.37		0.62	J	0.34	J	1.08		0.69	J
Chrysene	3.40		1.54		0.69	J	2.24		1.41	
C1-Chrysenes	2.64		0.28	U	0.28	U	0.28	U	0.28	U
C2-Chrysenes	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
C3-Chrysenes	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
C4-Chrysenes	0.28	U	0.28	U	0.28	U	0.28	U	0.28	U
Benzo(b)fluoranthene	2.98		1.34		0.33	U	2.17		1.23	
Benzo(k)fluoranthene	2.47		1.02		0.33	U	1.75		0.89	J
Benzo(e)pyrene	2.03		1.46		0.34	U	1.59		1.00	
Benzo(a)pyrene	1.84		0.49	U	0.49	U	1.50		0.74	J
Perylene	0.53	U	0.53	U	0.53	U	0.53	U	0.53	U
Indeno(1,2,3-cd)pyrene	1.43	B	0.69	JB	0.45	JB	0.97	B	0.56	JB
Dibenz(a,h)anthracene	0.79	U	0.78	U	0.79	U	0.78	U	0.79	U
Benzo(g,h,i)perylene	1.54	B	0.68	JB	0.54	JB	1.27	B	0.48	JB
Total Priority Pollutant PAHs	44.36		28.59		19.04		35.84		33.23	
Naphthalene-d8	54		57		69		55		65	
Phenanthrene-d10	70		69		77		70		72	
Chrysene-d12	85		88		81		85		86	



## PAHs QA/QC

**PROJECT:** SPAWAR TO0011, Contaminant Analysis of Stormwater and San Diego Bay Seawater

**PARAMETER:** PAH

**LABORATORY:** Battelle, Duxbury, MA

**MATRIX:** Water

**SAMPLE CUSTODY:** The water samples were collected February 25, 2003. They were received in Duxbury on February 28, 2003 in good condition in six coolers. The cooler temperature on arrival ranged from 0.2 °C to 1.3 °C. Samples were stored at 4 °C until processing.

### QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	LCS/MS Recovery	Sample Replicate Relative Precision	Procedural Blank
PAH	General NS&T	30-130% Recovery	LCS: 40-120% Recovery for at least 80% of analytes  MS: 50-150% Recovery for at least 70% of analytes; analyte conc. in MS must be >5x background	≤30% RSD  analyte conc. in MS must be <5x background	<3X MDL

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Full water samples were spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with Recovery Internal Standard (RIS) and split for analysis. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) with the MS operating in the selected ion monitoring (SIM) mode, following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch.

Samples were extracted with in the 7-day holding time for waters. Extracts were analyzed within the 40-day holding time for extracts

<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
03-0203	3/4/2003	3/19/2003 – 3/20/2003

**BLANKS:** A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.

**03-0203** – Several target analytes were detected at concentrations greater than 3X the MDL.

~~Comments – All samples are appropriately flagged. The contamination in the blank does not appear to have the same PAH homologue pattern as the samples indicating that the contamination is likely isolated to the blank and that the samples are not impacted by the blank contamination. This is supported by the fact that no alkyl homologues were detected in the LCS (blank spike) sample – the LCS is prepared in the same manner as the blank, with the addition of a spike of the target analytes of interest (in this case, the parent PAH).~~

**LABORATORY CONTROL** Note: The 2003 MDL for substituted naphthalenes were updated.  
A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**SAMPLE:**

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client.

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS)/matrix spike duplicate (MSD) pair was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy; the relative percent difference between the pair was calculated to measure data quality in terms of precision.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client. The relative percent differences between the MS and MSD recoveries were within the laboratory control limits for all target PAH.

**Comments** – None.

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**03-0203** – All surrogate percent recoveries were within the laboratory control limits specified by the client.

**Comments** – None.

# PAHs QA/QC (CONT.)

CLIENT SAMPLE ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE-NAV-BAY9-SDB2-PRE			MATRIX SPIKE DUPLICATE-NAV-BAY9-SDB2-PRE			PROCEDURAL BLANK	
Battelle Sample ID	BB584LCS			U7067MS			U7067MSD			BB583PB	
Battelle Batch ID	03-0200			03-0200			03-0200			03-0200	
Data File	A1849.D			A1851.D			A1852.D			A1848.D	
Extraction Date	03/03/03			3/3/2003			03/03/03			03/03/03	
Acquired Date	03/18/03			3/18/2003			37698			03/18/03	
Matrix	Water			Water			Water			Water	
Sample Size (L)	2			0.65			0.65			2	
Dilution Factor	1.667			1.667			1.667			1.667	
PIV (mL)	0.3			0.30			0.30			0.3	
Min Reporting Limit	1.25			3.85			3.85			1.25	
Amount Units	ng		Rec%	Q		ng/L	Rec%		ng/L	Rec%	
Naphthalene	368.77		74	1019.92		66	1010.15		65	1.89	
C1-Naphthalenes	0.66	U	NA	2.04	U	NA	2.04	U	NA	1.14	J
C2-Naphthalenes	0.66	U	NA	2.04	U	NA	2.04	U	NA	0.66	U
C3-Naphthalenes	0.66	U	NA	2.04	U	NA	2.04	U	NA	0.66	U
C4-Naphthalenes	0.66	U	NA	2.04	U	NA	2.04	U	NA	0.66	U
2-Methylnaphthalene	371.20		74	983.20		64	982.48		64	0.95	J
1-Methylnaphthalene	347.39		69	946.06		61	940.09		61	0.63	J
2,6-Dimethylnaphthalene	354.90		71	916.90		60	894.33		58	0.47	U
2,3,5-Trimethylnaphthalene	378.08		76	1001.89		65	975.25		63	0.50	U
Biphenyl	373.48		74	958.19		62	931.34		60	0.42	U
Acenaphthylene	384.65		77	1086.17		70	1084.45		70	0.41	U
Acenaphthene	369.53		74	1021.95		66	1027.95		66	0.54	U
Fluorene	399.58		80	1119.79		73	1121.97		73	0.49	U
C1-Fluorenes	0.49	U	NA	1.51	U	NA	1.51	U	NA	0.49	U
C2-Fluorenes	0.49	U	NA	1.51	U	NA	1.51	U	NA	0.49	U
C3-Fluorenes	0.49	U	NA	1.51	U	NA	1.51	U	NA	0.49	U
Phenanthrene	416.86		83	1205.14		78	1189.70		77	0.53	J
Anthracene	418.43		84	1193.24		77	1170.26		76	0.35	U
C1-Phenanthrenes/Anthracenes	0.38	U	NA	1.15	U	NA	1.15	U	NA	0.38	U
C2-Phenanthrenes/Anthracenes	0.38	U	NA	1.15	U	NA	1.15	U	NA	0.38	U
C3-Phenanthrenes/Anthracenes	0.38	U	NA	1.15	U	NA	1.15	U	NA	0.38	U
C4-Phenanthrenes/Anthracenes	0.38	U	NA	1.15	U	NA	1.15	U	NA	0.38	U
1-Methylphenanthrene	409.14		82	1204.04		78	1194.14		78	0.43	U
Dibenzothiophene	0.46	U	NA	1.43	U	NA	1.43	U	NA	0.46	U
C1-Dibenzothiophenes	0.46	U	NA	1.43	U	NA	1.43	U	NA	0.46	U
C2-Dibenzothiophenes	0.46	U	NA	1.43	U	NA	1.43	U	NA	0.46	U
C3-Dibenzothiophenes	0.46	U	NA	1.43	U	NA	1.43	U	NA	0.46	U
Fluoranthene	447.78		90	1342.42		87	1330.47		86	0.39	J
Pyrene	460.98		92	1406.44		91	1361.94		88	0.48	J
C1-Fluoranthenes/Pyrenes	0.44	U	NA	1.35	U	NA	1.35	U	NA	0.44	U
C2-Fluoranthenes/Pyrenes	0.44	U	NA	1.35	U	NA	1.35	U	NA	0.44	U
C3-Fluoranthenes/Pyrenes	0.44	U	NA	1.35	U	NA	1.35	U	NA	0.44	U
Benzo(a)anthracene	466.38		93	1434.42		93	1368.53		89	0.69	U
Chrysene	467.52		93	1447.34		94	1385.71		90	0.37	U
C1-Chrysenes	0.37	U	NA	1.13	U	NA	1.13	U	NA	0.37	U
C2-Chrysenes	0.37	U	NA	1.13	U	NA	1.13	U	NA	0.37	U
C3-Chrysenes	0.37	U	NA	1.13	U	NA	1.13	U	NA	0.37	U
C4-Chrysenes	0.37	U	NA	1.13	U	NA	1.13	U	NA	0.37	U
Benzo(b)fluoranthene	456.45		91	1398.10		91	1354.66		88	0.43	U
Benzo(k)fluoranthene	458.55		92	1408.51		92	1333.50		87	0.43	U
Benzo(e)pyrene	404.89		82	1251.12		82	1188.80		78	0.45	U
Benzo(a)pyrene	440.30		88	1348.53		88	1269.82		82	0.65	U
Perylene	399.28		80	1197.11		78	1158.92		75	0.70	U
Indeno(1,2,3-cd)pyrene	422.43		84	1254.97		81	1235.79		80	0.80	J
Dibenz(a,h)anthracene	456.49		91	1395.33		91	1356.43		88	1.04	U
Benzo(g,h,i)perylene	342.98		69	1035.28		67	1012.59		66	1.31	
Total Priority Pollutant PAHs											
Naphthalene-d8	74			69			72			76	
Phenanthrene-d10	77			72			73			75	
Chrysene-d12	90			88			86			91	

# PCBs

CLIENT SAMPLE ID:	NAV- PR5-SDB2- FF	NAV- PR5-SDB2- COMP	NAV- PR6-SDB2- FF	NAV- PR6-SDB2- COMP	NAV- OF9-SDB2- FF	NAV- OF9-SDB2- COMP	NAV- OF11-SDB2- FF	NAV- OF11-SDB2- COMP	NAV- OF14-SDB2- FF	NAV- OF14-SDB2- COMP	
Battelle Sample ID:	U7089	U7091	U7090	U7092	U7083	U7086	U7084	U7087	U7085	U7088	
Battelle Batch ID:	03-0203	03-0203	03-0203	03-0203	03-0203	03-0203	03-0203	03-0203	03-0203	03-0203	
Data File:	sc0382.49.1	sc0382.51.1	sc0382.50.1	sc0382.52.1	sc0382.39.1	sc0382.44.1	sc0382.42.1	sc0382.47.1	sc0382.45.1	sc0382.48.1	
Extraction Date:	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	3/04/03	
Acquired Date:	3/19/03	3/19/03	3/19/03	3/19/03	3/18/03	3/18/03	3/18/03	3/18/03	3/18/03	3/18/03	
Matrix:	Water	Water	Water	Water	Water	Water	Water	Water	Water	Water	
Sample Volume (L):	2.620	2.640	2.660	2.660	1.350	2.660	2.660	2.660	2.660	2.620	
Dilution Factor:	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	
Pre Injection Volume (µL):	300	300	300	300	300	300	300	300	300	300	
Minimum Reporting Limit (ng/L):	0.191	0.189	0.188	0.188	0.370	0.188	0.188	0.188	0.188	0.191	
Units:	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	
C12 08	1.833 U	11.781 NC	1.805 U	1.805 U	3.557 U	1.805 U	1.805 U	1.805 U	1.805 U	0.277 NC	15.762
C13 18	0.159 U	0.157 U	7.223 U	0.156 U	2.993 U	2.485 U	6.150 U	0.156 U	0.156 U	0.159 U	
C13 28	0.198 U	0.197 U	0.195 U	0.195 U	0.385 U	0.195 U	0.195 U	0.195 U	0.195 U	0.198 U	
C14 44	0.634 U	0.521 U	0.663 U	0.546 U	0.323 U	2.330 U	4.776 NC	0.649 U	1.120 U	0.166 U	
C14 49	0.170 U	0.169 U	0.168 U	0.168 U	0.330 U	0.168 U	11.503 NC	0.168 U	0.168 U	0.170 U	
C14 52	0.164 U	0.163 U	0.162 U	0.162 U	0.319 U	1.088 NC	0.162 U	0.162 U	0.162 U	0.164 U	
C14 66	0.171 U	0.169 U	0.168 U	0.168 U	0.331 U	0.168 U	0.168 U	0.168 U	0.168 U	0.171 U	
C14 77	0.243 U	0.489 NC	0.239 U	1.887 NC	1.361 NC	1.565 NC	3.689 NC	1.640 NC	1.375 U	1.171 NC	
C15 87	0.177 NC	0.350 NC	0.127 U	0.152 NC	0.704 U	0.894 U	4.045 NC	0.232 NC	0.848 U	0.940 NC	
C15 101	0.131 U	0.922 NC	0.129 U	1.659 NC	2.055 NC	2.818 U	11.255 U	1.184 U	3.290 U	0.131 U	
C15 105	0.066 U	0.065 U	0.065 U	0.065 U	0.353 NC	1.513 U	2.188 NC	0.167 NC	1.153 U	0.215 NC	
C15 114	0.113 U	0.112 U	0.111 U	0.111 U	0.219 U	0.111 U	1.623 U	0.111 U	0.111 U	0.113 U	
C15 118	2.355 U	1.733 NC	3.206 NC	3.620 NC	0.808 NC	1.753 NC	5.469 NC	0.333 NC	3.117 NC	0.374 NC	
C15 123	0.113 U	0.112 U	0.111 U	0.111 U	0.219 U	0.111 U	0.111 U	0.111 U	0.111 U	0.113 U	
C15 126	0.141 U	0.140 U	0.139 U	0.139 U	0.273 U	0.139 U	0.139 U	0.139 U	0.139 U	0.141 U	
C16 128	0.160 U	0.485 NC	0.508 NC	0.893 NC	1.336 NC	1.265 NC	4.836 NC	0.597 NC	2.128 NC	1.203 NC	
C16 138	0.321 NC	0.814 NC	0.133 NC	0.504 U	2.362 U	3.719 NC	17.547 NC	1.316 NC	3.099 NC	1.803 NC	
C16 153	0.122 U	0.231 U	0.120 U	1.069 U	1.883 U	5.412 U	21.543 NC	1.226 U	3.269 U	1.728 U	
C16 156	0.137 U	0.136 U	0.135 U	0.130 U	0.265 U	0.226 U	0.786 U	0.135 U	0.612 U	0.137 U	
C16 157	0.137 U	0.136 U	0.135 U	0.135 U	0.265 U	0.135 U	0.135 U	0.135 U	0.135 U	0.137 U	
C16 167	0.137 U	0.426 U	0.135 U	0.389 U	1.059 U	2.020 U	5.665 U	0.889 U	3.229 U	0.137 U	
C16 169	0.109 U	0.109 U	0.238 NC	0.108 U	0.212 U	0.108 U	0.108 U	0.108 U	0.108 U	0.109 U	
C17 170	0.116 U	0.115 U	0.290 NC	0.114 U	0.861 U	1.424 U	8.071 NC	0.420 U	0.473 U	0.216 U	
C17 180	0.110 U	0.109 U	0.427 U	0.108 U	2.074 U	3.483 U	18.727 NC	1.264 U	1.565 U	0.110 U	
C17 183	0.107 U	0.106 U	0.105 U	0.105 U	0.207 U	0.466 U	5.751 NC	0.105 U	0.105 U	0.107 U	
C17 184	0.105 U	0.104 U	0.104 U	0.104 U	0.204 U	0.104 U	0.104 U	0.104 U	0.119 NC	0.105 U	
C17 187	0.099 U	0.182 U	0.097 U	0.384 U	0.694 U	0.887 U	7.818 U	0.345 U	0.466 U	0.247 U	
C17 189	0.108 U	0.107 U	0.106 U	0.106 U	0.209 U	0.106 U	0.106 U	0.106 U	0.106 U	0.108 U	
C18 195	0.124 U	0.123 U	0.122 U	0.122 U	0.241 U	0.236 NC	1.453 NC	0.061 NC	0.122 U	0.095 NC	
C19 206	0.139 U	0.138 U	0.371 U	0.137 U	0.270 U	0.137 U	2.957 U	0.137 U	0.457 U	0.139 U	
C10 209	0.702 U	0.772 U	0.593 U	0.143 U	1.427 NC	0.143 U	6.227 U	0.143 U	1.794 U	0.145 U	
Total PCB	4.190	18.281	13.652	10.846	18.911	31.563	144.788	9.432	25.162	23.753	
Surrogate Recoveries:											
C13(34)	80	79	75	83	86	81	91	91	85	82	
C15(112)	79	80	71	80	78	76	93	81	78	82	

## PCBs QA/QC

**PROJECT:** SPAWAR TO0011, Contaminant Analysis of Stormwater and San Diego Bay Seawater  
**PARAMETER:** PCB Congener  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** The water samples were collected on February 25, 2003. They were received in Duxbury on February 28, 2003 in good condition in six coolers. The cooler temperature on arrival ranged from 0.2 °C to 1.3 °C. Samples were stored at 4 °C until processing.

### QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	LCS/MS Recovery	Sample Replicate Relative Precision	Procedural Blank
PAH	General NS&T	30-130% Recovery	LCS: 40-120% Recovery for at least 80% of analytes  MS: 50-150% Recovery for at least 70% of analytes; analyte conc. in MS must be >5x background	≤30% RSD  analyte conc. in MS must be <5x background	<3X MDL

**METHOD:** Water samples were extracted for PCB Congener following general NS&T methods. Full water samples were spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with Recovery Internal Standard (RIS) and split for analysis. Extracts were analyzed using gas chromatography/electron capture detection (GC/ECD), following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch.

Samples were extracted with in the 7-day holding time for waters. Extracts were analyzed within the 40-day holding time for extracts

<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
03-0203	3/4/2003	3/17/2003 – 3/22/2003

**BLANKS:** A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.

**03-0203** – No analytes identified at greater than 3X the MDL.

**LABORATORY CONTROL SAMPLE:** **Comments** – None.  
A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB Congeners were calculated to measure data quality in terms of accuracy.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

**Comments** – None.

A matrix spike (MS)/matrix spike duplicate (MSD) pair was prepared with each analytical batch. The percent recoveries of target PCB Congeners were calculated to measure data quality in terms of accuracy; the relative percent difference between the pair was calculated to measure data quality in terms of precision.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client. The relative percent differences between the MS and MSD recoveries were within the laboratory control limits for all target PCB Congeners.

**SURROGATES:**

**Comments** – None.

Two surrogate compounds were added prior to extraction, including PCB34 and PCB112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**03-0203** – All surrogate percent recoveries were within the laboratory control limits specified by the client.

**Samples:**

**Comments** – None.

The condition of the confirmation column was in question after the analysis. It was decided to report all “hits” from the primary column regardless if confirmed or not confirmed. The analytes are appropriately flagged if reported, but not confirmed.

## PCBs QA/QC (CONT.)

CLIENT SAMPLE ID:	LABORATORY CONTROL SAMPLE		MATRIX SPIKE-NAV-OF9-SDB2-FF		MATRIX SPIKE DUPLICATE-NAV-OF9-SDB2-FF				PROCEDURAL BLANK	
Battelle Sample ID:	BB593LCS		U7083MS		U7083MSD				BB592PB	
Battelle Batch ID:	03-0203		03-0203		03-0203				03-0203	
Data File:	sc0382.38.1		sc0382.40.1		sc0382.41.1				sc0382.37.1	
Extraction Date:	3/04/03		3/04/03		3/04/03				3/04/03	
Acquired Date:	3/17/03		3/18/03		3/18/03				03/17/03	
Matrix:	Water		Water		Water				Water	
Sample Volume (L):	2.000		1.175		1.175				2.000	
Dilution Factor:	1.667		1.667		1.667				1.667	
Pre Injection Volume (µL):	300		300		300				300	
Minimum Reporting Limit (ng/L):	0.250		0.426		0.426				0.250	
Units:	ng	% Recovery	ng/L	% Recovery	ng/L	% Recovery	% RPD		ng/L	
CI2 08	20.509	68	17.345	68	20.449	80	16		2.401	U
CI3 18	21.498	72	19.854	66	20.959	70	6		0.208	U
CI3 28	35.064	117	21.372	84	25.258	99	17		0.260	U
CI4 44	25.535	85	21.262	83	23.531	92	10		0.218	U
CI4 49	25.348	84	24.907	97	25.302	99	2		0.223	U
CI4 52	24.280	81	20.705	81	21.345	84	3		0.215	U
CI4 66	27.632	92	22.603	89	25.267	99	11		0.224	U
CI4 77	24.023	80	20.028	73	22.256	82	11		0.318	U
CI5 87	24.470	82	20.388	77	21.738	82	7		0.169	U
CI5 101	25.400	85	21.352	76	23.998	86	13		0.172	U
CI5 105	26.157	87	20.806	80	21.916	84	5		0.086	U
CI5 114	NA	NA	NS	NA	NS	NA	NA		0.148	U
CI5 118	23.286	78	19.969	75	21.834	82	9		0.130	U
CI5 123	NA	NA	NS	NA	NS	NA	NA		0.148	U
CI5 126	28.227	94	19.566	77	20.869	82	6		0.184	U
CI6 128	26.487	88	23.105	85	21.485	79	8		0.210	U
CI6 138	25.310	84	22.841	80	24.760	88	9		0.199	U
CI6 153	22.656	76	22.155	79	23.904	86	8		0.160	U
CI6 156	NA	NA	NS	NA	NS	NA	NA		0.179	U
CI6 157	NA	NA	NS	NA	NS	NA	NA		0.179	U
CI6 167	NA	NA	NS	NA	NS	NA	NA		0.179	U
CI6 169	28.949	96	23.429	91	25.035	98	7		0.143	U
CI7 170	25.778	86	22.468	85	24.052	91	7		0.152	U
CI7 180	25.907	86	23.798	85	26.011	94	10		0.144	U
CI7 183	25.158	84	21.384	84	22.322	87	4		0.140	U
CI7 184	23.828	79	19.885	78	20.606	80	4		0.138	U
CI7 187	23.085	77	19.872	75	20.867	79	5		0.129	U
CI7 189	NA	NA	NS	NA	NS	NA	NA		0.141	U
CI8 195	25.317	84	20.354	80	21.844	86	7		0.163	U
CI9 206	23.978	80	20.081	79	21.885	86	9		0.183	U
CI10 209	23.396	78	18.226	66	19.594	71	8		0.190	U
Total PCB	631.280	NA	527.755	NA	567.085	NA	NA		0.000	
Surrogate Recoveries:										
CI3(34)	84		90		99				78	
CI5(112)	78		74		77				78	

## SDB4- 10/17/2004

### METALS

SAMPLE ID	DISSOLVED Cu (µg/L)	TOTAL Cu (µg/L)	DISSOLVED Zn (µg/L)	TOTAL Zn (µg/L)
NAV-BAY SDB4 PRE	3.0	3.5	9.5	12
NAV-OF11-SDB4-FF	89	244	2453	3631
NAV-BAY14-SDB4-DUR	14	21	182	238

### TSS

SAMPLE LABEL	TSS (mg/L)
NAV-OF14-SDB4-FF	838.75
NAV-BAY14-SDB4-DUR	20.66



## SDB45- 10/26/2004

### METALS

MSL Code	Rep	Sponsor I.D.	Al (µg/L) ICP-OES	Fe (µg/L) ICP-OES	Cr (µg/L) ICP-MS	Mn (µg/L) ICP-OES	Ni (µg/L) ICP-MS	Cu (µg/L) ICP-MS
<b>SAMPLE RESULTS</b>								
2173*27		NAV-OF14-SD45-FF	1322	2138	6.93	66.2	7.19	45.3
2173*28		NAV-OF14-SD45-FF (F)	14.7	26.4	2.22	29.2	3.67	18.9
2173*29		NAV-OF14-SD45-COMP	2618	4481	12.9	71.5	4.81	38.0
2173*30		NAV-OF14-SD45-COMP (F)	17.7	25.0	9.99	13.2	1.66	9.89
2173*31		NAV-OF14-SD45-Blank (F)	3.36	U 2.51	U 0.724	0.025	U 0.009	U 0.008

MSL Code	Rep	Sponsor I.D.	Zn (µg/L) ICP-MS	As (µg/L) ICP-MS	Se (µg/L) ICP-MS	Ag (µg/L) ICP-MS	Cd (µg/L) ICP-MS	Sn (µg/L) ICP-MS	Pb (µg/L) ICP-MS	Hg (µg/L) CVAF
<b>SAMPLE RESULTS</b>										
2173*27		NAV-OF14-SD45-FF	362	3.20	1.30	0.0741	1.18	0.663	21.7	0.0629
2173*28		NAV-OF14-SD45-FF (F)	175	2.04	0.848	0.00601	0.492	0.50	U 0.493	0.00597
2173*29		NAV-OF14-SD45-COMP	220	2.39	0.530	0.0632	0.871	0.536	21.6	0.0694
2173*30		NAV-OF14-SD45-COMP (F)	68.4	1.72	0.356	0.00378	0.244	0.50	U 0.441	0.00330
2173*31		NAV-OF14-SD45-Blank (F)	0.0713	0.015	U 0.101	U 0.002	U 0.002	U 0.50	U 0.00266	0.000510

SAMPLE ID	DISSOLVED COPPER (µg/L)	TOTAL COPPER (µg/L)	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
NAV-BAY-SD45-PRE	3.94	6.97	7.79	8.42
NAV-BAY14-SD45-DUR 1	4.32	7.05	10.21	12.79
NAV-BAY14-SD45-DUR 2	4.32	6.19	9.15	9.26
NAV-BAY14-SD45-DUR 3	4.55	6.82	9.06	9.51
NAV-BAY14-SD45-DUR 4	3.32	5.89	7.70	8.60
NAV-BAY14-SD45-AFT 1	3.41	6.05	8.07	8.98
NAV-BAY14-SD45-AFT 2	3.66	5.97	7.89	8.98
NAV-BAY14-SD45-AFT 3	3.98	6.26	10.08	11.22

## METALS QA/QC

**PROGRAM:** SPAWAR, Task 16  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/OES	50-150%	±20%	±50%	50.0
Iron	ICP/OES	50-150%	±20%	±50%	10.0
Manganese	ICP/OES	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Five (5) samples were analyzed: ten (10) metals; chromium (Cr), nickel (Ni), copper, (Cu), zinc (Zn), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1638m, aluminum (Al), iron (Fe), and manganese (Mn) by inductively coupled plasma optic emission spectroscopy following EPA Method 200.7 and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. Samples were analyzed by EPA Method 1638m. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Five (5) samples were received on 10/29/2004 and were logged into Battelle's sample tracking system. Five samples were analyzed within the six month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:

### QA/QC SUMMARY/METALS - PRISM Task 16 (continued)

Task	Date Performed
Hg	11/16/04
ICP-MS	11/29/04 & 12/8/04
ICP-OES	11/21/04

<b>DETECTION LIMITS</b>	The target detection limit was met for all metals. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.
<b>METHOD BLANKS</b>	One method blank was analyzed with this batch of samples. Results were less than 5 times the MDL for all metals.
<b>BLANK SPIKES</b>	One sample of reagent water was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.
<b>MATRIX SPIKES</b>	One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.
<b>REPLICATES</b>	One sample was analyzed in duplicate. All results were within the project criteria.
<b>SRM</b>	<p>Two matrix-appropriate standard reference materials (SRM) were analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.</p> <p>SRM 1640 has 22 certified metals. Recovery for all metals reported were within the control limit of <math>\pm 20\%</math> of the certified value, except Se that had a % difference of 21%. All other QC for this metal were within acceptable criteria. No corrective action was taken. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of <math>\pm 25\%</math> of the certified value.</p>
<b>REFERENCES</b>	EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4- 91-010. Environmental Services Division, Monitoring Management Branch.

## METALS QA/QC (CONT.)

MSL Code	Rep	Sponsor I.D.	Al (µg/L) ICP-OES	Fe (µg/L) ICP-OES	Cr (µg/L) ICP-MS	Mn (µg/L) ICP-OES	Ni (µg/L) ICP-MS	Cu (µg/L) ICP-MS
<b>PROCEDURAL BLANK</b>			3.36	2.51	0.018	0.025	0.009	0.008
<b>METHOD DETECTION LIMIT</b>			3.36	2.51	0.018	0.025	0.009	0.008
<b>Project Target Detection Limit</b>			50.0	10.0	1.00	0.50	0.05	0.05
<b>STANDARD REFERENCE MATERIAL</b>								
1640			50.5	36.0	39.9	121	28.5	88.8
1640		certified value	52.0	34.3	38.6	122	27.4	85.2
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2
		% difference	3%	5%	3%	1%	4%	4%
1641d			NA	NA	NA	NA	NA	NA
1641d		certified value	NC	NC	NC	NC	NC	NC
1641d		range	NC	NC	NC	NC	NC	NC
		% difference	N/A	N/A	N/A	N/A	N/A	N/A
<b>ICV,CCV RESULTS</b>								
ICV			99%	104%	104%	100%	103%	104%
CCV			98%	102%	103%	95%	102%	103%
CCV			99%	103%	106%	95%	101%	104%
CCV			NA	NA	107%	NA	103%	104%
<b>BLANK SPIKE RESULTS</b>								
		Amount Spiked	100	50.0	10.0	50.0	10.0	10.0
		Blank	3.36	2.51	0.018	0.03	0.01	0.008
		Blank + Spike	98.6	53.1	10.9	51.8	9.64	9.83
		Amount Recovered	98.6	53.1	10.9	51.8	9.64	9.83
		Percent Recovery	99%	106%	109%	104%	96%	98%
<b>MATRIX SPIKE RESULTS</b>								
		Amount Spiked	250	200	NS	50.0	NS	NS
		NAV-OF14-SD45-FF (F)	14.7	26.4	N/A	29.2	N/A	N/A
		NAV-OF14-SD45-FF (F) + Spike	258	238	NA	79.5	NA	NA
		Amount Recovered	243	212	N/A	50.3	N/A	N/A
		Percent Recovery	97%	106%	N/A	101%	N/A	N/A
		Amount Spiked	NS	NS	50.0	NS	10.0	50.0
		NAV-OF14-SD45-COMP	N/A	N/A	12.9	N/A	4.81	38.0
		NAV-OF14-SD45-COMP + Spike	NA	NA	65.4	NA	15.0	88.7
		Amount Recovered	N/A	N/A	52.5	N/A	10.2	50.7
		Percent Recovery	N/A	N/A	105%	N/A	102%	101%
		Amount Spiked	NS	NS	NS	NS	NS	NS
		NAV-OF14-SD45-COMP (F)	N/A	N/A	N/A	N/A	N/A	N/A
		NAV-OF14-SD45-COMP (F) + Spike	NA	NA	NA	NA	NA	NA
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A
MSL Code	Rep	Sponsor I.D.	Al (µg/L) ICP-OES	Fe (µg/L) ICP-OES	Cr (µg/L) ICP-MS	Mn (µg/L) ICP-OES	Ni (µg/L) ICP-MS	Cu (µg/L) ICP-MS
<b>REPLICATE RESULTS</b>								
2173*27	1	NAV-OF14-SD45-FF	1322	2138	6.93	66.2	7.19	45.3
2173*27	2	NAV-OF14-SD45-FF	NA	NA	7.22	NA	7.14	44.9
		RPD	N/A	N/A	4%	N/A	1%	1%
2173*28	1	NAV-OF14-SD45-FF (F)	14.7	26.4	2.22	29.2	3.67	18.9
2173*28	2	NAV-OF14-SD45-FF (F)	14.9	31.2	NA	29.4	NA	NA
		RPD	1%	17%	N/A	1%	N/A	N/A

## METALS QA/QC (CONT.)

MSL Code	Rep	Sponsor I.D.	Zn (µg/L) ICP-MS	As (µg/L) ICP-MS	Se (µg/L) ICP-MS	Ag (µg/L) ICP-MS	Cd (µg/L) ICP-MS	Sn (µg/L) ICP-MS	Pb (µg/L) ICP-MS	Hg (µg/L) CVAF
PROCEDURAL BLANK			0.028 U	0.015 U	0.101 U	0.002 U	0.002 U	0.50 U	0.001 U	0.00012 U
METHOD DETECTION LIMIT			0.028	0.015	0.101	0.002	0.002	NA	0.001	0.00012
Project Target Detection Limit			0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01
STANDARD REFERENCE MATERIAL										
1640			61.2	29.8	26.6	7.78	24.5	1.68	29.4	NA
1640		certified value	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC
1640		range	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC
		% difference	15%	12%	21% #	2%	7%	N/A	5%	N/A
1641d			NA	NA	NA	NA	NA	NA	NA	1641
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	1590
1641d		range	NC	NC	NC	NC	NC	NC	NC	±4.00
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	3%
ICV,CCV RESULTS										
ICV			103%	104%	102%	103%	103%	100%	105%	99%
CCV			101%	104%	103%	104%	104%	105%	107%	100%
CCV			101%	103%	103%	102%	102%	104%	106%	NA
CCV			102%	103%	103%	102%	100%	103%	106%	NA
BLANK SPIKE RESULTS										
		Amount Spiked	10	10.0	10.0	10.0	10.0	0.100	10.0	0.00506
		Blank	0.028 U	0.015 U	0.101 U	0.002 U	0.002 U	0.50 U	0.001 U	0.00012 U
		Blank + Spike	8.66	9.22	8.87	9.71	9.34	0.111	10.3	0.00534
		Amount Recovered	8.66	9.22	8.87	9.71	9.34	0.111	10.3	0.00522
		Percent Recovery	87%	92%	89%	97%	93%	111%	103%	103%
MATRIX SPIKE RESULTS										
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	NS
		NAV-OF14-SD45-FF (F)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		NAV-OF14-SD45-FF (F) + Spike	NA	NA	NA	NA	NA	NA	NA	NA
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	50.0	10.0	10.0	10.0	10.0	1.00	50.0	NS
		NAV-OF14-SD45-COMP	220	2.39	0.530	0.0632	0.871	0.536	21.6	N/A
		NAV-OF14-SD45-COMP + Spike	270	12.9	10.8	10.0	10.9	1.43	73.5	NA
		Amount Recovered	50.0	10.5	10.3	9.9	10.0	0.894	51.9	N/A
		Percent Recovery	100%	105%	103%	99%	100%	89%	104%	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0298
		NAV-OF14-SD45-COMP (F)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00331
		NAV-OF14-SD45-COMP (F) + Spike	NA	NA	NA	NA	NA	NA	NA	0.0349
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0316
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	106%
MSL Code	Rep	Sponsor I.D.	Zn (µg/L) ICP-MS	As (µg/L) ICP-MS	Se (µg/L) ICP-MS	Ag (µg/L) ICP-MS	Cd (µg/L) ICP-MS	Sn (µg/L) ICP-MS	Pb (µg/L) ICP-MS	Hg (µg/L) CVAF
REPLICATE RESULTS										
2173*27	1	NAV-OF14-SD45-FF	362	3.20	1.30	0.0741	1.18	0.663	21.7	0.0629
2173*27	2	NAV-OF14-SD45-FF	362	3.32	1.27	0.0743	1.15	0.631	21.3	NA
		RPD	0%	4%	2%	0%	3%	5%	2%	N/A
2173*28	1	NAV-OF14-SD45-FF (F)	175	2.04	0.848	0.00601	0.492	0.0371	0.493	0.00597
2173*28	2	NAV-OF14-SD45-FF (F)	NA	NA	NA	NA	NA	NA	NA	0.00572
		RPD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4%

# PAHs

CLIENT ID	NAV- OF14-SD45-FF		NAV- OF14-SD45-COMP	
Battelle ID	S5983-P		S5984-P	
Sample Type	SA		SA	
Collection Date	10/27/04		10/27/04	
Extraction Date	11/02/04		11/02/04	
Analysis Date	01/04/05		11/17/04	
Analytical Instrument	MS		MS	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	1.64		2.63	
Size Unit-Basis	L LIQUID		L LIQUID	
Units	NG/L LIQUID		NG/L LIQUID	
Naphthalene	11.28	T	9.23	
C1-Naphthalenes	7.37	T	7.37	
C2-Naphthalenes	16.31	T	0.5	U
C3-Naphthalenes	158.2	T	0.5	U
C4-Naphthalenes	21.76	T	0.5	U
2-Methylnaphthalene	6.93	T	5.32	
1-Methylnaphthalene	4.34	JT	3.62	
Biphenyl	4.46	JT	2.5	J
2,6-dimethylnaphthalene	4.36	JT	0.63	U
Acenaphthylene	3.23	JT	2	J
Acenaphthene	4.19	JT	1.67	J
2,3,5-trimethylnaphthalene	5.44	JT	0.44	U
Fluorene	5.97	JT	3.03	J
C1-Fluorenes	9.55	T	0.52	U
C2-Fluorenes	115.68	T	0.52	U
C3-Fluorenes	68.19	T	0.52	U
Anthracene	6.17	JT	0.38	U
Phenanthrene	64.76	T	41.97	
C1-Phenanthrenes/Anthracene	45.92	T	36.23	
C2-Phenanthrenes/Anthracene	105.52	T	76.88	
C3-Phenanthrenes/Anthracene	54.03	T	65.96	
C4-Phenanthrenes/Anthracene	32.13	T	0.82	U
1-Methylphenanthrene	12.92	T	8.5	
Dibenzothiophene	11.03	T	7.54	
C1-Dibenzothiophenes	78.5	T	0.38	U
C2-Dibenzothiophenes	54.81	T	54.93	
C3-Dibenzothiophenes	62.53	T	72.57	
C4-Dibenzothiophenes	41.57	T	0.38	U
Fluoranthene	95.74	T	63.01	
Pyrene	97.66	T	60.55	
C1-Fluoranthenes/Pyrenes	41.41	T	40.49	
C2-Fluoranthenes/Pyrenes	59.33	T	0.68	U
C3-Fluoranthenes/Pyrenes	57.53	T	0.68	U
Benzo(a)anthracene	23.09	T	12.25	
Chrysene	71.52	T	48.34	
C1-Chrysenes	56.41	T	38.79	
C2-Chrysenes	73.5	T	54.85	
C3-Chrysenes	74.63	T	0.45	U
C4-Chrysenes	1.79	UT	0.45	U
Benzo(b)fluoranthene	43.83	T	30.59	
Benzo(k)fluoranthene	34.62	T	26.34	
Benzo(e)pyrene	48.6	T	33.67	
Benzo(a)pyrene	31.31	T	17.58	
Perylene	12.59	T	9.35	
Indeno(1,2,3-cd)pyrene	33.58	T	22.7	
Dibenz(a,h)anthracene	7.22	T	3.93	
Benzo(g,h,i)perylene	62.28	T	43.59	
Total Priority Pollutant PAHs	596.45		387.16	
Naphthalene-d8	66		60	
Phenanthrene-d10	85		84	
Chrysene-d12	82		78	

## PAHs QA/QC

**PROJECT:** Task Order TO0016 – YO817 Stormwater FY04  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 10/27/04. The samples were received at Battelle Duxbury on 10/29/04. Upon arrival, the cooler temperature was recorded at 1.7°C. No custody issues were noted. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0432, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PAH	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.47 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds. Initial analysis of sample S5983 yielded low surrogate recoveries. This was due to a concentration issue as noted in the sample preparation records. The archived non-fractionated extract for this sample was re-processed through the HPLC, concentrated, fortified with RIS and sent to GC/MS for PAH analysis only. Results from the second analysis have been reported.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection. All extracts were analyzed within the 40-day holding time, except for S5983. The data that was reported for this sample came from the second analysis, as noted above, which occurred outside of the 40-day holding time.

Batch	Extraction Date	Analysis Date
04-0432	11/2/04	11/16/04 – 11/17/04; reanalysis 1/4/05

**BLANK:** One procedural blank (PB) sample was prepared with the analytical batch. The procedural blank was analyzed to ensure the sample extraction and analysis methods were free of contamination.

**04-0432** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank except for Naphthalene. Naphthalene was detected at a concentration greater than the MDL, yet less than the RL. The data was qualified with an “J”. Any field concentration for this target analyte, that was not greater than five times the concentration detected in the PB, was qualified with a “B”. This resulted in Naphthalene data for sample S5991 (Duxbury Bay Water) being qualified with a “B”.

**LABORATORY  
CONTROL  
SAMPLE:**

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits.

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair was prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**04-0432** – All target analytes were recovered within the laboratory control limits. All RPDs were within the laboratory control limits.

**Comments** – None.

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Note: At the time of extraction, no certified second source material was available. In lieu of a certified second source, the SRM sample was generated by spiking target analyte solution into a clean seawater sample from Duxbury Bay. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including Naphthalene-d8, Phenanthrene-d10, and Chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**04-0432** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery).

**Comments** – After initial analysis Naphthalene-d8 was under-recovered in sample S5983 (OF14-SD45-FF). In the sample preparation records, an issue was noted regarding the concentration step after HPLC clean-up. It was determined that this sample was blow down too quickly on the N-evaporator. The archived portion of the extract was re-fractionated and re-analyzed. Since all SIS recoveries were acceptable in the second analysis, these results are reported.





# PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE-NAV-OF14-SD45-FF			MATRIX SPIKE DUPLICATE-NAV-OF14-SD45-FF			PROCEDURAL BLANK	
Battelle ID	BF359LCS-P			S5983MS-P			S5983MSD-P			BF358PB-P	
Sample Type	LCS			MS			MSD			PB	
Collection Date	11/02/04			10/27/2004			10/27/2004			11/02/04	
Extraction Date	11/02/04			11/2/2004			11/2/2004			11/02/04	
Analysis Date	11/16/04			11/17/2004			11/17/2004			11/16/04	
Analytical Instrument	MS			MS			MS			MS	
% Moisture	NA			NA			NA			NA	
% Lipid	NA			NA			NA			NA	
Matrix	LIQUID			LIQUID			WATER			LIQUID	
Sample Size	2.00			0.5			0.5			2.00	
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID			L LIQUID	
Units	NG/L LIQUID		% Recovery	NG/L LIQUID		% Recovery	NG/L LIQUID		% Recovery	NG/L LIQUID	
Naphthalene	635.23		63	2426.22		60	2348.43		58	1.84	J
C1-Naphthalenes	0.66	U		3672.35			3591.42			0.66	U
C2-Naphthalenes	0.66	U		2.65	U		2.65	U		0.66	U
C3-Naphthalenes	0.66	U		2.65	U		2.65	U		0.66	U
C4-Naphthalenes	0.66	U		2.65	U		2.65	U		0.66	U
2-Methylnaphthalene	706.72		71	2767.73		69	2715.61		68	0.47	U
1-Methylnaphthalene	626.85		63	2507.63		63	2441.57		61	0.5	U
Biphenyl	673.04		67	2704.17		67	2645.34		66	0.62	U
2,6-dimethylnaphthalene	715.93		72	2879.07		72	2845.32		71	0.83	U
Acenaphthylene	674.62		67	2745.32		69	2689.21		67	0.7	U
Acenaphthene	679.43		68	2808.53		70	2751.59		69	0.75	U
2,3,5-trimethylnaphthalene	734.65		73	3058.87		76	3003.23		75	0.58	U
Fluorene	712.63		71	3026.87		75	3016.1		75	0.68	U
C1-Fluorenes	0.68	U		2.72	U		2.72	U		0.68	U
C2-Fluorenes	0.68	U		2.72	U		2.72	U		0.68	U
C3-Fluorenes	0.68	U		2.72	U		2.72	U		0.68	U
Anthracene	807.28		81	3399.95		85	3402.93		85	0.51	U
Phenanthrene	774.53		77	3340.67		82	3296.59		81	1.08	U
C1-Phenanthrenes/Anthracene	1.08	U		4.32	U		4.32	U		1.08	U
C2-Phenanthrenes/Anthracene	1.08	U		4.32	U		4.32	U		1.08	U
C3-Phenanthrenes/Anthracene	1.08	U		4.32	U		4.32	U		1.08	U
C4-Phenanthrenes/Anthracene	1.08	U		4.32	U		4.32	U		1.08	U
1-Methylphenanthrene	834.72		83	3505.36		87	3490.79		87	0.61	U
Dibenzothiophene	0.5	U		57.47			55.56			0.5	U
C1-Dibenzothiophenes	0.5	U		2.01	U		2.01	U		0.5	U
C2-Dibenzothiophenes	0.5	U		134.99			116.79			0.5	U
C3-Dibenzothiophenes	0.5	U		138.25			122.43			0.5	U
C4-Dibenzothiophenes	0.5	U		2.01	U		2.01	U		0.5	U
Fluoranthene	866.46		87	3567.22		87	3516.93		85	0.77	U
Pyrene	878.52		88	3591.63		87	3584.54		87	0.9	U
C1-Fluoranthenes/Pyrenes	0.9	U		60.32			55.66			0.9	U
C2-Fluoranthenes/Pyrenes	0.9	U		3.59	U		3.59	U		0.9	U
C3-Fluoranthenes/Pyrenes	0.9	U		3.59	U		3.59	U		0.9	U
Benzo(a)anthracene	948.49		95	3474.22		86	3527.93		88	1.36	U
Chrysene	900.23		90	3393.36		83	3409.71		83	0.59	U
C1-Chrysenes	0.59	U		64.31			61.27			0.59	U
C2-Chrysenes	0.59	U		95.62			81.94			0.59	U
C3-Chrysenes	0.59	U		2.36	U		2.36	U		0.59	U
C4-Chrysenes	0.59	U		2.36	U		2.36	U		0.59	U
Benzo(b)fluoranthene	931.17		93	3566.1		88	3600.42		89	1.16	U
Benzo(k)fluoranthene	528.84		53	4035.04		100	4090.67		101	1.31	U
Benzo(e)pyrene	955.65		96	3761.95		93	3764.49		93	0.51	U
Benzo(a)pyrene	918.28		92	3621.84		90	3606.61		89	1	U
Perylene	912.89		91	3636.06		91	3677.71		92	1.93	U
Indeno(1,2,3-cd)pyrene	964.78		96	3732.44		92	3795.29		94	0.99	U
Dibenz(a,h)anthracene	969.69		97	3850.92		96	3797.73		95	0.84	U
Benzo(g,h,i)perylene	929.97		93	3781.88		93	3821.02		94	0.99	U
<b>Surrogate Recoveries (%)</b>											
Naphthalene-d8	67			60			59			78	
Phenanthrene-d10	78			83			83			87	

# PCBs

CLIENT ID	NAV- OF14-SD45-FF		NAV- OF14-SD45-COMP	
Battelle ID	S5983-P		S5984-P	
Sample Type	SA		SA	
Collection Date	10/27/04		10/27/04	
Extraction Date	11/02/04		11/02/04	
Analysis Date	12/13/04		12/14/04	
Analytical Instrument	MS		MS	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	1.64		2.63	
Size Unit-Basis	L_LIQUID		L_LIQUID	
Units	NG/L_LIQUID		NG/L_LIQUID	
CI2(8)	0.11	UT	0.07	UT
CI3(18)	0.13	UT	0.08	UT
CI3(28)	0.13	UT	0.08	UT
CI4(44)	3.63	JT	0.15	UT
CI4(49)	0.23	UT	0.15	UT
CI4(52)	6.26	T	2.37	JT
CI4(66)	1.56	JT	0.69	JT
CI4(77)	0.23	UT	0.14	UT
CI5(87)	7.29	T	2.29	JT
CI5(101)	11.76	T	4.58	T
CI5(105)	5.4	T	1.97	JT
CI5(114)	0.37	UT	0.23	UT
CI5(118)	7.05	T	2.67	JT
CI5(123)	0.13	UT	0.08	UT
CI5(126)	0.19	UT	0.12	UT
CI6(128)	0.43	UT	0.27	UT
CI6(138)	8.92	T	4.03	T
CI6(153)	10.3	T	4.96	T
CI6(156)	0.12	UT	0.08	UT
CI6(157)	0.23	UT	0.15	UT
CI6(167)	0.43	UT	0.27	UT
CI6(169)	0.18	UT	0.11	UT
CI7(170)	1.88	JT	1.05	JT
CI7(180)	2.23	JT	2.33	JT
CI7(183)	0.71	JT	0.58	JT
CI7(184)	0.3	UT	0.19	UT
CI7(187)	1.13	JT	1.02	JT
CI7(189)	0.13	UT	0.08	UT
CI8(195)	0.58	UT	0.36	UT
CI9(206)	0.54	UT	0.34	UT
CI10(209)	0.65	UT	0.41	UT
<b>Surrogate Recoveries (%)</b>				
CI2(14)	86		82	
CI3(34)	90		82	

## PCBs QA/QC (CONT.)

**PROJECT:** Task Order TO0016 – YO817 Stormwater FY04  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 10/27/04. The samples were received at Battelle Duxbury on 10/29/04. Upon arrival, the cooler temperature was recorded at 1.7°C. No custody issues were noted. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0432, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.09 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection. However, extracts were not analyzed within the 40-day holding time.

Batch	Extraction Date	Analysis Date
04-0432	11/2/04	12/13/04 – 12/14/04

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**04-0432** – No exceedences noted.

**Comments** – No target analytes were detected in sample BF358PB.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**04-0432** – Eight percent recovery exceedences noted. All RPDs were within the laboratory limits specified by the client.

**Comments** – In sample S5983MS (background OF14-SD45-FF), PCB 126, PCB 169, PCB 180, PCB 206, and PCB 209 were all over-recovered at 127%, 121%, 125%, 129%, and 129%, respectively. In sample S5983MSD (same background), PCB 126, PCB 206, and PCB 209 were all over-recovered at 121%, 123%, and 124%, respectively. Chromatography and calculations were reviewed. No discrepancies were found. The exceedences have been qualified with an “N”.

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Note: At the time of extraction, no certified second source material was available. In lieu of a certified second source, the SRM sample was generated by spiking target analyte solution into a clean seawater sample from Duxbury Bay. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None

**SURROGATES:**

Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**04-0432** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

## PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE		MATRIX SPIKE NAV-OF14- SD45-FF		MATRIX SPIKE DUPLICATE- NAV- OF14-SD45-FF		PROCEDURAL BLANK	STANDARD REFERENCE MATERIAL- 041102- 01: DUXBURY BAY WATER
Battelle ID	BF359LCS-P		S5983MS-P		S5983MSD-P		BF358PB-P	BF360SRM-P
Sample Type	LCS		MS		MSD		PB	LCS
Collection Date	11/02/04		10/27/2004		10/27/2004		11/02/04	11/2/2004
Extraction Date	11/02/04		11/2/2004		11/2/2004		11/02/04	11/2/2004
Analysis Date	12/13/04		12/13/2004		12/14/2004		12/13/04	12/13/2004
Analytical Instrument	MS		MS		MS		MS	MS
% Moisture	NA		NA		NA		NA	NA
% Lipid	NA		NA		NA		NA	NA
Matrix	LIQUID		LIQUID		WATER		LIQUID	LIQUID
Sample Size	2.00		0.5		0.5		2.00	2
Size Unit-Basis	L LIQUID		L LIQUID		L LIQUID		L LIQUID	L LIQUID
Units	NG/L LIQUID	% Recovery	NG/L LIQUID	% Recovery	NG/L LIQUID	% Recovery	NG/L LIQUID	NG/L LIQUID
C12(8)	20.49 T	69	97.51 T	82	94.59 T	80	0.09 UT	22.4 T
C13(18)	22.04 T	73	102.38 T	85	100.85 T	84	0.11 UT	24.2 T
C13(28)	24.09 T	81	108.62 T	91	106.31 T	89	0.11 UT	26.88 T
C14(44)	23.45 T	79	119.95 T	98	116.81 T	95	0.19 UT	26.13 T
C14(49)	26.7 T	89	117.08 T	97	114.22 T	95	0.19 UT	29.56 T
C14(52)	20.68 T	70	109.85 T	87	105.83 T	84	0.19 UT	23.38 T
C14(66)	15.27 T	51	92.31 T	76	88.55 T	72	0.19 UT	17.41 T
C14(77)	16.25 T	54	106.02 T	88	102.53 T	85	0.18 UT	18.5 T
C15(87)	24.55 T	82	142.5 T	113	137.64 T	109	0.31 UT	27.32 T
C15(101)	22.85 T	76	130.88 T	99	125.23 T	95	0.31 UT	25.85 T
C15(105)	20.01 T	67	139.89 T	113	132.87 T	107	0.14 UT	23.1 T
C15(114)	0.31 UT		1.23 UT		1.23 UT		0.31 UT	0.31 UT
C15(118)	13.72 T	46	93.47 T	73	89.9 T	70	0.1 UT	15.75 T
C15(123)	0.11 UT		0.43 UT		0.43 UT		0.11 UT	0.11 UT
C15(126)	23.41 T	78	152.1 T	127	144.81 T	121	0.16 UT	26.58 T
C16(128)	19.08 T	64	120.73 T	101	118.1 T	99	0.35 UT	21.65 T
C16(138)	22.65 T	76	145.4 T	114	139.45 T	109	0.35 UT	25.61 T
C16(153)	21.22 T	71	142.62 T	111	136.45 T	106	0.35 UT	24.64 T
C16(156)	0.1 UT		0.4 UT		0.4 UT		0.1 UT	0.1 UT
C16(157)	0.19 UT		0.76 UT		0.76 UT		0.19 UT	0.19 UT
C16(167)	0.35 UT		1.42 UT		1.42 UT		0.35 UT	0.35 UT
C16(169)	21 T	70	145.22 T	121	136.65 T	113	0.15 UT	24.12 T
C17(170)	19.2 T	65	134.29 T	111	127.26 T	105	0.25 UT	21.2 T
C17(180)	27.25 T	91	152.23 T	125	140.92 T	115	0.14 UT	30.08 T
C17(183)	21.78 T	73	141.01 T	117	134.65 T	112	0.25 UT	25.63 T
C17(184)	21.41 T	71	131.49 T	109	123.6 T	103	0.25 UT	25 T
C17(187)	20.72 T	70	131.33 T	109	127.82 T	107	0.25 UT	23.03 T
C17(189)	0.11 UT		0.42 UT		0.42 UT		0.11 UT	0.11 UT
C18(195)	17.12 T	57	120.89 T	101	112.53 T	94	0.48 UT	19.35 T
C19(206)	22.47 T	76	153.55 T	129	146.21 T	123	0.44 UT	26.26 T
C10(209)	27.88 T	93	154.24 T	129	148.54 T	124	0.53 UT	31.68 T
Surrogate Recoveries (%)								
C12(14)	69		82		80		72	76
C13(34)	68		82		80		68	77

## PESTICIDES

CLIENT ID	NAV- OF14-SD45-FF		NAV- OF14-SD45-COMP	
Battelle ID	S5983-P		S5984-P	
Sample Type	SA		SA	
Collection Date	10/27/04		10/27/04	
Extraction Date	11/02/04		11/02/04	
Analysis Date	11/12/04		11/12/04	
Analytical Instrument	ECD		ECD	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	1.64		2.63	
Size Unit-Basis	L_LIQUID		L_LIQUID	
Units	NG/L_LIQUID		NG/L_LIQUID	
2,4'-DDD	0.99	U	0.62	U
2,4'-DDE	0.84	U	0.52	U
2,4'-DDT	0.59	U	0.37	U
4,4'-DDD	1.16	U	1.49	
4,4'-DDE	1.62		1.1	
4,4'-DDT	4.12		0.45	U
TOTAL DDT MDL	9.32		4.55	
aldrin	0.48	U	0.3	U
a-chlordane	2.16		1.67	
g-chlordane	0.49	U	0.31	U
a-BHC	0.42	U	0.26	U
b-BHC	0.58	U	0.36	U
d-BHC	0.47	U	0.3	U
Lindane	0.6	U	1.49	
cis-nonachlor	0.79	U	0.49	U
trans-nonachlor	2.03		1.44	
oxychlordane	0.48	U	0.3	U
TCHLOR	2.65		1.98	
dieldrin	0.93	U	0.58	U
endosulfan I	0.33	U	0.21	U
endosulfan II	0.84	U	0.53	U
endosulfan sulfate	0.79	U	0.49	U
endrin	0.92	U	0.57	U
endrin aldehyde	1.03	U	0.65	U
endrin ketone	1.08	U	0.68	U
heptachlor	0.72	U	0.45	U
heptachlor epoxide	1.92	U	1.2	U
Hexachlorobenzene	1.01	U	0.63	U
methoxychlor	1.19	U	0.74	U
Mirex	0.75	U	0.47	U
<b>Surrogate Recoveries (%)</b>				
CI2(14)	73		98	
CI3(34)	75		86	
CI5(104)	89		89	
CI5(112)	100		94	

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0016 – YO817 Stormwater FY04  
**PARAMETER:** Pesticides  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 10/27/04. The samples were received at Battelle Duxbury on 10/29/04. Upon arrival, the cooler temperature was recorded at 1.7°C. No custody issues were noted. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0432, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.27– 1.58

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
04-0432	11/2/04	11/11/04 – 11/12/04

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**04-0432** – No exceedences noted.

**Comments** – No target analytes were detected in sample BF358PB.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with the analytical batch. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Note: At the time of extraction, no certified second source material was available. In lieu of a certified second source, the SRM sample was generated by spiking target analyte solution into a clean seawater sample from Duxbury Bay. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**04-0432** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None

**SURROGATES:**

Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**04-0432** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.



# PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE		MATRIX SPIKE- OF14-SD45-FF		MATRIX SPIKE DUPLICATE-OF14- SD45-FF		PROCEDURAL BLANK	
Battelle ID	BF359LCS-P		S5983MS-P		S5983MSD-P		BF358PB-P	
Sample Type	LCS		MS		MSD		PB	
Collection Date	11/02/04		10/27/2004		10/27/2004		11/02/04	
Extraction Date	11/02/04		11/2/2004		11/2/2004		11/02/04	
Analysis Date	11/11/04		11/12/2004		11/12/2004		11/11/04	
Analytical Instrument	ECD		ECD		ECD		ECD	
% Moisture	NA		NA		NA		NA	
% Lipid	NA		NA		NA		NA	
Matrix	LIQUID		LIQUID		WATER		LIQUID	
Sample Size	2.00		0.5		0.5		2.00	
Size Unit-Basis	L LIQUID		L LIQUID		L LIQUID		L LIQUID	
Units	NG/L LIQUID	% Recovery	NG/L LIQUID	% Recovery	NG/L LIQUID	% Recovery	NG/L LIQUID	
2,4'-DDD	28.43	95	121.16	101	121.34	101	0.81 U	
2,4'-DDE	23.21	77	99.26	82	90.73	75	0.69 U	
2,4'-DDT	22.43	75	83.59	70	95.01	79	0.48 U	
4,4'-DDD	29.17	97	121.61	101	121.33	101	0.95 U	
4,4'-DDE	26.95	90	113.95	94	115.18	95	0.68 U	
4,4'-DDT	30.23	101	135.23	109	133.98	108	0.59 U	
aldrin	27.37	91	110.02	92	110.67	92	0.4 U	
a-chlordane	27.84	92	112.32	91	110.3	90	0.38 U	
g-chlordane	25.73	86	103.51	86	104.21	87	0.4 U	
a-BHC	16.43	55	72.56	60	72.04	60	0.34 U	
b-BHC	28.2	94	113.26	94	114.96	96	0.47 U	
d-BHC	28.61	95	116.88	97	118.22	98	0.39 U	
Lindane	27.72	92	115.43	96	113.94	95	0.49 U	
cis-nonachlor	28.59	95	118.57	99	119.95	100	0.65 U	
trans-nonachlor	28.11	94	112.6	92	112.73	92	0.4 U	
oxychlordane	29.09	97	117.48	98	118.69	99	0.39 U	
dieldrin	28.97	97	116.9	97	121.34	101	0.76 U	
endosulfan I	27.44	91	115.78	96	114.19	95	0.27 U	
endosulfan II	23.95	80	108.3	90	113.41	94	0.69 U	
endosulfan sulfate	28.91	96	128.84	107	127.41	106	0.65 U	
endrin	29.12	97	127.89	107	131.53	110	0.75 U	
endrin aldehyde	21.79	73	80.78	67	75.85	63	0.85 U	
endrin ketone	28.78	96	120.09	100	119.23	99	0.89 U	
heptachlor	25.63	85	109.66	91	107.2	89	0.59 U	
heptachlor epoxide	27.44	91	107	89	109.04	91	1.58 U	
Hexachlorobenzene	24.75	82	108.4	90	109.34	91	0.83 U	
methoxychlor	30.38	101	134.06	112	129.9	108	0.98 U	
Mirex	28.14	94	117.15	98	116.76	97	0.62 U	
<b>Surrogate Recoveries (%)</b>								
CI2(14)	76		83		95		86	
CI3(34)	85		82		82		83	
CI5(104)	81		85		81		88	
CI5(112)	83		88		91		91	

## TSS

SAMPLE ID	TSS (mg/L)
NAV-OF14-SD45-FF	61.24
NAV-OF14-SD45-COMP	78.73
NAV-OF14-SD45-COMP/BTL1	60.69
NAV-OF14-SD45-COMP/BTL2	44.97
NAV-OF14-SD45-COMP/BTL5	162.88
NAV-OF14-SD45-COMP/BTL11	46.78
NAV-BAY14-SD45-PRE	1.40
NAV- BAY14-SD45-DUR1	3.97
NAV-BAY14-SD45-DUR2	6.50
NAV-BAY14-SD45-DUR3	1.89
NAV-BAY14-SD45-DUR4	2.87
NAV-BAY14-SD45-AFT1	2.49
NAV-BAY14-SD45-AFT2	1.16
NAV-BAY14-SD45-AFT3	2.92

## DOC

Sample ID	MEAN DOC (mg/L)
NAV-OF14-SD45-FF	11.73
NAV-OF14-SD45-COMP	6.00
NAV-BAY14-SD45-PRE	0.91
NAV-BAY14-SD45-DUR1	0.62
NAV-BAY14-SD45-DUR2	1.63
NAV-BAY14-SD45-DUR3	1.73
NAV-BAY14-SD45-DUR4	0.95
NAV-BAY14-SD45-AFT1	1.34
NAV-BAY14-SD45-AFT2	0.74
NAV-BAY14-SD45-AFT3	0.62

## **Appendix D2**

### **SUB**

**SDB2- 2/24/2003**

**SDB3- 2/2/2004**

**SDB4- 10/17/2004**

## SDB2- 2/24/2003

### METALS

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
1979-14		SUB-OF11B-SDB2-FF (T)	0.0563 J	3040	1.46	0.556	5.60	130	5770	0.0253	306	12.5	43.5	0.237	0.686	588
1979-29		SUB-OF11B-SDB2-FF (D)	0.010 U	25.2 J	0.448 J	0.165	0.511 J	27.2	53.6	0.00979 J	44.8	7.49	0.575	0.276	0.136 J	139

MSL		Instrument:	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
1979-15		SUB-OF24-SDB2-FF (T)	0.0949 J	453	1.24	1.26	3.44	129	751	0.00679 J	22.6	6.58	9.85	0.301	0.521	267
1979-30		SUB-OF24-SDB2-FF (D)	0.0165 J	32.9 J	1.13	0.645	1.16	75.1	33.6	0.00342 J	11.0	3.30	0.370	0.255	0.0646 J	179
1979-13		SUB-OF26-SDB2-FF (T)	0.152 J	459	1.23	1.08	6.23	116	750	0.00666 J	30.7	16.6	14.3	0.261	0.444 J	248
1979-28		SUB-OF26-SDB2-FF (D)	0.0140 J	18.6 J	1.14	0.472	1.59	61.9	15.3	0.00355 J	12.4	11.8	0.184	0.0991 U	0.0386 J	88.2

## METALS QA/QC

**PROJECT:** SPAWARS Task 11, San Diego Bay Stormwater  
**PARAMETER:** Metals  
**LABORATORY:** Battelle Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Seawater and Freshwater

**SAMPLE CUSTODY AND PROCESSING:** Eighteen seawater and twelve freshwater samples were received in on 03/03/03. All samples were received in good condition (i.e., all sample containers were intact). Samples were assigned a Battelle Central File (CF) identification number (1979) and were entered into Battelle's sample tracking system.

The following lists information on sample receipt and processing activities:

<b>Chemistry Lab ID</b>	1979-1 through -30
<b>Collection dates</b>	02/25/03
<b>Laboratory arrival dates</b>	03/03/03
<b>Cooler temperatures, on arrival</b>	NA – Samples arrived preserved
<b>Fe/Pd Preconcentration (seawater)</b>	03/14/03
<b>FIAS (As – seawater)</b>	03/14/03
<b>FIAS (Se – seawater)</b>	03/17/03
<b>GFAA (Ag – seawater)</b>	03/20/03
<b>CVAA analyses (Hg)</b>	03/13/03, 03/14/03, 03/18/03
<b>ICP-MS analyses:</b>	
<b>Fe/Pd Seawater</b> (Cd, Cr, Cu, Ni, Pb)	03/18/03
<b>Direct Seawater</b> (Al, Fe, Mn, Sn, Zn)	03/27/03
<b>Freshwater</b> (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, Zn)	03/24/03
<b>Rerun Freshwater</b> (Al, Fe)	04/11/03

### QA/QC DATA QUALITY OBJECTIVES:

Analyte	Analytical Method Seawater	Analytical Method Freshwater	Range of Recovery	SRM Accuracy	Relative Precision	Detection Limits (µg/L)		
						Target MDL <sup>(1)</sup>	Achieved MDL Seawater <sup>(2)</sup>	Achieved MDL Freshwater <sup>(2)</sup>
Silver	GFAA	ICP-MS	50-150%	≤20%	≤50%	0.50	0.010	0.0038
Aluminum	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	50.0	0.823	0.823
Arsenic	FIAS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.0275	0.0087
Cadmium	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.0094	0.0008
Chromium	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	1.00	1.00	0.024
Copper	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.05	0.0029
Iron	ICP-MS	ICP-MS	50-150%	≤20%	≤50%	10.0	0.983	0.983
Mercury	CVAA	CVAA	50-150%	≤25%	≤30%	0.01	0.00014	0.00014
Manganese	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.50	0.003
Nickel	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.05	0.0114
Lead	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.05	0.0035	0.0044
Selenium	FIAS	ICP-MS	50-150%	≤20%	≤30%	0.20	0.0352	0.0991
Tin	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.0024	0.0024
Zinc	ICP-MS	ICP-MS	50-150%	≤20%	≤30%	0.50	0.50	0.0493

(1) As stated in the Statement of Work for Chemical Analysis of Marine and Estuarine Samples 15 May 2001.

(2) Reported from the 2003 MDL study.

**METHODS:**

Battelle MSL analyzed both seawater and freshwater samples for fourteen metals: silver (Ag), aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn) and zinc (Zn). The samples were submitted for analyses by four analytical methods: GFAA, ICP-MS, FIAS and CVAA.

Seawater samples were preconcentrated using iron (Fe) and palladium (Pd) in accordance with the Battelle SOP MSL-I-025, *Methods of Sample Preconcentration*, which is derived from EPA Method 1640. The sample preconcentration was submitted for analysis by ICP-MS and GFAA.

Seawater samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) in accordance with Battelle SOP MSL-I-022, *Determination of Elements in Aqueous and Digestate Samples by ICP-MS*. This method is based on two EPA Methods: 200.8 and 1638. Analytes reported from the preconcentrated seawater samples include: Cd, Cr, Cu, Ni, and Pb. Analytes reported from the direct analysis of the seawater samples include: Al, Fe, Mn, Sn, and Zn. Freshwater samples were analyzed directly by ICP-MS for all analytes, except Hg.

Ag was analyzed in the Fe-Pd preconcentrate by graphite furnace atomic absorption (GFAA) following Battelle SOP MSL-I-029, *Determination of Metals in Aqueous and Digestate Samples by GFAA*, which is derived from EPA Method 200.9.

Seawater samples were analyzed by hydride generation flow injection atomic spectroscopy (FIAS) for As and Se according to Battelle SOP MSL-I-030 *Determination of Metals in Aqueous and Digestate Samples by HGAA-FIAS*.

Seawater and freshwater samples were analyzed by cold-vapor atomic fluorescence spectroscopy (CVAF) for Hg according to Battelle SOP MSL-I-013, *Total Mercury in Aqueous Samples by CVAF*, which is derived from EPA Method 1631.

All results are reported in units of µg/L.

**HOLDING TIMES:**

The holding times for metals analyses are 90 days from sample collection for Hg analysis, and 6 months from sample collection for analysis of all other metals. The holding times for all metals were achieved.

**DETECTION LIMITS:**

Target detection limits (TDL) were achieved for all analytes. Achieved method detection limits are reported from the 2003 MDL study. Sample concentrations were evaluated and flagged to the following criteria:

- U Analyte not detected at or above the detection limit, MDL reported
- J Analyte detected above MDL, but below TDL
- \* Duplicate out of QC criteria
- e SRM recovery out of QC criteria
- w Spike recovery out of QC criteria due to inappropriate spiking level
- # Continuing calibration recovered outside of acceptable method criteria

**NOTE ON Hg QA/QC SAMPLES:**

Seawater and freshwater samples were analyzed concurrently for Hg. The QC samples are reported in both the seawater and freshwater tables.

<b>METHOD BLANKS:</b>	<p><b>Seawater:</b> A minimum of one method blank was analyzed with each analysis batch. Metals concentrations in the method blanks were below the TDL, with the exception of one method blank for Ni and Cu. All sample concentrations for Ni and Cu are greater than five times the detected blank. No corrective action was required. The data were not blank-corrected.</p> <p><b>Freshwater:</b> A minimum of one method blank was analyzed with each analysis batch. All metals concentrations in the method blanks were below the TDL. The data were not blank-corrected.</p>
<b>BLANK SPIKE or OPR ACCURACY:</b>	<p><b>Seawater:</b> A minimum of one blank spike or on-going precision and recovery (OPR) sample was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.005 µg/L for Hg; 5 µg/L for As and Se; and 10 µg/L for Ag, Cd, Cr, Cu, Ni, and Pb. BS recoveries among all metals analyzed ranged from 82% to 107% and were within the QC acceptance criteria of 50% to 150% for all metals.</p> <p><b>Freshwater:</b> A minimum of one blank spike or on-going precision and recovery (OPR) sample was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.005 µg/L for Hg; 10 µg/L for Cr, Mn, Ni, Cu, Zn, As, Se, Ag, Cd, Sn, and Pb; and 100 µg/L for Al and Fe. BS recoveries among all metals analyzed ranged from 91% to 119% and were within the QC acceptance criteria of 50% to 150% for all metals.</p>
<b>MATRIX SPIKE ACCURACY:</b>	<p><b>Seawater:</b> A minimum of one matrix spike was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.01 µg/L for Hg; 5 µg/L for As and Se; 10 µg/L for Cr, Ni, Cu, Ag, Cd, Sn, and Pb; and 100 µg/L for Al, Fe, Mn and Zn. Matrix spike recoveries among all metals analyzed ranged from 83% to 117% and were within the QC acceptance criteria of 50% to 150% for all metals, with the exception of one MS for Al (240%) and two replicates for Fe (0%, 220%). Low recoveries for the matrix spikes are due to an inappropriate spiking level relative to the native sample concentration. Spiking levels were less than 10% of the native sample concentration, therefore not appropriate for evaluating matrix spike accuracy. Acceptable MS accuracy for Al and Fe was demonstrated in the alternate matrix spike samples.</p> <p><b>Freshwater:</b> A minimum of one matrix spike was analyzed with each analysis batch. Recoveries were reported for spikes at approximate concentrations of 0.01 µg/L for Hg; 10 µg/L for Cr, Mn, Ni, Cu, As, Se, Ag, Cd, Sn, and Pb; and 100 µg/L for Al, Fe and Zn. Matrix spike recoveries among all metals analyzed ranged from 94% to 118% and were within the QC acceptance criteria of 50% to 150% for all metals.</p>
<b>REPLICATE PRECISION:</b>	<p>Analytical precision for each analysis batch was evaluated by the analysis of laboratory duplicates and expressed as the relative percent deviation (RPD) of duplicate results.</p> <p><b>Seawater:</b> A minimum of one set of laboratory duplicates was analyzed with each analysis batch. Precision for all metals, except Fe, ranged from 0% to 18% RPD and were within the QC limits of <math>\leq 30\%</math>. RPD values for Fe were 9% and 32% and were within the QC limits of <math>\leq 50\%</math>.</p> <p><b>Freshwater:</b> A minimum of one set of laboratory duplicates was analyzed with each analysis batch. Precision for all metals ranged from 1% to 19% RPD and</p>

**STANDARD  
REFERENCE  
MATERIAL  
ACCURACY:**

were within the QC limits of  $\leq 30\%$ .

Accuracy of recovery of SRM analytes was expressed as the percent difference (PD) between the measured and certified SRM concentrations. The target QC criterion is  $\leq 20\%$  PD.

**Seawater:** Standard reference material analyzed for seawater samples include: SRM 1640, SRM CASS-4, and SRM 1641 for Hg. The SRM 1640 is not certified for Sn and the certified value for Fe is not at a level appropriate for data quality evaluation. Percent differences for SRM 1640 and SRM 1641 ranged from 0% to 17% and were within the QC criterion.

The SRM CASS-4 is a low-level seawater reference material. Analytes of interest certified in CASS-4 are less than 10 times the laboratory achieved MDL for all metals except Cu. Currently, there is not seawater SRM certified at a practical quantification level for all analytes of interest. The SRM CASS-4 was analyzed with the preconcentrated seawater samples, and applies only to the metals obtained from this method (Ag, Cr, Ni, Cu, Cd, Pb). Percent differences for analytes within the QC criteria for CASS-4 include As (9%) and Cd (15%). The required preconcentration procedure for low level seawater samples includes the addition of chelating agents to induce precipitation of metals under specific conditions. Subsequently, reagents added to the samples should be of the purest quality to result in zero addition of metals to the samples. The current reagents available contain traces of Cr, Cu and Ni. Correcting CASS-4 results for reagent contributions provide PD values within the QC criterion for Cr (9%), Ni (2%), and Cu (1%). Since CASS-4 is not certified for Ag or Hg and is not certified at practical levels for a majority of the analytes of interest, the alternate SRM (1640 or 1641, respectively) should be used to evaluate the accuracy of this data set. The data were not blank corrected, as the sample concentrations are greater than five times the detected blank for these analytes.

**Freshwater:** Standard reference material analyzed for freshwater samples include: SRM 1640, SLRS-3 for Fe, and SRM 1641 for Hg. The SRM 1640 is not certified for Sn and the certified value for Fe is not at a level appropriate for data quality evaluation. Percent differences for all SRMs ranged from 0% to 19% and were within the QC acceptance criterion for all metals, with the following exceptions. One replicate of 1640 for Se (28%) and one replicate of 1640 for Zn (21%). In both cases, an alternate replicate of SRM 1640 was analyzed within the batch, which demonstrated acceptable accuracy for Se (0% PD) and Zn (3% PD).



# METALS QA/QC (CONT.)

MSL		Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
<b>METHOD BLANK</b>																
blk TRM r1		ICP-MS Direct	NA	0.823 U	NA	NA	NA	NA	0.983 U	NA	0.003 U	NA	NA	NA	0.00578 J	0.5 U
blk TRM r2		ICP-MS Direct	NA	0.823 U	NA	NA	NA	NA	0.983 U	NA	0.003 U	NA	NA	NA	0.00754 J	0.5 U
1979-blk		Fe/Pd ICP-MS or GFAA-Ag	0.0174 J	NA	NA	0.0094 U	0.0913 J	0.151	NA	NA	NA	0.105	0.0203 J	NA	NA	NA
Method Blank		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
Method Blank		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	0.00014 U	NA	NA	NA	NA	NA	NA
BLANK		FIAS - As	NA	NA	0.0275 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
BLANK		FIAS - Se	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.0352 U	NA	NA
<b>METHOD DETECTION LIMIT <sup>1</sup></b>			<b>0.010</b>	<b>0.823</b>	<b>0.0275</b>	<b>0.0094</b>	<b>0.0218</b>	<b>0.0540</b>	<b>0.983</b>	<b>0.00014</b>	<b>0.003</b>	<b>0.0286</b>	<b>0.0035</b>	<b>0.0352</b>	<b>0.0024</b>	<b>0.5</b>
Project Target Detection Limit			0.50	50.0	0.50	0.05	1.00	0.05	10.0	0.01	0.50	0.05	0.05	0.20	0.50	0.50
<b>STANDARD REFERENCE MATERIAL</b>																
1640 Direct		ICP-MS Direct	NA	51.8	NA	NA	NA	NA	N/A	NA	123	NA	NA	NA	1.58	62.3
1640 TRM		ICP-MS Direct	NA	48.8	NA	NA	NA	NA	N/A	NA	117	NA	NA	NA	1.52	50.6
1640 Direct		Fe/Pd ICP-MS or GFAA-Ag	6.96	NA	NA	24.7	39.4	87.2	N/A	NA	NA	28.2	28.0	NA	NA	NA
1640 Direct		Fe/Pd ICP-MS or GFAA-Ag	NA	NA	NA	24.5	37.1	83.0	N/A	NA	NA	26.7	27.3	NA	NA	NA
1641 Direct		FIAS- Se	NA	NA	NA	NA	NA	NA	N/A	NA	NA	NA	NA	21.0	NA	NA
1640		certified value	7.6	52.0	26.7	22.8	38.6	85.2	34.3	NC	122	27.4	27.9	22.0	NC	53.2
1640		range	±0.25	±1.5	±0.73	±0.96	±1.6	±1.2	±1.6	NC	±1.1	±0.8	±0.14	±0.51	NC	±1.1
		% difference	NA	0%	NA	NA	NA	NA	N/A	NA	1%	NA	NA	NA	NA	17%
		% difference	NA	6%	NA	NA	NA	NA	N/A	NA	4%	NA	NA	NA	NA	5%
			9%	NA	NA	8%	2%	2%	N/A	NA	NA	3%	0%	NA	NA	NA
			NA	NA	NA	8%	4%	3%	N/A	NA	NA	3%	2%	NA	NA	NA
			NA	NA	NA	NA	NA	NA	N/A	NA	NA	NA	4%	NA	NA	NA
1979-cass4		Fe/Pd ICP-MS or GFAA-Ag	0.0369	N/A	N/A	0.0299	0.222	0.749	N/A	N/A	N/A	0.425	0.0265	N/A	N/A	N/A
CASS-4		FIAS - As	N/A	N/A	1.01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
CASS-4		certified value	NC	NC	1.11	0.026	0.144	0.592	0.71	N/A	2.78	0.314	0.0098	NC	NC	0.381
CASS-4		range	NC	NC	±0.16	±0.003	±0.029	±0.055	±0.058	N/A	±0.19	±0.030	±0.0036	NC	NC	±0.057
		% difference	N/A	N/A	N/A	15%	54% e	27% e	N/A	N/A	N/A	35% e	170% e	N/A	N/A	N/A
		% difference	N/A	N/A	9%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1641d031203		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1565	N/A	N/A	N/A	N/A	N/A	N/A
1641d031303		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1466	N/A	N/A	N/A	N/A	N/A	N/A
1641d031703		Hg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1573	N/A	N/A	N/A	N/A	N/A	N/A
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	1590	NC	NC	NC	NC	NC	NC
1641d		range	NC	NC	NC	NC	NC	NC	NC	±4.00	NC	NC	NC	NC	NC	NC
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2%	N/A	N/A	N/A	N/A	N/A	N/A
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	8%	N/A	N/A	N/A	N/A	N/A	N/A
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1%	N/A	N/A	N/A	N/A	N/A	N/A
<b>ICV,CCV RESULTS</b>																
ICV		ICP-MS Direct or Hg		101%					109%	93%	104%				108%	105%
CCV		ICP-MS Direct or Hg		98%					99%	100%	105%				104%	105%
CCV		ICP-MS Direct or Hg		106%					113%	98%	104%				105%	107%
CCV		ICP-MS Direct or Hg		101%					101%	101%	104%				101%	100%
CCV		ICP-MS Direct or Hg		107%					112%	94%	100%				101%	98%
ICV		Fe/Pd ICP-MS or Hg	102%			102%	103%	102%		94%		102%	100%			
CCV		Fe/Pd ICP-MS or Hg	104%			100%	99%	98%		92%		97%	102%			
CCV		Fe/Pd ICP-MS or Hg	101%			101%	98%	96%		94%		97%	105%			
CCV		Fe/Pd ICP-MS or Hg	101%			100%	98%	96%		97%		96%	102%			
CCV		Fe/Pd ICP-MS	N/A			99%	96%	95%		NA		94%	100%			
ICV		FIAS-As or Hg			103%					100%						
CCV		FIAS-As or Hg			100%					101%						
CCV		FIAS-As or Hg			98%					103%						
CCV		FIAS-As or Hg			99%					98%						
ICV		FIAS-Se												104%		
CCV		FIAS-Se												100%		
CCV		FIAS-Se												99%		
CCV		FIAS-Se												95%		

# METALS QA/QC (CONT.)

MSL	Instrument:	GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAH	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
<b>BLANK SPIKE RESULTS</b>																
		Amount Spiked	10	NS	NS	10	10	10	NS	0.00497	NS	10	10	NS	NS	NS
1979-SB Bk or		0.0246 J				0.0721	0.180 J	0.488		0.000419 J		0.475	0.0279 J			
1979-SB LCS or		9.30				8.94	9.54	9.21		0.00569		9.19	8.26			
		Amount Recovered	9.28	N/A	N/A	8.94	9.36	8.72	N/A	0.00527	N/A	8.72	8.23	N/A	N/A	N/A
		Percent Recovery	93%	N/A	N/A	89%	94%	87%	N/A	106%	N/A	87%	82%	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00497	NS	NS	NS	NS	NS	NS
BLANK031203										0.000419 J						
OPR031203run2										0.00545						
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00503	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	101%	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS
BLANK031303										0.000172 J						
OPR031303run1										0.00490						
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00473	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	97%	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487	NS	NS	NS	NS	NS	NS
BLANK031303										0.000172 J						
OPR031303run2										0.00502						
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00485	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	100%	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	5	NS	NS	NS	NS	0.00491	NS	NS	NS	NS	NS	NS
BLANK (FIAS)					0.0275 U					0.000202 J						
LCS or					5.14					0.00528						
		Amount Recovered	N/A	N/A	5.14	N/A	N/A	N/A	N/A	0.00508	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	103%	N/A	N/A	N/A	N/A	103%	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00491	NS	NS	NS	5.0	NS	NS
BLANK(FIAS)										0.000202 J				0.0352 U		
LCS or										0.00547				4.92		
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00527	N/A	N/A	N/A	4.92	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	107%	N/A	N/A	N/A	98%	N/A	N/A
<b>MATRIX SPIKE RESULTS</b>																
		Amount Spiked	NS	100	NS	NS	NS	NS	100	NS	100	NS	NS	NS	10	100
1979-1		NAV-OF9-SDB2-FF		1840					2390		92.6				1.00	433
		MS		1920					2360		192				9.29	534
		Amount Recovered	N/A	80.0	N/A	N/A	N/A	N/A	-30	N/A	99.4	N/A	N/A	N/A	8.29	101
		Percent Recovery	N/A	80%	N/A	N/A	N/A	N/A	0%	N/A	99%	N/A	N/A	N/A	83%	101%
		Amount Spiked	NS	100	NS	NS	NS	NS	100	NS	100	NS	NS	NS	10	100
1979-1		NAV-OF9-SDB2-FF		1840					2390		92.6				1.00	433
		MSD		2080					2610		189				9.70	540
		Amount Recovered	N/A	240	N/A	N/A	N/A	N/A	220	N/A	96.4	N/A	N/A	N/A	8.70	107
		Percent Recovery	N/A	240%	N/A	N/A	N/A	N/A	220%	N/A	96%	N/A	N/A	N/A	87%	107%
		Amount Spiked	NS	100	5.0	NS	NS	NS	100	NS	100	NS	NS	5.0	10	100
1979-16		NAV-OF9-SDB2-FF		16.6 J	0.695				18.5		28.7			0.132 J	0.165 J	218
		MS		119	5.38				104		138			4.80	10.6	335
		Amount Recovered	N/A	102	4.69	N/A	N/A	N/A	85.5	N/A	109	N/A	N/A	4.67	10.4	117
		Percent Recovery	N/A	102%	94%	N/A	N/A	N/A	86%	N/A	109%	N/A	N/A	93%	104%	117%
		Amount Spiked	NS	100	NS	NS	NS	NS	100	NS	100	NS	NS	NS	10	100
1979-16		NAV-OF9-SDB2-FF		16.6 J					18.5		28.7				0.165 J	218
		MSD		125					102		133				10.5	328
		Amount Recovered	N/A	108	N/A	N/A	N/A	N/A	83.5	N/A	104	N/A	N/A	N/A	10.3	110
		Percent Recovery	N/A	108%	N/A	N/A	N/A	N/A	84%	N/A	104%	N/A	N/A	N/A	103%	110%
		Amount Spiked	10	NS	NS	10	10	10	NS	NS	NS	10	10	NS	NS	NS
1979-18		NAV-OF14-SDB2-FF	0.0267 J			0.983	0.804 J	22.1				5.78	0.916			
		MS	9.90			9.46	9.46	30.3				14.6	9.47			
		Amount Recovered	9.87	N/A	N/A	8.48	8.66	8.20	N/A	N/A	N/A	8.82	8.55	N/A	N/A	N/A
		Percent Recovery	99%	N/A	N/A	85%	87%	82%	N/A	N/A	N/A	88%	86%	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0158	NS	NS	NS	NS	NS	NS
1979-12		NAV-BAY14-SDB2-D								0.00229 J						
		MS								0.0188						
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0165	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	104%	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0155	NS	NS	NS	NS	NS	NS
1979-12		NAV-BAY14-SDB2-D								0.00229 J						
		MSD								0.01820						
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0159	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	103%	N/A	N/A	N/A	N/A	N/A	N/A

## METALS QA/QC (CONT.)

MSL	Instrument:		GFAA	ICP-MS	FIAS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	FIAS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn
REPLICATE RESULTS															
1979-1		NAV-OF9-SDBZ-FF	0.168 J	1840	1.58	0.987	6.56	54.2	2390	0.0173	92.6	12.5	22.7	0.187 J	1.00
1979-1	2	NAV-OF9-SDBZ-FF	NA	1790	NA	NA	NA	NA	2180	0.0174	87.8	NA	NA	NA	1.02
		% difference	NA	3%	NA	NA	NA	NA	9%	1%	5%	NA	NA	NA	2%
1979-12		NAV-BAY14-SDBZ-D	0.0324 J	107	1.17	0.109	1.75	5.01	152	0.00230 J	12.5	1.93	0.623	0.0539 J	0.253 J
1979-12	2	NAV-BAY14-SDBZ-D	0.0388 J	NA	1.20	0.113	1.74	4.99	NA	NA	NA	1.94	0.602	0.0352 U	NA
		% difference	18%	NA	3%	4%	1%	0%	NA	NA	NA	1%	3%	NA	NA
1979-16		OF9-SDBZ-FF	0.0203 J	16.6 J	0.695	0.388	1.22	25.8	18.5	0.00367 J	28.7	6.95	0.369	0.132 J	0.165 J
1979-16	2	OF9-SDBZ-FF	NA	16.4 J	NA	NA	NA	NA	25.5	NA	29.9	NA	NA	NA	0.149 J
		% difference	NA	1%	NA	NA	NA	NA	32%	NA	4%	NA	NA	NA	10%
(1)= Fe/Pd MDL Study, Ag from Graphite Furnace report, and Hg from 2002 MDL Study; NC = Analyte not certified; NS= Analyte not spike; # = Data quality outside the accuracy criteria of ±20% or precision/MS recovery criteria of ±25%; U= Analyte not detected above the laboratory achieved MDL, which is reported; J = Analyte detected above the MDL, but below the reporting limit.															

# METALS QA/QC (CONT.)

MSL		Instrument:	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS												
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg		Mn	Ni	Pb	Se	Sn	Zn												
METHOD BLANK																													
Method Blank		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	0.00014	U	NA	NA	NA	NA	NA	NA												
Method Blank		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	0.00014	U	NA	NA	NA	NA	NA	NA												
Method Blank		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	0.00014	U	NA	NA	NA	NA	NA	NA												
1979-blk TRM r1		ICP-MS	0.0038	U	NA	0.0087	U	0.0008	U	0.245	J	0.0029	U	NA	0.003	U	0.0114	U	0.0044	U	0.0991	U	0.0185	J	0.0493	U			
1979-blk TRM r2		ICP-MS	0.0038	U	NA	0.00929	J	0.0008	U	0.321	J	0.0029	U	NA	0.003	U	0.0114	U	0.0044	U	0.0991	U	0.00810	J	0.0493	U			
1979- dissolved		ICP-MS	0.00463	J	0.823	U	0.0087	U	0.0039	J	0.024	U	0.0029	U	0.983	U	NA	0.003	U	0.0259	J	0.0044	U	0.0991	U	0.0103	J	0.0493	U
Blank trm r1		ICP-MS (Al, Fe)	NA	0.823	U	NA	NA	NA	NA	0.983	U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
METHOD DETECTION LIMIT			0.0038	0.823	0.0087	0.0008	0.024	0.0029	0.983	0.00014	0.003	0.0114	0.0044	0.0991	0.0024	0.0493													
Project Target			0.50	50.0	0.50	0.05	1.00	0.05	10.0	0.01	0.50	0.05	0.05	0.05	0.20	0.50	0.50												
STANDARD REFERENCE MATERIAL																													
1979-1640 TRM		ICP-MS	7.49	58.2	28.3	23.1	41.5	87.8	NA	NA	132	29.2	27.7	21.9	1.54	54.9													
1640 Direct		ICP-MS	7.63	53.7	30.8	25.3	40.4	89.9	NA	NA	127	29.2	27.6	28.2	1.56	64.4													
1640 TRM		ICP-MS (Al, Fe)	NA	50.6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA												
1640		certified value	7.6	52.0	26.7	22.8	38.6	85.2	34.3	NC	122	27.4	27.9	22.0	NC	53.2													
1640		range	±0.25	±1.5	±0.73	±0.96	±1.6	±1.2	±1.6	NC	±1.1	±0.8	±0.14	±0.51	NC	±1.1													
		% difference	2%	12%	6%	1%	8%	3%	NA	NA	9%	7%	1%	0%	NA	3%													
		% difference	0%	3%	15%	11%	5%	6%	NA	NA	5%	7%	1%	28%	e	21%	e												
		% difference	NA	3%	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA													
SLRS-3 (Fe)		ICP-MS	NA	NA	NA	NA	NA	NA	119	NA	NA	NA	NA	NA	NA	NA	NA												
SLRS-3 (Fe)		ICP-MS (Al, Fe)	NA	NA	NA	NA	NA	NA	92.2	NA	NA	NA	NA	NA	NA	NA	NA												
		certified value	NA	NA	NA	NA	NA	NA	100	NA	NA	NA	NA	NA	NA	NA	NA												
		range	NA	NA	NA	NA	NA	NA	±2	NA	NA	NA	NA	NA	NA	NA	NA												
		% difference	NA	NA	NA	NA	NA	NA	19%	NA	NA	NA	NA	NA	NA	NA	NA												
		% difference	NA	NA	NA	NA	NA	NA	8%	NA	NA	NA	NA	NA	NA	NA	NA												
1641d031203		Hg- 03/13/03	NA	NA	NA	NA	NA	NA	NA	1565	NA	NA	NA	NA	NA	NA	NA												
1641d031303		Hg- 03/14/03	NA	NA	NA	NA	NA	NA	NA	1466	NA	NA	NA	NA	NA	NA	NA												
1641d031703		Hg- 03/18/03	NA	NA	NA	NA	NA	NA	NA	1573	NA	NA	NA	NA	NA	NA	NA												
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	1590	NC	NC	NC	NC	NC	NC	NC												
1641d		range	NC	NC	NC	NC	NC	NC	NC	±4.00	NC	NC	NC	NC	NC	NC	NC												
		% difference	NA	NA	NA	NA	NA	NA	NA	2%	NA	NA	NA	NA	NA	NA	NA												
		% difference	NA	NA	NA	NA	NA	NA	NA	8%	NA	NA	NA	NA	NA	NA	NA												
		% difference	NA	NA	NA	NA	NA	NA	NA	1%	NA	NA	NA	NA	NA	NA	NA												
ICV,CCV RESULTS																													
ICV		ICP-MS or Hg 1	102%	102%	103%	100%	103%	102%	104%	93%	103%	103%	101%	104%	101%	102%													
CCV		ICP-MS or Hg 1	103%	113%	107%	102%	109%	105%	110%	100%	110%	106%	100%	104%	102%	107%													
CCV		ICP-MS or Hg 1	104%	113%	105%	102%	108%	106%	115%	98%	109%	106%	98%	104%	102%	105%													
CCV		ICP-MS or Hg 1	103%	113%	105%	100%	108%	106%	113%	101%	109%	106%	98%	104%	101%	105%													
CCV		ICP-MS or Hg 1	101%	114%	104%	100%	108%	103%	111%	94%	108%	104%	98%	101%	100%	105%													
ICV		ICP-MS (Al, Fe) or Hg 2	NA	97%	NA	NA	NA	NA	92%	94%	NA	NA	NA	NA	NA	NA	NA												
CCV		ICP-MS (Al, Fe) or Hg 2	NA	101%	NA	NA	NA	NA	96%	92%	NA	NA	NA	NA	NA	NA	NA												
CCV		ICP-MS (Al, Fe) or Hg 2	NA	NA	NA	NA	NA	NA	NA	94%	NA	NA	NA	NA	NA	NA	NA												
CCV		ICP-MS (Al, Fe) or Hg 2	NA	NA	NA	NA	NA	NA	NA	97%	NA	NA	NA	NA	NA	NA	NA												
ICV		Hg 3	NA	NA	NA	NA	NA	NA	NA	100%	NA	NA	NA	NA	NA	NA	NA												
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	101%	NA	NA	NA	NA	NA	NA	NA												
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	103%	NA	NA	NA	NA	NA	NA	NA												
CCV		Hg 3	NA	NA	NA	NA	NA	NA	NA	98%	NA	NA	NA	NA	NA	NA	NA												

# METALS QA/QC (CONT.)

MSL	Rep	Instrument:	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAI	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Code		Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg		Mn	Ni	Pb	Se	Sn	Zn
BLANK SPIKE RESULTS																	
		Amount Spiked	10	100	10	10	10	10	100	0.00497		10	10	10	10	10	10
1979-blk TRM r1 or			0.0038 U	0.823 U	0.0087 U	0.0008 U	0.245 J	0.0029 U	36.7	0.000419 J	0.003 U	0.0114 U	0.0044 U	0.0091 U	0.0185 U	0.0493 U	
1979-blk spike r1 or			10.6	114	9.40	9.96	12.1	10.9	149	0.00569		11.7	11.0	10.8	9.56	11.6	10.2
		Amount Recovered	10.6	114	9.40	9.96	11.9	10.9	112	0.00527		11.7	11.0	10.8	9.56	11.6	10.2
		Percent Recovery	106%	114%	94%	100%	119%	109%	112%	106%		117%	110%	108%	96%	116%	102%
		Amount Spiked	10	100	10	10	10	10	100	0.00497		10	10	10	10	10	10
1979-blk TRM r2 or			0.0038 U	0.823 U	0.00929 J	0.0008 U	0.321 J	0.0029 U	36.5	0.000419 J	0.003 U	0.0114 U	0.0044 U	0.0091 U	0.00810 U	0.0493 U	
1979-blk spike r2 or			10.7	113	9.30	9.89	12.1	10.9	150	0.00545		11.8	11.0	10.6	9.05	11.7	9.76
		Amount Recovered	10.7	113	9.29	9.89	11.8	10.9	114	0.00503		11.8	11.0	10.6	9.05	11.7	9.76
		Percent Recovery	107%	113%	93%	99%	118%	109%	114%	101%		118%	110%	106%	91%	117%	98%
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487		NS	NS	NS	NS	NS	NS
BLANK031303										0.00172 J							
OPR031303run1										0.00490 J							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00473		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	97%		NA	NA	NA	NA	NA	NA
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00487		NS	NS	NS	NS	NS	NS
BLANK031303										0.00172 J							
OPR031303run2										0.00502							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00485		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	100%		NA	NA	NA	NA	NA	NA
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00491		NS	NS	NS	NS	NS	NS
BLANK031403										0.000202 J							
OPR031403run1										0.00528							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00508		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	103%		NA	NA	NA	NA	NA	NA
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.00491		NS	NS	NS	NS	NS	NS
BLANK031403										0.000202 J							
OPR031403run2										0.00547							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.00527		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	107%		NA	NA	NA	NA	NA	NA
MATRIX SPIKE RESULTS																	
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0161		NS	NS	NS	NS	NS	NS
1979-15		SUB-OF24-SDB2-FF								0.00679 J							
		MS								0.0223							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.0155		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	96%		NA	NA	NA	NA	NA	NA
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	0.0157		NS	NS	NS	NS	NS	NS
1979-15		SUB-OF24-SDB2-FF								0.00679 J							
		MSD								0.0215							
		Amount Recovered	NA	NA	NA	NA	NA	NA	NA	0.0147		NA	NA	NA	NA	NA	NA
		Percent Recovery	NA	NA	NA	NA	NA	NA	NA	94%		NA	NA	NA	NA	NA	NA
		Amount Spiked	10	100	10	10	10	10	100	NS		10	10	10	10	10	100
1979-24		NAV-PR5-SDB2-COMP	0.00809 J	15.1	1.18	0.303	1.12	14.2	17.6			5.94	1.88	0.533	0.247	0.0603 J	80.8
		MS	10.6	131	11.4	10.7	12.6	24.3	130			17.3	12.8	10.5	11.0	11.6	185
		Amount Recovered	10.6	116	10.2	10.4	11.5	10.1	112	NA		11.4	10.9	10.0	10.8	11.5	104
		Percent Recovery	106%	116%	102%	104%	115%	101%	112%	NA		114%	109%	100%	108%	115%	104%
		Amount Spiked	10	100	10	10	10	10	100	NS		10	10	10	10	10	100
1979-24		NAV-PR5-SDB2-COMP	0.00809 J	15.1	1.18	0.303	1.12	14.2	17.6			5.94	1.88	0.533	0.247	0.0603 J	80.8
		MSD	10.7	129	11.7	10.8	12.7	24.5	132			17.3	12.9	10.9	11.1	11.9	184
		Amount Recovered	10.7	114	10.5	10.5	11.6	10.3	114	NA		11.4	11.0	10.4	10.9	11.8	103
		Percent Recovery	107%	114%	105%	105%	116%	103%	114%	NA		114%	110%	104%	109%	118%	103%

## METALS QA/QC (CONT.)

MSL		Instrument:	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
Code	Rep	Sponsor I.D.	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
REPLICATE RESULTS																
1979-23		NAV-PR6-SDB2-FF	0.0266	30.4	1.41	1.23	3.58	177	161	0.0133	81.5	17.2	0.879	1.33	0.289	J 288
1979-23	2	NAV-PR6-SDB2-FF	NA	NA	NA	NA	NA	NA	NA	0.0132	NA	NA	NA	NA	NA	NA
		% difference	NA	NA	NA	NA	NA	NA	NA	1%	NA	NA	NA	NA	NA	NA
1979-24		NAVPR5-SDB2-COMP	0.00809	15.1	1.18	0.303	1.12	14.2	17.6	0.00219	J 5.94	1.88	0.533	0.247	0.0603	J 80.8
1979-24	2	NAV-PR5-SDB2-COMP	0.00670	14.8	1.10	0.295	1.14	13.6	16.2	NA	5.88	1.91	0.502	0.0991	U 0.0688	J 79.7
		% difference	19%	2%	7%	3%	2%	4%	8%	NA	1%	2%	6%	NA	13%	1%

(1)= Fe/Pd MDL Study, Ag from Graphite Furnace report, and Hg from 2002 MDL Study; NC = Analyte not certified; NS= Analyte not spike; # = Data quality outside the accuracy criteria of  $\pm 20\%$  or precision/MS recovery criteria of  $\pm 25\%$ ; U= Analyte not detected above the laboratory achieved MDL, which is reported; J = Analyte detected above the MDL, but below the reporting limit.

# PAHs

CLIENT SAMPLE ID	SUB-OF11B-SDB2-FF	SUB-OF24-SDB2-FF	SUB-OF26-SDB2-FF	
Battelle Sample ID	U7094	U7093	U7095	
Battelle Batch ID	03-0203	03-0203	03-0203	
Data File	A1890.D	A1889.D	A1891.D	
Extraction Date	03/04/03	03/04/03	03/04/03	
Acquired Date	03/20/03	03/20/03	03/20/03	
Matrix	Water	Water	Water	
Sample Size (L)	2.66	2.66	2.66	
Dilution Factor	1.667	1.667	1.667	
PIV (mL)	0.3	0.3	0.3	
Min Reporting Limit	0.94	0.94	0.94	
Amount Units	ng/L	ng/L	ng/L	
Naphthalene	5.02 B	3.57 B	5.73 B	B
C1-Naphthalenes	2.78 B	2.87 B	4.62	
C2-Naphthalenes	5.20	6.25	5.17	
C3-Naphthalenes	5.55	4.86	4.95	
C4-Naphthalenes	11.32	11.31	10.95	
2-Methylnaphthalene	2.73 B	2.60 B	4.13	
1-Methylnaphthalene	1.72 B	1.67 B	2.11 B	B
2,6-Dimethylnaphthalene	1.27	1.50	1.38	
2,3,5-Trimethylnaphthalene	0.95	0.99	0.37	U
Biphenyl	2.43	1.61	2.60	
Acenaphthylene	1.37	0.56 J	1.40	
Acenaphthene	0.96	0.59 J	4.93	
Fluorene	1.91	1.25 B	7.16	
C1-Fluorenes	3.62	3.82	3.78	
C2-Fluorenes	7.61 B	18.92	35.65	
C3-Fluorenes	29.93 B	45.48	48.59	
Phenanthrene	18.47	20.80	59.33	
Anthracene	1.46 B	1.72 B	3.08	
C1-Phenanthrenes/Anthracenes	15.40 B	17.01 B	17.91 B	B
C2-Phenanthrenes/Anthracenes	34.66 B	24.22 B	33.99 B	B
C3-Phenanthrenes/Anthracenes	27.77 B	11.19 B	21.92 B	B
C4-Phenanthrenes/Anthracenes	13.41 B	2.74 B	7.38 B	B
1-Methylphenanthrene	4.32 B	4.54 B	4.56 B	B
Dibenzothiophene	7.27	4.62	9.30	
C1-Dibenzothiophenes	13.07	8.54 B	14.98	
C2-Dibenzothiophenes	42.40 B	23.78 B	28.80 B	B
C3-Dibenzothiophenes	42.08 B	16.79 B	28.21 B	B
Fluoranthene	28.49	16.92	42.51	
Pyrene	31.56 B	15.45 B	28.96 B	B
C1-Fluoranthenes/Pyrenes	18.74 B	9.61 B	14.74 B	B
C2-Fluoranthenes/Pyrenes	22.76 B	7.37 B	16.75 B	B
C3-Fluoranthenes/Pyrenes	25.77 B	7.12 B	13.95 B	B
Benzo(a)anthracene	5.68	1.76	2.20	
Chrysene	29.63	9.65	18.35	
C1-Chrysenes	25.16	6.55 B	10.57 B	B
C2-Chrysenes	29.19 B	10.97 B	11.54 B	B
C3-Chrysenes	28.50 B	0.28 U	0.28 U	U
C4-Chrysenes	0.28 U	0.28 U	0.28 U	U
Benzo(b)fluoranthene	11.63	4.70	9.75	
Benzo(k)fluoranthene	9.02	3.81	5.41	
Benzo(e)pyrene	12.23	4.78	7.21	
Benzo(a)pyrene	6.62	2.81	3.15	
Perylene	4.47	0.91 J	0.73 J	J
Indeno(1,2,3-cd)pyrene	7.20	2.87	4.26	
Dibenz(a,h)anthracene	1.89	0.45 J	0.74 J	J
Benzo(g,h,i)perylene	17.99	7.40	10.12	
Total Priority Pollutant PAHs	178.90	94.32	207.07	
<b>Surrogate Recoveries (%)</b>				
Naphthalene-d8	61	58	69	
Phenanthrene-d10	70	67	77	
Chrysene-d12	69	80	89	

## PAHs QA/QC

**PROJECT:** SPAWAR TO0011, Contaminant Analysis of Stormwater and San Diego Bay Seawater

**PARAMETER:** PAH

**LABORATORY:** Battelle, Duxbury, MA

**MATRIX:** Water

**SAMPLE CUSTODY:** The water samples were collected February 25, 2003. They were received in Duxbury on February 28, 2003 in good condition in six coolers. The cooler temperature on arrival ranged from 0.2 °C to 1.3 °C. Samples were stored at 4 °C until processing.

### QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	LCS/MS Recovery	Sample Replicate Relative Precision	Procedural Blank
PAH	General NS&T	30-130% Recovery	LCS: 40-120% Recovery for at least 80% of analytes  MS: 50-150% Recovery for at least 70% of analytes; analyte conc. in MS must be >5x background	≤30% RSD  analyte conc. in MS must be <5x background	<3X MDL

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Full water samples were spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with Recovery Internal Standard (RIS) and split for analysis. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) with the MS operating in the selected ion monitoring (SIM) mode, following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch.

Samples were extracted with in the 7-day holding time for waters. Extracts were analyzed within the 40-day holding time for extracts

<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
03-0203	3/4/2003	3/19/2003 – 3/20/2003

**BLANKS:** A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.

**03-0203** – Several target analytes were detected at concentrations greater than 3X the MDL.

**Comments** – ~~All samples are appropriately flagged. The contamination in the blank does not appear to have the same PAH homologue pattern as the samples indicating that the contamination is likely isolated to the blank and that the samples are not impacted by the blank contamination. This is supported by the fact that no alkyl homologues were detected in the LCS (blank spike) sample — the LCS is prepared in the same manner as the blank, with the addition of a spike of the target analytes of interest (in this case, the parent PAH).~~

**LABORATORY** **Note: The 2003 MDL for substituted naphthalenes were updated.** A laboratory control sample (LCS) was prepared with each analytical batch. The percent



**CONTROL  
SAMPLE:**

recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client.

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS)/matrix spike duplicate (MSD) pair was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy; the relative percent difference between the pair was calculated to measure data quality in terms of precision.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client. The relative percent differences between the MS and MSD recoveries were within the laboratory control limits for all target PAH.

**Comments** – None.

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**03-0203** – All surrogate percent recoveries were within the laboratory control limits specified by the client.

**Comments** – None.

# PAHs QA/QC (CONT.)

CLIENT SAMPLE ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE-NAV-OF9-SDB2-FF			MATRIX SPIKE DUPLICATE-NAV-OF9-SDB2-FF					PROCEDURAL BLANK	
Battelle Sample ID	BB593LCS			U7083MS			U7083MSD					BB592PB	
Battelle Batch ID	03-0203			03-0203			03-0203					03-0203	
Data File	A1873.D			A1875A.D			A1876.D					A1872.D	
Extraction Date	03/04/03			3/4/2003			03/04/03					03/04/03	
Acquired Date	03/19/03			3/19/2003			37699					03/19/03	
Matrix	Water			Water			Water					Water	
Sample Size (L)	2			1.18			1.18					2	
Dilution Factor	1.667			1.67			1.67					1.667	
PIV (mL)	0.30			0.30			0.30					0.3	
Min Reporting Limit	1.25			2.13			2.13					1.25	
Amount Units	ng	Rec%	Q	ng/L	Rec%		ng/L	Rec%	Q	RPD	Q	ng/L	
Naphthalene	352.38		70	543.19		63	554.69		64	2.14		2.33	B
C1-Naphthalenes	0.66	U	NA	1.13	U	NA	1.13	U	NA	NA		1.23	J
C2-Naphthalenes	0.66	U	NA	1.13	U	NA	1.13	U	NA	NA		0.66	U
C3-Naphthalenes	0.66	U	NA	1.13	U	NA	1.13	U	NA	NA		0.66	U
C4-Naphthalenes	0.66	U	NA	1.13	U	NA	1.13	U	NA	NA		0.66	U
2-Methylnaphthalene	360.50		72	577.66		67	577.08		67	0.10		1.09	J
1-Methylnaphthalene	339.07		68	553.60		64	554.86		64	0.23		0.82	J
2,6-Dimethylnaphthalene	343.64		69	579.78		68	595.69		70	2.72		0.47	U
2,3,5-Trimethylnaphthalene	371.42		74	645.28		76	686.38		80	6.19		0.50	U
Biphenyl	337.28		67	583.63		68	594.79		69	1.91		0.28	J
Acenaphthylene	379.80		76	644.53		75	674.66		79	4.59		0.41	U
Acenaphthene	361.28		72	612.93		72	636.85		74	3.84		0.54	U
Fluorene	398.80		80	685.50		80	731.35		85	6.51		0.57	J
C1-Fluorenes	0.49	U	NA	0.83	U	NA	0.83	U	NA	NA		1.13	J
C2-Fluorenes	0.49	U	NA	0.83	U	NA	0.83	U	NA	NA		4.77	B
C3-Fluorenes	0.49	U	NA	0.83	U	NA	0.83	U	NA	NA		13.84	B
Phenanthrene	419.23		84	774.11		82	869.69		94	12.77		5.78	B
Anthracene	430.88		86	683.27		80	747.23		87	9.00		0.84	J
C1-Phenanthrenes/Anthracene	0.38	U	NA	0.64	U	NA	0.64	U	NA	NA		15.14	B
C2-Phenanthrenes/Anthracene	0.38	U	NA	0.64	U	NA	0.64	U	NA	NA		58.14	B
C3-Phenanthrenes/Anthracene	0.38	U	NA	0.64	U	NA	0.64	U	NA	NA		81.62	B
C4-Phenanthrenes/Anthracene	0.38	U	NA	0.64	U	NA	0.64	U	NA	NA		108.36	B
1-Methylphenanthrene	425.88		85	721.31		84	796.73		92	10.07		2.70	B
Dibenzothiophene	5.39		NA	21.83		NA	23.72		NA	NA		0.82	J
C1-Dibenzothiophenes	0.46	U	NA	0.79	U	NA	0.79	U	NA	NA		3.14	B
C2-Dibenzothiophenes	0.46	U	NA	0.79	U	NA	0.79	U	NA	NA		22.71	B
C3-Dibenzothiophenes	0.46	U	NA	0.79	U	NA	0.79	U	NA	NA		47.04	B
Fluoranthene	464.01		93	861.68		89	1001.92		106	16.88		5.12	B
Pyrene	477.18		95	879.40		92	1033.03		110	17.89		17.73	B
C1-Fluoranthenes/Pyrenes	0.44	U	NA	0.75	U	NA	0.75	U	NA	NA		31.70	B
C2-Fluoranthenes/Pyrenes	0.44	U	NA	0.75	U	NA	0.75	U	NA	NA		66.39	B
C3-Fluoranthenes/Pyrenes	0.44	U	NA	0.75	U	NA	0.75	U	NA	NA		68.03	B
Benzo(a)anthracene	472.04		94	760.93		88	892.16		103	16.14		0.69	U
Chrysene	469.94		94	820.97		88	995.84		108	20.99		0.37	U
C1-Chrysenes	0.37	U	NA	0.62	U	NA	0.62	U	NA	NA		6.13	B
C2-Chrysenes	0.37	U	NA	0.62	U	NA	0.62	U	NA	NA		25.02	B
C3-Chrysenes	0.37	U	NA	0.62	U	NA	0.62	U	NA	NA		30.09	B
C4-Chrysenes	0.37	U	NA	0.62	U	NA	0.62	U	NA	NA		0.37	U
Benzo(b)fluoranthene	432.60		86	776.18		86	964.01		108	22.83		0.43	U
Benzo(k)fluoranthene	439.70		88	747.55		83	919.30		103	21.64		0.43	U
Benzo(e)pyrene	388.05		78	685.24		77	836.81		95	21.05		1.48	B
Benzo(a)pyrene	418.30		84	725.55		81	893.33		101	21.63		0.65	U
Perylene	384.14		77	659.17		77	789.49		92	18.15		0.70	U
Indeno(1,2,3-cd)pyrene	390.28		78	728.87		81	810.93		91	11.20		0.43	J
Dibenz(a,h)anthracene	421.03		84	740.55		86	814.99		95	9.65		1.04	U
Benzo(g,h,i)perylene	347.96		70	658.67		71	751.71		82	14.29		0.69	J
Total Priority Pollutant PAHs												33.49	
<b>Surrogate Recoveries (%)</b>													
Naphthalene-d8	74			63			66					74	
Phenanthrene-d10	81			77			82					77	
Chrysene-d12	93			83			95					91	

# PCBs

CLIENT SAMPLE ID:	SUB-OF11B-SDB2-FF		SUB-OF24-SDB2-FF		SUB-OF26-SDB2-FF	
Battelle Sample ID:	U7094		U7093		U7095	
Battelle Batch ID:	03-0203		03-0203		03-0203	
Data File:	sc0382,54,1		sc0382,53,1		sc0382,55,1	
Extraction Date:	3/04/03		3/04/03		3/04/03	
Aquired Date:	3/19/03		3/19/03		3/19/03	
Matrix:	Water		Water		Water	
Sample Volume (L):	2.660		2.660		2.660	
Dilution Factor:	1.667		1.667		1.667	
Pre Injection Volume (µL):	300		300		300	
Minimum Reporting Limit (ng/L):	0.188		0.188		0.188	
Units:	ng/L		ng/L		ng/L	
Cl2 08	1.805	U	1.805	U	1.805	U
Cl3 18	0.156	U	0.156	U	0.156	U
Cl3 28	0.195	U	0.279	NC	0.195	U
Cl4 44	0.164	U	0.475	NC	0.731	NC
Cl4 49	4.229	NC	0.168	U	0.168	U
Cl4 52	0.162	U	0.162	U	0.162	U
Cl4 66	0.168	U	0.168	U	0.168	U
Cl4 77	1.320	NC	1.841	NC	0.239	U
Cl5 87	0.086	NC	0.127	U	0.127	U
Cl5 101	0.129	U	1.338	NC	0.129	U
Cl5 105	0.065	U	0.065	U	0.065	U
Cl5 114	0.111	U	0.111	U	0.111	U
Cl5 118	0.098	U	0.098	U	0.098	U
Cl5 123	0.111	U	0.111	U	0.111	U
Cl5 126	0.139	U	0.139	U	0.139	U
Cl6 128	0.732	NC	0.281	NC	0.304	NC
Cl6 138	0.413	NC	0.149	U	0.149	U
Cl6 153	0.120	U	0.698		0.120	U
Cl6 156	0.135	U	0.135	U	0.135	U
Cl6 157	0.135	U	0.135	U	0.135	U
Cl6 167	0.815		0.135	U	0.135	U
Cl6 169	0.108	U	0.108	U	0.108	U
Cl7 170	0.114	U	0.114	U	0.114	U
Cl7 180	0.893		0.221	NC	0.108	U
Cl7 183	0.105	U	0.105	U	0.105	U
Cl7 184	0.104	U	0.104	U	0.104	U
Cl7 187	0.097	U	0.197		0.097	U
Cl7 189	0.106	U	0.106	U	0.106	U
Cl8 195	0.122	U	0.122	U	0.122	U
Cl9 206	0.137	U	0.363		0.137	U
Cl10 209	1.463		0.793		0.346	
Total PCB	9.136		6.488		1.381	
Surrogate Recoveries:						
Cl3(34)	89		77		85	
Cl5(112)	66		69		75	

## PCBs QA/QC

**PROJECT:** SPAWAR TO0011, Contaminant Analysis of Stormwater and San Diego Bay Seawater  
**PARAMETER:** PCB Congener  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** The water samples were collected on February 25, 2003. They were received in Duxbury on February 28, 2003 in good condition in six coolers. The cooler temperature on arrival ranged from 0.2 °C to 1.3 °C. Samples were stored at 4 °C until processing.

### QA/QC DATA QUALITY OBJECTIVES:

	Reference Method	Surrogate Recovery	LCS/MS Recovery	Sample Replicate Relative Precision	Procedural Blank
PAH	General NS&T	30-130% Recovery	LCS: 40-120% Recovery for at least 80% of analytes  MS: 50-150% Recovery for at least 70% of analytes; analyte conc. in MS must be >5x background	≤30% RSD  analyte conc. in MS must be <5x background	<3X MDL

**METHOD:** Water samples were extracted for PCB Congener following general NS&T methods. Full water samples were spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with Recovery Internal Standard (RIS) and split for analysis. Extracts were analyzed using gas chromatography/electron capture detection (GC/ECD), following general NS&T methods. Sample data were quantified by the method of internal standards, using the RIS compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch.

Samples were extracted with in the 7-day holding time for waters. Extracts were analyzed within the 40-day holding time for extracts

<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
03-0203	3/4/2003	3/17/2003 – 3/22/2003

**BLANKS:** A procedural blank (PB) was prepared with each analytical batch. Blanks were analyzed to ensure the sample extraction and analysis methods were free of contamination.

**03-0203** – No analytes identified at greater than 3X the MDL.

**LABORATORY CONTROL SAMPLE:** **Comments** – None.  
A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB Congeners were calculated to measure data quality in terms of accuracy.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

**Comments** – None.

A matrix spike (MS)/matrix spike duplicate (MSD) pair was prepared with each analytical batch. The percent recoveries of target PCB Congeners were calculated to measure data quality in terms of accuracy; the relative percent difference between the pair was calculated to measure data quality in terms of precision.

**03-0203** – All target analytes were recovered within the laboratory control limits specified by the client. The relative percent differences between the MS and MSD recoveries were within the laboratory control limits for all target PCB Congeners.

**SURROGATES:**

**Comments** – None.

Two surrogate compounds were added prior to extraction, including PCB34 and PCB112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**03-0203** – All surrogate percent recoveries were within the laboratory control limits specified by the client.

**Samples:**

**Comments** – None.

The condition of the confirmation column was in question after the analysis. It was decided to report all “hits” from the primary column regardless if confirmed or not confirmed. The analytes are appropriately flagged if reported, but not confirmed.

## PCBs QA/QC (CONT.)

CLIENT SAMPLE ID:	LABORATORY CONTROL SAMPLE		MATRIX SPIKE-NAV-OF9-SDB2-FF		MATRIX SPIKE DUPLICATE-NAV-OF9-SDB2-FF		
Battelle Sample ID:	BB593LCS		U7083MS		U7083MSD		
Battelle Batch ID:	03-0203		03-0203		03-0203		
Data File:	sc0382.38.1		sc0382.40.1		sc0382.41.1		
Extraction Date:	3/04/03		3/04/03		3/04/03		
Aquired Date:	3/17/03		3/18/03		3/18/03		
Matrix:	Water		Water		Water		
Sample Volume (L):	2.000		1.175		1.175		
Dilution Factor:	1.667		1.667		1.667		
Pre Injection Volume (µL):	300		300		300		
Minimum Reporting Limit (ng/L):	0.250		0.426		0.426		
Units:	ng	% Recovery	ng/L	% Recovery	ng/L	% Recovery	% RPD
CI2 08	20.509	68	17.345	68	20.449	80	16
CI3 18	21.498	72	19.854	66	20.959	70	6
CI3 28	35.064	117	21.372	84	25.258	99	17
CI4 44	25.535	85	21.262	83	23.531	92	10
CI4 49	25.348	84	24.907	97	25.302	99	2
CI4 52	24.280	81	20.705	81	21.345	84	3
CI4 66	27.632	92	22.603	89	25.267	99	11
CI4 77	24.023	80	20.028	73	22.256	82	11
CI5 87	24.470	82	20.388	77	21.738	82	7
CI5 101	25.400	85	21.352	76	23.998	86	13
CI5 105	26.157	87	20.806	80	21.916	84	5
CI5 114	NA	NA	NS	NA	NS	NA	NA
CI5 118	23.286	78	19.969	75	21.834	82	9
CI5 123	NA	NA	NS	NA	NS	NA	NA
CI5 126	28.227	94	19.566	77	20.869	82	6
CI6 128	26.487	88	23.105	85	21.485	79	8
CI6 138	25.310	84	22.841	80	24.760	88	9
CI6 153	22.656	76	22.155	79	23.904	86	8
CI6 156	NA	NA	NS	NA	NS	NA	NA
CI6 157	NA	NA	NS	NA	NS	NA	NA
CI6 167	NA	NA	NS	NA	NS	NA	NA
CI6 169	28.949	96	23.429	91	25.035	98	7
CI7 170	25.778	86	22.468	85	24.052	91	7
CI7 180	25.907	86	23.798	85	26.011	94	10
CI7 183	25.158	84	21.384	84	22.322	87	4
CI7 184	23.828	79	19.885	78	20.606	80	4
CI7 187	23.085	77	19.872	75	20.867	79	5
CI7 189	NA	NA	NS	NA	NS	NA	NA
CI8 195	25.317	84	20.354	80	21.844	86	7
CI9 206	23.978	80	20.081	79	21.885	86	9
CI10 209	23.396	78	18.226	66	19.594	71	8
Total PCB	631.280	NA	527.755	NA	567.085	NA	NA
Surrogate Recoveries:							
CI3(34)	84		90		99		
CI5(112)	78		74		77		

## SDB3- 2/2/2004

### METALS

MSL	Rep	Sponsor	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code		I.D.	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
<b>SAMPLE RESULTS</b>									
2157*1		SUB-OF11B-SDB3-COMP (T)	1.09	0.561	0.0403	0.237	0.50	12.2	0.04315
2157*4		SUB-OF11B-SDB3-COMP (D)	0.721	0.650	0.009	0.0880	0.50	0.400	0.01546
2157*3		SUB-OF23CE-SDB3-COMP (T)	2.08	0.260	0.0633	2.60	0.874	20.1	0.01657
2157*6		SUB-OF23CE-SDB3-COMP (D)	1.52	0.237	0.009	0.855	0.50	0.742	0.02654
2157*2		SUB-OF26-SDB3-COMP (T)	4.62	0.629	0.0722	0.995	0.537	7.82	0.01740
2157*5		SUB-OF26-SDB3-COMP (D)	4.31	0.20	0.0256	0.451	0.50	0.521	0.00740
2157*8		Field Blank-Filtered	0.129	0.20	0.009	0.023	0.50	0.0345	0.01046

MSL	Rep	Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)
Code		I.D.	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-OES
<b>SAMPLE RESULTS</b>									
2157*1		SUB-OF11B-SDB3-COMP (T)	2190	3210	6.16	78.4	6.76	24.9	123
2157*4		SUB-OF11B-SDB3-COMP (D)	9.05	31.6	0.890	11.1	3.18	15.2	37.4
2157*3		SUB-OF23CE-SDB3-COMP (T)	1550	1980	6.71	89.7	7.68	37.3	792
2157*6		SUB-OF23CE-SDB3-COMP (D)	18.2	33.5	0.948	35.9	3.14	18.0	505
2157*2		SUB-OF26-SDB3-COMP (T)	529	2300	4.79	48.7	9.31	216	442
2157*5		SUB-OF26-SDB3-COMP (D)	17.5	30.9	1.80	23.8	5.76	142	263
2157*8		Field Blank-Filtered	0.638	10.0	0.0712	0.50	0.01	0.018	0.140

SAMPLE ID	DISSOLVED COPPER (ppb)	TOTAL COPPER (ppb)	DISSOLVED ZINC (ppb)	TOTAL ZINC (ppb)
SUB-SDB3-BAY11B-PRE	1.1	1.6	3.8	4.3
SUB-SDB3-BAY11B-DUR	1.6	1.9	7.6	7.0
SUB-SDB3-BAY11B-AFT	0.66	1.1	2.5	2.9
SUB-SDB3-BAY23CE-PRE	1.1	1.6	4.5	4.5
SUB-SDB3-BAY23CE-DUR	0.78	1.2	2.8	3.4
SUB-SDB3-BAY23CE-AFT	0.60	0.80	1.9	2.07
SUB-SDB3-BAY26-PRE	1.6	2.4	4.0	4.6
SUB-SDB3-BAY26-DUR	1.4	1.8	6.3	6.2
SUB-SDB3-BAY26-AFT	0.59	0.88	1.6	1.93
SUB-SDB3-BAY26A-PRE	0.79	1.1	2.2	2.7
SUB-SDB3-BAY26A-DUR	0.34	0.55	1.2	1.19
SUB-SDB3-BAY26A-AFT	0.42	0.62	1.3	1.24

## METALS QA/QC

### QA/QC SUMMARY

**PROGRAM:** SPAWAR STORMWATER, Task 15  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/MS	50-150%	±20%	±50%	50.0
Iron	ICP/MS	50-150%	±20%	±50%	10.0
Manganese	ICP/MS	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Seven (7) samples were analyzed for ten (10) metals; chromium (Cr), manganese (Mn), nickel (Ni), copper, (Cu), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1638m, three (3) metals: aluminum (Al), iron (Fe), and zinc (Zn) by inductively coupled plasma optic emission spectroscopy (ICP/OES) following EPA Method 200.7, and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. The samples were analyzed for all metals except Hg by ICP/MS. Results for Al, Fe, and Zn were outside the range of the ICP/MS and were then analyzed by ICP/OES. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Eight (8) samples were received on 2/5/2004 and were logged into Battelle's sample tracking system. Following a phone call from Joel Guerrero, sample 7 was designated for archive instead of analysis. Seven samples were digested and analyzed within the six-month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:



Task	Date Performed
Hg	2/12/04
ICP-MS	2/17/04
ICP-OES	3/9/04
ICP-OES (reanalysis of sample 2159*4)	3/12/04

#### **DETECTION LIMITS**

The target detection limit was met for all metals. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.

#### **METHOD BLANKS**

One method blank was analyzed with this batch of samples. Results were less than 3 times the MDL for all metals, except Al. Sample results that are less than 3 x the blank have been "b" flagged.

#### **BLANK SPIKES**

One sample of reagent water was spiked at one level with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **MATRIX SPIKES**

One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **REPLICATES**

A duplicate was not requested for this task.

#### **SRM**

Two matrix-appropriate standard reference materials (SRM) were analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.

SRM 1640 has 22 certified metals. Recovery for all metals reported were within the control limit of  $\pm 20\%$  of the certified value. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of  $\pm 25\%$  of the certified value.

#### **REFERENCES**

EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4-91-010. Environmental Services Division, Monitoring Management Branch.

## METALS QA/QC (CONT.)

MSL	Rep	Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)	
Code		I.D.	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF	
<b>PROCEDURAL BLANK</b>			0.785	10.0 U	0.107	0.50 U	0.01 U	0.018 U	0.160	0.051 U	0.20 U	0.009 U	0.023 U	0.50 U	0.0110 U	0.00014 U	
METHOD DETECTION LIMIT			0.20	NA	0.047	NA	0.01	0.018	0.140	0.051	NA	0.009	0.023	NA	0.011	0.00014	
Project Target Detection Limit			50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01	
<b>STANDARD REFERENCE MATERIAL</b>																	
1640			61.3	36.9	38.7	124	27.9	86.3	56.8	25.7	21.3	7.59	22.9	1.47	27.3	NA	
1640		certified value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC	
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC	
		% difference	18%	8%	0%	2%	2%	1%	7%	4%	3%	0%	0%	N/A	2%	N/A	
1641d			NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1613	
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1557	
1641d		range	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	±4.00	
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4%	
<b>ICV,CCV RESULTS</b>																	
ICV			101%	100%	101%	103%	101%	101%	103%	102%	102%	102%	102%	102%	102%	93%	
CCV			99%	98%	98%	101%	98%	99%	102%	99%	100%	101%	101%	101%	99%	101%	
CCV			99%	98%	99%	101%	97%	99%	101%	99%	100%	100%	100%	101%	100%	94%	
CCV			100%	98%	102%	104%	100%	102%	103%	103%	102%	102%	101%	103%	101%	NA	
CCV			NA	NA	98%	95%	95%	97%	NA	99%	99%	102%	102%	106%	106%	NA	
<b>BLANK SPIKE RESULTS</b>																	
		Amount Spiked	2500	2500	50.0	50.0	50.0	50.0	250	50.0	50.0	50.0	50.0	50.0	50.0	0.00496	
		Blank	0.785	10.0 U	0.107	0.50 U	0.010 U	0.018 U	0.160	0.051 U	0.20 U	0.009 U	0.023 U	0.50 U	0.011 U	0.000368	
		Blank + Spike	2538	2477	48.5	47.4	46.5	50.7	255	48.1	47.7	50.3	50.9	52.5	52.6	0.00543	
		Amount Recovered	2537	2477	48.4	47.4	46.5	50.7	255	48.1	47.7	50.3	50.9	52.5	52.6	0.00506	
		Percent Recovery	101%	99%	97%	95%	93%	101%	102%	96%	95%	101%	102%	105%	105%	102%	
<b>MATRIX SPIKE RESULTS</b>																	
		Amount Spiked	NS	NS	50.0	50.0	50.0	50.0	NS	10.0	10.0	10.0	10.0	10.0	50.0	NS	
		SUB-OF11B-SDB3-COMP (T)	N/A	N/A	6.16	78.4	6.76	24.9	N/A	1.09	0.561	0.0403	0.237	0.50 U	12.2	N/A	
		SUB-OF11B-SDB3-COMP (T)+ Spike	NS	NS	59.4	127	59.5	76.1	NS	12.3	11.8	10.6	11.3	8.00	62.4	NS	
		Amount Recovered	N/A	N/A	53.2	48.6	52.7	51.2	N/A	11.2	11.2	10.6	11.1	8.00	50.2	N/A	
		Percent Recovery	N/A	N/A	106%	97%	105%	102%	N/A	112%	112%	106%	111%	80%	100%	N/A	
		Amount Spiked	2336.0	2336	NS	NS	NS	NS	234	NS	NS	NS	NS	NS	NS	0.0103	
		SUB-OF26-SDB3-COMP (T)	529	2300	N/A	N/A	N/A	N/A	442	N/A	N/A	N/A	N/A	N/A	N/A	0.01740	
		SUB-OF26-SDB3-COMP (T) + Spike	2970	4794	NS	NS	NS	NS	703	NS	NS	NS	NS	NS	NS	0.0274	
		Amount Recovered	2441	2494	N/A	N/A	N/A	N/A	261	N/A	N/A	N/A	N/A	N/A	N/A	0.0100	
		Percent Recovery	104%	107%	N/A	N/A	N/A	N/A	112%	N/A	N/A	N/A	N/A	N/A	N/A	97%	

U = not detected at or above detection limit; NC = not certified; NA = not analyzed or available; N/A = not applicable; b = Sample results are less than 5 x the blank; w = spike recovery is out of control due to inappropriate spiking level; t = 0.1 LLS recovery was outside default limits of 50-150%, result reported is an estimate.

# PAHs

CLIENT ID	SUB-OF11B-SDB3-FF	SUB-OF11B-SDB3-COMP	SUB-BAY11B-SDB3-PRE	SUB-BAY11B-SDB3-DUR	SUB-BAY11B-SDB3-AFT	SUB-OF23CE-SDB3-FF	SUB-OF23CE-SDB3-COMP	SUB-BAY23CE-SDB3-PRE
Battelle ID	S0887-P	S0890-P	S0875-P	S0879-P	S0883-P	S0889-P	S0892-P	S0877-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	02/03/04	02/03/04	02/02/04	02/03/04	02/04/04	02/03/04	02/03/04	02/02/04
Extraction Date	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04
Analysis Date	02/21/04	02/22/04	02/21/04	02/21/04	02/21/04	02/22/04	02/22/04	02/21/04
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	FRESHWATER	FRESHWATER	SEAWATER	SEAWATER	SEAWATER	FRESHWATER	FRESHWATER	SEAWATER
Sample Size	2.62	2.64	2.64	2.62	2.62	2.64	1.32	2.65
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Naphthalene	6.28 B	10.72	6.39 B	129.92	5.15 B	10.83	16.08	34.76
C1-Naphthalenes	3.39 B	6.6	3.5 B	140.93	3.28 B	5.87	9.08	26.19
C2-Naphthalenes	3.76 B	6.56	2.75 J	59.53	2.6 J	6.45	9.45	12.37
C3-Naphthalenes	12.41	17.46	1.28 J	23.5	0.85 J	38.59	47.96	4.36
C4-Naphthalenes	6.3	10.82	1.27 J	9.23	0.51 U	8.38	17.55	2.9 J
2-Methylnaphthalene	3.87 B	7.67	3.41 B	155.82	3.43 B	6.33	9.9	28.03
1-Methylnaphthalene	1.74 J	3.39	2.35 J	81.94	2.01 J	3.36	5.13 J	16.51
Biphenyl	2.34 J	4.09	0.72 J	8.87	0.78 J	5.31	7.94	2.13 J
2,6-dimethylnaphthalene	1.24 J	2.06 J	0.95 J	30.79	0.83 J	2.4 J	3.61 J	5.61
Acenaphthylene	1.21 J	1.83 J	1.59 J	17.54	0.57 J	2.4 J	2.44 J	4.87
Acenaphthene	0.62 J	1.12 J	2.09 J	3.12 J	1.78 J	1.04 J	1.29 J	1.75 J
2,3,5-trimethylnaphthalene	0.88 J	1.22 J	0.38 J	3.89	0.17 J	1.61 J	2.1 J	1.14 J
Dibenzofuran	1.94 J	3.33	1.23 J	2.03 J	1.02 J	5	5.6 J	0.98 J
Fluorene	2.09 J	2.82 J	1.38 J	5.93	1.09 J	3.29	3.64 J	1.93 J
C1-Fluorenes	3.18	3.55	0.44 J	3.05 J	0.35 J	3.87	4.65 J	1.01 J
C2-Fluorenes	9	20.72	0.74 J	4.9	0.52 U	18.23	27.9	1.79 J
C3-Fluorenes	23.58	29.04	0.52 U	4.55	0.52 U	60.59	65.07	0.51 U
Anthracene	2.79 J	3.11 J	0.65 J	2.32 J	0.48 J	4.77	4.1 J	0.91 J
Phenanthrene	18.33	25	1.76 J	9.92	2.16 J	41.96	41.21	3.22
C1-Phenanthrenes/Anthracenes	13.79	18.47	1.16 J	7.84	0.78 J	33.69	36.06	2.47 J
C2-Phenanthrenes/Anthracenes	17.49	22.91	0.87 J	6.88	0.62 J	37.64	45.4	2.07 J
C3-Phenanthrenes/Anthracenes	18.58	22.66	0.98 J	3.2	0.82 U	28.5	31.93	1.55 J
C4-Phenanthrenes/Anthracenes	9.7	14.9	0.82 U	0.8 J	0.82 U	18.7	18.14	0.81 U
1-Methylphenanthrene	4.27	5.56	0.37 J	1.53 J	0.17 J	9.74	10.54	0.54 J
Dibenzothiophene	2.11 J	7.33	0.22 J	0.56 J	0.21 J	5.13	10.7	0.22 J
C1-Dibenzothiophenes	8.82	17.4	0.36 J	0.83 J	0.34 J	15.46	27.9	0.51 J
C2-Dibenzothiophenes	23.98	43.08	0.59 J	1.53 J	0.41 J	39.54	59.87	0.7 J
C3-Dibenzothiophenes	26.73	41.94	0.38 U	1.05 J	0.38 U	40.45	54.5	0.38 U
C4-Dibenzothiophenes	19.14	27.41	0.38 U	0.38 U	0.38 U	31.6	32.6	0.38 U
Fluoranthene	31.6	33.09	4.97	9.03	2.89 J	70.33	61.54	4.4
Pyrene	34.4	36.9	2.58 J	10.89	1.75 J	58.98	51.2	3.5
C1-Fluoranthenes/Pyrenes	12.04	15.75	0.94 J	2.76 J	0.7 J	20.03	19.91	1.23 J
C2-Fluoranthenes/Pyrenes	16.43	24.07	0.68 U	1.42 J	0.68 U	29.84	32.14	0.68 U
C3-Fluoranthenes/Pyrenes	17.04	28.76	0.68 U	0.68 U	0.68 U	30.94	31.38	0.68 U
Benzo(a)anthracene	3.27	6.37	0.43 J	0.65 J	0.24 J	7.94	8.49	0.33 J
Chrysene	21.96	25.1	0.84 J	1.32 J	0.48 J	43.25	38.21	0.69 J
C1-Chrysenes	12.38	22.06	0.27 J	0.38 J	0.45 U	22.32	21.03	0.24 J
C2-Chrysenes	14.04	28.34	0.45 U	0.45 U	0.45 U	24.31	23.03	0.44 U
C3-Chrysenes	11.84	28.93	0.45 U	0.45 U	0.45 U	22.3	23.09	0.44 U
C4-Chrysenes	0.45 U	15.53	0.45 U	0.45 U	0.45 U	10.5	11.37	0.44 U
Benzo(b)fluoranthene	10.31	13.42	0.76 J	0.65 J	0.29 J	23.11	22.95	0.55 J
Benzo(j,k)fluoranthene	9.14	11.28	0.72 J	0.69 J	0.31 J	18.07	18.56	0.51 J
Benzo(e)pyrene	10.06	15.37	0.47 J	0.51 J	0.31 J	20.67	20.32	0.37 J
Benzo(a)pyrene	4.56	8.54	0.47 J	0.55 J	0.32 J	9.15	11.49	0.35 J
Perylene	2.01 J	4.96	0.14 J	0.16 J	1.47 U	2.69 J	3.31 J	1.46 U
Indeno(1,2,3-cd)pyrene	4.67	8.9	0.35 J	0.31 J	0.11 J	11.48	13.29	0.25 J
Dibenz(a,h)anthracene	1.35 J	1.9 J	0.3 J	0.2 J	0.64 U	1.98 J	2.47 J	0.11 J
Benzo(g,h,i)perylene	7.51	16.78	0.29 J	0.68 J	0.11 J	16.46	16.93	0.27 J

## PAHs (CONT.)

CLIENT ID	SUB- OF11B-SDB3-FF	SUB- OF11B-SDB3- COMP	SUB- BAY11B-SDB3- PRE	SUB- BAY11B-SDB3- DUR	SUB- BAY11B-SDB3- AFT	SUB- OF23CE-SDB3-FF	SUB- OF23CE-SDB3- COMP	SUB- BAY23CE-SDB3- PRE
<i>Surrogate Recoveries (%)</i>								
Naphthalene-d8	54	61	51	49	55	59	54	48
Phenanthrene-d10	78	85	73	79	74	86	79	70
Chrysene-d12	81	86	84	89	83	87	83	80

# PAHs (CONT.)

CLIENT ID	SUB-BAY23CE-SDB3-DUR	SUB-BAY23CE-SDB3-AFT	SUB-OF26-SDB3-FF	SUB-OF26-SDB3-COMP	SUB-BAY26-SDB3-PRE	SUB-BAY26-SDB3-DUR	SUB-BAY26-SDB3-AFT	SUB-BAY26A-SDB3-PRE	SUB-BAY26A-SDB3-DUR	SUB-BAY26A-SDB3-AFT
Battelle ID	S0881-P	S0885-P	S0888-P	S0891-P	S0876-P	S0880-P	S0884-P	S0878-P	S0882-P	S0886-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	02/03/04	02/04/04	02/03/04	02/03/04	02/02/04	02/03/04	02/04/04	02/02/04	02/03/04	02/04/04
Extraction Date	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04	02/06/04
Analysis Date	02/21/04	02/21/04	02/22/04	02/22/04	02/21/04	02/21/04	02/21/04	02/21/04	02/21/04	02/21/04
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	SEAWATER	SEAWATER	FRESHWATER	FRESHWATER	SEAWATER	SEAWATER	SEAWATER	SEAWATER	SEAWATER	SEAWATER
Sample Size	2.64	2.64	2.64	2.64	2.63	2.64	2.64	2.64	2.64	2.64
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Naphthalene	3.66 B	7.52 B	11.9	9.37 B	14.18	3.33 B	9.76 B	2.03 J	7.56 B	6.93 B
C1-Naphthalenes	1.7 J	4.39 B	5.68	5.9	12.56	1.83 J	6.13	0.94 J	4.95 B	3.79 B
C2-Naphthalenes	2.13 J	2.63 J	5.86 B	6.67	8.72	1.95 J	2.97 J	1.08 J	2.83 J	1.89 J
C3-Naphthalenes	0.89 J	0.81 J	14.62	42.09	3.52	1.11 J	0.87 J	0.67 J	0.99 J	0.72 J
C4-Naphthalenes	1.01 J	0.89 J	6.49	69.49	2.44 J	1.29 J	0.85 J	0.5 U	0.98 J	0.79 J
2-Methylnaphthalene	1.62 J	4.57	6.11	5.57	12.76	1.7 J	6.55	0.96 J	5.12	4.01 B
1-Methylnaphthalene	1.09 J	2.72 J	3.42	3.66	8.49	1.22 J	3.72	0.62 J	3.1 J	2.28 J
Biphenyl	0.51 J	0.6 J	3.43	3.44	1.38 J	0.52 J	0.76 J	0.43 J	0.67 J	0.64 J
2,6-dimethylnaphthalene	0.58 J	0.78 J	1.95 J	1.87 J	3.74	0.59 J	1.06 J	0.27 J	1.02 J	0.59 J
Acenaphthylene	0.77 J	0.63 J	3.11 J	2.9 J	3.34	1.01 J	0.84 J	0.38 J	1.04 J	0.59 J
Acenaphthene	0.87 J	1.15 J	1.8 J	2.06 J	1.35 J	1.1 J	0.99 J	0.35 J	0.2 J	0.53 J
2,3,5-trimethylnaphthalene	0.19 J	0.18 J	1.02 J	0.99 J	0.81 J	0.32 J	0.21 J	0.15 J	0.21 J	0.16 J
Dibenzofuran	0.53 J	0.59 J	5.6	3.94	0.85 J	0.8 J	0.68 J	0.48 J	0.28 J	0.4 J
Fluorene	0.57 J	0.89 J	3.28	3.66	1.38 J	0.83 J	0.89 J	0.33 J	0.46 J	0.53 J
C1-Fluorenes	0.32 J	0.31 J	2.52 J	4.46	0.81 J	0.39 J	0.32 J	0.34 J	0.23 J	0.52 U
C2-Fluorenes	0.72 J	0.52 U	19.36	39.6	1.61 J	1.04 J	0.52 U	0.52 U	0.52 U	0.52 U
C3-Fluorenes	0.52 U	0.52 U	63.92	69.71	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U
Anthracene	0.54 J	0.38 J	4.62	1.73 J	0.69 J	0.59 J	0.36 J	0.25 J	0.14 J	0.19 J
Phenanthrene	0.74 J	1.71 J	50.61	31.03	1.95 J	0.22 J	2.11 J	0.47 J	0.92 J	1.15 J
C1-Phenanthrenes/Anthracenes	0.87 J	0.77 J	23.82	21.28	2.01 J	1.07 J	0.82 J	0.68 J	0.75 J	0.64 J
C2-Phenanthrenes/Anthracenes	0.78 J	0.7 J	29.52	25.69	1.7 J	1.08 J	0.72 J	0.8 J	0.7 J	0.68 J
C3-Phenanthrenes/Anthracenes	0.82 U	0.82 U	37.69	23.51	1.43 J	1.11 J	0.82 U	1.02 J	0.82 U	0.82 U
C4-Phenanthrenes/Anthracenes	0.82 U	0.82 U	32.56	13.78	0.82 U	0.82 U	0.82 U	0.82 U	0.82 U	0.82 U
1-Methylphenanthrene	0.2 J	0.16 J	6.27	6.29	0.47 J	0.24 J	0.27 J	0.24 J	0.22 J	0.21 J
Dibenzothiophene	0.12 J	0.17 J	4.15	10.34	0.19 J	0.2 J	0.19 J	0.07 J	0.08 J	0.09 J
C1-Dibenzothiophenes	0.25 J	0.36 J	9.78	24.24	0.47 J	0.55 J	0.34 J	0.29 J	0.28 J	0.12 J
C2-Dibenzothiophenes	0.48 J	0.51 J	29.55	50.5	0.76 J	0.79 J	0.48 J	0.55 J	0.44 J	0.38 U
C3-Dibenzothiophenes	0.38 U	0.38 U	34.25	46.69	0.38 U	0.63 J	0.38 U	0.38 U	0.38 U	0.38 U
C4-Dibenzothiophenes	0.38 U	0.38 U	28.76	37.25	0.38 U	0.38 U	0.38 U	0.38 U	0.38 U	0.38 U
Fluoranthene	2.76 J	2.43 J	71.87	24.57	4.48	4.72	2.61 J	2.4 J	0.68 J	1.15 J
Pyrene	1.5 J	1.25 J	53.39	20.45	3.3	2.64 J	1.42 J	0.96 J	0.59 J	0.64 J
C1-Fluoranthenes/Pyrenes	0.78 J	0.62 J	22.34	12.94	1.09 J	0.9 J	0.65 J	0.66 J	0.32 J	0.36 J
C2-Fluoranthenes/Pyrenes	0.68 U	0.68 U	41.41	14.82	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U
C3-Fluoranthenes/Pyrenes	0.68 U	0.68 U	32.59	15.5	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U
Benzo(a)anthracene	0.15 J	0.23 J	7.12	2.7 J	0.34 J	0.21 J	0.15 J	0.18 J	0.07 J	0.07 J
Chrysene	0.46 J	0.4 J	39.53	10.05	0.65 J	0.97 J	0.51 J	0.36 J	0.23 J	0.31 J
C1-Chrysenes	0.45 U	0.45 U	16.53	6.9	0.23 J	0.22 J	0.45 U	0.45 U	0.45 U	0.45 U
C2-Chrysenes	0.45 U	0.45 U	21.55	8.26	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U
C3-Chrysenes	0.45 U	0.45 U	22.7	7.7	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U
C4-Chrysenes	0.45 U	0.45 U	8.39	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U
Benzo(b)fluoranthene	0.26 J	0.19 J	17.6	7.07	0.45 J	0.34 J	0.2 J	0.3 J	0.88 U	0.88 U
Benzo(k)fluoranthene	0.39 J	0.28 J	16.34	5.82 J	0.35 J	0.3 J	0.27 J	0.21 J	0.99 U	0.99 U
Benzo(e)pyrene	0.18 J	0.17 J	15.95	6.7	0.38 J	0.31 J	0.2 J	0.22 J	0.39 U	0.39 U
Benzo(a)pyrene	0.23 J	0.2 J	7.92	4.21	0.37 J	0.22 J	0.17 J	0.26 J	0.76 U	0.76 U
Perylene	1.46 U	1.46 U	2.18 J	0.79 J	1.47 U	1.46 U	1.46 U	1.46 U	1.46 U	1.46 U
Indeno(1,2,3-cd)pyrene	0.1 J	0.08 J	8.15	4.54	0.24 J	0.13 J	0.06 J	0.12 J	0.75 U	0.05 J
Dibenz(a,h)anthracene	0.63 U	0.63 U	1.62 J	0.82 J	0.19 J	0.11 J	0.63 U	0.08 J	0.63 U	0.63 U
Benzo(g,h,i)perylene	0.13 J	0.06 J	15.94	5.63	0.33 J	0.19 J	0.09 J	0.12 J	0.75 U	0.05 J

## PAHs (CONT.)

CLIENT ID	SUB- BAY23CE-SDB3- DUR	SUB- BAY23CE-SDB3- AFT	SUB- OF26-SDB3-FF	SUB- OF26-SDB3- COMP	SUB- BAY26-SDB3-PRE	SUB- BAY26-SDB3- DUR	SUB- BAY26-SDB3-AFT	SUB- BAY26A-SDB3- PRE	SUB- BAY26A-SDB3- DUR	SUB- BAY26A-SDB3- AFT
<i>Surrogate Recoveries (%)</i>										
Naphthalene-d8	61	68	53	68	50	51	51	57	56	64
Phenanthrene-d10	81	82	76	86	73	80	76	77	75	79
Chrysene-d12	88	89	78	88	83	89	84	85	85	86

## PAHs QA/QC

**PROJECT:** Task Order TO0015 –Contaminant Analysis of Stormwater and San Diego Bay Seawater

**PARAMETER:** PAH

**LABORATORY:** Battelle, Duxbury, MA

**MATRIX:** Water

**SAMPLE CUSTODY:** Water samples were collected over three days 2/2/04 – 2/4/04. Samples were shipped in three containers to Battelle Duxbury via Federal Express. The samples were received on 2/5/04. The cooler temperatures were recorded at 2.1°C, 2.6°C, and 3.4°C upon arrival. No custody issues were noted. Samples were stored at 4° C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0039.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PAH	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery	≤30% PD on average (target spike must be >5 x native conc.)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.50 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
04-0039	2/6/04	2/20/04 – 2/22/04

**SURROGATES:** Three surrogate compounds were added prior to extraction, including Naphthalene-d8, Phenanthrene-d10, and Chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**04-0039** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery).

**Comments** – None.

(BD935PB), however all compounds were below the laboratory control limit (< 5 times MDL) and below the reporting limit (RL). These data points were qualified with a “J” in the procedural blank. Any authentic field sample concentrations that were less than five times the concentration detected in the blank were qualified with a “B”. No further corrective action is necessary.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**04-0039** – All target analytes were recovered within the laboratory control limits.

**Comments** – None.

**MATRIX SPIKE/MATRIX SPIKE DUPLICATE:** A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair was prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**04-0039** – All target analytes were recovered within the laboratory control limits. All RPDs were within the laboratory control limits.

**Comments** – None.

**SRM:** A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. The percent difference (PD) between the measured value and the certified range was calculated to measure data quality in terms of accuracy.

**04-0039** – No exceedences noted.

**Comments** – None.

**SURROGATES:** Three surrogate compounds were added prior to extraction, including Naphthalene-d8, Phenanthrene-d10, and Chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**04-0039** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery).

**Comments** – None.



# PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE		MATRIX SPIKE- OF23CE-SDB3-COMP		MATRIX SPIKE DUPLICATE- OF23CE-SDB3-COMP				PROCEDURAL BLANK	PROCEDURAL BLANK- DUXBURY BAY SEAWATER BACKGROUND
Battelle ID	BD936LCS-P		S0892MS-P		S0892MSD-P				BD935PB-P	BD938PB-P
Sample Type	LCS		MS		MSD				PB	PB
Collection Date	02/06/04		2/3/2004		2/3/2004				02/06/04	2/6/2004
Extraction Date	02/06/04		2/6/2004		2/6/2004				02/06/04	2/6/2004
Analysis Date	02/20/04		2/22/2004		2/22/2004				02/20/04	2/20/2004
Analytical Instrument	MS		MS		MS				MS	MS
% Moisture	NA		NA		NA				NA	NA
% Lipid	NA		NA		NA				NA	NA
Matrix	LIQUID		LIQUID		LIQUID				LIQUID	LIQUID
Sample Size	2.00		0.65		0.65				2.00	2
Size Unit-Basis	L LIQUID		L LIQUID		L LIQUID				L LIQUID	L LIQUID
Units	NG/L LIQUID	% Rec	NG/L LIQUID	% Rec	NG/L LIQUID	% Rec	RPD (%)		NG/L LIQUID	NG/L LIQUID
Naphthalene	864.16	69	1811.73	47	1735.32	45	4.3		2.11	J 8.27
C1-Naphthalenes	0.66	U	2.04	U	2.04	U			1.1	J 3.18
C2-Naphthalenes	0.66	U	2.04	U	2.04	U			1.18	J 2.23
C3-Naphthalenes	0.66	U	2.04	U	2.04	U			0.54	J 1.3
C4-Naphthalenes	0.66	U	2.04	U	2.04	U			0.66	U 0.66
2-Methylnaphthalene	988.62	79	2195.25	57	2115.43	55	3.6		0.85	J 3.17
1-Methylnaphthalene	861.6	69	1941.62	50	1891.28	49	2.0		0.56	J 2.19
Biphenyl	929.05	74	2239.03	58	2272.63	59	1.7		0.45	J 1.28
2,6-dimethylnaphthalene	927.6	74	2260.22	59	2276.76	59	0.0		0.36	J 0.92
Acenaphthylene	1038.32	83	2685.66	70	2749.98	71	1.4		0.7	U 0.61
Acenaphthene	945.09	76	2409.61	63	2473.72	64	1.6		0.75	U 1.25
2,3,5-trimethylnaphthalene	985.41	79	2743.51	71	2849.58	74	4.1		0.17	J 0.44
Dibenzofuran	0.3	U	13.18		0.93	U			0.3	U 1.39
Fluorene	945.1	76	2630.92	68	2733.85	71	4.3		0.16	J 1.37
C1-Fluorenes	0.68	U	2.09	U	2.09	U			0.68	U 0.43
C2-Fluorenes	0.68	U	2.09	U	2.09	U			0.68	U 0.68
C3-Fluorenes	0.68	U	2.09	U	2.09	U			0.68	U 0.68
C4-Fluorenes	0.68	U	2.09	U	2.09	U			0.68	U 0.68
Anthracene	1131.51	90	3117.3	81	3211.72	83	2.4		0.51	U 0.25
Phenanthrene	1006.84	81	2923.26	75	3080.18	79	5.2		0.37	J 3.44
C1-Phenanthrenes/Anthracenes	1.08	U	3.32	U	3.32	U			0.52	J 1.19
C2-Phenanthrenes/Anthracenes	1.08	U	3.32	U	3.32	U			0.48	J 1.02
C3-Phenanthrenes/Anthracenes	1.08	U	3.32	U	3.32	U			1.08	J 1.38
C4-Phenanthrenes/Anthracenes	1.08	U	3.32	U	3.32	U			1.08	U 1.08
1-Methylphenanthrene	1168.53	93	3368.48	87	3524.52	91	4.5		0.18	J 0.4
Dibenzothiophene	12.33		52.04		54.37				0.08	J 0.25
C1-Dibenzothiophenes	0.5	U	1.55	U	1.55	U			0.5	U 0.36
C2-Dibenzothiophenes	0.5	U	1.55	U	1.55	U			0.54	J 0.6
C3-Dibenzothiophenes	0.5	U	1.55	U	1.55	U			0.5	U 0.5
C4-Dibenzothiophenes	0.5	U	1.55	U	1.55	U			0.5	U 0.5
Fluoranthene	1177.07	94	3370.11	86	3523.89	90	4.5		0.37	J 2.37
Pyrene	1183.96	95	3337.92	85	3510.25	90	5.7		0.39	J 1.34
C1-Fluoranthenes/Pyrenes	0.9	U	2.76	U	2.76	U			0.32	J 0.62
C2-Fluoranthenes/Pyrenes	0.9	U	2.76	U	2.76	U			0.9	U 0.52
C3-Fluoranthenes/Pyrenes	0.9	U	2.76	U	2.76	U			0.9	U 0.9
Benzo(a)anthracene	1240.16	99	3478.77	90	3635.88	94	4.3		0.16	J 0.46
Chrysene	1127.61	90	3141.02	81	3288.97	84	3.6		0.39	J 1.07
C1-Chrysenes	0.59	U	1.81	U	1.81	U			0.2	J 0.27
C2-Chrysenes	0.59	U	1.81	U	1.81	U			0.59	U 0.59
C3-Chrysenes	0.59	U	1.81	U	1.81	U			0.59	U 0.59
C4-Chrysenes	0.59	U	1.81	U	1.81	U			0.59	U 0.59
Benzo(b)fluoranthene	1192.45	95	3395.92	88	3518.19	91	3.4		0.15	J 0.63
Benzo(i/k)fluoranthene	1320.96	106	3792.52	98	3910.57	101	3.0		0.2	J 0.67
Benzo(e)pyrene	1187.42	96	3394.05	89	3538.22	93	4.4		0.15	J 0.53
Benzo(a)pyrene	1213.38	97	3462.33	90	3604.14	93	3.3		0.14	J 0.59
Perylene	1187.17	95	3514.76	91	3651.85	95	4.3		1.93	U 0.17
Indeno(1,2,3-cd)pyrene	1136.94	91	3400.22	88	3531.49	91	3.4		0.25	J 0.61
Dibenz(a,h)anthracene	1169.01	93	3508.51	91	3633.68	94	3.2		0.56	J 0.55
Benzo(g,h,i)perylene	850.35	68	2454.91	63	2554.38	66	4.7		0.23	J 0.49

CLIENT ID	LABORATORY CONTROL SAMPLE		MATRIX SPIKE- OF23CE-SDB3-COMP		MATRIX SPIKE DUPLICATE- OF23CE-SDB3-COMP				PROCEDURAL BLANK	PROCEDURAL BLANK- DUXBURY BAY SEAWATER BACKGROUND
Surrogate Recoveries (%)										
Naphthalene-d8	76		53		52				71	67
Phenanthrene-d10	87		80		85				80	80
Chrysene-d12	94		83		86				84	88

# PCBs

CLIENT ID	SUB-OF11B-SDB3-COMP	SUB-OF23CE-SDB3-COMP	SUB-OF26-SDB3-COMP	
Battelle ID	S0890-P	S0892-P	S0891-P	
Sample Type	SA	SA	SA	
Collection Date	02/03/04	02/03/04	02/03/04	
Extraction Date	02/06/04	02/06/04	02/06/04	
Analysis Date	02/17/04	02/17/04	02/17/04	
Analytical Instrument	MS	MS	MS	
% Moisture	NA	NA	NA	
% Lipid	NA	NA	NA	
Matrix	FRESHWATER	FRESHWATER	FRESHWATER	
Sample Size	2.64	1.32	2.64	
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	
CI2(8)	0.06 U	0.13 U	0.06 U	
CI3(18)	0.06 U	0.12 U	0.06 U	
CI3(28)	0.06 U	0.12 U	0.06 U	
CI4(44)	0.11 U	0.23 U	0.11 U	
CI4(49)	0.11 U	0.23 U	0.11 U	
CI4(52)	0.11 U	0.23 U	0.11 U	
CI4(66)	0.11 U	0.23 U	0.11 U	
CI4(77)	0.14 U	0.28 U	0.14 U	
CI5(87)	0.11 U	0.23 U	0.11 U	
CI5(101)	U	0.23 U	0.11 U	
CI5(105)	0.11 U	0.21 U	0.11 U	
CI5(114)	0.23 U	0.46 U	0.23 U	
CI5(118)	0.07 U	0.14 U	0.07 U	
CI5(123)	0.08 U	0.16 U	0.08 U	
CI5(126)	0.12 U	0.24 U	0.12 U	
CI6(128)	0.15 U	0.31 U	0.15 U	
CI6(138)	0.15 U	0.31 U	0.15 U	
CI6(153)	0.15 U	0.31 U	0.15 U	
CI6(156)	0.08 U	0.15 U	0.08 U	
CI6(157)	0.14 U	0.29 U	0.14 U	
CI6(167)	0.27 U	0.54 U	0.27 U	
CI6(169)	0.11 U	0.22 U	0.11 U	
CI7(170)	0.19 U	0.37 U	0.19 U	
CI7(180)	0.11 U	0.21 U	0.11 U	
CI7(183)	0.11 U	0.23 U	0.11 U	
CI7(184)	0.11 U	0.23 U	0.11 U	
CI7(187)	0.11 U	0.23 U	0.11 U	
CI7(189)	0.08 U	0.16 U	0.08 U	
CI8(195)	0.21 U	0.42 U	0.21 U	
CI9(206)	0.34 U	0.67 U	0.34 U	
CI10(209)	0.4 U	0.81 U	0.4 U	
<b>Surrogate Recoveries (%)</b>				
CI2(14)	86	76	89	
CI3(34)	83	76	87	
CI5(104)	83	77	86	
CI5(112)	86	82	86	

## PCBs QA/QC

**PROJECT:** Task Order TO0015 –Contaminant Analysis of Stormwater and San Diego Bay Seawater

**PARAMETER:** PCB

**LABORATORY:** Battelle, Duxbury, MA

**MATRIX:** Water

**SAMPLE CUSTODY:** Water samples were collected over three days 2/2/04 – 2/4/04. Samples were shipped in three containers to Battelle Duxbury via Federal Express. The samples were received on 2/5/04. Upon arrival, the cooler temperatures were recorded at 2.1°C, 2.6°C, and 3.4°C. No custody issues were noted. Samples were stored in the upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0039.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.08 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
04-0039	2/6/04	2/17/04

<b>BLANK:</b>	<p>Two blank (PB) samples were prepared with the analytical batch. One procedural blank BD935PB was analyzed to ensure the sample extraction and analysis methods were free of contamination. The other blank, BD938PB, was analyzed to give a background value for "clean" seawater. All analytical data has been qualified according to the concentrations detected in BD935PB.</p> <p><b>04-0039</b> – No exceedences noted.</p> <p><b>Comments</b> – No target analytes were detected in the procedural blank.</p>
<b>LABORATORY CONTROL SAMPLE:</b>	<p>A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.</p> <p><b>04-0039</b> – One exceedence noted.</p> <p><b>Comments</b> – All target analytes were recovered within the laboratory control limits specified by the client (40-120%), except for PCB 180. PCB 180 was over-recovered at 130%. The chromatograms and calculations were reviewed. The analyst notes an interfering compound, possibly a phthalate, co-eluting with this peak. A spectral comparison versus a standard has been included in the data a package. The exceedence was qualified with an "N". No further corrective action was taken.</p>
<b>MATRIX SPIKE/MATRIX SPIKE DUPLICATE:</b>	<p>A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair was prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.</p> <p><b>04-0039</b> – Two percent recovery exceedences noted. No RPD exceedences noted.</p> <p><b>Comments</b> – All RPDs were within the laboratory control limits (&lt;30% RPD). All target analytes were recovered within the laboratory control limits specified by the client (40-120%), except for PCB 170. PCB 170 was over-recovered in both the MS and MSD samples at 131% and 126%, respectively. Calculations and chromatograms were reviewed. No discrepancies were found. Accuracy for this compound was demonstrated in both the LCS and SRM samples. The exceedences</p>
<b>SRM:</b>	<p>A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. The percent difference (PD) between the measured value and the certified range was calculated to measure data quality in terms of accuracy.</p> <p><b>04-0039</b> – No exceedence noted.</p> <p><b>Comments</b> – None.</p>
<b>SURROGATES:</b>	<p>Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).</p> <p><b>04-0039</b> – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).</p> <p><b>Comments</b> – None.</p>

# PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE				PROCEDURAL BLANK	PROCEDURAL BLANK - DUXBURY BAY SEAWATER BACKGROUND		MATRIX SPIKE SUB-OF23CE- SDB3-COMP	MATRIX SPIKE- SUB-OF23CE- SDB3-COMP				MATRIX SPIKE DUPLICATE- SUB-OF23CE- SDB3-COMP				FW21: NIST SRM SPIKING SOLUTION			
Battelle ID	BD936LCS-P				BD935PB-P	BD938PB-P		S0892MS-P	S0892MS-P				S0892MSD-P				BD937SRM-P			
Sample Type	LCS				PB	PB		MS	MS				MSD				SRM			
Collection Date	02/06/04				02/06/04	2/6/2004		02/03/04	2/3/2004				2/3/2004				02/06/04			
Extraction Date	02/06/04				02/06/04	2/6/2004		02/06/04	2/6/2004				2/6/2004				02/06/04			
Analysis Date	02/17/04				02/17/04	2/17/2004		02/17/04	2/17/2004				2/17/2004				02/17/04			
Analytical Instrument	MS				MS	MS		MS	MS				MS				MS			
% Moisture	NA				NA	NA		NA	NA				NA				NA			
% Lipid	NA				NA	NA		NA	NA				NA				NA			
Matrix	LIQUID				LIQUID	LIQUID		LIQUID	LIQUID				LIQUID				LIQUID			
Sample Size	2.00				2.00	2		0.65	0.65				0.65				2.00			
Size Unit-Basis	L LIQUID				L LIQUID	L LIQUID		L LIQUID	L LIQUID				L LIQUID				L LIQUID			
Units	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	NG/L LIQUID		NG/L LIQUID	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	Target	% Difference	
C12(8)	30.97	37.54	82		0.09 U	0.09 U		96.15	96.15	115.50	83		105.53	115.50	91	9.2	28.63	34.24	16.4	
C13(18)	29.49	37.50	79		0.08 U	0.08 U		91.46	91.46	115.38	79		97.97	115.38	85	7.3	27.05	32.93	17.9	
C13(28)	34.38	37.50	92		0.08 U	0.08 U		104.82	104.82	115.38	91		113.46	115.38	98	7.4	30			
C14(44)	28.95	37.50	77		0.15 U	0.15 U		95.92	95.92	115.38	83		102.52	115.38	89	7.0	28.55	32.86	13.1	
C14(49)	32.65	37.65	87		0.15 U	0.15 U		100.77	100.77	115.85	87		107.9	115.85	93	6.7	0.15 U			
C14(52)	39.17	37.54	104		0.15 U	0.15 U		102.41	102.41	115.50	89		106.08	115.50	92	3.3	30.96	33.07	6.4	
C14(66)	34.66	37.50	92		0.15 U	0.15 U		122.23	122.23	115.38	106		126.27	115.38	109	2.8	35.32	32.82	7.6	
C14(77)	29.82	37.54	79		0.18 U	0.18 U		128.19	128.19	115.50	111		130.02	115.50	113	1.8	32.9	33.55	1.9	
C15(87)	28.7	37.50	77		0.15 U	0.15 U		111.7	111.7	115.38	97		115.88	115.38	100	3.0	31.15	33.10	5.9	
C15(101)	32.07	37.54	85		0.15 U	0.15 U		105.05	105.05	115.50	91		106.65	115.50	92	1.1	29.12	32.56	10.6	
C15(105)	29.78	37.54	79		0.14 U	0.14 U		128.47	128.47	115.50	111		128.82	115.50	112	0.9	35.43	32.67	8.4	
C15(114)	0.31 U				0.31 U	0.31 U		0.94 U	0.94 U				0.94 U				0.31 U			
C15(118)	29.05	37.54	77		0.1 U	0.1 U		127.9	127.9	115.50	111		129.74	115.50	112	0.9	34.39	33.02	4.1	
C15(123)	0.11 U				0.11 U	0.11 U		0.33 U	0.33 U				0.33 U				0.11 U			
C15(126)	30.58	37.50	82		0.16 U	0.16 U		136.08	136.08	115.38	118		133.16	115.38	115	2.6	33.24	33.22	0.1	
C16(128)	31.1	37.50	83		0.2 U	0.2 U		119.57	119.57	115.38	104		115.14	115.38	100	3.9	31.22	32.94	5.2	
C16(138)	26.88	37.54	72		0.2 U	0.2 U		113.99	113.99	115.50	99		111.37	115.50	96	3.1	28.52	32.43	12.1	
C16(153)	29.4	37.50	78		0.2 U	0.2 U		111.8	111.8	115.38	97		112.82	115.38	98	1.0	28.8	32.64	11.8	
C16(156)	0.1 U				0.1 U	0.1 U		0.31 U	0.31 U				0.31 U				0.1 U			
C16(157)	0.19 U				0.19 U	0.19 U		0.59 U	0.59 U				0.59 U				0.19 U			
C16(167)	0.35 U				0.35 U	0.35 U		1.09 U	1.09 U				1.09 U				0.35 U			
C16(169)	28.41	37.65	75		0.15 U	0.15 U		137.99	137.99	115.85	119		132.09	115.85	114	4.3	0.15 U			
C17(170)	37.83	37.54	101		0.25 U	0.25 U		151.2	151.2	115.50	131	N	145.2	115.50	126	N	38.26	32.72	16.9	
C17(180)	48.96	37.54	130	N	0.14 U	0.14 U		132.18	132.18	115.50	114		125.12	115.50	108	5.4	38.29	32.96	16.2	
C17(183)	35.2	37.50	94		0.15 U	0.15 U		125.74	125.74	115.38	109		120.85	115.38	105	3.7	0.15 U			
C17(184)	26.69 J	37.65	71		0.15 U	0.15 U		100.96 JE	100.96 JE	115.85	87		98.79 JE	115.85	85	2.3	0.15 U			
C17(187)	30.05	37.54	80		0.15 U	0.15 U		118.09	118.09	115.50	102		116.63	115.50	101	1.0	31.78	32.75	3.0	
C17(189)	0.11 U				0.11 U	0.11 U		0.33 U	0.33 U				0.33 U				0.11 U			
C18(195)	31.85	37.50	85		0.28 U	0.28 U		127.27	127.27	115.38	110		120.3	115.38	104	5.6	31.32	32.83	4.6	
C19(206)	27.58	37.50	74		0.44 U	0.44 U		114.22	114.22	115.38	99		111.79	115.38	97	2.0	27.05	32.02	15.5	
C10(209)	42.01	37.50	112		0.53 U	0.53 U		115.69	115.69	115.38	100		117.65	115.38	102	2.0	32.54	32.99	1.4	
<b>Surrogate Recoveries (%)</b>																				
C12(14)	72				67	71		75	75				83				85			
C13(34)	73				66	70		75	75				82				83			
C15(104)	83				76	77		79	79				84				89			
C15(112)	79				63	71		82	82				85				89			

# PESTICIDES

CLIENT ID	SUB-OF11B-SDB3-COMP		SUB-OF26-SDB3-COMP		SUB-OF23CE-SDB3-COMP	
Battelle ID	S0890-P		S0891-P		S0892-P	
Sample Type	SA		SA		SA	
Collection Date	02/03/04		02/03/04		02/03/04	
Extraction Date	02/06/04		02/06/04		02/06/04	
Analysis Date	02/27/04		02/27/04		02/27/04	
Analytical Instrument	ECD		ECD		ECD	
% Moisture	NA		NA		NA	
% Lipid	NA		NA		NA	
Matrix	FRESHWATER		FRESHWATER		FRESHWATER	
Sample Size	2.64		2.64		1.32	
Size Unit-Basis	L LIQUID		L LIQUID		L LIQUID	
Units	NG/L LIQUID		NG/L LIQUID		NG/L LIQUID	
2,4'-DDD	0.62 U		0.62 U		1.23 U	
2,4'-DDE	0.52 U		0.52 U		1.04 U	
2,4'-DDT	0.37 U		0.37 U		0.73 U	
4,4'-DDD	0.72 U		0.72 U		1.44 U	
4,4'-DDE	0.52 U		0.52 U		1.04 U	
4,4'-DDT	0.45 U		0.45 U		0.89 U	
aldrin	0.3 U		0.3 U		0.6 U	
a-chlordane	0.29 U		0.29 U		0.57 U	
g-chlordane	0.31 U		0.31 U		0.61 U	
a-BHC	0.26 U		0.26 U		0.52 U	
b-BHC	0.36 U		0.36 U		0.72 U	
d-BHC	0.29 U		0.29 U		0.59 U	
Lindane	0.37 U		0.37 U		0.75 U	
cis-nonachlor	0.49 U		0.49 U		0.98 U	
trans-nonachlor	0.31 U		0.31 U		0.61 U	
Chlorpyrifos	0.39 U		0.39 U		0.77 U	
oxychlordane	0.3 U		0.3 U		0.59 U	
dieldrin	0.58 U		0.58 U		1.16 U	
endosulfan I	0.21 U		0.21 U		0.42 U	
endosulfan II	0.52 U		0.52 U		1.05 U	
endosulfan sulfate	0.49 U		0.49 U		0.98 U	
endrin	0.57 U		0.57 U		1.14 U	
endrin aldehyde	0.64 U		0.64 U		1.29 U	
endrin ketone	0.67 U		0.67 U		1.34 U	
heptachlor	0.44 U		0.44 U		0.89 U	
heptachlor epoxide	1.19 U		1.19 U		2.39 U	
Hexachlorobenzene	0.63 U		0.63 U		1.25 U	
methoxychlor	0.74 U		0.74 U		1.48 U	
Mirex	0.47 U		0.47 U		0.94 U	
<b>Surrogate Recoveries (%)</b>						
CI2(14)	70		64		77	
CI3(34)	96		87		79	
CI5(104)	90		76		69	
CI5(112)	79		90		71	

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0015 –Contaminant Analysis of Stormwater and San Diego Bay Seawater

**PARAMETER:** Pesticides

**LABORATORY:** Battelle, Duxbury, MA

**MATRIX:** Water

**SAMPLE CUSTODY:** Water samples were collected over three days 2/2/04 – 2/4/04. Samples were shipped in three containers to Battelle Duxbury via Federal Express. The samples were received on 2/5/04. Upon arrival, the cooler temperatures were recorded at 2.1°C, 2.6°C, and 3.4°C. No custody issues were noted. Samples were stored in the upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 04-0039. Selected samples were chosen for pesticide analysis.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery	≤30% PD on average	≤30% RPD	MDL: ~0.34 – 1.58
				(target spike must be >5 x native conc.)	(for analytes >5x MDL)	(calculated between the MS and MSD samples)	

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
04-0039	2/6/04	2/27/04



<b>BLANK:</b>	<p>Two blank (PB) samples were prepared with the analytical batch. One procedural blank BD935PB was analyzed to ensure the sample extraction and analysis methods were free of contamination. The other blank, BD938PB, was analyzed to give a background value for "clean" seawater. All analytical data has been qualified according to the concentrations detected in BD935PB.</p> <p><b>04-0039</b> – No exceedences noted.</p> <p><b>Comments</b> – No target analytes were detected in sample BD935PB. Lindane, a-BHC, and Heptachlor were detected in sample BD938PB, however these analytes were both below the RL. These detections were qualified with a "J". No further corrective action was taken.</p>
<b>LABORATORY CONTROL SAMPLE:</b>	<p>A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.</p> <p><b>04-0039</b> – All target analytes were recovered within the laboratory control limits specified by the client (40-120%)</p> <p><b>Comments</b> – None.</p>
<b>MATRIX SPIKE/MATRIX SPIKE DUPLICATE:</b>	<p>A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.</p> <p><b>04-0039</b> – Six percent recovery exceedences noted. No RPD exceedences noted.</p> <p><b>Comments</b> – Chlorpyrifos, endrin, and heptachlor were over-recovered in both samples S0892MS and S0892MSD (background sample OF23CE-SDB3-Comb). In</p>
<b>SRM:</b>	<p>A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. The percent difference (PD) between the measured value and the certified range was calculated to measure data quality in terms of accuracy.</p> <p><b>04-0039</b> – No exceedence noted.</p> <p><b>Comments</b> – None.</p>
<b>SURROGATES:</b>	<p>Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).</p> <p><b>04-0039</b> – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).</p> <p><b>Comments</b> – None.</p>



# PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE SUB-OF23CE-SDB3-COMP				MATRIX SPIKE DUPLICATE-SUB-OF23CE-COMP				PROCEDURAL BLANK	PROCEDURAL - DUXBURY BAY SEATWATER BACKGROUND	FW21: NIST SRM SPIKING SOLUTION		
Battelle ID	BD936LCS-P			S0892MS-P				S0892MSD-P				BD935PB-P	BD938PB-P	BD937SRM-P		
Sample Type	LCS			MS				MSD				PB	PB	SRM		
Collection Date	02/06/04			2/3/2004				2/3/2004				02/06/04	2/6/2004	02/06/04		
Extraction Date	02/06/04			2/6/2004				2/6/2004				02/06/04	2/6/2004	02/06/04		
Analysis Date	02/27/04			2/27/2004				2/27/2004				02/27/04	2/27/2004	02/27/04		
Analytical Instrument	ECD			ECD				ECD				ECD	ECD	ECD		
% Moisture	NA			NA				NA				NA	NA	NA		
% Lipid	NA			NA				NA				NA	NA	NA		
Matrix	LIQUID			LIQUID				LIQUID				LIQUID	LIQUID	LIQUID		
Sample Size	2.00			0.65				0.65				2.00	2	2.00		
Size Unit-Basis	L LIQUID			L LIQUID				L LIQUID				L LIQUID	L LIQUID	L LIQUID		
Units	NG LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Target	% Difference
2,4'-DDD	28.05	37.52	75	93.48	115.43	81		99.13	115.43	86	6.0	0.81 U	0.81 U	39.76	31.62	25.7
2,4'-DDE	31.96	37.62	85	116.95	115.75	101		111.86	115.75	97	4.0	0.69 U	0.69 U	31.33	31.34	0.0
2,4'-DDT	16.62	37.62	44	65.3	115.75	56		67.32	115.75	58	3.5	0.48 U	0.48 U	34.7	31.87	8.9
4,4'-DDD	32.76	37.64	87	118.82	115.52	103		118.19	115.52	102	1.0	0.95 U	0.95 U	33.09	31.62	4.6
4,4'-DDE	31.23	37.53	83	94.78	115.47	82		96.85	115.47	84	2.4	0.68 U	0.68 U	34.04	31.47	8.2
4,4'-DDT	29.08	37.55	77	117.85	115.52	102		114.79	115.52	99	3.0	0.59 U	0.59 U	30.04		
aldrin	31.89	37.55	85	105.69	115.53	91		104.96	115.53	91	0.0	0.4 U	0.4 U	36.05	31.55	14.3
a-chlordane	34.92	37.69	93	117.49	115.96	101		117.8	115.96	102	1.0	0.38 U	0.38 U	0.4 U		
g-chlordane	34.17	37.51	91	117.46	115.41	102		116.42	115.41	101	1.0	0.4 U	0.4 U	0.25 J		
a-BHC	27.98	37.54	75	80.54	115.51	70		82.2	115.51	71	1.4	0.34 U	0.19 J	0.47 U		
b-BHC	30.01	37.55	80	106.82	115.53	92		107.19	115.53	93	1.1	0.47 U	0.47 U	0.39 U		
d-BHC	33.29	37.55	89	128.64	115.53	111		125.63	115.53	109	1.8	0.39 U	0.39 U	28.6	31.55	9.4
Lindane	27.99	37.53	75	113.27	115.47	98		112.27	115.47	97	1.0	0.49 U	0.25 J	0.65 U		
cis-nonachlor	30.11	37.80	80	92.92	116.30	80		94.04	116.30	81	1.2	0.65 U	0.65 U	37.54	31.78	18.1
trans-nonachlor	35.23	37.52	94	117.92	115.43	102		118.17	115.43	102	0.0	0.4 U	0.4 U	0.51 U		
Chlorpyrifos	44.14	37.53	118	159.74	115.49	138 N		163.25	115.49	141 N	2.2	0.51 U	0.51 U	0.39 U		
oxychlordane	38.16	37.73	101	127.53	116.10	110		129.9	116.10	112	1.8	0.39 U	0.39 U	29.83	31.55	5.5
dieldrin	28.12	37.53	75	89.4	115.49	77		91.56	115.49	79	2.6	0.76 U	0.76 U	0.27 U		
endosulfan I	37.47	37.54	100	121.34	115.51	105		119.19	115.51	103	1.9	0.27 U	0.27 U	0.69 U		
endosulfan II	25.79	37.54	69	91.27	115.51	79		95.68	115.51	83	4.9	0.69 U	0.69 U	0.65 U		
endosulfan sulfate	32.31	37.54	86	108.45	115.50	94		111.42	115.50	96	2.1	0.65 U	0.65 U	0.75 U		
endrin	44.98	37.54	120	179.68	115.50	158 N		183.01	115.50	158 N	1.3	0.75 U	0.75 U	0.85 U		
endrin aldehyde	15.34	37.53	41	59.47	115.49	51		59.1	115.49	51	0.0	0.85 U	0.85 U	0.89 U		
endrin ketone	27.71	37.54	74	90.13	115.52	78		91.17	115.52	79	1.3	0.89 U	0.89 U	36.51	31.63	15.4
heptachlor	33.69	37.54	90	161.5	115.52	140 N		151.61	115.52	131 N	6.6	0.59 U	0.23 J	35.15	31.63	11.1
heptachlor epoxide	34.01	37.55	91	116.35	115.55	101		116	115.55	100	1.0	1.58 U	1.58 U	29.85	31.49	5.2
Hexachlorobenzene	30.06	37.53	80	93.54	115.47	81		96.17	115.47	83	2.4	0.83 U	0.83 U	0.98 U		
methoxychlor	30.04	37.54	80	110.3	115.51	95		112.73	115.51	98	3.1	0.98 U	0.98 U	29.96	31.86	6.0
Mirex	26.84	37.65	71	79.4	115.83	69		81.38	115.83	70	1.4	0.62 U	0.62 U			
Surrogate Recoveries (%)																
C13(14)	78			73				78				72	74	82		
C13(34)	79			80				83				73	75	73		
C15(104)	74			71				73				70	71	77		
C15(112)	77			72				76				73	73			

## TSS

SAMPLE LABEL	TSS (mg/L)
SUB-OF11B-SDB3-FF	37.15
SUB-OF11B-SDB3-COMP	96.58
SUB-BAY11B-SDB3-DUR	2.33
SUB-BAY11B-SDB3-AFT	3.52
SUB-OF23CE-SDB3-FF	45.10
SUB-OF23CE-SDB3-COMP	54.67
SUB-BAY23CE-SDB3-PRE	3.43
SUB-BAY23CE-SDB3-DUR	3.19
SUB-BAY23CE-SDB3-AFT	2.37
SUB-OF26-SDB3-FF	38.79
SUB-OF26-SDB3-COMP	21.18
SUB-BAY26-SDB3-PRE	2.18
SUB-BAY26-SDB3-DUR	2.46
SUB-BAY26-SDB3-AFT	2.42
SUB-BAY26A-SDB3-PRE	2.99
SUB-BAY26A-SDB3-DUR	2.05
SUB-BAY26A-SDB3-AFT	3.67

## DOC

CLIENT SAMPLE ID	MEAN DOC (mg/L)
SUB-OF11B-SDB3-FF	11.40
SUB-OF11B-SDB3-COMP	11.32
SUB-BAY11B-SDB3-PRE	0.72
SUB-BAY11B-SDB3-DUR	0.47
SUB-BAY11B-SDB3-AFT	0.80
SUB-OF23CE-SDB3-FF	8.97
SUB-OF23CE-SDB3-COMP	13.00
SUB-BAY23CE-SDB3-PRE	0.71
SUB-BAY23CE-SDB3-DUR	0.57
SUB-BAY23CE-SDB3-AFT	0.61
SUB-OF26-SDB3-FF	4.47
SUB-OF26-SDB3-COMP	12.43
SUB-BAY26-SDB3-PRE	0.83
SUB-BAY26-SDB3-DUR	0.70
SUB-BAY26-SDB3-AFT	0.58
SUB-BAY26A-SDB3-PRE	0.52
SUB-BAY26A-SDB3-DUR	0.59
SUB-BAY26A-SDB3-AFT	0.49

## SDB4- 10/17/2004

### METALS

SAMPLE ID	DISSOLVED COPPER (µg/L)	TOTAL COPPER (µg/L)	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
SUB-OF11B-SDB4-FF	93	149	1255	1291
SUB-BAY11B-SDB4-DUR	5	10	53	71

### TSS

SAMPLE LABEL	TSS (mg/L)
SUB-OF11B-SDB4-FF	152.94
SUB-BAY11B-SDB4-DUR	8.60

## **Appendix D3**

### **NAB**

**SDB4- 10/17/2004**

**SDB6- 2/10/2005**

**SDB7- 4/27/2005**

## SDB4- 10/17/2004

### METALS

SAMPLE ID	DISSOLVED Cu (µg/L)	TOTAL Cu (µg/L)
NAB-OF9-SDB4-FF	172	668
NAB-BAY9-SDB4-DUR	17	23

SAMPLE ID	DISSOLVED Zn (µg/L)	TOTAL Zn (µg/L)
NAB-OF9-SDB4-FF	7134	8051
NAB-BAY9-SDB4-DUR	176	256

### TSS

SAMPLE LABEL	TSS (mg/L)
NAB-OF9-SDB4-FF	130.40
NAB-BAY9-SDB4-DUR	12.12

## SDB6- 2/10/2005

### METALS

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES
2157*13		NAB-SDB6-OF9-COMP (T)	192	847	2.11	71.3	4.37	59.5	522
2157*10		NAB-SDB6-OF9-COMP (D)	13.9	31.5	1.18	59.6	3.87	40.0	356
2157*14		NAB-SDB6-OF18-COMP (T)	507	832	2.30	26.1	2.45	44.4	214
2157*11		NAB-SDB6-OF18-COMP (D)	15.0	29.5	0.574	8.58	1.27	26.2	101

MSL		Sponsor	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code	Rep	I.D.	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
2157*13		NAB-SDB6-OF9-COMP (T)	4.93	14.1	0.040 U	0.551	0.50 U	3.21	0.00838
2157*10		NAB-SDB6-OF9-COMP (D)	4.80	14.1	0.040 U	0.414	0.50 U	0.132	0.00309
2157*14		NAB-SDB6-OF18-COMP (T)	2.28	1.47 U	0.0411	0.794	0.550	5.74	0.00711
2157*11		NAB-SDB6-OF18-COMP (D)	1.77	1.47 U	0.040 U	0.322	0.50 U	0.291	0.00410

SAMPLE ID	DISSOLVED COPPER (µg/L)	TOTAL COPPER (µg/L)	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
NAB-OF9-SDB6-FF	37.5	39.8	197	315
NAB-BAY9-SDB6-PRE	2.4	3.6	6.2	8.5
NAB-BAY9-SDB6-DUR	3.5	6.2	32	44
NAB-OF18-SDB6-FF	38.2	43.7	134	137
NAB-BAY18-SDB6-PRE	2.0	3.2	8.3	8.7
NAB-BAY18-SDB6-DUR	7.9	14.9	55	85

## METALS QA/QC

**PROGRAM:** SPAWAR, Task 19  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/OES	50-150%	±20%	±50%	50.0
Iron	ICP/OES	50-150%	±20%	±50%	10.0
Manganese	ICP/OES	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Three (3) samples were analyzed for fourteen (14) metals: nickel (Ni), copper, (Cu), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1631m, aluminum (Al), iron (Fe), chromium (Cr), manganese (Mn), and zinc (Zn) by inductively coupled plasma optical emission spectroscopy following EPA Method 200.7 and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Three (3) samples were received on 2/11/2005 and were logged into Battelle's sample tracking system. The samples were analyzed within the six month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:

Task	Date Performed
Hg	2/23/05
ICP-MS	2/22/05
ICP-OES	3/1 & 4/05

### DETECTION LIMITS

The target detection limit was met for all metals, except Ni, Cu, Se and Cd. The MDL for seawater analysis by dilution is somewhat higher than

our typical MDL's for direct analysis. Sample concentrations were substantially greater than the MDL, except Se. All Se results were less than our MDL for this method. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.

#### **METHOD BLANKS**

One method blank was analyzed with this batch of samples. Results were less than 3 times the MDL for all metals, except the TRM blank for Zn. The TRM field sample was greater than 10 x the blank concentration and therefore was not impacted by the blank contamination.

#### **BLANK SPIKES**

One sample of reagent water was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **MATRIX SPIKES**

One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **REPLICATES**

One sample was analyzed in duplicate. All results were within the QC limits of  $\pm 30\%$  ( $\pm 50\%$  for Al and Fe).

#### **SRM**

One matrix-appropriate standard reference material (SRM) was analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.

SRM 1640 has 22 certified and reference metals. Recovery for all metals reported were within the control limit of  $\pm 20\%$  of the certified or reference value. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of  $\pm 25\%$  of the certified value.

#### **REFERENCES**

EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4- 91-010. Environmental Services Division, Monitoring Management Branch.



# METALS QA/QC (CONT.)

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
<b>PROCEDURAL BLANK</b>																
		Dissolved	3.36 U	2.51 U	0.155 U	0.025 U	0.074 U	0.883 U	0.283 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.00017 U
		Dissolved - OES reanalysis	3.36 U	2.51 U	0.119 U	0.025 U	N/A	N/A	0.113 U	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		TRM	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.705 b	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	N/A
<b>METHOD DETECTION LIMIT</b>			<b>3.36</b>	<b>2.51</b>	<b>0.119</b>	<b>0.025</b>	<b>0.074</b>	<b>0.883</b>	<b>0.113</b>	<b>0.158</b>	<b>1.47</b>	<b>0.040</b>	<b>0.054</b>	<b>NA</b>	<b>0.009</b>	<b>0.00012</b>
Project Target Detection Limit			50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01
<b>STANDARD REFERENCE MATERIAL</b>																
1640		Dissolved	52.8	36.3	37.4	125	26.9	83.9	54.7	28.9	26.2	7.57	24.1	1.63	29.0	NA
1640		Dissolved - OES reanalysis	54.6	34.4	39.0	123	N/A	N/A	54.1	N/A	N/A	N/A	N/A	N/A	N/A	NA
1640		TRM	N/A	N/A	N/A	N/A	26.7	82.3	N/A	25.7	21.1	7.42	22.2	1.71	31.4	NA
1640		certified/reference value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC
		% difference	2%	6%	3%	2%	2%	2%	3%	8%	19%	1%	6%	N/A	4%	N/A
		% difference	5%	0%	1%	1%	N/A	N/A	2%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		% difference	N/A	N/A	N/A	N/A	3%	3%	N/A	4%	4%	3%	3%	N/A	13%	N/A
1641d		% difference	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1497
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1590
1641d		range	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	±18.0
1641d		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	6%
<b>ICV, CCV RESULTS</b>																
ICV			99%	101%	99%	100%	100%	101%	101%	98%	100%	101%	100%	104%	101%	95%
CCV			99%	102%	98%	99%	101%	101%	100%	99%	99%	102%	99%	104%	105%	98%
CCV			101%	105%	98%	98%	98%	98%	100%	97%	97%	100%	99%	101%	107%	NA
CCV			100%	104%	98%	98%	98%	98%	100%	97%	96%	99%	97%	99%	109%	NA
CCV			NA	NA	NA	NA	96%	97%	NA	98%	96%	100%	100%	102%	108%	NA
ICV		OES reanalysis	98%	100%	102%	101%	100%	101%	103%	98%	100%	101%	100%	104%	101%	NA
CCV		OES reanalysis	100%	102%	99%	96%	101%	101%	100%	99%	99%	102%	99%	104%	105%	NA
CCV		OES reanalysis	100%	99%	100%	97%	98%	98%	100%	97%	97%	100%	99%	101%	107%	NA
CCV		OES reanalysis	99%	100%	100%	97%	96%	98%	100%	97%	96%	99%	97%	99%	109%	NA
<b>BLANK SPIKE RESULTS</b>																
		Amount Spiked	100	100	50.0	100	10.0	50.0	50.0	10.0	10.0	10.0	10.0	10.0	10.0	0.00472
		Blank	3.36 U	2.51 U	0.155 U	0.025 U	0.074 U	0.883 U	0.283 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.000407
		Blank + Spike	95.8	108	53.9	125	9.80	50.1	56.7	9.88	9.96	10.3	10.1	10.2	11.2	0.00484
		Amount Recovered	95.8	108	53.7	125	9.80	50.1	56.4	9.88	9.96	10.3	10.1	10.2	11.2	0.00443
		Percent Recovery	96%	108%	107%	125%	98%	100%	113%	99%	100%	103%	101%	102%	112%	94%
<b>MATRIX SPIKE RESULTS</b>																
		Amount Spiked	100	50.0	50.0	50.0	NS	NS	50.0	NS	NS	NS	NS	NS	NS	NS
		NI-SDB6-OF23A-FF (D) + Spike	17.1	20.4	1.02	0.154	N/A	N/A	134	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		NI-SDB6-OF23A-FF (D) + Spike	119	74.2	56.9	54.0	NA	NA	189	NA	NA	NA	NA	NA	NA	NA
		Amount Recovered	102	53.8	55.9	53.8	N/A	N/A	55.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	102%	108%	112%	108%	N/A	N/A	110%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	10.0	50.0	NS	10.0	10.0	10.0	10.0	100.0	10.0	0.0102
		NI-SDB6-OF23A-FF (T)	N/A	N/A	N/A	N/A	3.83	49.4	N/A	1.22	1.47 U	0.0308	0.552	0.251	3.78	0.0118
		NI-SDB6-OF23A-FF (T) + Spike	NA	NA	NA	NA	13.6	102	NA	11.3	11.5	9.72	10.4	95.3	14.9	0.0196
		Amount Recovered	N/A	N/A	N/A	N/A	10	52.6	N/A	10.1	11.5	9.69	9.85	95.0	11.1	0.00780
		Percent Recovery	N/A	N/A	N/A	N/A	98%	105%	N/A	101%	115%	97%	98%	95%	111%	76%
<b>REPLICATE RESULTS</b>																
2360*1	1	NI-SDB6-OF23A-FF (D)	17.1	20.4	1.02	0.154	3.45	42.6	134	0.968	1.47 U	0.04 U	0.369	0.50 U	0.201	0.00593
2360*1	2	NI-SDB6-OF23A-FF (D)	17.6	19.4	1.08	0.153	NA	NA	133	NA	NA	NA	NA	NA	NA	0.00600
		RPD	3%	5%	6%	1%	N/A	N/A	1%	N/A	N/A	N/A	N/A	N/A	N/A	1%
2360*3	1	NI-SDB6-OF23A-FF (T)	290	388	1.47	15.1	3.83	49.4	185	1.22	1.47 U	0.04 U	0.552	0.50 U	3.78	0.0118
2360*3	2	NI-SDB6-OF23A-FF (T)	NA	NA	NA	NA	3.71	48.6	NA	1.15	1.47 U	0.0444	0.541	0.50 U	3.85	NA
		RPD	N/A	N/A	N/A	N/A	3%	2%	N/A	6%	N/A	N/A	2%	N/A	2%	N/A

U = not detected at or above detection limit; NC = not certified; NA = not analyzed or available; N/A = not applicable; b = Sample results are less than 3 x the blank.

# PAHs

CLIENT ID	NAB- OF9-SDB6-FF	NAB- OF9-SDB6- COMP	NAB- BAY9-SDB6- PRE	NAB- BAY9-SDB6- DUR	NAB- OF18-SDB6-FF	NAB- OF18-SDB6- COMP	NAB- BAY18-SDB6- PRE	NAB- BAY18-SDB6- DUR
Battelle ID	S7118-P	S7119-P	S7120-P	S7121-P	S7122-P	S7123-P	S7124-P	S7125-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05
Extraction Date	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05
Analysis Date	03/05/05	03/05/05	03/05/05	03/05/05	03/06/05	03/06/05	03/06/05	03/06/05
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.62	2.60	2.61	2.61	2.60	1.00	2.61	2.60
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Naphthalene	4.14 B	7.85	2.31 J	1.42 J	4.59 B	6.65 J	1.93 J	3.54 B
C1-Naphthalenes	2.88 J	2.08 J	0.51 U	0.51 U	3.29	5.46 J	0.51 U	1.48 J
C2-Naphthalenes	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	1.33 U	0.51 U	0.51 U
C3-Naphthalenes	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	1.33 U	0.51 U	0.51 U
C4-Naphthalenes	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	1.33 U	0.51 U	0.51 U
2-Methylnaphthalene	2.84 J	2.16 J	0.36 U	0.36 U	2.82 J	4.01 J	0.36 U	1.51 J
1-Methylnaphthalene	2.04 J	2.02 J	0.38 U	0.38 U	2.49 J	4.58 J	0.38 U	0.99 J
Biphenyl	2.39 J	4.52	0.48 U	0.48 U	3.24	1.24 U	0.48 U	0.48 U
2,6-dimethylnaphthalene	0.63 U	0.64 U	0.63 U	0.63 U	0.64 U	1.65 U	0.63 U	0.64 U
Acenaphthylene	0.54 U	0.54 U	0.54 U	0.54 U	0.54 U	1.4 U	0.54 U	1.35 J
Acenaphthene	0.57 U	2.29 J	0.57 U	0.57 U	0.57 U	1.49 U	0.57 U	0.57 U
2,3,5-trimethylnaphthalene	0.44 U	0.45 U	0.44 U	0.44 U	0.45 U	1.16 U	0.44 U	0.45 U
Dibenzofuran	1.39 J	2.77 J	0.23 U	0.23 U	1.52 J	0.6 U	0.23 U	0.23 U
Fluorene	1.52 J	2.93 J	0.87 J	0.52 U	1.85 J	1.36 U	0.52 U	1.54 J
C1-Fluorenes	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U	1.36 U	0.52 U	0.52 U
C2-Fluorenes	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U	1.36 U	0.52 U	0.52 U
C3-Fluorenes	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U	1.36 U	0.52 U	0.52 U
Anthracene	1.4 J	2.49 J	0.39 U	0.39 U	1.36 J	1.01 U	0.39 U	0.39 U
Phenanthrene	5.59	11.38	1.32 J	6.92	8.98	10.5	0.83 J	13.64
C1-Phenanthrenes/Anthracenes	3.3	8.2	0.83 U	0.83 U	5.65	2.16 U	0.83 U	7.55
C2-Phenanthrenes/Anthracenes	0.82 U	11.28	0.83 U	0.83 U	8.69	2.16 U	0.83 U	14.31
C3-Phenanthrenes/Anthracenes	0.82 U	8.07	0.83 U	0.83 U	5.13	2.16 U	0.83 U	8.08
C4-Phenanthrenes/Anthracenes	0.82 U	0.83 U	0.83 U	0.83 U	0.83 U	2.16 U	0.83 U	0.83 U
1-Methylphenanthrene	1.45 J	2.95 J	0.47 U	0.47 U	1.92 J	1.22 U	0.47 U	2.86 J
Dibenzothiophene	8.83	14.57	0.39 U	0.39 U	8.41	3.56 J	0.39 U	2.05 J
C1-Dibenzothiophenes	9.15	13.85	0.39 U	0.39 U	12.94	8.2 J	0.39 U	2.35 J
C2-Dibenzothiophenes	24.2	47.41	0.39 U	0.39 U	37.14	28.72	0.39 U	12.9
C3-Dibenzothiophenes	21.76	32.51	0.39 U	0.39 U	31.41	26.22	0.39 U	15.06
C4-Dibenzothiophenes	8.38	16.7	0.39 U	0.39 U	14.14	12.58	0.39 U	7.67
Fluoranthene	6.56	19.95	3.63	21.72	9.62	6.71 J	3.03 J	20.94
Pyrene	4.99	14.35	2.55 J	13.58	10.23	9.04	1.69 J	18.51
C1-Fluoranthenes/Pyrenes	0.68 U	6.31	0.69 U	0.69 U	4.51	1.79 U	0.69 U	6.96
C2-Fluoranthenes/Pyrenes	0.68 U	0.69 U	0.69 U	0.69 U	0.69 U	1.79 U	0.69 U	6.94
C3-Fluoranthenes/Pyrenes	0.68 U	0.69 U	0.69 U	0.69 U	0.69 U	1.79 U	0.69 U	0.69 U
Benzo(a)anthracene	1.21 J	1.02 J	1.04 U	0.63 J	2.11 J	2.73 U	1.04 U	1.15 J
Chrysene	1.91 J	7.74	0.89 J	5.82	4.48	5.67 J	0.45 U	8.45
C1-Chrysenes	0.45 U	4.84	0.45 U	0.45 U	0.45 U	1.18 U	0.45 U	6.52
C2-Chrysenes	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	1.18 U	0.45 U	11.38
C3-Chrysenes	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	1.18 U	0.45 U	0.45 U
C4-Chrysenes	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	1.18 U	0.45 U	0.45 U
Benzo(b)fluoranthene	0.89 U	4.22	0.89 U	3.5	2.1 J	2.32 U	0.89 U	5.42
Benzo(i)k)fluoranthene	1 U	1.53 J	1 U	2.74 J	1.5 J	2.62 U	1 U	3.25 J
Benzo(e)pyrene	0.39 U	0.4 U	0.39 U	2.77 J	2.15 J	1.03 U	0.39 U	6.36
Benzo(a)pyrene	0.77 U	0.77 U	0.77 U	0.77 U	0.77 U	2.01 U	0.77 U	0.77 U
Perylene	1.47 U	1.48 U	1.48 U	1.48 U	1.48 U	3.86 U	1.48 U	1.48 U
Indeno(1,2,3-cd)pyrene	0.76 U	0.76 U	0.76 U	0.76 U	0.76 U	1.98 U	0.76 U	2.7 J
Dibenz(a,h)anthracene	0.64 U	0.64 U	0.64 U	0.64 U	0.64 U	1.68 U	0.64 U	1.98 J
Benzo(g,h,i)perylene	1.39 J	3.81	0.76 U	1.18 J	1.73 J	4.82 J	0.76 U	10.46

## PAHs (CONT.)

CLIENT ID	NAB- OF9-SDB6-FF		NAB- OF9-SDB6- COMP		NAB- BAY9-SDB6- PRE		NAB- BAY9-SDB6- DUR		NAB- OF18-SDB6-FF		NAB- OF18-SDB6- COMP		NAB- BAY18-SDB6- PRE		NAB- BAY18-SDB6- DUR	
<i>Surrogate Recoveries (%)</i>																
Naphthalene-d8	32	N	63		56		41		59		40		62		49	
Phenanthrene-d10	45		80		74		62		71		64		68		76	
Chrysene-d12	39	N	69		72		61		59		56		66		67	

## PAHs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PAH	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.47 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for PAH were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	2/25/05 – 3/6/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected above the laboratory control limit (>5 x MDL), however naphthalene was detected in the procedural blank at a concentration less than the reporting limit (RL). The data was qualified with a “J” in the procedural blank. Any authentic field sample naphthalene concentrations that are greater than the reporting limit but less than five times the concentration detected in

**LABORATORY  
CONTROL  
SAMPLE:**

the associated blank, were qualified with a “B”. This resulted in three samples having “B” qualified naphthalene data; S7118 (OF-NAB9-SDB6-FF), S7122 (OF-NAB18-SDB6-FF), and S7125 (BAY-NAB18-SD86-D). No further corrective action was taken.

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**Comments** – None.

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Two exceedences noted.

**CALIBRATIONS:**

**Comments** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery), except for naphthalene-d8 and chrysene-d12 in sample S7118 (OF-NAB9-SDB6-FF). The recoveries for these compounds were calculated to be 32% and 39%, respectively. Chromatography and calculations were reviewed. No discrepancies were found. The exceedences were qualified with an “N”. No further corrective action taken. The GC/MS is calibrated with a minimum of a 5 level curve. The RSD between response factors for the individual target analytes must be  $<25\%$ . Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of minimally every 10 samples. This PD between the initial calibration RF and the check should be  $<25\%$  for individual analytes.

**04-0103** – No calibration exceedences.

**Comments** – None.

# PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE NAB-OF18-SDB6-COMP				MATRIX SPIKE DUPLICATE-NAB-OF18-SDB6-COMP					PROCEDURAL BLANK	GG73: PCB/PESTICIDE SRM SOLUTION			
Battelle ID	BF876LCS-P			S7123MS-P				S7123MSD-P					BF875PB-P	BF877SRM-P			
Sample Type	LCS			MS				MSD					PB	SRM			
Collection Date	02/17/05			2/11/2005				2/11/2005					02/17/05	02/17/05			
Extraction Date	02/17/05			2/17/2005				2/17/2005					02/17/05	02/17/05			
Analysis Date	02/25/05			3/6/2005				3/6/2005					02/25/05	02/25/05			
Analytical Instrument	MS			MS				MS					MS	MS			
% Moisture	NA			NA				NA					NA	NA			
% Lipid	NA			NA				NA					NA	NA			
Matrix	LIQUID			WATER				WATER					LIQUID	LIQUID			
Sample Size	2.00			0.825				0.825					2.00	2.00			
Size Unit-Basis	L LIQUID			L LIQUID				L LIQUID					L LIQUID	L LIQUID			
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	Target	% Recovery	RPD (%)		NG/L LIQUID	NG/L LIQUID	Certified Range	% Difference	
Naphthalene	579.24	1000.60	58	1379.31	2425.70	57		1415.95	2425.70	58	1.7		0.94	1064.46	1000.60 - 1000.60	6.4	
C1-Naphthalenes	0.66	U		1758.57				1835.46					0.66	0.66	U		
C2-Naphthalenes	0.66	U		1.61	U			1.61	U				0.66	0.66	U		
C3-Naphthalenes	0.66	U		1.61	U			1.61	U				0.66	0.66	U		
C4-Naphthalenes	0.66	U		1.61	U			1.61	U				0.66	0.66	U		
2-Methylnaphthalene	604.62	1002.00	60	1550.81	2429.09	64		1622.32	2429.09	67	4.6		0.47	891.98	1002.00 - 1002.00	11.0	
1-Methylnaphthalene	578.63	1001.20	58	1441.76	2427.15	59		1524.17	2427.15	63	6.6		0.5	855.14	1001.20 - 1001.20	14.6	
Biphenyl	587.69	1000.20	59	1683.06	2424.73	69		1779.39	2424.73	73	5.6		0.62	861.16	1000.20 - 1000.20	13.9	
2,6-dimethylnaphthalene	614.44	1001.00	61	1620.23	2426.67	67		1724.13	2426.67	71	5.8		0.83	909.31	1001.00 - 1001.00	9.2	
Acenaphthylene	597.78	1000.65	60	1497.71	2425.82	62		1600.06	2425.82	66	6.3		0.7	877.83	1000.65 - 1000.65	12.3	
Acenaphthene	616.18	1000.75	62	1505.37	2426.06	62		1607.01	2426.06	66	6.3		0.75	918.77	1000.75 - 1000.75	8.2	
2,3,5-trimethylnaphthalene	602.88	1000.30	60	1629.66	2424.97	67		1767.26	2424.97	73	8.6		0.58	890.92	1000.30 - 1000.30	10.9	
Dibenzofuran	621.82	1002.20	62	1865.44	2429.58	77		2020.42	2429.58	83	7.5		0.3	933.56	1002.20 - 1002.20	6.8	
Fluorene	620.55	1000.70	62	1697.98	2425.94	70		1848.13	2425.94	76	8.2		0.68	916.71	1000.70 - 1000.70	8.4	
C1-Fluorenes	0.68	U		1.65	U			1.65	U				0.68	0.68	U		
C2-Fluorenes	0.68	U		1.65	U			1.65	U				0.68	0.68	U		
C3-Fluorenes	0.68	U		1.65	U			1.65	U				0.68	0.68	U		
Anthracene	703.01	1000.65	70	1819.86	2425.82	75		2059.39	2425.82	85	12.5		0.51	1037	1000.65 - 1000.65	3.6	
Phenanthrene	677.73	1000.65	68	1837.78	2425.82	75		2059.16	2425.82	84	11.3		1.08	1005.31	1000.65 - 1000.65	0.5	
C1-Phenanthrenes/Anthracenes	1.08	U		1292.49				1434.89					1.08	1.08	U		
C2-Phenanthrenes/Anthracenes	1.08	U		27.92				35.44					1.08	1.08	U		
C3-Phenanthrenes/Anthracenes	1.08	U		30.03				36.58					1.08	1.08	U		
C4-Phenanthrenes/Anthracenes	1.08	U		2.62	U			2.62	U				1.08	1.08	U		
1-Methylphenanthrene	693.54	1000.30	69	1890.47	2424.97	78		2124.46	2424.97	88	12.0		0.61	1021.46	1000.30 - 1000.30	2.1	
Dibenzothiophene	687.95	1001.00	69	1834.13	2426.67	75		2061.43	2426.67	85	12.5		0.5	1019.19	1001.00 - 1001.00	1.8	
C1-Dibenzothiophenes	0.5	U		12.59				12.51					0.5	0.5	U		
C2-Dibenzothiophenes	0.5	U		48.6				43.67					0.5	0.5	U		
C3-Dibenzothiophenes	0.5	U		49.59				53.46					0.5	0.5	U		
C4-Dibenzothiophenes	0.5	U		33.75				35.06					0.5	0.5	U		
Fluoranthene	703.26	1000.50	70	1862.97	2425.45	77		2104.3	2425.45	86	11.0		0.77	1041.81	1000.50 - 1000.50	4.1	
Pyrene	718.86	1000.50	72	1865.04	2425.45	77		2089.62	2425.45	86	11.0		0.9	1067.39	1000.50 - 1000.50	6.7	
C1-Fluoranthenes/Pyrenes	0.9	U		17.67				19.81					0.9	0.9	U		
C2-Fluoranthenes/Pyrenes	0.9	U		2.17	U			2.17	U				0.9	0.9	U		
C3-Fluoranthenes/Pyrenes	0.9	U		2.17	U			2.17	U				0.9	0.9	U		
Benzo(a)anthracene	621.47	1000.60	62	1462.91	2425.70	60		1604.23	2425.70	66	9.5		1.36	856.76	1000.60 - 1000.60	14.4	
Chrysene	730.19	1000.75	73	1556.53	2426.06	64		1657.64	2426.06	68	6.1		0.59	1045.65	1000.75 - 1000.75	4.5	
C1-Chrysenes	0.59	U		17.96				26.53					0.59	0.59	U		
C2-Chrysenes	0.59	U		30.65				38.76					0.59	0.59	U		
C3-Chrysenes	0.59	U		1.43	U			3.54	J				0.59	0.59	U		
C4-Chrysenes	0.59	U		1.43	U			1.43	U				0.59	0.59	U		
Benzo(b)fluoranthene	673.96	1000.75	67	1818.68	2426.06	75		2085.1	2426.06	86	13.7		1.16	935.5	1000.75 - 1000.75	6.5	
Benzo(k)fluoranthene	777.31	1000.65	78	1891.52	2425.82	78		2136.71	2425.82	88	12.0		1.31	1086.15	1000.65 - 1000.65	8.5	
Benzo(a)pyrene	702.15	1001.80	70	1823.17	2428.61	75		2063.07	2428.61	85	12.5		0.51	979.25	1001.80 - 1001.80	2.3	
Benzo(a)pyrene	629.4	1000.65	63	1716.19	2425.82	71		1960.11	2425.82	81	13.2		1	876.77	1000.65 - 1000.65	12.4	
Perylene	656.25	1000.20	66	1707.57	2424.73	70		1955.41	2424.73	81	14.6		1.93	909.5	1000.20 - 1000.20	9.1	
Indeno(1,2,3-cd)pyrene	723.98	1000.60	72	1676.14	2425.70	69		1869.45	2425.70	77	11.0		0.99	1033.73	1000.60 - 1000.60	3.3	
Dibenz(a,h)anthracene	685.03	1000.55	68	1982.27	2425.58	82		2274.52	2425.58	94	13.6		0.84	916.9	1000.55 - 1000.55	8.4	
Benzo(g,h,i)perylene	705.89	1000.70	71	1939.71	2425.94	80		2258.51	2425.94	93	15.0		0.99	971.43	1000.70 - 1000.70	2.9	

## PAHs QA/QC

CLIENT ID	LABORATORY CONTROL SAMPLE				MATRIX SPIKE NAB-OF18-SDB6- COMP				MATRIX SPIKE DUPLICATE-NAB- OF18-SDB6-COMP						PROCEDURAL BLANK	GG73: PCB/PESTICIDE SRM SOLUTION			
<i>Surrogate Recoveries (%)</i>																			
Naphthalene-d8	61				55				58						42	51			
Phenanthrene-d10	71				77				84						44	63			
Chrysene-d12	72				66				69						43	66			

## PCBs

CLIENT ID	NAB- OF9-SDB6-FF	NAB- OF9-SDB6- COMP	NAB- BAY9-SDB6- PRE	NAB- BAY9-SDB6- DUR	NAB- OF18-SDB6-FF	NAB- OF18-SDB6- COMP	NAB- BAY18-SDB6- PRE	NAB- BAY18-SDB6- DUR
Battelle ID	S7118-P	S7119-P	S7120-P	S7121-P	S7122-P	S7123-P	S7124-P	S7125-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005
Extraction Date	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005
Analysis Date	3/6/2005	3/6/2005	3/6/2005	3/6/2005	3/6/2005	3/6/2005	3/7/2005	3/7/2005
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.62	2.60	2.61	2.61	2.60	1.00	2.61	2.60
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Cl2(8)	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.18 U	0.07 U	0.07 U
Cl3(18)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.22 U	0.08 U	0.08 U
Cl3(28)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.22 U	0.08 U	0.08 U
Cl4(44)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.38 U	0.15 U	0.15 U
Cl4(49)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.38 U	0.15 U	0.15 U
Cl4(52)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.38 U	0.15 U	0.15 U
Cl4(66)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.38 U	0.15 U	0.15 U
Cl4(77)	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.37 U	0.14 U	0.14 U
Cl5(87)	0.23 U	0.24 U	0.24 U	0.24 U	0.24 U	0.61 U	0.24 U	0.24 U
Cl5(101)	0.23 U	0.24 U	0.24 U	0.24 U	0.24 U	0.61 U	0.24 U	0.24 U
Cl5(105)	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.28 U	0.11 U	0.11 U
Cl5(114)	0.23 U	0.24 U	0.24 U	0.24 U	0.24 U	0.61 U	0.24 U	0.24 U
Cl5(118)	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.19 U	0.07 U	0.07 U
Cl5(123)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.21 U	0.08 U	0.08 U
Cl5(126)	0.12 U	0.12 U	0.12 U	0.12 U	0.12 U	0.31 U	0.12 U	0.12 U
Cl6(128)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.71 U	0.27 U	0.27 U
Cl6(138)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.71 U	0.27 U	0.27 U
Cl6(153)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.71 U	0.27 U	0.27 U
Cl6(156)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.2 U	0.08 U	0.08 U
Cl6(157)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.38 U	0.15 U	0.15 U
Cl6(167)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.71 U	0.27 U	0.27 U
Cl6(169)	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.29 U	0.11 U	0.11 U
Cl7(170)	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.49 U	0.19 U	0.19 U
Cl7(180)	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.28 U	0.11 U	0.11 U
Cl7(183)	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.49 U	0.19 U	0.19 U
Cl7(184)	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.49 U	0.19 U	0.19 U
Cl7(187)	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.49 U	0.19 U	0.19 U
Cl7(189)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.21 U	0.08 U	0.08 U
Cl8(195)	0.36 U	0.37 U	0.37 U	0.37 U	0.37 U	0.95 U	0.37 U	0.37 U
Cl9(206)	0.34 U	0.34 U	0.34 U	0.34 U	0.34 U	0.89 U	0.34 U	0.34 U
Cl10(209)	0.41 U	0.41 U	0.41 U	0.41 U	0.41 U	1.07 U	0.41 U	0.41 U
Surrogate Recoveries (%)								
Cl2(14)	41	77	63	51	64	56	63	70
Cl3(34)	43	76	67	57	67	61	64	74



## PCBs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.09 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate and concentrated. The extract was then fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	3/5/05 – 3/7/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.

**LABORATORY  
CONTROL  
SAMPLE:**

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**Comments** – None.

**SURROGATES:**

Two surrogate compounds were added prior to extraction, including PCB 14 and PCB 34. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATIONS:**

The GC/MS is calibrated with a minimum of a 6-point curve. The co-efficient of determination must be  $\geq 0.995$  for each target analyte. Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of every 12 hours (minimally). This PD between the initial calibration RF and the check should be  $<20\%$  for individual analytes; 15% on average. Additionally an ICC check was run with the initial calibration. The PD for the ICC should be  $< 15\%$ , for each analyte.

**05-0056** – No calibration exceedences.

**Comments** – None.

## PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE- NAB-OF18- SDB6-COMP			MATRIX SPIKE DUPLICATE- NAB-OF18- SDB6-COMP					PRODECURAL BLANK		GG73: PCB/PESTICIDE SRM SOLUTION											
Battelle ID	BF876LCS-P			S7123MS-P			S7123MSD-P					BF875PB-P		BF877SRM-P											
Sample Type	LCS			MS			MSD					PB		SRM											
Collection Date	2/17/2005			2/11/2005			2/11/2005					2/17/2005		2/17/2005											
Extraction Date	2/17/2005			2/17/2005			2/17/2005					2/17/2005		2/17/2005											
Analysis Date	3/5/2005			3/6/2005			3/7/2005					3/5/2005		3/5/2005											
Analytical Instrument	MS			MS			MS					MS		MS											
% Moisture	NA			NA			NA					NA		NA											
% Lipid	NA			NA			NA					NA		NA											
Matrix	LIQUID			WATER			WATER					LIQUID		LIQUID											
Sample Size	2.00			0.825			0.825					2.00		2.00											
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID					L LIQUID		L LIQUID		Certified	Value	+/-	Passing		Passing				
Units	NG/L LIQUID	Target	% Recovery	Q	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID											
C1(8)	20.94	40.12	52		57.93	97.26	60		65.69	97.26	68	12.5	0.09 U	28.71		34.24	2.88	23.41		8.5					
C1(18)	23.48	40.12	59		63.17	97.26	65		72.28	97.26	74	12.9	0.11 U	33.26		32.93	0.30	15.92		0.1					
C1(28)	21.18	40.04	53		58.47	97.07	60		66.61	97.07	69	14.0	0.11 U	31.4				15							
C1(44)	23.36	40.08	58		67.71	97.16	70		80.77	97.16	83	17.0	0.19 U	31.8		32.86	0.59	16.8		1.5					
C1(49)	26.89	40.16	67		72.7	97.36	75		86.35	97.36	89	17.1	0.19 U	0.19 U				15							
C1(52)	22.65	40.00	57		64.69	96.97	67		76.93	96.97	79	16.4	0.19 U	30.17		33.07	0.38	16.16		7.7					
C1(66)	16.82	40.04	42		56	97.07	58		65.49	97.07	67	14.4	0.19 U	23.19		32.82	0.62	16.9		28					
C1(77)	17.85	40.00	45		60.54	96.97	62		69.94	96.97	72	14.9	0.18 U	24.75		33.55	1.10	18.29		23.7					
C1(87)	25.33	40.00	63		82.81	96.97	85		96.23	96.97	99	15.2	0.31 U	35.34		33.1	0.27	15.82		5.9					
C1(101)	23.84	40.08	59		72.85	97.16	75		86.65	97.16	89	17.1	0.31 U	31.49		33.6	0.47	16.43		1.9					
C1(105)	23.38	40.04	58		78.35	97.07	81		90.65	97.07	93	13.8	0.14 U	34.77		32.67	1.01	18.09		3.2					
C1(114)	0.31 U				0.74 U				0.74 U				0.31 U	0.31 U					15						
C1(118)	16.89	40.04	42		58.07	97.07	61		70.11	97.07	72	16.5	0.1 U	30.68		32.74	1.06	18.23		3.2					
C1(123)	0.11 U				0.26 U				0.26 U				0.11 U	0.11 U				15							
C1(126)	21.05	40.24	52		73.18	97.55	75		83.73	97.55	86	13.7	0.16 U	32.14		33.22	1.38	19.14		1					
C1(128)	20.67	40.24	51		70.52	97.55	72		81.83	97.55	84	15.4	0.35 U	28.54		32.94	0.27	15.83		12.6					
C1(138)	23.4	40.08	58		83.59	97.16	86		93.09	97.16	96	11.0	0.35 U	32.27		32.43	0.38	16.18		1					
C1(153)	23.31	40.04	58		78.01	97.07	80		91.91	97.07	95	17.1	0.35 U	31.88		32.64	0.62	16.91		0.4					
C1(156)	0.1 U				0.24 U				0.24 U				0.1 U	0.1 U				15							
C1(157)	0.19 U				0.46 U				0.46 U				0.19 U	0.19 U				15							
C1(167)	0.35 U				0.86 U				0.86 U				0.35 U	0.35 U				15							
C1(169)	23.83	40.16	59		80.81	97.36	83		95.7	97.36	98	16.6	0.15 U	31.5		32.83	0.35	16.3							
C1(170)	20.19	40.20	50		66.97	97.45	69		81.17	97.45	83	18.4	0.25 U	28.45		32.72	0.54	16.66		11.6					
C1(180)	23.14	40.16	58		78.45	97.36	81		93.41	97.36	96	16.9	0.14 U	32.98		32.96	0.32	15.97		1					
C1(183)	24.37	40.16	61		83	97.36	85		96.91	97.36	100	16.2	0.25 U	0.25 U				15							
C1(184)	24.69	40.16	61		80.23	97.36	82		94.21	97.36	97	16.8	0.25 U	0.25 U				15							
C1(187)	20.63	40.12	51		73.67	97.26	76		89.41	97.26	92	19.0	0.25 U	31.89		32.75	0.30	15.93		1.7					
C1(189)	0.11 U				0.26 U				0.26 U				0.11 U	0.11 U				15							
C1(195)	20.93	40.12	52		72.11	97.26	74		85.1	97.26	87	16.1	0.48 U	28.04		32.83	0.66	17		12.8					
C1(206)	22.82	40.12	57		74.32	97.26	76		90.8	97.26	93	20.1	0.44 U	32.94		32.02	0.59	16.85							
C1(209)	29.36	40.04	73		81.36	97.07	84		99.02	97.07	102	19.4	0.53 U	40.51		32.99	0.45	16.36		21.1					
Surrogate Recoveries (%)																									
C1(14)	58				67				78				40	55											
C1(34)	59				69				79				40	56											

# PESTICIDES

CLIENT ID	NAB- OF9-SDB6-FF	NAB- OF9-SDB6- COMP	NAB- OF9-SDB6-PRE	NAB OF9-SDB6-DUR	NAB- OF18-SDB6-FF	NAB- OF18-SDB6- COMP	NAB- BAY18-SDB6- PRE	NAB- BAY18-SDB6- DUR
Battelle ID	S7118-P	S7119-P	S7120-P	S7121-P	S7122-P	S7123-P	S7124-P	S7125-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05
Extraction Date	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05
Analysis Date	02/27/05	02/27/05	02/27/05	02/27/05	02/27/05	02/27/05	02/28/05	02/28/05
Analytical Instrument	ECD	ECD	ECD	ECD	ECD	ECD	ECD	ECD
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.62	2.60	2.61	2.61	2.60	1.00	2.61	2.60
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
2,4'-DDD	0.62 U	0.63 U	0.62 U	0.62 U	0.63 U	1.63 U	0.62 U	0.63 U
2,4'-DDE	0.41 J	0.76 U	0.53 U	0.53 U	0.53 U	1.37 U	0.53 U	0.53 U
2,4'-DDT	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	0.97 U	0.37 U	0.37 U
4,4'-DDD	0.73 U	0.73 U	0.73 U	0.73 U	0.73 U	1.9 U	0.73 U	0.73 U
4,4'-DDE	0.52 U	0.53 U	0.52 U	0.52 U	0.53 U	1.37 U	0.52 U	0.53 U
4,4'-DDT	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	1.18 U	0.45 U	0.45 U
aldrin	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.79 U	0.3 U	0.3 U
a-chlordane	0.29 U	0.29 U	0.29 U	0.29 U	0.29 U	0.76 U	0.29 U	0.29 U
g-chlordane	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.81 U	0.31 U	0.31 U
a-BHC	0.26 U	0.26 U	0.26 U	0.26 U	0.26 U	0.69 U	0.26 U	0.26 U
b-BHC	0.36 U	0.36 U	0.36 U	0.36 U	0.36 U	0.95 U	0.36 U	0.36 U
d-BHC	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.78 U	0.3 U	0.3 U
Lindane	0.38 U	0.38 U	0.38 U	0.38 U	0.38 U	0.99 U	0.38 U	0.38 U
cis-nonachlor	0.49 U	0.5 U	0.5 U	0.5 U	0.5 U	1.29 U	0.5 U	0.5 U
trans-nonachlor	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.81 U	0.31 U	0.31 U
Chlorpyrifos	0.39 U	0.39 U	0.39 U	0.39 U	0.39 U	1.02 U	0.39 U	0.39 U
oxychlordane	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.78 U	0.3 U	0.3 U
dieldrin	0.58 U	0.59 U	0.59 U	0.59 U	0.59 U	1.53 U	0.59 U	0.59 U
endosulfan I	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.55 U	0.21 U	0.21 U
endosulfan II	0.53 U	0.53 U	0.53 U	0.53 U	0.53 U	1.38 U	0.53 U	0.53 U
endosulfan sulfate	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	1.3 U	0.5 U	0.5 U
endrin	0.57 U	0.58 U	0.58 U	0.58 U	0.58 U	1.5 U	0.58 U	0.58 U
endrin aldehyde	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	1.7 U	0.65 U	0.65 U
endrin ketone	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U	1.78 U	0.68 U	0.68 U
heptachlor	0.45 U	4.57 U	0.45 U	0.45 U	5.65 U	1.17 U	0.45 U	0.45 U
heptachlor epoxide	1.2 U	1.21 U	1.21 U	1.21 U	1.21 U	3.15 U	1.21 U	1.21 U
Hexachlorobenzene	0.63 U	0.64 U	0.63 U	0.63 U	0.64 U	1.65 U	0.63 U	0.64 U
methoxychlor	0.75 U	0.75 U	0.75 U	0.75 U	0.75 U	1.76 U	0.75 U	0.75 U
Mirex	0.47 U	0.48 U	0.47 U	0.47 U	0.48 U	1.24 U	0.47 U	0.48 U
<b>Surrogate Recoveries (%)</b>								
Cl2(14)	61	92	80	65	96	74	77	92
Cl3(34)	59	86	78	66	92	65	74	82
Cl5(104)	47	73	77	66	68	67	72	86
Cl5(112)	49	84	79	68	71	67	75	81

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Conataminant Analysis of Stormwater  
**PARAMETER:** Pesticides  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.38 – 1.58

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	2/25/05 – 2/28/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with the analytical batch. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – Two exceedences noted.

**Comments** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD), except for 2,4-DDD and 2,4-DDT. The percent differences calculated for these two compounds are 58.5% and 51.0%, respectively. Chromatography and calculations were reviewed. No discrepancies were found. The data has been qualified with an “N”. Accuracy for this compound has adequately been demonstrated in the LCS, MS, and MSD QC samples.

**SURROGATES**

Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATIONS:**

The instrument is calibrated with a 5-level (minimum) calibration, ranging in concentration from ~0.001 ng/uL to ~0.125 ng/uL. Calibration checks are analyzed minimally every 10 samples. The samples must be bracketed by passing calibrations.

**04-0275** – No exceedences noted.

**Comments** – All calibration criteria were met except for two percent differences calculated for HCB in two calibration checks. However since this compound was not detected in any field samples, and accuracy for this compound was adequately demonstrated in all other QC samples, no further corrective action was taken.



# PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE-NAB-OF18-SDB6-COMP			MATRIX SPIKE DUPLICATE-NAB-OF18-SDB6-COMP				PROCEDURAL BLANK	GG73: PCB/PESTICIDE SRM SOLUTION			
Battelle ID	BF876LCS-P			S7123MS-P			S7123MSD-P				BF875PB-P	BF877SRM-P			
Sample Type	LCS			MS			MSD				PB	SRM			
Collection Date	02/17/05			2/11/2005			2/11/2005				02/17/05	02/17/05			
Extraction Date	02/17/05			2/17/2005			2/17/2005				02/17/05	02/17/05			
Analysis Date	02/25/05			2/27/2005			2/27/2005				02/25/05	02/25/05			
Analytical Instrument	ECD			ECD			ECD				ECD	ECD			
% Moisture	NA			NA			NA				NA	NA			
% Lipid	NA			NA			NA				NA	NA			
Matrix	LIQUID			WATER			WATER				LIQUID	LIQUID			
Sample Size	2.00			0.825			0.825				2.00	2.00			
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	L LIQUID			
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	Certified Range	% Difference	
2,4'-DDD	25.61	40.12	64	67.68	97.26	70	75.58	97.26	78	10.8	0.81 U	50.48	31.30 - 31.84	58.5	N
2,4'-DDE	23.38	40.01	58	59.57	97.00	61	68.91	97.00	71	15.2	0.69 U	21.94	31.35 - 31.89	30.0	
2,4'-DDT	21.07	40.23	52	52.73	97.53	54	59.9	97.53	61	12.2	0.48 U	15.3	31.20 - 31.48	51.0	N
4,4'-DDD	26.02	40.01	65	68.94	96.98	71	77.31	96.98	80	11.9	0.95 U	24.59	31.44 - 32.30	21.8	
4,4'-DDE	25.33	40.01	63	65.61	96.98	68	74.09	96.98	76	11.1	0.68 U	27.41	31.46 - 31.78	12.9	
4,4'-DDT	28.23	40.02	71	88.61	97.02	91	98.05	97.02	101	10.4	0.59 U	31.36	31.28 - 31.66	1.0	
aldrin	24.44	40.01	61	64.72	97.00	67	73.01	97.00	75	11.3	0.4 U	24.22			
a-chlordane	23.46	40.03	59	63	97.04	65	71.99	97.04	74	12.9	0.38 U	26.5	31.36 - 31.74	15.5	
g-chlordane	23.1	40.06	58	62.91	97.12	65	71.26	97.12	73	11.6	0.4 U	0.4 U			
a-BHC	23.05	40.02	58	61.5	97.01	63	70	97.01	72	13.3	0.34 U	0.34 U			
g-BHC	26.04	40.01	65	71.33	96.98	74	81.52	96.98	84	12.7	0.47 U	0.47 U			
g-BHC	26.74	40.02	67	75.54	97.01	78	86.61	97.01	89	13.2	0.39 U	0.39 U			
Lindane	26.6	40.01	66	72.67	96.99	75	82.78	96.99	85	12.5	0.49 U	30.23	31.39 - 31.71	3.7	
cis-nonachlor	25.29	40.03	63	66.56	97.04	69	74.86	97.04	77	11.0	0.65 U	0.65 U			
trans-nonachlor	24.46	40.06	61	67.21	97.11	69	76.42	97.11	79	13.5	0.4 U	27.77	31.56 - 32.00	12.0	
Chlorpyrifos	26	40.10	65	75.11	97.21	77	86.23	97.21	89	14.5	0.51 U	0.51 U			
oxychlordane	24.48	40.03	61	66.19	97.04	68	74.74	97.04	77	12.4	0.39 U	0.39 U			
dieldrin	25.77	40.01	64	66.66	96.99	69	75.03	96.99	77	11.0	0.76 U	28.21	31.34 - 31.76	10.0	
endosulfan I	25.15	40.03	63	73.26	97.04	75	73.82	97.04	76	1.3	0.27 U	0.27 U			
endosulfan II	24.17	40.02	60	65.82	97.02	68	76.63	97.02	79	15.0	0.69 U	0.69 U			
endosulfan sulfate	25.59	40.02	64	74.76	97.01	77	84.21	97.01	87	12.2	0.65 U	0.65 U			
endrin	25.18	40.01	63	72.34	97.00	75	81.04	97.00	84	11.3	0.75 U	0.75 U			
endrin aldehyde	19.49	40.01	49	51.31	96.99	53	65.18	96.99	67	23.3	0.85 U	13.8			
endrin ketone	26.63	40.02	67	72.67	97.01	75	82.31	97.01	85	12.5	0.89 U	0.89 U			
heptachlor	25.65	40.00	64	77.01	96.98	79	87.83	96.98	91	14.1	0.59 U	29.59	31.39 - 31.87	5.7	
heptachlor epoxide	25.41	40.01	64	66.79	96.98	69	76.31	96.98	79	13.5	1.58 U	27.77	31.36 - 31.90	11.4	
Hexachlorobenzene	28.14	40.06	70	72.56	97.12	75	82.98	97.12	85	12.5	0.83 U	32.05	31.35 - 31.63	1.3	
methoxychlor	28.49	40.01	74	91.3	97.00	92	101.57	97.00	103	11.3	0.98 U	7.8			
Mirex	26.25	40.03	66	69.14	97.05	71	77.47	97.05	80	11.9	0.62 U	29.19	31.41 - 32.31	7.1	
<b>Surrogate Recoveries (%)</b>															
Cl2(14)	71			81			95				51	69			
Cl3(34)	72			76			87				51	68			
Cl5(104)	69			80			92				50	60			
Cl5(112)	72			77			85				53	69			

## TSS

SAMPLE LABEL	TSS (mg/L)
NAB-OF9-SDB6-FF	6.30
NAB-OF9-SDB6-COMP	10.00
NAB-BAY9-SDB6-PRE	5.51
NAB-BAY9-SDB6-DUR	8.29
NAB-OF18-SDB6-FF	5.83
NAB-OF18-SDB6-COMP	20.30
NAB-BAY18-SDB6-PRE	2.15
NAB-BAY18-SDB6-DUR	11.47



## SDB7- 4/27/2005

### METALS

MSL		Sponsor	Al (µg/L)		Fe (µg/L)		Cr (µg/L)		Mn (µg/L)		Ni (µg/L)		Cu (µg/L)		Zn (µg/L)	
Code	Rep	I.D.	ICP-OES		ICP-OES		ICP-OES		ICP-OES		ICP-MS		ICP-MS		ICP-OES	
2360*11		NAB-OF9-SDB7-COMP (T)	1085		5394		6.41		159		11.6		108		1832	
2360*6		NAB-OF9-SDB7-COMP (D)	13.2		14.3		1.60		95.9		8.68		37.8		709	
2360*12		NAB-OF18-SDB7-COMP (T)	4717		6550		11.1		197		9.96		108		752	
2360*7		NAB-OF18-SDB7-COMP (D)	46.4		145		0.729		34.2		3.81		31.2		149	
2360*8		Field Blank - Filtered	3.36	U	2.66		0.119	U	0.025	U	0.436		0.883	U	11.9	

MSL		Sponsor	As (µg/L)		Se (µg/L)		Ag (µg/L)		Cd (µg/L)		Sn (µg/L)		Pb (µg/L)		Hg (µg/L)	
Code	Rep	I.D.	ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		ICP-MS		CVAF	
2360*11		NAB-OF9-SDB7-COMP (T)	23.4		52.4		0.125		1.59		0.896		13.2		0.0127	
2360*6		NAB-OF9-SDB7-COMP (D)	20.2		48.8		0.04	U	1.04		0.50	U	0.139		0.00192	
2360*12		NAB-OF18-SDB7-COMP (T)	2.51		1.47	U	0.0915		2.91		0.724		23.0		0.0201	
2360*7		NAB-OF18-SDB7-COMP (D)	1.20		1.47	U	0.04	U	0.507		0.50	U	0.853		0.00456	
2360*8		Field Blank - Filtered	0.158	U	1.47	U	0.04	U	0.054	U	0.50	U	0.0602		0.000871	

SAMPLE ID	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
NAB-BAY9-SDB7-FF	10	10
NAB-BAY9-SDB7-PRE	12.7	22.7
NAB-BAY9-SDB7-DUR	14.8	17.7
NAB-BAY18-SDB7-FF	30	46
NAB-BAY18-SDB7-PRE	307.6	519.0
NAB-BAY18-SDB7-DUR	312.6	600.7

SAMPLE ID	DISSOLVED COPPER (µg/L)	TOTAL COPPER (µg/L)
NAB-BAY9-SDB7-FF	18	33
NAB-BAY9-SDB7-PRE	2.3	3.9
NAB-BAY9-SDB7-DUR	3.1	6.9
NAB-BAY18-SDB7-FF	32	67
NAB-BAY18-SDB7-PRE	2.1	3.1
NAB-BAY18-SDB7-DUR	2.5	4.3

## METALS QA/QC

**PROGRAM:** SPAWAR, Task 19, batch 2  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/OES	50-150%	±20%	±50%	50.0
Iron	ICP/OES	50-150%	±20%	±50%	10.0
Manganese	ICP/OES	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Nine (9) samples were analyzed for fourteen (14) metals: nickel (Ni), copper, (Cu), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1631m, aluminum (Al), iron (Fe), chromium (Cr), manganese (Mn), and zinc (Zn) by inductively coupled plasma optic emission spectroscopy following EPA Method 200.7 and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Nine (9) samples were received on 5/03/2005 and were logged into Battelle's sample tracking system. The samples were analyzed within the six month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:

Task	Date Performed
Hg	5/20/05
ICP-MS	5/11/05
ICP-OES	5/23/05

### DETECTION LIMITS

The target detection limit was met for all metals, except Ni, Cu, Se and Cd. The MDL for seawater analysis by dilution is somewhat higher than

our typical MDL's for direct analysis. Sample concentrations were substantially greater than the MDL, except Se. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.

**METHOD BLANKS**

One method blank was analyzed with this batch of samples. Results were less than 3 times the MDL for all metals.

**BLANK SPIKES**

One sample of reagent water was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

**MATRIX SPIKES**

One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

**REPLICATES**

One sample was analyzed in duplicate. All results were within the QC limits of  $\pm 30\%$  ( $\pm 50\%$  for Al and Fe).

**SRM**

One matrix-appropriate standard reference material (SRM) was analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.

SRM 1640 has 22 certified and reference metals. Recovery for all metals reported were within the control limit of  $\pm 20\%$  of the certified or reference value. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of  $\pm 25\%$  of the certified value.

**REFERENCES**

EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4- 91-010. Environmental Services Division, Monitoring Management Branch.

# METALS QA/QC (CONT.)

MSL Code	Rep	Sponsor I.D.	Al (µg/L) ICP-OES	Fe (µg/L) ICP-OES	Cr (µg/L) ICP-OES	Mn (µg/L) ICP-OES	Ni (µg/L) ICP-MS	Cu (µg/L) ICP-MS	Zn (µg/L) ICP-OES	As (µg/L) ICP-MS	Se (µg/L) ICP-MS	Ag (µg/L) ICP-MS	Cd (µg/L) ICP-MS	Sn (µg/L) ICP-MS	Pb (µg/L) ICP-MS	Hg (µg/L) CVAF
<b>PROCEDURAL BLANK</b>																
		Dissolved	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.248 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.00017 U
		TRM	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.113 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	N/A
<b>METHOD DETECTION LIMIT</b>			<b>3.36</b>	<b>2.51</b>	<b>0.119</b>	<b>0.025</b>	<b>0.074</b>	<b>0.883</b>	<b>0.113</b>	<b>0.158</b>	<b>1.47</b>	<b>0.04</b>	<b>0.054</b>	<b>0.50</b>	<b>0.009</b>	<b>0.00017</b>
Project Target Detection Limit			50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01
<b>STANDARD REFERENCE MATERIAL</b>																
1640		Dissolved	56.3	34.0	37.4	119	26.0	78.1	53.7	26.2	23.2	7.10	22.3	1.58	27.4	NA
1640		TRM	N/A	N/A	N/A	N/A	25.3	81.4	N/A	25.2	20.4	7.38	21.8	1.72	27.7	NA
1640		certified/reference value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC
		% difference	8%	1%	3%	2%	5%	8%	1%	2%	5%	7%	2%	N/A	2%	N/A
		% difference	N/A	N/A	N/A	N/A	8%	4%	N/A	6%	7%	3%	4%	N/A	1%	N/A
1641d		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1602
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1590
1641d		range	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	±18.0
		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1%
<b>ICV,CCV RESULTS</b>																
ICV			99%	96%	99%	99%	101%	101%	98%	99%	96%	102%	100%	102%	102%	97%
CCV			99%	106%	101%	97%	98%	100%	103%	101%	94%	100%	99%	105%	102%	98%
CCV			100%	107%	98%	99%	98%	96%	102%	97%	96%	101%	96%	106%	100%	99%
CCV			98%	102%	99%	100%	93%	94%	101%	93%	89%	100%	99%	103%	100%	97%
<b>BLANK SPIKE RESULTS</b>																
		Amount Spiked	500	500	100.0	100	10.0	50.0	100.0	10.0	10.0	10.0	10.0	10.0	10.0	0.00496
		Blank	3.36 U	2.51 U	0.245 U	0.038 U	0.005 U	0.015 U	0.248	0.008 U	0.096 U	0.005 U	0.004 U	0.011 U	0.06 U	0.000379
		Blank + Spike	587.0	499	99.6	97.3	9.60	49.3	98.0	9.66	9.31	10.1	9.99	9.99	9.93	0.00517
		Amount Recovered	587.0	499	99.6	97.3	9.60	49.3	97.8	9.66	9.31	10.1	10.0	10.0	9.93	0.00479
		Percent Recovery	117%	100%	100%	97%	96%	99%	98%	97%	93%	101%	100%	100%	99%	97%
<b>MATRIX SPIKE RESULTS</b>																
		Amount Spiked	NS	NS	NS	NS	10.0	50.0	NS	10.0	10.0	10.0	10.0	10.0	10.0	NS
		NI-OF26-SDB7-COMP (D)	N/A	N/A	N/A	N/A	5.95	18.9	N/A	1.15	1.47	0.04 U	0.882	0.50 U	1.50	N/A
		NI-OF26-SDB7-COMP (D) + Spike	NA	NA	NA	NA	15.3	65.2	NA	11.5	11.2	9.03	10.9	11.2	11.3	NA
		Amount Recovered	N/A	N/A	N/A	N/A	9.35	46.3	N/A	10.4	11.2	9.03	10.0	11.2	9.80	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	94%	93%	N/A	104%	112%	90%	100%	112%	98%	N/A
		Amount Spiked	500	500	100	NS	NS	NS	100	NS	NS	NS	NS	NS	NS	NS
		NI-OF23A-SDB7-FF (D)	11.1	12.4	0.295	2.57	N/A	N/A	33.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		NI-OF23A-SDB7-FF (D) + Spike	583	515	97.8	100	NA	NA	129	NA	NA	NA	NA	NA	NA	NA
		Amount Recovered	572	503	97.5	97.7	N/A	N/A	95.6	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	114%	101%	98%	98%	N/A	N/A	96%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	0.0098
		NI-OF23A-SDB7-FF (T)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0164
		NI-OF23A-SDB7-FF (T) + Spike	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.0249
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00850
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	87%
<b>REPLICATE RESULTS</b>																
2360*4	1	NI-OF26-SDB7-COMP (D)	121	103	1.90	23.6	5.95	18.9	79.5	1.15	1.47 U	0.04 U	0.882	0.50 U	1.50	0.0547
2360*4	2	NI-OF26-SDB7-COMP (D)	130	107	2.00	23.9	5.94	18.6	81.6	1.14	1.47 U	0.04 U	0.863	0.50 U	1.54	NA
		RPD	7%	4%	5%	1%	0%	2%	3%	1%	N/A	N/A	2%	N/A	3%	N/A
		NAB-OF9-SDB7-COMP (D)														
2360*6	1	NAB-OF9-SDB7-COMP (D)	13.2	14.3	1.60	95.9	8.68	37.8	709	20.2	48.8	0.04 U	1.04	0.50 U	0.139	0.00192
2360*6	2	NAB-OF9-SDB7-COMP (D)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.00177
		RPD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	8%

U = not detected at or above detection limit; NC = not certified; NA= not analyzed or available.

# PAHs

CLIENT ID	NAB- OF9-SDB7-FF	NAB- OF9-SDB7- COMP	NAB- BAY9-SDB7- PRE	NAB- BAY9-SDB7- DUR	NAB- OF18-SDB7-FF	NAB- OF18-SDB7- COMP	NAB- BAY18-SDB7- PRE	NAB- BAY18-SDB7- DUR
Battelle ID	S7473-P	S7474-P	S7475-P	S7476-P	S7477-P	S7478-P	S7479-P	S7480-P
Sample Type	SA	SA	SA	SA	SA	SA	SA	SA
Collection Date	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005
Extraction Date	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005
Analysis Date	5/18/2005	5/18/2005	5/18/2005	5/18/2005	5/18/2005	5/18/2005	5/18/2005	5/18/2005
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.65	2.65	2.65	2.65	2.65	2.65	2.65	2.65
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Naphthalene	11.1	11.05	1.26 J	1.03 J	6.62 J	11.15	1.11 J	0.94 J
C1-Naphthalenes	30.17	12.79	0.42 J	0.81 J	4.6 J	5.44 J	0.45 J	0.45 J
C2-Naphthalenes	92.08	53.04	0.5 U	0.5 U	7.26	15.2	0.5 U	0.5 U
C3-Naphthalenes	128.36	108.99	0.5 U	0.5 U	0.5 U	30.58	0.5 U	0.5 U
C4-Naphthalenes	106.87	169	0.5 U	0.5 U	0.5 U	31.63	0.5 U	0.5 U
2-Methylnaphthalene	24.24	9.71	0.4 J	0.73 J	4.36 J	5.51 J	0.39 J	0.37 J
1-Methylnaphthalene	19.05	8.22	0.23 J	0.39 J	2.92 J	3.17 J	0.23 J	0.24 J
Biphenyl	25.03	12.32	0.33 J	0.66 J	4.82 J	4.91 J	0.47 U	0.47 U
2,6-dimethylnaphthalene	34.62	15.6	0.62 U	0.98 J	2.09 J	3.74 J	0.62 U	0.62 U
Acenaphthylene	1.92 J	2.41 J	0.66 J	1.17 J	2.01 J	4.48 J	0.63 J	0.73 J
Acenaphthene	3.68 J	6.15 J	1.2 J	0.9 J	0.56 U	0.56 U	0.98 J	2 J
2,3,5-trimethylnaphthalene	24.89	16.67	0.44 U	0.44 U	0.44 U	3.92 J	0.44 U	0.44 U
Dibenzofuran	4.22 J	4.51 J	0.76 J	1.09 J	1.54 J	4.08 J	0.9 J	1.08 J
Fluorene	7.46	7.32	0.95 J	1.07 J	1.37 J	3.16 J	0.67 J	0.67 J
C1-Fluorenes	18.54	0.51 U	0.51 U	0.51 U	0.51 U	10.89	0.51 U	0.51 U
C2-Fluorenes	60.11	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U
C3-Fluorenes	49.79	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U	0.51 U
Anthracene	4.45 J	6.66	0.87 J	2.15 J	1.53 J	4.42 J	0.69 J	1.3 J
Phenanthrene	27.9	36.65	4.17 J	6.97	22.72	78.07	2.59 J	3.22 J
C1-Phenanthrenes/Anthracenes	31.47	42.81	0.81 U	3.39 J	27.34	75.21	0.81 U	1.72 J
C2-Phenanthrenes/Anthracenes	54.75	103.67	0.81 U	0.81 U	54.96	122.08	0.81 U	0.81 U
C3-Phenanthrenes/Anthracenes	39.51	102.28	0.81 U	0.81 U	50.18	100.41	0.81 U	0.81 U
C4-Phenanthrenes/Anthracenes	13.6	38.91	0.81 U	0.81 U	21.76	52.62	0.81 U	0.81 U
1-Methylphenanthrene	7.61	11.81	0.46 U	1.09 J	7	17.92	0.46 U	0.36 J
Dibenzothiophene	7.15	8.61	0.38 U	1.2 J	6.73	9.86	0.38 U	0.65 J
C1-Dibenzothiophenes	15.2	24.15	0.38 U	1.24 J	18.75	30.94	0.38 U	1.26 J
C2-Dibenzothiophenes	32.08	55.21	0.38 U	3.58 J	45.18	84.7	0.38 U	2.77 J
C3-Dibenzothiophenes	32.04	64.39	0.38 U	3.19 J	50.01	115.47	0.38 U	3.12 J
C4-Dibenzothiophenes	20.54	51.97	0.38 U	0.38 U	50.82	86.74	0.38 U	0.38 U
Fluoranthene	46.09	97.53	8.42	19.73	34.34	117.3	7.96	11.51
Pyrene	31.89	85.54	4.97 J	12.91	53.06	156.6	4.67 J	7.82
C1-Fluoranthenes/Pyrenes	16.36	49.87	1.28 J	3.67 J	20.74	56.82	1.25 J	2.2 J
C2-Fluoranthenes/Pyrenes	0.68 U	62.66	0.68 U	0.68 U	28.56	89.66	0.68 U	0.68 U
C3-Fluoranthenes/Pyrenes	0.68 U	43.51	0.68 U	0.68 U	38.2	97.27	0.68 U	0.68 U
Benzo(a)anthracene	2.85 J	8.84	0.55 J	1.44 J	3.41 J	14.22	0.39 J	0.98 J
Chrysene	18.09	66.76	3.17 J	9	30.02	84.75	3.06 J	4.7 J
C1-Chrysenes	6.7	31.12	0.44 U	1.31 J	29.92	79.73	0.44 U	1.13 J
C2-Chrysenes	6.85	39.11	0.44 U	0.44 U	33.96	113.91	0.44 U	0.44 U
C3-Chrysenes	0.44 U	45.38	0.44 U	0.44 U	39.23	144.28	0.44 U	0.44 U
C4-Chrysenes	0.44 U	23.57	0.44 U	0.44 U	20.9	81.24	0.44 U	0.44 U
Benzo(b)fluoranthene	8.84	27.03	1.73 J	5.74 J	12.78	44.78	1.64 J	2.75 J
Benzo(j,k)fluoranthene	6.12 J	17.8	1.48 J	4.47 J	8.13	28.11	1.47 J	2.44 J
Benzo(e)pyrene	6.37	24.43	1.18 J	3.8 J	16.04	51.95	1.2 J	2.09 J
Benzo(a)pyrene	2.28 J	10.23	0.76 U	2.01 J	6.77	25.57	0.76 U	0.82 J
Perylene	1.46 U	3.88 J	1.28 J	1.22 J	2.17 J	9.03	1.46 U	1.46 U
Indeno(1,2,3-cd)pyrene	3.06 J	13.48	0.62 J	2.35 J	9.77	32.14	0.54 J	1.17 J
Dibenz(a,h)anthracene	0.58 J	2.72 J	0.63 U	0.63 U	1.54 J	6.34	0.63 U	0.63 U
Benzo(g,h,i)perylene	6.86 J	38.76	0.94 J	2.42 J	38.09	123.15	0.77 J	1.58 J

## PAHs (CONT.)

CLIENT ID	NAB- OF9-SDB7-FF	NAB- OF9-SDB7- COMP	NAB- BAY9-SDB7- PRE	NAB- BAY9-SDB7- DUR	NAB- OF18-SDB7-FF	NAB- OF18-SDB7- COMP	NAB- BAY18-SDB7- PRE	NAB- BAY18-SDB7- DUR	
<i>Surrogate Recoveries (%)</i>									
Naphthalene-d8	51	58	59	44	54	50	56	47	
Phenanthrene-d10	67	75	68	65	73	72	67	65	
Chrysene-d12	83	91	88	85	83	82	87	86	

## PAHs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PAH	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD plus variance (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.50 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for PAH were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0129	5/04/05	5/17/05 – 5/19/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0129** – No exceedences noted.

**Comments** – No target analytes were detected above the laboratory control limit (>5 x MDL), however naphthalene and 2-Methylnaphthalene were detected in the procedural blank at a concentration less than the reporting limit (RL). The data was qualified with a “J” in the procedural blank. All authentic field sample concentrations for these compounds were either greater than five times the

**LABORATORY  
CONTROL  
SAMPLE:**

concentration in the associated blank, or less than the RL.

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**05-0129** – All target analytes were recovered within the laboratory control limits (40-120%).

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

**Comments** – None.

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**SRM:**

**Comments** – None

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**SURROGATES:**

**Comments** – None.

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0129** – One exceedence noted.

**Comments** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery), except for naphthalene-d8 in sample S7468 (OF-NI26-SDB7-FF). The recovery for this compound was calculated to be 38%. Chromatography and calculations were reviewed. No discrepancies were found. The sample prep records indicate an emulsion formed during the extraction of this sample, and that this extract had difficulty passing through the alumina cleanup column. The exceedences were qualified with an “N”. No further corrective action taken.

**CALIBRATIONS:**

The GC/MS is calibrated with a minimum of a 6 level curve. The RSD between response factors for the individual target analytes must be  $<25\%$ , the mean RSD  $< 15\%$ . Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of minimally every 10 samples. This PD between the initial calibration RF and the check should be  $<25\%$  for individual analytes, and again the mean PD should be  $<15\%$ .

**05-0129** – No calibration exceedences.

**Comments** – None.



# PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MARTIX SPIKE NI-OF23A- SD87-FF			MARTIX SPIKE DUPLICATE- NI-OF23A- SD87-FF					PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION				
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P					BG247PB-P	BG275PB-P	BG276SRM-P				
Sample Type	LCS			MS			MSD					PB	PB	SRM				
Collection Date	5/4/2005			4/28/2005			4/28/2005					5/4/2005	5/4/2005	5/4/2005				
Extraction Date	5/4/2005			5/4/2005			5/4/2005					5/4/2005	5/4/2005	5/4/2005				
Analysis Date	5/17/2005			5/18/2005			5/18/2005					5/17/2005	5/17/2005	5/17/2005				
Analytical Instrument	MS			MS			MS					MS	MS	MS				
% Moisture	NA			NA			NA					NA	NA	NA				
% Lipid	NA			NA			NA					NA	NA	NA				
Matrix	LIQUID			WATER			WATER					LIQUID	LIQUID	LIQUID				
Sample Size	2.00			0.5			0.5					2.00	2	2.00				
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID					L LIQUID	L LIQUID	L LIQUID				
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Certified Value	+/-	Passing %Difference	Actual %Difference
Naphthalene	686.93	1000.60	69	2051.39	4002.40	51	1973.11	4002.40	49	4.0	1.22	4.35	J	1022.26	1000.6			2.2
C1-Naphthalenes	0.66 U			2801.42	NA		2651.74	NA			0.66 U	2.28	J	1353.64				
C2-Naphthalenes	0.66 U			2.65	UNA		1236.05	UNA			0.66 U	0.66	U	0.66 U				
C3-Naphthalenes	0.66 U			2.65	UNA		2.65	UNA			0.66 U	0.66	U	0.66 U				
C4-Naphthalenes	0.66 U			2.65	UNA		2.65	UNA			0.66 U	0.66	U	0.66 U				
2-Methylnaphthalene	699.17	1002.00	70	2138.17	4008.00	53	2035.88	4008.00	51	3.8	0.6 J	1.92	J	938.81	1002			6.3
1-Methylnaphthalene	701.45	1001.20	70	2124.31	4004.80	53	2032.5	4004.80	51	3.8	0.5 U	1.35	J	940.5	1001.2			6.1
Biphenyl	883.83	1000.20	89	2186.87	4000.80	55	2056.84	4000.80	51	7.5	0.63 U	0.63	U	927.81	1000.2			7.2
2,6-dimethylnaphthalene	871.72	1001.00	87	2149.4	4004.00	54	2055.97	4004.00	51	5.7	0.83 U	0.83	U	898.7	1001			10.2
Acenaphthylene	696.61	1000.65	70	2330.15	4002.60	58	2230.88	4002.60	56	3.5	0.7 U	0.7 U	U	965.76	1000.65			3.5
Acenaphthene	705.01	1000.75	70	2351.79	4003.00	59	2236.53	4003.00	56	5.2	0.75 U	0.75	U	972.35	1000.75			2.8
2,3,5-trimethylnaphthalene	696.21	1000.30	70	2463.11	4001.20	62	2320.61	4001.20	58	6.7	0.58 U	0.58	U	953.76	1000.3			4.7
Dibenzofuran	688.85	1002.20	69	2360.31	4008.80	59	2254.7	4008.80	56	5.2	0.3 U	0.65	J	953.67	1002.2			4.8
Fluorene	716.57	1000.70	72	2582.59	4002.80	64	2455.24	4002.80	61	4.8	0.68 U	0.57	J	985.56	1000.7			1.5
C1-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
C2-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
C3-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
Anthracene	764.04	1000.65	76	2991.32	4002.60	75	2868.53	4002.60	72	4.1	0.51 U	0.51	U	1024.04	1000.65			2.3
Phenanthrene	739.01	1000.65	74	2909.16	4002.60	72	2772.41	4002.60	68	5.7	1.08 U	1.67	J	1001.33	1000.65			0.1
C1-Phenanthrenes/Anthracenes	1.08 U			2310.61	NA		2235.23	NA			1.08 U	1.08	U	1.08 U				
C2-Phenanthrenes/Anthracenes	1.08 U			87.84	NA		88.37	NA			1.08 U	1.08	U	1.08 U				
C3-Phenanthrenes/Anthracenes	1.08 U			58.53	NA		51.04	NA			1.08 U	1.08	U	1.08 U				
C4-Phenanthrenes/Anthracenes	1.08 U			4.32	UNA		4.32	UNA			1.08 U	1.08	U	1.08 U				
1-Methylphenanthrene	769.45	1000.30	77	3032.32	4001.20	76	2916.84	4001.20	73	4.0	0.61 U	0.61	U	1029.72	1000.3			2.9
Dibenzothiophene	727.14	1001.00	73	2828.38	4004.00	71	2702.91	4004.00	67	5.8	0.5 U	0.5 U	U	991.17	1001			1
C1-Dibenzothiophenes	0.5 U			138.06	NA		130.53	NA			0.5 U	0.5 U	U	0.5 U				
C2-Dibenzothiophenes	0.5 U			29.62	JNA		33.61	NA			0.5 U	0.5 U	U	0.5 U				
C3-Dibenzothiophenes	0.5 U			31.49	JNA		36.17	NA			0.5 U	0.5 U	U	0.5 U				
C4-Dibenzothiophenes	0.5 U			24.27	JNA		22.05	JNA			0.5 U	0.5 U	U	0.5 U				
Fluoranthene	821.94	1000.50	82	3251.87	4002.00	80	3170.94	4002.00	78	2.5	0.77 U	1.55	J	1104.38	1000.5			10.4
Pyrene	824.46	1000.50	82	3271.32	4002.00	80	3176.64	4002.00	78	2.5	0.9 U	1.01	J	1107.39	1000.5			10.7
C1-Fluoranthenes/Pyrenes	0.9 U			29.03	JNA		31.31	JNA			0.9 U	0.9 U	U	0.9 U				
C2-Fluoranthenes/Pyrenes	0.9 U			23.18	JNA		25.07	JNA			0.9 U	0.9 U	U	0.9 U				
C3-Fluoranthenes/Pyrenes	0.9 U			24.42	JNA		30.07	JNA			0.9 U	0.9 U	U	0.9 U				
Benzo(a)anthracene	829.99	1000.60	83	3342.41	4002.40	83	3185.28	4002.40	79	4.9	1.36 U	0.31	J	876.32	1000.6			12.4
Chrysene	823.75	1000.75	82	3181.59	4003.00	78	3113.69	4003.00	77	1.3	0.59 U	0.72	J	857.67	1000.75			14.3
C1-Chrysenes	0.59 U			34.57	NA		38.44	NA			0.59 U	0.59	U	0.59 U				
C2-Chrysenes	0.59 U			51.96	NA		58.75	NA			0.59 U	0.59	U	0.59 U				
C3-Chrysenes	0.59 U			38.83	NA		44.77	NA			0.59 U	0.59	U	0.59 U				
C4-Chrysenes	0.59 U			2.36	UNA		2.36	UNA			0.59 U	0.59	U	0.59 U				
Benzo(b)fluoranthene	851.64	1000.75	85	3402.73	4003.00	84	3290.1	4003.00	81	3.6	1.16 U	1.16	U	893.46	1000.75			10.7
Benzo(k)fluoranthene	881.56	1000.65	88	3353.44	4002.60	83	3254.85	4002.60	81	2.4	1.31 U	1.31	U	921.45	1000.65			7.9
Benzo(e)pyrene	776.8	1001.80	78	3028.88	4007.20	75	2982.69	4007.20	74	1.3	0.51 U	0.51	U	815.6	1001.8			18.6
Benzo(a)pyrene	839.45	1000.65	84	3257.28	4002.60	81	3122.06	4002.60	78	3.8	1 U	1 U	U	882.23	1000.65			11.8
Perylene	819.83	1000.20	82	3320.82	4000.80	83	3226.69	4000.80	81	2.4	1.93 U	1.93	U	866.73	1000.2			13.3
Indeno(1,2,3-cd)pyrene	812.86	1000.60	81	3339.86	4002.40	83	3224.82	4002.40	80	3.7	0.99 U	0.99	U	853.56	1000.6			14.7
Dibenz(a,h)anthracene	882.52	1000.55	88	3440.18	4002.20	86	3281.85	4002.20	82	4.8	0.84 U	0.84	U	924.45	1000.55			7.6
Benzo(g,h,i)perylene	814.87	1000.70	81	3214.16	4002.80	79	3128.86	4002.80	77	2.6	0.99 U	0.99	U	854.95	1000.7			14.6

## PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MARTIX SPIKE- NI-OF23A- SDB7-FF				MATRIX SPIKE DUPLICATE- NI-OF23A- SDB7-FF					PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION				
Surrogate Recoveries (%)																			
Naphthalene-d8	83			51				43					83	52	68				
Phenanthrene-d10	80			72				68					78	71	75				
Chrysene-d12	102			89				86					98	87	95				

PCBs

CLIENT ID	NAB-OF9-SDB7-COMP		NAB-OF18-SDB7-COMP	
Battelle ID	S7474-P		S7478-P	
Sample Type	SA		SA	
Collection Date	4/28/2005		4/28/2005	
Extraction Date	5/4/2005		5/4/2005	
Analysis Date	5/29/2005		5/30/2005	
Analytical Instrument	MS		MS	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	2.65		2.65	
Size Unit-Basis	L_LIQUID		L_LIQUID	
Units	NG/L_LIQUID		NG/L_LIQUID	
Cl2(8)	0.07	U	0.07	U
Cl3(18)	0.08	U	0.08	U
Cl3(28)	0.08	U	0.08	U
Cl4(44)	0.14	U	0.14	U
Cl4(49)	0.14	U	0.14	U
Cl4(52)	0.14	U	0.14	U
Cl4(66)	0.14	U	3.52	
Cl4(77)	0.14	U	2.15	J
Cl5(87)	0.23	U	2.73	J
Cl5(101)	0.23	U	3.57	
Cl5(105)	0.11	U	4.44	
Cl5(114)	0.23	U	0.23	U
Cl5(118)	0.07	U	6.05	
Cl5(123)	0.08	U	0.08	U
Cl5(126)	0.12	U	0.12	U
Cl6(128)	0.27	U	0.27	U
Cl6(138)	0.27	U	4.18	
Cl6(153)	1.83	J	4	
Cl6(156)	0.08	U	0.08	U
Cl6(157)	0.14	U	0.14	U
Cl6(167)	0.27	U	0.27	U
Cl6(169)	0.11	U	0.11	U
Cl7(170)	0.18	U	0.18	U
Cl7(180)	0.1	U	2.57	J
Cl7(183)	0.18	U	0.18	U
Cl7(184)	0.18	U	0.18	U
Cl7(187)	0.18	U	1.86	J
Cl7(189)	0.08	U	0.08	U
Cl8(195)	0.36	U	0.36	U
Cl9(206)	0.33	U	0.33	U
Cl10(209)	0.4	U	0.4	U
<b>Surrogate Recoveries (%)</b>				
Cl2(14)	87		76	
Cl3(34)	89		82	

## PCBs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery  (target spike must be >5 x native conc.)	≤30% PD on average  (for analytes >5x MDL)	≤30% RPD  (calculated between the MS and MSD samples)	MDL: ~0.09 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate and concentrated. The extract was then fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

	<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
	05-0129	5/4/05	5/28/05 – 5/30/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0129** – No exceedences noted.

**LABORATORY CONTROL SAMPLE:** **Comments** – No target analytes were detected in the procedural blank. A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.

**05-0129** – One exceedence noted.

**Comments** – All target analytes were recovered within the specified laboratory control limits (40-120%), except for PCB 169. This analyte was over-recovered at

**MATRIX  
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SPIKE  
DUPLICATE:**

141%. It was also over-recovered in both the MS and MSD samples. Chromatography and calculations were reviewed. No discrepancies were found. The exceedence has been qualified with an "N". Since PCB 169 was not detected in any field samples, the affect of this exceedence on the data is minimal. No further corrective action is necessary.

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair was prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0129** – Three percent recovery exceedences noted.  
No RPD exceedences noted.

**Comments** – All target analytes were recovered within the specified laboratory control limits (40-120%), except for PCB 169 in samples S7470MS and S7470MSD (background OF-NI23A-SDB7-FF) and PCB 209 in sample S7470MS. All exceedences were due to over-recoveries. Chromatography and calculations were reviewed, no discrepancies were found. The exceedences were qualified with an "N". Since PCB 169 was not detected in any field samples, and PCB 209 was not detected above the RL, the affect of these exceedences on the data is minimal. No further corrective action is necessary.

**SRM:**

A standard reference material was prepared with each analytical batch. The percent difference (PD) between the measured value and the certified range was calculated to measure data quality in terms of accuracy. The MQO criteria of 30% PD was added to the variance of each analyte. The variance of each analyte is determined by dividing the range value by the target.

**05-0129** – All PDs were within the specified laboratory control limits.

**Comments** – None.

**SURROGATES:**

Two surrogate compounds were added prior to extraction, including PCB 14 and PCB 34. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0129** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATION:**

The GC/MS is calibrated with a minimum of a 6-point curve. The co-efficient of determination must be  $\geq 0.995$  for each target analyte. Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of every 12 hours (minimally). This PD between the initial calibration RF and the check should be  $<20\%$  for individual analytes; 15% on average. Additionally an ICC check was run with the initial calibration. The PD for the ICC should be  $< 15\%$ , for each analyte.

**05-0129** – One exceedence noted.

**Comments** – In mid C1466.d PCB 105 was over-recovered and had a PD of 31%. Two samples S7468 and S7478 (Samples OF-NI26-SDB7-Comp and OF-NAB18-SDB7-Comp, respectively) had PCB 105 detected in them. Chromatography and calculations were reviewed. No discrepancies were found. The deviation has been documented and the data reviewed. No further corrective action was taken.

# PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE- NI-OF23A-SDB7-FF				PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION					
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P				BG247PB-P	BG275PB-P	BG276SRM-P					
Sample Type	LCS			MS			MSD				PB	PB	SRM					
Collection Date	5/4/2005			4/28/2005			4/28/2005				5/4/2005	5/4/2005	5/4/2005					
Extraction Date	5/4/2005			5/4/2005			5/4/2005				5/4/2005	5/4/2005	5/4/2005					
Analysis Date	5/28/2005			5/29/2005			5/29/2005				5/28/2005	5/28/2005	5/28/2005					
Analytical Instrument	MS			MS			MS				MS	MS	MS					
% Moisture	NA			NA			NA				NA	NA	NA					
% Lipid	NA			NA			NA				NA	NA	NA					
Matrix	LIQUID			WATER			WATER				LIQUID	LIQUID	LIQUID					
Sample Size	2.00			0.5			0.5				2.00	2	2.00					
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	L LIQUID	L LIQUID	Certified				
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Value	+/-	Passing %Difference	Actual %Difference	
C12(8)	27.49	40.12	69	98.76	160.48	62	111.42	160.48	69	10.7	0.09 U	0.09 U	27.52	34.24	2.88	38.41	19.6	
C13(18)	32.94	40.12	82	117.38	160.48	73	123.26	160.48	77	5.3	0.11 U	0.11 U	31.47	32.93	0.30	30.92	4.4	
C13(28)	29.26	40.04	73	118.72	160.16	74	114.24	160.16	71	4.1	0.11 U	0.11 U	30.54					
C14(44)	34.28	40.08	86	134.47	160.32	84	124.95	160.32	78	7.4	0.19 U	0.19 U	30.39	32.86	0.59	31.8	7.5	
C14(49)	40.18	40.16	100	150.87	160.64	94	145.68	160.64	91	3.2	0.19 U	0.19 U	0.19 U					
C14(52)	31.65	40.00	79	122.5	160.00	77	119.2	160.00	75	2.6	0.19 U	0.19 U	30.03	33.07	0.38	31.16	9.2	
C14(66)	31.54	40.04	79	141.85	160.16	89	118.9	160.16	74	18.4	0.19 U	0.19 U	30.09	32.82	0.62	31.9	8.3	
C14(77)	31.71	40.00	79	160.6	160.00	100	131.34	160.00	82	19.8	0.18 U	0.18 U	31.48	33.55	1.10	33.29	6.2	
C15(87)	35.98	40.00	90	165.64	160.00	104	136.48	160.00	85	20.1	0.31 U	0.31 U	34.88	33.1	0.27	30.82	5.4	
C15(101)	34.94	40.08	87	155.41	160.32	97	124.41	160.32	78	21.7	0.31 U	0.31 U	31.45	32.56	0.47	31.43	3.4	
C15(105)	32.22	40.04	80	187.32	160.16	117	144.07	160.16	90	26.1	0.14 U	0.14 U	33.85	32.67	1.01	33.09	3.6	
C15(114)	0.31 U			1.23 U			1.23 U				0.31 U	0.31 U	0.31 U	U				
C15(119)	32.35	40.04	81	163.33	160.16	102	126.35	160.16	79	25.4	0.11 U	0.11 U	29.41	32.74	1.06	33.23	10.2	
C15(123)	0.11 U			0.43 U			0.43 U				0.11 U	0.11 U	0.11 U	U				
C15(126)	29.27	40.24	73	166.74	160.96	104	130.52	160.96	81	24.9	0.16 U	0.16 U	32.45	33.22	1.38	34.14	2.3	
C16(128)	29.39	40.24	73	149.58	160.96	93	117.39	160.96	73	24.1	0.35 U	0.35 U	27.53	32.94	0.27	30.83	16.4	
C16(138)	33.24	40.08	83	176.99	160.32	110	139.78	160.32	87	23.4	0.35 U	0.35 U	31.99	32.43	0.38	31.18	1.4	
C16(153)	34.07	40.04	85	168.47	160.16	105	131.73	160.16	82	24.6	0.35 U	0.35 U	30.86	32.64	0.62	31.91	5.5	
C16(156)	0.1 U			0.4 U			0.4 U				0.1 U	0.1 U	0.1 U	U				
C16(157)	0.19 U			0.76 U			0.76 U				0.19 U	0.19 U	0.19 U	U				
C16(167)	0.35 U			1.42 U			1.42 U				0.35 U	0.35 U	0.35 U	U				
C16(169)	56.68	40.16	141	309.8	160.64	193	248.63	160.64	155	21.8	0.15 U	0.15 U	0.15 U					
C17(170)	29.13	40.20	72	163.63	160.80	102	131.34	160.80	82	21.7	0.25 U	0.25 U	27.28	32.72	0.54	31.66	16.6	
C17(180)	29.47	40.16	73	175.36	160.64	109	146.13	160.64	91	18.0	0.14 U	0.14 U	29.53	32.96	0.32	30.97	10.4	
C17(183)	32.99	40.16	82	169.17	160.64	105	137.46	160.64	86	19.9	0.25 U	0.25 U	0.25 U					
C17(184)	34.92	40.16	87	163.2	160.64	102	132	160.64	82	21.7	0.25 U	0.25 U	0.25 U	U				
C17(187)	30.23	40.12	75	152.19	160.48	95	127.03	160.48	79	18.4	0.25 U	0.25 U	30.46	32.75	0.30	30.93	7	
C17(189)	0.11 U			0.42 U			0.42 U				0.11 U	0.11 U	0.11 U	U				
C18(195)	29.27	40.12	73	148.26	160.48	92	120.19	160.48	75	20.4	0.48 U	0.48 U	27.7	32.83	0.66	32	15.6	
C19(206)	33.76	40.12	84	172.85	160.48	108	143.4	160.48	89	19.3	0.44 U	0.44 U	32.46	32.02	0.59	31.85	1.4	
C110(209)	46.77	40.04	117	223.66	160.16	140	182.47	160.16	114	20.5	0.53 U	0.53 U	42.96	32.99	0.45	31.36	30.2	
Surrogate Recoveries (%)																		
C12(14)	87			74			77				77	68	80					
C13(34)	94			79			82				80	70	82					

# PESTICIDES

CLIENT ID	NAB- OF9-SDB7-COMP		NAB- OF18-SDB7-COMP	
Battelle ID	S7474-P		S7478-P	
Sample Type	SA		SA	
Collection Date	4/28/2005		4/28/2005	
Extraction Date	5/4/2005		5/4/2005	
Analysis Date	5/14/2005		5/14/2005	
Analytical Instrument	ECD		ECD	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	2.65		2.65	
Size Unit-Basis	L LIQUID		L LIQUID	
Units	NG/L LIQUID		NG/L LIQUID	
2,4'-DDD	0.61	U	0.61	U
2,4'-DDE	0.25	J	0.52	U
2,4'-DDT	0.37	U	0.37	U
4,4'-DDD	0.72	U	0.72	U
4,4'-DDE	0.52	U	0.9	
4,4'-DDT	1.39		0.44	U
aldrin	1.65		0.3	U
a-chlordane	0.34	J	0.28	U
g-chlordane	0.3	U	0.3	U
a-BHC	0.26	U	0.26	U
b-BHC	0.36	U	0.36	U
d-BHC	0.99		0.67	
Lindane	0.37	U	0.37	U
cis-nonachlor	0.49	U	0.49	U
trans-nonachlor	1.14		0.31	U
Chlorpyrifos	0.39	U	0.39	U
oxychlordane	0.3	U	0.3	U
dieldrin	0.58	U	0.58	U
endosulfan I	0.21	U	0.21	U
endosulfan II	0.52	U	0.52	U
endosulfan sulfate	0.49	U	0.49	U
endrin	0.57	U	0.57	U
endrin aldehyde	0.64	U	0.64	U
endrin ketone	0.67	U	0.67	U
heptachlor	0.44	U	0.44	U
heptachlor epoxide	1.19	U	1.19	U
Hexachlorobenzene	0.62	U	0.62	U
methoxychlor	0.74	U	5.28	
Mirex	0.47	U	0.47	U
<b>Surrogate Recoveries (%)</b>				
CI2(14)	88		88	
CI3(34)	94		84	
CI5(104)	94		83	
CI5(112)	91		90	

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** Pesticides  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD plus variance (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.27 – 1.58

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, copper cleaned, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0129	5/04/05	5/14/05 – 5/16/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0129** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.

**LABORATORY** A laboratory control sample (LCS) was prepared with the analytical batch. The



**CONTROL  
SAMPLE:**

percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0129** – All percent differences for reported target analytes were within the laboratory control limits ( $<30\%$  difference plus variance).

**Comments** – None.

**SURROGATES**

Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0129** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATIONS:**

The instrument is calibrated with a 6-level (minimum) calibration, ranging in concentration from  $\sim 0.001$  ng/uL to  $\sim 0.125$  ng/uL. The initial correlation coefficient must be  $> 0.995$ . Calibration checks are analyzed minimally every 12 hours. The samples must be bracketed by passing calibrations. Calibration checks must have a percent difference  $\leq 25\%$ .

**05-0129** – No exceedences noted.

**Comments** – None.



# PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE-NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE-NI-OF23A-SDB7-FF					PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION					
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P					BG247PB-P	BG275PB-P	BG276SRM-P					
Sample Type	LCS			MS			MSD					PB	PB	SRM					
Collection Date	5/4/2005			4/28/2005			4/28/2005					5/4/2005	5/4/2005	5/4/2005					
Extraction Date	5/4/2005			5/4/2005			5/4/2005					5/4/2005	5/4/2005	5/4/2005					
Analysis Date	5/16/2005			5/14/2005			5/14/2005					5/16/2005	5/16/2005	5/14/2005					
Analytical Instrument	ECD			ECD			ECD					ECD	ECD	ECD					
% Moisture	NA			NA			NA					NA	NA	NA					
% Lipid	NA			NA			NA					NA	NA	NA					
Matrix	LIQUID			WATER			WATER					LIQUID	LIQUID	LIQUID					
Sample Size	2.00			0.5			0.5					2.00	2	2.00					
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID					L LIQUID	L LIQUID	L LIQUID					
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Certified Value	+/-	Passing	Actual	%Difference
2,4'-DDD	33.25	40.12	83	126.17	160.48	79	121.46	160.48	76	3.9	0.81 U	0.81 U	65.74						
2,4'-DDE	29.51	40.01	74	116.42	160.05	73	110.03	160.05	69	5.6	0.69 U	0.69 U	22.4		31.62	0.27	30.86	29.2	
2,4'-DDT	26.38	40.23	66	110.77	160.93	69	104.02	160.93	65	6.0	0.48 U	0.48 U	27.15		31.34	0.14	30.46	13.4	
4,4'-DDD	33.01	40.01	83	128.85	160.02	81	123.46	160.02	77	5.1	0.95 U	0.95 U	24.85		31.87	0.43	31.36	22	
4,4'-DDE	32.85	40.01	82	125.33	160.02	78	118.75	160.02	74	5.3	0.68 U	0.68 U	28.26		31.62	0.16	30.51	10.6	
4,4'-DDT	32.99	40.02	82	130.94	160.09	81	124.55	160.09	77	5.1	0.59 U	0.59 U	27.74		31.47	0.19	30.61	11.9	
aldrin	27.61	40.01	69	105.56	160.06	66	97.41	160.06	61	7.9	0.4 U	0.4 U	21.28						
a-chlordane	29.84	40.03	75	113.71	160.11	71	108.08	160.11	67	5.8	0.38 U	0.38 U	26.85		31.55	0.19	30.61	14.9	
g-chlordane	28.59	40.06	71	107.53	160.26	66	103.45	160.26	64	3.1	0.4 U	0.4 U	0.4	U					
a-BHC	23.22	40.02	58	84.2	160.06	53	72.71	160.06	45	16.3	0.34 U	0.28 U	0.32	J					
b-BHC	26.75	40.01	67	100.77	160.02	63	93.5	160.02	58	8.3	0.47 U	0.47 U	0.47	U					
g-BHC	31.05	40.02	76	123.12	160.07	77	113.38	160.07	71	8.1	0.39 U	0.39 U	0.39	U					
Lindane	26.45	40.01	66	103.5	160.04	65	92.09	160.04	58	11.4	0.49 U	0.49 U	22.74		31.55	0.16	30.51	27.9	
cis-nonachlor	33.3	40.03	83	124.04	160.11	77	119.47	160.11	75	2.6	0.65 U	0.65 U	0.65	U					
trans-nonachlor	30.91	40.06	77	117.4	160.22	73	112.61	160.22	70	4.2	0.4 U	0.4 U	27.72		31.78	0.22	30.7	12.8	
Chlorpyrifos	32.53	40.10	81	127.35	160.40	79	121.06	160.40	75	5.2	0.51 U	0.51 U	0.51	U					
oxychlordane	28.88	40.03	72	108.92	160.11	68	102.88	160.11	64	6.1	0.39 U	0.39 U	0.39	U					
dieldrin	32.5	40.01	81	119.69	160.03	75	115.7	160.03	72	4.1	0.76 U	0.76 U	27.43						
endosulfan I	31.23	40.03	78	114.7	160.11	72	110.45	160.11	69	4.3	0.27 U	0.27 U	0.27	U	31.55	0.21	30.66	13.1	
endosulfan II	31.53	40.02	79	121.66	160.08	76	116.01	160.08	72	5.4	0.69 U	0.69 U	0.69	U					
endosulfan sulfate	35.11	40.02	88	133.4	160.07	83	127.81	160.07	80	3.7	0.65 U	0.65 U	0.65	U					
endrin	34.35	40.01	86	136.19	160.05	85	128.49	160.05	80	6.1	0.75 U	0.75 U	0.75	U					
endrin aldehyde	27.27	40.01	68	105.84	160.03	66	99.74	160.03	62	6.3	0.85 U	0.85 U	0.85	U					
endrin ketone	35.14	40.02	88	132.66	160.06	83	123.21	160.06	81	2.4	0.89 U	0.89 U	0.89	U					
heptachlor	29.47	40.03	74	114.63	160.02	72	104.8	160.02	65	10.2	0.59 U	0.59 U	25.28		31.63	0.24	30.76	20.1	
heptachlor epoxide	28.54	40.01	71	102.62	160.02	64	98.63	160.02	62	3.2	1.58 U	1.58 U	23.46		31.63	0.27	30.86	25.8	
Hexachlorobenzene	30.22	40.06	75	114.74	160.24	72	107.22	160.24	67	7.2	0.83 U	0.83 U	27.24		31.49	0.14	30.46	13.5	
methoxychlor	33.31	40.01	83	133.39	160.05	82	127.62	160.05	78	5.0	0.98 U	0.98 U	0.98	U					
Mirex	34	40.03	85	124.94	160.13	78	121.75	160.13	76	2.6	0.62 U	0.62 U	29.34		31.86	0.45	31.41	7.9	
Surrogate Recoveries (%)																			
C12(14)	93			83			76				85	79	87						
C13(14)	99			87			76				86	80	84						
C15(104)	91			80			77				86	77	75						
C15(112)	96			82			79				96	81	86						

## TSS

SAMPLE LABEL	TSS (mg/L)
NAB-OF9-SDB7-FF	11.690
NAB-OF9-SDB7-COMP	60.289
NAB-BAY9-SDB7-PRE	3.277
NAB-BAY9-SDB7-DUR	15.239
NAB-OF18-SDB7-FF	45.573
NAB-OF18-SDB7-COMP	234.378
NAB-BAY18-SDB7-PRE	4.280
NAB-BAY18-SDB7-DUR	6.139

## DOC

SAMPLE LABEL	DOC (mg/L)
NAB-OF9-SDB7-FF	7.562
NAB-OF9-SDB7-FF	7.770
NAB-OF9-SDB7-FF	7.943
NAB-OF9-SDB7-COMP	14.439
NAB-OF9-SDB7-COMP	15.064
NAB-OF9-SDB7-COMP	15.188
NAB-BAY9-SDB7-PRE	1.919
NAB-BAY9-SDB7-PRE	1.750
NAB-BAY9-SDB7-PRE	1.552
NAB-BAY9-SDB7-DUR	1.709
NAB-BAY9-SDB7-DUR	1.690
NAB-BAY9-SDB7-DUR	1.742
NAB-OF18-SDB7-FF	11.079
NAB-OF18-SDB7-FF	11.584
NAB-OF18-SDB7-FF	11.442
NAB-OF18-SDB7-COMP	14.983
NAB-OF18-SDB7-COMP	15.441
NAB-OF18-SDB7-COMP	15.169
NAB-BAY18-SDB7-PRE	2.070
NAB-BAY18-SDB7-PRE	1.713
NAB-BAY18-SDB7-PRE	1.756
NAB-BAY18-SDB7-DUR	1.775
NAB-BAY18-SDB7-DUR	1.759
NAB-BAY18-SDB7-DUR	1.952

## **Appendix D4**

**NI**

**SDB4- 10/17/2004**

**SBD6-2/10/2005**

**SDB7- 4/027/2005**

## SDB4- 10/17/2004

### METALS

SAMPLE ID	DISSOLVED Cu (µg/L)	TOTAL Cu (µg/L)
NI-OF23A SDB4 FF	74	172
NI-BAY23A SDB4 DUR	5.2	8.0

SAMPLE ID	DISSOLVED Zn (µg/L)	TOTAL Zn (µg/L)
NI-OF23A SDB4 FF	778	1125
NI-BAY23A SDB4 DUR	20.8	21.3

### TSS

SAMPLE LABEL	TSS (mg/L)
NI-OF23A-SDB4-FF	201.33
NI-BAY23A-SDB4-DUR	9.89

## SDB6- 2/10/2005

### METALS

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES
2360*3		NI-OF23A-SDB6-FF (T)	290	388	1.47	15.1	3.83	49.4	185
2360*1		NI-OF23A-SDB6-FF (D)	17.1	20.4	1.02	0.154	3.45	42.6	134
2360*2		Field Blank - Filtered	1.64	0.217	0.119 U	0.025 U	0.074 U	0.883 U	0.274

MSL		Sponsor	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code	Rep	I.D.	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
2360*3		NI-OF23A-SDB6-FF (T)	1.22	1.47 U	0.04 U	0.552	0.50 U	3.78	0.0118
2360*1		NI-OF23A-SDB6-FF (D)	0.968	1.47 U	0.04 U	0.369	0.50 U	0.201	0.00593
2360*2		Field Blank - Filtered	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.000566

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES
2157*12		NI-SDB6-O26-COMP (T)	540	756	3.65	51.0	5.93	41.0	87.3
2157*9		NI-SDB6-OF26-COMP (D)	19.8	22.1	1.31	7.12	4.62	29.1	36.6

MSL		Sponsor	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code	Rep	I.D.	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
2157*12		NI-SDB6-O26-COMP (T)	11.5	38.9	0.0719	1.14	0.739	10.8	0.0212
2157*9		NI-SDB6-OF26-COMP (D)	11.0	38.3	0.040 U	0.791	0.50 U	0.512	0.00213

SAMPLE ID	DISSOLVED COPPER ( µg/L)	TOTAL COPPER (µg/L)
NI-BAY23A-SDB6-PRE	2.2	2.3
NI-BAY23A-SDB6-DUR	3.3	6.0
NI-OF26-SDB6-FF	22.2	33.4
NI-BAY26-SDB6-PRE	2.2	2.7
NI-BAY26-SDB6-DUR	4.1	9.7

SAMPLE ID	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
NI-BAY23A-SDB6-PRE	6.2	6.3
NI-BAY23A-SDB6-DUR	10.7	11.1
NI-OF26-SDB6-FF	101	129
NI-BAY26-SDB6-PRE	5.1	6.7
NI-BAY26-SDB6-DUR	18	29

## METALS QA/QC

**PROGRAM:** SPAWAR, Task 19  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/OES	50-150%	±20%	±50%	50.0
Iron	ICP/OES	50-150%	±20%	±50%	10.0
Manganese	ICP/OES	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Three (3) samples were analyzed for fourteen (14) metals: nickel (Ni), copper, (Cu), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1631m, aluminum (Al), iron (Fe), chromium (Cr), manganese (Mn), and zinc (Zn) by inductively coupled plasma optical emission spectroscopy following EPA Method 200.7 and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Three (3) samples were received on 2/11/2005 and were logged into Battelle's sample tracking system. The samples were analyzed within the six month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:

Task	Date Performed
Hg	2/23/05
ICP-MS	2/22/05
ICP-OES	3/1 & 4/05

### DETECTION LIMITS

The target detection limit was met for all metals, except Ni, Cu, Se and Cd. The MDL for seawater analysis by dilution is somewhat higher than

our typical MDL's for direct analysis. Sample concentrations were substantially greater than the MDL, except Se. All Se results were less than our MDL for this method. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.

#### **METHOD BLANKS**

One method blank was analyzed with this batch of samples. Results were less than 3 times the MDL for all metals, except the TRM blank for Zn. The TRM field sample was greater than 10 x the blank concentration and therefore was not impacted by the blank contamination.

#### **BLANK SPIKES**

One sample of reagent water was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **MATRIX SPIKES**

One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

#### **REPLICATES**

One sample was analyzed in duplicate. All results were within the QC limits of  $\pm 30\%$  ( $\pm 50\%$  for Al and Fe).

#### **SRM**

One matrix-appropriate standard reference material (SRM) was analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.

SRM 1640 has 22 certified and reference metals. Recovery for all metals reported were within the control limit of  $\pm 20\%$  of the certified or reference value. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of  $\pm 25\%$  of the certified value.

#### **REFERENCES**

EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4- 91-010. Environmental Services Division, Monitoring Management Branch.



# METALS QA/QC

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)	
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
<b>PROCEDURAL BLANK</b>																	
		Dissolved	3.36 U	2.51 U	0.155	0.025 U	0.074 U	0.883 U	0.283 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.00017 U	U
		Dissolved - OES reanalysis	3.36 U	2.51 U	0.119 U	0.025 U	N/A	N/A	0.113 U	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		TRM	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.705 b	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	N/A	N/A
<b>METHOD DETECTION LIMIT</b>			<b>3.36</b>	<b>2.51</b>	<b>0.119</b>	<b>0.025</b>	<b>0.074</b>	<b>0.883</b>	<b>0.113</b>	<b>0.158</b>	<b>1.47</b>	<b>0.040</b>	<b>0.054</b>	<b>NA</b>	<b>0.009</b>	<b>0.00012</b>	
Project Target Detection Limit			50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01	
<b>STANDARD REFERENCE MATERIAL</b>																	
1640		Dissolved	52.8	36.3	37.4	125	26.9	83.9	54.7	28.9	26.2	7.57	24.1	1.63	29.0	NA	
1640		Dissolved - OES reanalysis	54.6	34.4	39.0	123	N/A	N/A	54.1	N/A	N/A	N/A	N/A	N/A	N/A	NA	
1640		TRM	N/A	N/A	N/A	N/A	26.7	82.3	N/A	25.7	21.1	7.42	22.2	1.71	31.4	NA	
1640		certified/reference value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC	
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC	
		% difference	2%	6%	3%	2%	2%	2%	3%	8%	19%	1%	6%	N/A	4%	N/A	
		% difference	5%	0%	1%	1%	N/A	N/A	2%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
		% difference	N/A	N/A	N/A	N/A	3%	3%	N/A	4%	3%	3%	3%	N/A	13%	N/A	
1641d		% difference	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1497	
1641d		certified value	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1590	
1641d		range	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	±18.0	
1641d		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	6%	
<b>ICV, CCV RESULTS</b>																	
ICV			99%	101%	99%	100%	100%	101%	101%	98%	100%	101%	100%	104%	101%	95%	
CCV			99%	102%	98%	99%	101%	101%	100%	99%	99%	102%	99%	104%	108%	98%	
CCV			101%	105%	98%	98%	98%	98%	100%	97%	97%	100%	99%	101%	107%	NA	
CCV			100%	104%	98%	98%	96%	98%	100%	97%	96%	99%	97%	99%	108%	NA	
CCV			NA	NA	NA	NA	96%	97%	NA	98%	96%	100%	100%	102%	108%	NA	
ICV		OES reanalysis	98%	100%	102%	101%	100%	101%	103%	98%	100%	101%	100%	104%	101%	NA	
CCV		OES reanalysis	100%	102%	99%	96%	101%	101%	100%	99%	99%	102%	99%	104%	105%	NA	
CCV		OES reanalysis	100%	99%	100%	97%	98%	98%	100%	97%	97%	100%	99%	101%	107%	NA	
CCV		OES reanalysis	99%	100%	100%	97%	96%	98%	100%	97%	96%	99%	97%	99%	109%	NA	
<b>BLANK SPIKE RESULTS</b>																	
		Amount Spiked	100	100	50.0	100	10.0	50.0	50.0	10.0	10.0	10.0	10.0	10.0	10.0	0.00472	
		Blank	3.36 U	2.51 U	0.155	0.025 U	0.074 U	0.883 U	0.283 U	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.000407	
		Blank + Spike	95.8	108	53.9	125	9.80	50.1	56.7	9.88	9.96	10.3	10.1	10.2	11.2	0.00484	
		Amount Recovered	95.8	108	53.7	125	9.80	50.1	56.4	9.88	9.96	10.3	10.1	10.2	11.2	0.00443	
		Percent Recovery	96%	108%	107%	125%	98%	100%	113%	99%	100%	103%	101%	102%	112%	94%	
<b>MATRIX SPIKE RESULTS</b>																	
		Amount Spiked	100	50.0	50.0	50.0	NS	NS	50.0	NS	NS	NS	NS	NS	NS	NS	
		NI-OF23A-SDB6-FF (D) + Spike	17.1	20.4	1.02	0.154	N/A	N/A	134	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
		NI-OF23A-SDB6-FF (D) + Spike	119	74.2	56.9	54.0	NA	NA	189	NA	NA	NA	NA	NA	NA	NA	
		Amount Recovered	102	53.8	55.9	53.8	N/A	N/A	55.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
		Percent Recovery	102%	108%	112%	108%	N/A	N/A	110%	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
		Amount Spiked	NS	NS	NS	NS	10.0	50.0	NS	10.0	10.0	10.0	10.0	10.0	10.0	0.0102	
		NI-OF23A-SDB6-FF (T)	N/A	N/A	N/A	N/A	3.83	49.4	N/A	1.22	1.47 U	0.0308	0.552	0.251	3.78	0.0118	
		NI-OF23A-SDB6-FF (T) + Spike	NA	NA	NA	NA	13.6	102	NA	11.3	11.5	9.72	10.4	95.3	14.9	0.0196	
		Amount Recovered	N/A	N/A	N/A	N/A	10	52.6	N/A	10.1	11.5	9.69	9.85	95.0	11.1	0.00780	
		Percent Recovery	N/A	N/A	N/A	N/A	98%	105%	N/A	101%	115%	97%	98%	95%	111%	76%	
<b>REPLICATE RESULTS</b>																	
2360*1	1	NI-OF23A-SDB6-FF (D)	17.1	20.4	1.02	0.154	3.45	42.6	134	0.968	1.47 U	0.04 U	0.369	0.50 U	0.201	0.00593	
2360*1	2	NI-OF23A-SDB6-FF (D)	17.6	19.4	1.08	0.153	NA	NA	133	NA	NA	NA	NA	NA	NA	0.00600	
		RPD	3%	5%	6%	1%	N/A	N/A	1%	N/A	N/A	N/A	N/A	N/A	N/A	1%	
2360*3	1	NI-OF23A-SDB6-FF (T)	290	388	1.47	15.1	3.83	49.4	185	1.22	1.47 U	0.04 U	0.552	0.50 U	3.78	0.0118	
2360*3	2	NI-OF23A-SDB6-FF (T)	NA	NA	NA	NA	3.71	48.6	NA	1.15	1.47 U	0.0444	0.541	0.50 U	3.85	NA	
		RPD	N/A	N/A	N/A	N/A	3%	2%	N/A	6%	N/A	N/A	2%	N/A	2%	N/A	

U = not detected at or above detection limit; NC = not certified; N/A = not applicable; b = Sample results are less than 3x the blank.

# METALS QA/QC (CONT.)

MSL	Code	Rep	Sponsor I.D.	Al (µg/L) ICP-OES	Fe (µg/L) ICP-OES	Cr (µg/L) ICP-OES	Mn (µg/L) ICP-OES	Ni (µg/L) ICP-MS	Cu (µg/L) ICP-MS	Zn (µg/L) ICP-OES	As (µg/L) ICP-MS	Se (µg/L) ICP-MS	Ag (µg/L) ICP-MS	Cd (µg/L) ICP-MS	Sn (µg/L) ICP-MS	Pb (µg/L) ICP-MS	Hg (µg/L) CVAF
<b>PROCEDURAL BLANK</b>																	
			Dissolved	3.36 U	2.51 U	0.155	0.025 U	0.074 U	0.883 U	0.283	0.158 U	1.47 U	0.040 U	0.054 U	0.50 U	0.009 U	0.00017 U
			Dissolved Hg reanalysis	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00017 U
			Dissolved - OES reanalysis	3.36 U	2.51 U	0.119 U	0.025 U	N/A	N/A	0.113 U	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			TRM	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.705 b	0.158 U	1.47 U	0.040 U	0.054 U	0.50 U	0.009 U	N/A
<b>METHOD DETECTION LIMIT</b>				3.36	2.51	0.119	0.025	0.074	0.883	0.113	0.158	1.47	0.040	0.054	NA	0.009	0.00012
Project Target Detection Limit				50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50	0.20	0.50	0.05	0.50	0.05	0.01
<b>STANDARD REFERENCE MATERIAL</b>																	
	1640		Dissolved	52.8	36.3	37.4	125	26.9	83.9	54.7	28.9	26.2	7.57	24.1	1.63	29.0	NA
	1640		Dissolved - OES reanalysis	54.6	34.4	39.0	123	N/A	N/A	54.1	N/A	N/A	N/A	N/A	N/A	N/A	NA
	1640		TRM	N/A	N/A	N/A	N/A	26.7	82.3	N/A	25.7	21.1	7.42	22.2	1.71	31.4	NA
	1640		certified/reference value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7	22.0	7.62	22.8	NC	27.9	NC
	1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73	±0.51	±0.25	±0.96	NC	±0.14	NC
			% difference	2%	6%	3%	3%	2%	2%	3%	8%	19%	1%	6%	N/A	4%	N/A
			% difference	5%	0%	1%	1%	N/A	N/A	2%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			% difference	N/A	N/A	N/A	N/A	3%	3%	N/A	4%	4%	3%	3%	N/A	13%	N/A
	1641d			NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1497
	1641d		Hg reanalysis	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1544
	1641d		certified value	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1590
	1641d		range	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	±18.0
			% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	6%
			% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	3%
<b>ICV,CCV RESULTS</b>																	
	ICV			99%	101%	99%	100%	100%	101%	101%	98%	100%	101%	100%	104%	101%	95%
	CCV			99%	102%	98%	99%	101%	100%	99%	99%	99%	102%	99%	104%	105%	98%
	CCV			101%	105%	98%	98%	98%	98%	100%	97%	97%	100%	99%	101%	107%	92%
	CCV			100%	104%	98%	98%	96%	98%	100%	97%	96%	99%	97%	99%	109%	NA
	CCV			NA	NA	NA	NA	96%	97%	NA	98%	96%	100%	100%	102%	108%	NA
	ICV		Hg reanalysis	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	96%
	CCV		Hg reanalysis	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	105%
	ICV		OES reanalysis	98%	100%	102%	101%	101%	101%	103%	98%	100%	101%	100%	104%	101%	NA
	CCV		OES reanalysis	100%	102%	99%	96%	100%	101%	100%	99%	99%	102%	104%	104%	105%	NA
	CCV		OES reanalysis	100%	99%	100%	97%	98%	98%	100%	97%	97%	100%	99%	101%	107%	NA
	CCV		OES reanalysis	99%	100%	100%	97%	96%	98%	100%	97%	96%	99%	97%	99%	109%	NA
<b>BLANK SPIKE RESULTS</b>																	
			Amount Spiked	100	100	50.0	100	10.0	50.0	50.0	50.0	50.0	10.0	10.0	10.0	10.0	0.00472
			Blank	3.36 U	2.51 U	0.155	0.025 U	0.074 U	0.883 U	0.283	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.009 U	0.000407
			Blank + Spike	95.8	108	53.9	125	9.80	50.1	56.7	48.8	49.5	10.3	10.1	10.2	11.2	0.00484
			Amount Recovered	95.8	108	53.7	125	9.80	50.1	56.4	48.8	49.5	10.3	10.1	10.2	11.2	0.00443
			Percent Recovery	96%	108%	107%	125%	98%	100%	113%	98%	99%	103%	101%	102%	112%	94%
<b>MATRIX SPIKE RESULTS</b>																	
			Amount Spiked	NS	NS	NS	NS	10.0	50.0	NS	50.0	50.0	10.0	10.0	100	10.0	NS
			NI-OF26-SDB6-COMP	N/A	N/A	N/A	N/A	4.62	29.1	N/A	11.0	38.3	0.04 U	0.791	0.50 U	0.512	N/A
			NI-OF26-SDB6-COMP + Spike	NS	NS	NS	NS	14.3	72.3	NS	57.6	83.8	8.67	10.1	94.4	9.86	NS
			Amount Recovered	N/A	N/A	N/A	N/A	9.68	43.2	N/A	46.6	45.5	8.67	9.31	94.4	9.35	N/A
			Percent Recovery	N/A	N/A	N/A	N/A	97%	86%	N/A	93%	91%	87%	93%	94%	93%	N/A
			Amount Spiked	100	50.0	50.0	50.0	NS	NS	50.0	NS	NS	NS	NS	NS	NS	NS
			NAB-OF9-SDB6-COMP	13.9	31.5	1.18	59.6	N/A	N/A	356	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			NAB-OF9-SDB6-COMP + Spike	120	80.6	54.1	111	NS	NS	412	NS	NS	NS	NS	NS	NS	NS
			Amount Recovered	106	49.1	52.9	51.4	N/A	N/A	56.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			Percent Recovery	106%	98%	106%	103%	N/A	N/A	112%	N/A	N/A	N/A	N/A	N/A	N/A	N/A
			Amount Spiked	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	0.0103
			NAB-OF9-SDB6-COMP	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.00838
			NAB-OF9-SDB6-COMP + Spike	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	0.0187
			Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.0103
			Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	100%
<b>REPLICATE RESULTS</b>																	
	2157*9	1	NI-OF26-SDB6-COMP (D)	19.8	22.1	1.31	7.12	4.62	29.1	36.6	11.0	38.3	0.04 U	0.791	0.50 U	0.512	0.00213
	2157*9	2	NI-OF26-SDB6-COMP (D)	20.9	17.1	1.17	7.04	4.76	28.7	36.9	11.0	40.8	0.04 U	0.746	0.50 U	0.463	NA
			RPD	5%	26%	11%	1%	3%	1%	1%	0%	6%	N/A	6%	N/A	10%	N/A
	2157*13	1	NAB-OF9-SDB6-COMP (T)	192	847	2.11	71.3	4.37	59.5	522	4.93	14.1	0.04 U	0.551	0.50 U	3.21	0.00838
	2157*13	2	NAB-OF9-SDB6-COMP (T)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.00815
			RPD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	3%

U = not detected at or above detection limit; NC = not certified; N/A = not applicable; b = Sample results are less than 3x the blank.

# PAHs

CLIENT ID	NI- OF23A-SDB6- FF	NI- BAY23A-SDB6- PRE	NI- BAY23A-SDB6- DUR	NI- OF26-SDB6-FF	NI- OF26-SDB6- COMP	NI- BAY26-SDB6- PRE	NI- BAY26-SDB6- DUR
Battelle ID	S7115-P	S7116-P	S7117-P	S7111-P	S7112-P	S7113-P	S7114-P
Sample Type	SA	SA	SA	SA	SA	SA	SA
Collection Date	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05
Extraction Date	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05
Analysis Date	02/25/05	02/26/05	03/05/05	03/06/05	03/06/05	02/25/05	03/06/05
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.60	2.64	2.63	2.62	2.62	2.62	2.60
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Naphthalene	12.63	0.76 J	1.73 J	115.33	67.79	0.72 J	2.18 J
C1-Naphthalenes	10.02	0.5 U	0.5 U	566.36	305.92	0.51 U	1.38 J
C2-Naphthalenes	11.68	0.5 U	0.5 U	1568.64	770.25	0.51 U	14.22
C3-Naphthalenes	51.43	0.5 U	0.5 U	1695.7	836.17	0.51 U	43.47
C4-Naphthalenes	11.93	0.5 U	0.5 U	1198.25	615.36	0.51 U	68.21
2-Methylnaphthalene	10.41	0.36 U	0.36 U	550.31	289.36	0.36 U	1.15 J
1-Methylnaphthalene	6.27	0.38 U	0.38 U	422.55	235.3	0.38 U	1.29 J
Biphenyl	1.81 J	0.47 U	0.47 U	113.71	29.82	0.47 U	0.48 U
2,6-dimethylnaphthalene	2.99 J	0.63 U	0.63 U	790.77	369.96	0.63 U	2.81 J
Acenaphthylene	0.54 U	0.53 U	11.52	0.54 U	0.54 U	0.54 U	3.71
Acenaphthene	8.29	0.57 U	4.39	70.26	40.82	0.57 U	4.76
2,3,5-trimethylnaphthalene	0.45 U	0.44 U	0.44 U	212.45	81.47	0.44 U	3.94
Dibenzofuran	1.31 J	0.23 U	8.32	90.86	47.54	0.23 U	3.96
Fluorene	3.07 J	0.52 U	2.88 J	142.16	79.66	0.52 U	3.65
C1-Fluorenes	3.81	0.52 U	0.52 U	421.13	209.69	0.52 U	14.89
C2-Fluorenes	21.57	0.52 U	0.52 U	634.23	333.91	0.52 U	57.66
C3-Fluorenes	19.5	0.52 U	0.52 U	754.05	315.52	0.52 U	39.6
Anthracene	1.93 J	0.38 U	31.98	79.35	31.18	0.39 U	12.51
Phenanthrene	14.59	0.82 U	64.16	343.48	221.11	0.82 U	56.55
C1-Phenanthrenes/Anthracenes	13.21	0.82 U	14.24	704.6	411.35	0.82 U	40.35
C2-Phenanthrenes/Anthracenes	29.91	0.82 U	6.06	856.47	492.7	0.82 U	85.08
C3-Phenanthrenes/Anthracenes	16.53	0.82 U	3.16 J	362.13	234.78	0.82 U	47.32
C4-Phenanthrenes/Anthracenes	5.94	0.82 U	0.82 U	91.94	71.35	0.82 U	13.8
1-Methylphenanthrene	3.55	0.46 U	3.48	205.09	109.38	0.46 U	13.4
Dibenzothiophene	11.22	0.38 U	13.72	161.69	87.1	0.38 U	11.36
C1-Dibenzothiophenes	16.5	0.38 U	2.29 J	309.2	163.27	0.38 U	18.55
C2-Dibenzothiophenes	45.95	0.38 U	3.42	593.52	331.39	0.38 U	66.96
C3-Dibenzothiophenes	41.28	0.38 U	0.38 U	402.74	255.88	0.38 U	54.3
C4-Dibenzothiophenes	22.32	0.38 U	0.38 U	134.77	92.93	0.38 U	22.56
Fluoranthene	11.91	3.2	295.63	765.03	291.07	3.62	235.42
Pyrene	17.65	1.7 J	156.21	579.54	254.27	1.95 J	194.17
C1-Fluoranthenes/Pyrenes	7.88	0.68 U	24	150.39	84.4	0.68 U	44.05
C2-Fluoranthenes/Pyrenes	5.73	0.68 U	0.68 U	68.08	110.12	0.68 U	0.69 U
C3-Fluoranthenes/Pyrenes	0.69 U	0.68 U	0.68 U	0.68 U	39.92	0.68 U	0.69 U
Benzo(a)anthracene	1.58 J	1.03 U	15.4	93.72	46.25	1.39 J	33.23
Chrysene	7.43	0.91 J	97.16	527.33	207.88	1.18 J	159.79
C1-Chrysenes	5.36	0.45 U	6.42	96.6	45.97	0.45 U	27.54
C2-Chrysenes	0.45 U	0.45 U	0.45 U	50.07	27.98	0.45 U	13.08
C3-Chrysenes	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U
C4-Chrysenes	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U
Benzo(b)fluoranthene	2.33 J	0.88 U	65.26	581.72	230.54	0.89 U	153.21
Benzo(j,k)fluoranthene	3.12 J	0.99 U	32.81	525.64	221.43	1 U	156.77
Benzo(e)pyrene	4.05	0.39 U	30.72	442.13	186.04	0.39 U	126.91
Benzo(a)pyrene	1.23 J	0.76 U	10.14	289.74	127.12	0.77 U	88.87
Perylene	1.48 U	1.46 U	1.47 U	54.79	26.65	1.47 U	16.24
Indeno(1,2,3-cd)pyrene	2.11 J	0.75 U	11	390.05	138.72	0.76 U	109.14
Dibenz(a,h)anthracene	1.54 J	0.63 U	2.3 J	68.08	32.03	0.64 U	19.46
Benzo(g,h,i)perylene	6.65	0.75 U	10.66	547.44	213.93	0.76 U	135.82
Surrogate Recoveries (%)							
Naphthalene-d8	46	55	57	49	43	46	52
Phenanthrene-d10	75	66	80	59	45	60	68
Chrysene-d12	63	66	77	54	43	60	65

## PAHS QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Referen ce Method	Method Blank	Surrogat e Recovery	LCS/M S Recover y	SRM % Diff. PD on average	Sample Replicat e Relative Precisio n	Detection Limits (ng/L)
PAH	General NS&T	<5xMD L	40-120% Recovery	40-120% Recovery  (target spike must be >5 x native conc.)	≤30%  (for analytes >5x MDL)	≤30% RPD  (calculated between the MS and MSD samples)	MDL: ~0.47 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for PAH were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	2/25/05 – 3/6/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected above the laboratory control limit (>5 x MDL), however naphthalene was detected in the procedural blank at a concentration less than the reporting limit (RL). The data was qualified with a “J” in

**LABORATORY  
CONTROL  
SAMPLE:**

the procedural blank. Any authentic field sample naphthalene concentrations that are greater than the reporting limit but less than five times the concentration detected in the associated blank, were qualified with a "B". This resulted in three samples having "B" qualified naphthalene data; S7118 (OF-NAB9-SDB6-FF), S7122 (OF-NAB18-SDB6-FF), and S7125 (BAY-NAB18-SD86-D). No further corrective action was taken.

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**Comments** – None.

**SURROGATES:**

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Two exceedences noted.

**Comments** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery), except for naphthalene-d8 and chrysene-d12 in sample S7118 (OF-NAB9-SDB6-FF). The recoveries for these compounds were calculated to be 32% and 39%, respectively. Chromatography and calculations were reviewed. No discrepancies were found. The exceedences were qualified with an "N". No further corrective action taken.

**CALIBRATIONS:**

The GC/MS is calibrated with a minimum of a 5 level curve. The RSD between response factors for the individual target analytes must be  $<25\%$ . Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of minimally every 10 samples. This PD between the initial calibration RF and the check should be  $<25\%$  for individual analytes.

**04-0103** – No calibration exceedences.

**Comments** – None.

# PAHS QA/QC

CLIENT ID	LABORATORY CONTROL SAMPLE				MATRIX SPIKE NAB-OF18-SDB6-COMP					MATRIX SPIKE DUPLICATE-NAB-OF18-SDB6-COMP					PROCEDURAL BLANK	CLIENT ID	GG73: PCB/PESTICIDE SRM SOLUTION				
Battelle ID	BF876LCS-P				S7123MS-P					S7123MS-P					BF875PB-P	Battelle ID	BF877SRM-P				
Sample Type	LCS				MS					MSD					PB	Sample Type	SRM				
Collection Date	02/17/05				2/11/2005					2/11/2005					02/17/05	Collection Date	02/17/05				
Extraction Date	02/17/05				2/17/2005					2/17/2005					02/17/05	Extraction Date	02/17/05				
Analysis Date	02/25/05				3/6/2005					3/6/2005					02/25/05	Analysis Date	02/25/05				
Analytical Instrument	MS				MS					MS					MS	Analytical Instrument	MS				
% Moisture	NA				NA					NA					NA	% Moisture	NA				
% Lipid	NA				NA					NA					NA	% Lipid	NA				
Matrix	LIQUID				WATER					WATER					LIQUID	Matrix	LIQUID				
Sample Size	2.00				0.825					0.825					2.00	Sample Size	2.00				
Size Unit-Basis	L LIQUID				L LIQUID					L LIQUID					L LIQUID	Size Unit-Basis	L LIQUID				
Units	NG/L LIQUID	Target	% Recovery		NG/L LIQUID	Target	% Recovery			NG/L LIQUID	Target	% Recovery	RPD (%)		NG/L LIQUID	Units	NG/L LIQUID	Certified Range	% Difference		
Naphthalene	579.24	1000.60	58		1379.31	2425.70	57			1415.95	2425.70	58	1.7		0.94	J Naphthalene	1064.46	1000.60 - 1000.60	6.4		
C1-Naphthalenes	0.66	U			1758.57					1835.46					0.66	U C1-Naphthalenes	0.66	U			
C2-Naphthalenes	0.66	U			1.61	U				1.61	U				0.66	U C2-Naphthalenes	0.66	U			
C3-Naphthalenes	0.66	U			1.61	U				1.61	U				0.66	U C3-Naphthalenes	0.66	U			
C4-Naphthalenes	0.66	U			1.61	U				1.61	U				0.66	U C4-Naphthalenes	0.66	U			
2-Methylnaphthalene	604.62	1002.00	60		1550.81	2429.09	64			1622.32	2429.09	67	4.6		0.47	U 2-Methylnaphthalene	891.98	1002.00 - 1002.00	11.0		
1-Methylnaphthalene	578.63	1001.20	58		1441.76	2427.15	59			1524.17	2427.15	63	6.6		0.5	U 1-Methylnaphthalene	855.14	1001.20 - 1001.20	14.6		
Biphenyl	587.69	1000.20	59		1683.06	2424.73	69			1779.39	2424.73	73	5.6		0.62	U Biphenyl	861.16	1000.20 - 1000.20	13.9		
2,6-dimethylnaphthalene	614.44	1001.00	61		1620.23	2426.67	67			1724.13	2426.67	71	5.8		0.83	U 2,6-dimethylnaphthalene	909.31	1001.00 - 1001.00	9.2		
Acenaphthylene	597.78	1000.65	60		1497.71	2425.82	62			1600.06	2425.82	66	6.3		0.7	U Acenaphthylene	877.83	1000.65 - 1000.65	12.3		
Acenaphthene	616.18	1000.75	62		1505.77	2426.06	62			1607.17	2426.06	66	8.3		0.75	U Acenaphthene	918.77	1000.75 - 1000.75	8.2		
2,3,5-trimethylnaphthalene	602.88	1000.30	60		1629.66	2424.97	67			1767.26	2424.97	73	8.6		0.58	U 2,3,5-trimethylnaphthalene	890.92	1000.30 - 1000.30	10.9		
Dibenzofuran	621.82	1002.20	62		1865.44	2429.58	77			2020.42	2429.58	83	7.5		0.3	U Dibenzofuran	933.56	1002.20 - 1002.20	6.8		
Fluorene	620.55	1000.70	62		1697.98	2425.94	70			1848.13	2425.94	76	8.2		0.68	U Fluorene	916.71	1000.70 - 1000.70	8.4		
C1-Fluorenes	0.68	U			1.65	U				1.65	U				0.68	U C1-Fluorenes	0.68	U			
C2-Fluorenes	0.68	U			1.65	U				1.65	U				0.68	U C2-Fluorenes	0.68	U			
C3-Fluorenes	0.68	U			1.65	U				1.65	U				0.68	U C3-Fluorenes	0.68	U			
Anthracene	703.01	1000.65	70		1819.46	2425.82	75			2059.49	2425.82	85	12.5		0.51	U Anthracene	1037.1	1000.65 - 1000.65	3.8		
Phenanthrene	677.73	1000.85	68		1837.78	2425.82	75			2059.16	2425.82	84	11.3		1.08	U Phenanthrene	1005.31	1000.85 - 1000.85	0.5		
C1-Phenanthrenes/Anthracenes	1.08	U			1292.49					1434.89					1.08	U C1-Phenanthrenes/Anthracenes	1.08	U			
C2-Phenanthrenes/Anthracenes	1.08	U			27.92					35.44					1.08	U C2-Phenanthrenes/Anthracenes	1.08	U			
C3-Phenanthrenes/Anthracenes	1.08	U			30.03					36.58					1.08	U C3-Phenanthrenes/Anthracenes	1.08	U			
C4-Phenanthrenes/Anthracenes	1.08	U			2.62	U				2.62	U				1.08	U C4-Phenanthrenes/Anthracenes	1.08	U			
1-Methylphenanthrene	693.54	1000.30	69		1890.47	2424.97	78			2124.46	2424.97	88	12.0		0.61	U 1-Methylphenanthrene	1021.46	1000.30 - 1000.30	2.1		
Dibenzothiophene	687.95	1001.00	69		1834.13	2426.67	75			2061.43	2426.67	85	12.5		0.5	U Dibenzothiophene	1019.19	1001.00 - 1001.00	1.8		
C1-Dibenzothiophenes	0.5	U			12.59					12.51					0.5	U C1-Dibenzothiophenes	0.5	U			
C2-Dibenzothiophenes	0.5	U			48.6					43.67					0.5	U C2-Dibenzothiophenes	0.5	U			
C3-Dibenzothiophenes	0.5	U			49.59					53.46					0.5	U C3-Dibenzothiophenes	0.5	U			
C4-Dibenzothiophenes	0.5	U			33.75					35.06					0.5	U C4-Dibenzothiophenes	0.5	U			
Fluoranthene	703.26	1000.50	70		1862.97	2425.45	77			2104.3	2425.45	86	11.0		0.77	U Fluoranthene	1041.81	1000.50 - 1000.50	4.1		
Pyrene	718.86	1000.50	72		1865.04	2425.45	77			2089.62	2425.45	86	11.0		0.9	U Pyrene	1067.39	1000.50 - 1000.50	6.7		
C1-Fluoranthenes/Pyrenes	0.9	U			17.67					19.81					0.9	U C1-Fluoranthenes/Pyrenes	0.9	U			
C2-Fluoranthenes/Pyrenes	0.9	U			2.17	U				2.17	U				0.9	U C2-Fluoranthenes/Pyrenes	0.9	U			
C3-Fluoranthenes/Pyrenes	0.9	U			2.17	U				2.17	U				0.9	U C3-Fluoranthenes/Pyrenes	0.9	U			
Benzo(a)anthracene	621.47	1000.60	62		1462.91	2425.70	60			1604.23	2425.70	66	9.5		1.36	U Benzo(a)anthracene	856.76	1000.60 - 1000.60	14.4		
Chrysene	730.19	1000.75	73		1556.53	2426.06	64			1657.64	2426.06	68	6.1		0.59	U Chrysene	1045.65	1000.75 - 1000.75	4.5		
C1-Chrysenes	0.59	U			17.96					26.53					0.59	U C1-Chrysenes	0.59	U			
C2-Chrysenes	0.59	U			30.65					38.76					0.59	U C2-Chrysenes	0.59	U			
C3-Chrysenes	0.59	U			1.43	U				3.54	U				0.59	U C3-Chrysenes	0.59	U			
C4-Chrysenes	0.59	U			1.43	U				1.43	U				0.59	U C4-Chrysenes	0.59	U			
Benzo(b)fluoranthene	673.98	1000.75	67		1818.88	2426.06	75			2085.1	2426.06	86	13.7		1.16	U Benzo(b)fluoranthene	935.5	1000.75 - 1000.75	6.5		
Benzo(k)fluoranthene	777.31	1000.65	78		1893.52	2426.06	78			2136.71	2426.06	88	12.0		1.31	U Benzo(k)fluoranthene	1086.15	1000.65 - 1000.65	8.5		
Benzo(e)pyrene	702.15	1001.80	70		1823.17	2428.61	75			2063.07	2428.61	85	12.5		0.51	U Benzo(e)pyrene	979.25	1001.80 - 1001.80	2.3		
Benzo(a)pyrene	629.4	1000.65	63		1716.19	2425.82	71			1960.11	2425.82	81	13.2		1	U Benzo(a)pyrene	876.77	1000.65 - 1000.65	12.4		
Perylene	656.25	1000.20	66		1707.57	2424.73	70			1955.41	2424.73	81	14.6		1.93	U Perylene	909.5	1000.20 - 1000.20	9.1		
Indeno(1,2,3-cd)pyrene	723.98	1000.60	72		1676.14	2425.70	69			1869.45	2425.70	77	11.0		0.99	U Indeno(1,2,3-cd)pyrene	1033.73	1000.60 - 1000.60	3.3		
Dibenz(a,h)anthracene	685.03	1000.55	68		1982.27	2425.58	84			2274.52	2425.58	94	13.6		0.84	U Dibenz(a,h)anthracene	916.9	1000.55 - 1000.55	8.4		
Benzo(g,h,i)perylene	705.89	1000.70	71		1939.71	2425.94	80			2258.51	2425.94	93	15.0		0.99	U Benzo(g,h,i)perylene	971.43	1000.70 - 1000.70	2.9		

CLIENT ID	LABORATORY CONTROL SAMPLE				MATRIX SPIKE OF-NAB18-SDB6-COMP					MATRIX SPIKE DUPLICATE-OF-NAB18-SDB6-COMP					PROCEDURAL BLANK	CLIENT ID	GG73: PCB/PESTICIDE SRM SOLUTION				
Surrogate Recoveries (%)																Surrogate Recoveries (%)					
Naphthalene-d8	61				55					58					42	Naphthalene-d8	51				
Phenanthrene-d10	71				77					84					44	Phenanthrene-d10	63				
Chrysene-d12	72				66					69					43	Chrysene-d12	66				

# PCBs

CLIENT ID	NI- OF26-SDB6-FF	NI- OF26-SDB6- COMP	NI- BAY26-SDB6- PRE	NI- BAY26-SDB6- DUR	NI- OF23A-SDB6- FF	NI- BAY23A-SDB6- PRE	NI- BAY23A-SDB6- DUR
Battelle ID	S7111-P	S7112-P	S7113-P	S7114-P	S7115-P	S7116-P	S7117-P
Sample Type	SA	SA	SA	SA	SA	SA	SA
Collection Date	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005	2/11/2005
Extraction Date	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005	2/17/2005
Analysis Date	3/5/2005	3/5/2005	3/5/2005	3/6/2005	3/6/2005	3/6/2005	3/6/2005
Analytical Instrument	MS	MS	MS	MS	MS	MS	MS
% Moisture	NA	NA	NA	NA	NA	NA	NA
% Lipid	NA	NA	NA	NA	NA	NA	NA
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER
Sample Size	2.62	2.62	2.62	2.60	2.60	2.64	2.63
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID
Cl2(8)	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U
Cl3(18)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U
Cl3(28)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U
Cl4(44)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U
Cl4(49)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U
Cl4(52)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U
Cl4(66)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U
Cl4(77)	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U	0.14 U
Cl5(87)	0.23 U	0.23 U	0.23 U	0.24 U	0.24 U	0.23 U	0.23 U
Cl5(101)	0.23 U	0.23 U	0.23 U	0.24 U	0.24 U	0.23 U	0.23 U
Cl5(105)	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U
Cl5(114)	0.23 U	0.23 U	0.23 U	0.24 U	0.24 U	0.23 U	0.23 U
Cl5(118)	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U	0.07 U
Cl5(123)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U
Cl5(126)	0.12 U	0.12 U	0.12 U	0.12 U	0.12 U	0.12 U	0.12 U
Cl6(128)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U
Cl6(138)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U
Cl6(153)	1.98 J	1.66 J	0.27 U	1.13 J	0.27 U	0.27 U	0.27 U
Cl6(156)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U
Cl6(157)	0.15 U	0.15 U	0.15 U	0.15 U	0.15 U	0.14 U	0.15 U
Cl6(167)	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U	0.27 U
Cl6(169)	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U	0.11 U
Cl7(170)	1.05 J	0.92 J	0.19 U	0.53 J	0.19 U	0.19 U	0.19 U
Cl7(180)	2.72 J	1.93 J	0.11 U	1.61 J	0.11 U	0.11 U	0.11 U
Cl7(183)	0.58 J	0.41 J	0.19 U	0.27 J	0.19 U	0.19 U	0.19 U
Cl7(184)	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U	0.19 U
Cl7(187)	1.01 J	0.91 J	0.19 U	0.74 J	0.19 U	0.19 U	0.19 U
Cl7(189)	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U	0.08 U
Cl8(195)	0.36 U	0.36 U	0.36 U	0.37 U	0.37 U	0.36 U	0.36 U
Cl9(206)	0.34 U	0.34 U	0.34 U	0.34 U	0.34 U	0.34 U	0.34 U
Cl10(209)	0.41 U	0.41 U	0.41 U	0.41 U	0.41 U	0.4 U	0.41 U
<b>Surrogate Recoveries (%)</b>							
Cl2(14)	67	52	55	66	65	59	68
Cl3(34)	71	53	59	67	65	61	70

## PCBs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/M S Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.09 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate and concentrated. The extract was then fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	3/5/05 – 3/7/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.



**LABORATORY  
CONTROL  
SAMPLE:**

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**Comments** – None.

**SURROGATES:**

Two surrogate compounds were added prior to extraction, including PCB 14 and PCB 34. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATIONS:**

The GC/MS is calibrated with a minimum of a 6-point curve. The co-efficient of determination must be  $\geq 0.995$  for each target analyte. Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of every 12 hours (minimally). This PD between the initial calibration RF and the check should be  $<20\%$  for individual analytes; 15% on average. Additionally an ICC check was run with the initial calibration. The PD for the ICC should be  $< 15\%$ , for each analyte.

**05-0056** – No calibration exceedences.

**Comments** – None.

# PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE- NAB-OF18- SDB6-COMP			MATRIX SPIKE DUPLICATE- NAB-OF18- SDB6-COMP				PRODECURAL BLANK		GG73- PCB/PESTICIDE SRM SOLUTION				
Battelle ID	BF876LCS-P			S7123MS-P			S7123MSD-P				BF875PB-P	BF877SRM-P					
Sample Type	LCS			MS			MSD				PB	SRM					
Collection Date	2/17/2005			2/11/2005			2/11/2005				2/17/2005	2/17/2005					
Extraction Date	2/17/2005			2/17/2005			2/17/2005				2/17/2005	2/17/2005					
Analysis Date	3/5/2005			3/6/2005			3/7/2005				3/5/2005	3/5/2005					
Analytical Instrument	MS			MS			MS				MS	MS					
% Moisture	NA			NA			NA				NA	NA					
% Lipid	NA			NA			NA				NA	NA					
Matrix	LIQUID			WATER			WATER				LIQUID	LIQUID					
Sample Size	2.00			0.825			0.825				2.00	2.00					
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	L LIQUID					
Units	NG/L LIQUID	Target	% Recovery	Q NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	Certified Value	+/-	Passing %Difference	Passing %Difference	
C12(8)	20.94	40.12	52	57.93	97.26	60	65.69	97.26	68	12.5	0.09 U	28.71	34.24	2.88	23.41	8.5	
C13(18)	23.46	40.12	59	63.17	97.26	65	72.28	97.26	74	12.9	0.11 U	33.26	32.93	0.30	15.92	0.1	
C13(28)	21.18	40.04	53	58.47	97.07	60	66.61	97.07	69	14.0	0.11 U	31.4			15		
C14(44)	23.36	40.08	58	67.71	97.16	70	80.77	97.16	83	17.0	0.19 U	31.8	32.86	0.59	16.8	1.5	
C14(49)	26.89	40.16	67	72.7	97.36	75	86.35	97.36	89	17.1	0.19 U	0.19 U			15		
C14(52)	22.65	40.00	57	64.69	96.97	67	76.93	96.97	79	16.4	0.19 U	30.17	33.07	0.38	16.16	7.7	
C14(66)	16.82	40.04	42	56	97.07	58	65.49	97.07	67	14.4	0.19 U	23.19	32.82	0.62	16.9	28	
C14(77)	17.85	40.00	45	60.54	96.97	62	69.94	96.97	72	14.9	0.18 U	24.75	33.55	1.10	18.29	23.7	
C15(87)	25.33	40.00	63	82.81	96.97	85	96.23	96.97	99	15.2	0.31 U	35.34	33.1	0.27	15.82	5.9	
C15(101)	23.84	40.08	59	72.85	97.16	75	86.65	97.16	89	17.1	0.31 U	31.49	32.56	0.47	16.43	1.9	
C15(105)	23.38	40.04	58	78.35	97.07	81	90.65	97.07	93	13.8	0.14 U	34.77	32.67	1.01	18.09	3.2	
C15(114)	0.31 U			0.74 U			0.74 U				0.31 U	0.31 U			15		
C15(118)	16.89	40.04	42	59.07	97.07	61	70.11	97.07	72	16.5	0.1 U	30.68	32.74	1.06	18.23	3.2	
C15(123)	0.11 U			0.26 U			0.26 U				0.11 U	0.11 U			15		
C15(126)	21.05	40.24	52	73.18	97.55	75	83.73	97.55	86	13.7	0.16 U	32.14	33.22	1.38	19.14	1	
C16(128)	20.67	40.24	51	70.52	97.55	72	81.83	97.55	84	15.4	0.35 U	28.54	32.94	0.27	15.83	12.6	
C16(138)	23.4	40.08	58	83.59	97.16	86	93.09	97.16	96	11.0	0.35 U	32.27	32.43	0.38	16.18	1	
C16(153)	23.31	40.04	58	78.01	97.07	80	91.91	97.07	95	17.1	0.35 U	31.88	32.64	0.62	16.91	0.4	
C16(156)	0.1 U			0.24 U			0.24 U				0.1 U	0.1 U			15		
C16(157)	0.19 U			0.46 U			0.46 U				0.19 U	0.19 U			15		
C16(167)	0.35 U			0.86 U			0.86 U				0.35 U	0.35 U			15		
C16(169)	23.83	40.16	59	80.81	97.36	83	95.7	97.36	98	16.6	0.15 U	0.15 U			15		
C17(170)	20.19	40.20	50	66.97	97.45	69	81.17	97.45	83	18.4	0.25 U	28.45	32.72	0.54	16.66	11.6	
C17(180)	23.14	40.16	58	78.45	97.36	81	93.41	97.36	96	16.9	0.14 U	32.98	32.96	0.32	15.97	1	
C17(183)	24.37	40.16	61	83	97.36	85	96.91	97.36	100	16.2	0.25 U	0.25 U			15		
C17(184)	24.69	40.16	61	80.23	97.36	82	94.21	97.36	97	16.8	0.25 U	0.25 U			15		
C17(187)	20.63	40.12	51	73.67	97.26	76	89.41	97.26	92	19.0	0.25 U	31.89	32.75	0.30	15.93	1.7	
C17(189)	0.11 U			0.26 U			0.26 U				0.11 U	0.11 U			15		
C18(195)	20.93	40.12	52	72.11	97.26	74	85.1	97.26	87	16.1	0.48 U	28.04	32.83	0.66	17	12.8	
C19(206)	22.82	40.12	57	74.32	97.26	76	90.8	97.26	93	20.1	0.44 U	32.94	32.02	0.59	16.85	1	
C10(209)	29.36	40.04	73	81.36	97.07	84	99.02	97.07	102	19.4	0.53 U	40.51	32.99	0.45	16.36	21.1	
Surrogate Recoveries (%)																	
C12(14)	58			67			78				40	55					
C13(34)	59			69			79				40	56					

# PESTICIDES

CLIENT ID	NI- OF23A-SDB6- FF	NI- BAY23A-SDB6- PRE	NI- BAY23A-SDB6- DUR	NI- OF26-SDB6-FF	NI- OF26-SDB6- COMP	NI- BAY26-SDB6- PRE	NI- BAY26-SDB6- DUR	
Battelle ID	S7115-P	S7116-P	S7117-P	S7111-P	S7112-P	S7113-P	S7114-P	
Sample Type	SA	SA	SA	SA	SA	SA	SA	
Collection Date	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	02/11/05	
Extraction Date	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	02/17/05	
Analysis Date	02/26/05	02/26/05	02/26/05	02/26/05	02/26/05	02/26/05	02/26/05	
Analytical Instrument	ECD	ECD	ECD	ECD	ECD	ECD	ECD	
% Moisture	NA	NA	NA	NA	NA	NA	NA	
% Lipid	NA	NA	NA	NA	NA	NA	NA	
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	WATER	
Sample Size	2.60	2.64	2.63	2.62	2.62	2.62	2.60	
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	
2,4'-DDD	0.63 U	0.62 U	0.62 U	0.62 U	0.62 U	0.62 U	0.63 U	
2,4'-DDE	1.16 U	0.52 U	0.52 U	0.52 U	0.52 U	0.52 U	0.53 U	
2,4'-DDT	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	0.37 U	
4,4'-DDD	0.73 U	0.72 U	0.72 U	3	2.1	0.73 U	1.19	
4,4'-DDE	0.53 U	0.52 U	0.52 U	0.52 U	0.82	0.52 U	0.71	
4,4'-DDT	0.45 U	0.45 U	0.45 U	0.45 U	4.58	0.45 U	3.37	
aldrin	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	
a-chlordane	0.29 U	0.29 U	0.29 U	0.29 U	1.7	0.29 U	0.47 J	
g-chlordane	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	0.31 U	
a-BHC	0.26 U	0.26 U	0.26 U	0.26 U	0.26 U	0.26 U	0.26 U	
b-BHC	0.36 U	0.36 U	0.36 U	0.36 U	0.36 U	0.36 U	0.36 U	
d-BHC	0.3 U	0.29 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	
Lindane	0.38 U	0.37 U	0.38 U	0.38 U	0.38 U	0.38 U	0.38 U	
cis-nonachlor	0.5 U	0.49 U	0.49 U	0.49 U	0.49 U	0.49 U	0.5 U	
trans-nonachlor	0.31 U	0.31 U	0.31 U	0.31 U	1.62	0.31 U	0.65	
Chlorpyrifos	0.39 U	0.39 U	0.39 U	0.39 U	0.39 U	0.39 U	0.39 U	
oxychlordane	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	0.3 U	
dieldrin	0.59 U	0.58 U	0.58 U	0.58 U	0.58 U	0.58 U	0.59 U	
endosulfan I	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	0.21 U	
endosulfan II	0.53 U	0.52 U	0.53 U	0.53 U	0.53 U	0.53 U	0.53 U	
endosulfan sulfate	0.5 U	0.49 U	0.49 U	0.5 U	0.5 U	0.5 U	0.5 U	
endrin	0.58 U	0.57 U	0.57 U	0.57 U	0.57 U	0.57 U	0.58 U	
endrin aldehyde	0.65 U	0.64 U	0.65 U	0.65 U	0.65 U	0.65 U	0.65 U	
endrin ketone	0.68 U	0.67 U	0.68 U	0.68 U	0.68 U	0.68 U	0.68 U	
heptachlor	8.67	0.44 U	0.45 U	0.45 U	0.45 U	0.45 U	0.45 U	
heptachlor epoxide	1.21 U	1.19 U	1.2 U	1.2 U	1.2 U	1.2 U	1.21 U	
Hexachlorobenzene	0.64 U	0.28 J	0.63 U	0.63 U	0.63 U	0.63 U	0.64 U	
methoxychlor	0.75 U	0.74 U	0.74 U	9.57	6.99	0.75 U	0.75 U	
Mirex	0.48 U	0.47 U	0.47 U	0.47 U	0.47 U	0.47 U	0.48 U	
<b>Surrogate Recoveries (%)</b>								
Cl2(14)	91	73	85	90	77	64	79	
Cl3(34)	97	70	84	108	66	66	73	
Cl5(104)	86	70	82	95	67	64	77	
Cl5(112)	81	72	82	65	55	67	71	

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Conataminant Analysis of Stormwater  
**PARAMETER:** Pesticides  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 2/11/05. The samples were received at Battelle Duxbury on 2/15/05. Upon arrival, the cooler temperatures ranged from 0.8°C – 3.7°C. No custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0056, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD on average (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.38 – 1.58

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0056	2/17/05	2/25/05 – 2/28/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0056** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.

**LABORATORY CONTROL SAMPLE:** A laboratory control sample (LCS) was prepared with the analytical batch. The percent recoveries of target pesticides were calculated to measure data quality in terms of accuracy.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).

**Comments** – None.

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0056** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**Comments** – None

**SRM:**

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0056** – Two exceedences noted.

**Comments** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD), except for 2,4-DDD and 2,4-DDT. The percent differences calculated for these two compounds are 58.5% and 51.0%, respectively. Chromatography and calculations were reviewed. No discrepancies were found. The data has been qualified with an “N”. Accuracy for this compound has adequately been demonstrated in the LCS, MS, and MSD QC samples.

**SURROGATES**

Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0056** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**Comments** – None.

**CALIBRATIONS:**

The instrument is calibrated with a 5-level (minimum) calibration, ranging in concentration from ~0.001 ng/uL to ~0.125 ng/uL. Calibration checks are analyzed minimally every 10 samples. The samples must be bracketed by passing calibrations.

**04-0275** – No exceedences noted.

**Comments** – All calibration criteria were met except for two percent differences calculated for HCB in two calibration checks. However since this compound was not detected in any field samples, and accuracy for this compound was adequately demonstrated in all other QC samples, no further corrective action was taken.

■

# PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE- NAB-OF19-SDB6- COMP			MATRIX SPIKE DUPLICATE-NAB-OF19-SDB6- COMP				PROCEDURAL BLANK	CLIENT ID	GG73- PCB/PESTICIDE SRM SOLUTION		
Battelle ID	BF876LCS-P			S7123MS-P			S7123MSD-P				BF875PB-P	Battelle ID	BF877SRM-P		
Sample Type	LCS			MS			MSD				PB	Sample Type	SRM		
Collection Date	02/17/05			2/11/2005			2/11/2005				02/17/05	Collection Date	02/17/05		
Extraction Date	02/17/05			2/17/2005			2/17/2005				02/17/05	Extraction Date	02/17/05		
Analysis Date	02/25/05			2/27/2005			2/27/2005				02/25/05	Analysis Date	02/25/05		
Analytical Instrument	ECD			ECD			ECD				ECD	Analytical Instrument	ECD		
% Moisture	NA			NA			NA				NA	% Moisture	NA		
% Lipid	NA			NA			NA				NA	% Lipid	NA		
Matrix	LIQUID			WATER			WATER				LIQUID	Matrix	LIQUID		
Sample Size	2.0g			0.825			0.825				2.0g	Sample Size	2.0g		
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	Size Unit-Basis	L LIQUID		
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	Units	NG/L LIQUID	Certified Range	% Difference
2,4'-DDD	25.61	40.12	64	67.68	97.26	70	75.58	97.26	78	10.8	0.81 U	2,4'-DDD	50.48	31.30 - 31.84	58.5 N
2,4'-DDE	23.38	40.01	58	59.57	97.00	61	68.91	97.00	71	15.2	0.69 U	2,4'-DDE	21.94	31.35 - 31.89	30.0
2,4'-DDT	21.07	40.23	52	52.73	97.53	54	59.9	97.53	61	12.2	0.48 U	2,4'-DDT	15.3	31.20 - 31.48	51.0 N
4,4'-DDD	28.02	40.01	65	63.94	96.98	71	77.31	96.98	80	11.9	0.95 U	4,4'-DDD	24.59	31.44 - 32.30	21.8
4,4'-DDE	25.33	40.01	63	65.61	96.98	68	74.09	96.98	76	11.1	0.68 U	4,4'-DDE	27.41	31.46 - 31.78	12.9
4,4'-DDT	28.23	40.02	71	88.61	97.02	91	98.05	97.02	101	10.4	0.59 U	4,4'-DDT	31.36	31.28 - 31.66	1.0
aldrin	24.44	40.01	61	64.72	97.00	67	73.01	97.00	75	11.3	0.4 U	aldrin	24.22		
a-chlordane	23.46	40.03	59	63	97.04	65	71.99	97.04	74	12.9	0.38 U	a-chlordane	26.5	31.36 - 31.74	15.5
g-chlordane	23.11	40.08	58	62.91	97.12	65	71.26	97.12	73	11.6	0.4 U	g-chlordane	0.4 U		
a-BHC	23.05	40.02	58	61.3	97.01	63	70	97.01	72	13.3	0.34 U	a-BHC	0.34 U		
b-BHC	26.04	40.01	65	71.33	96.98	74	81.52	96.98	84	12.7	0.47 U	b-BHC	0.47 U		
g-BHC	26.74	40.02	67	75.54	97.01	78	86.61	97.01	89	13.2	0.39 U	g-BHC	0.39 U		
Lindane	26.6	40.01	66	72.67	96.99	75	82.78	96.99	85	12.5	0.49 U	Lindane	30.23	31.39 - 31.71	3.7
cis-nonachlor	25.29	40.03	63	66.56	97.04	69	74.86	97.04	77	11.0	0.65 U	cis-nonachlor	0.65 U		
trans-nonachlor	24.46	40.06	61	67.21	97.11	69	76.42	97.11	78	13.5	0.4 U	trans-nonachlor	27.77	31.56 - 32.00	12.0
Chlorpyrifos	26	40.10	65	75.11	97.21	77	86.23	97.21	89	14.5	0.51 U	Chlorpyrifos	0.51 U		
oxychlordane	24.48	40.03	61	66.19	97.04	68	74.74	97.04	77	12.4	0.39 U	oxychlordane	0.39 U		
dieldrin	25.77	40.01	64	66.66	96.99	69	75.03	96.99	77	11.0	0.76 U	dieldrin	28.21	31.34 - 31.76	10.0
endosulfan I	25.15	40.03	63	73.26	97.04	75	73.82	97.04	76	1.3	0.27 U	endosulfan I	0.27 U		
endosulfan II	24.17	40.02	60	65.82	97.02	68	76.63	97.02	79	15.0	0.69 U	endosulfan II	0.69 U		
endosulfan sulfate	25.59	40.02	64	74.76	97.01	77	84.21	97.01	87	12.2	0.65 U	endosulfan sulfate	0.65 U		
endrin	25.18	40.01	63	72.34	97.00	75	81.04	97.00	84	11.3	0.75 U	endrin	0.75 U		
endrin aldehyde	19.49	40.01	49	51.31	96.99	53	65.18	96.99	67	23.3	0.85 U	endrin aldehyde	13.8		
endrin ketone	26.63	40.02	67	72.67	97.01	75	82.31	97.01	85	12.5	0.89 U	endrin ketone	0.89 U		
heptachlor	25.65	40.00	64	77.01	96.98	79	87.83	96.98	91	14.1	0.59 U	heptachlor	29.59	31.39 - 31.87	5.7
heptachlor epoxide	25.41	40.01	64	66.79	96.98	69	76.31	96.98	78	13.5	1.58 U	heptachlor epoxide	27.77	31.36 - 31.90	11.4
Hexachlorobenzene	28.14	40.06	70	72.56	97.12	75	82.38	97.12	85	12.5	0.83 U	Hexachlorobenzene	32.05	31.35 - 31.63	1.3
methoxychlor	29.49	40.01	74	91.3	97.00	92	101.57	97.00	103	11.3	0.98 U	methoxychlor	7.8		
Mirex	26.25	40.03	66	69.14	97.05	71	77.47	97.05	80	11.9	0.62 U	Mirex	29.19	31.41 - 32.31	7.1
Surrogate Recoveries (%)															
C12(14)	71			81			95				51	C12(14)	69		
C13(14)	72			76			87				51	C13(14)	68		
C15(104)	69						92				50	C15(104)	60		
C15(112)	72			77			85				53	C15(112)	69		

## TSS

SAMPLE LABEL	TSS (mg/L)
NI-OF23A-SDB6-FF	9.104
NI-BAY23A-SDB6-PRE	3.361
NI-BAY23A-SDB6-DUR	4.271
NI-OF26-SDB6-FF	14.714
NI-OF26-SDB6-COMP	21.742
NI-BAY26-SDB6-PRE	2.899
NI-BAY26-SDB6-DUR	12.674

## SDB7- 4/27/2005

### METALS

MSL		Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)
Code	Rep	I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES
2360*10		NI-OF23A-SDB7-FF (T)	1448	2557	9.61	44.2	11.8	40.8	289
2360*5		NI-OF23A-SDB7-FF (D)	11.1	12.4	0.295	2.57	1.41	3.69	33.4
2360*9		NI-OF26-SDB7-COMP (T)	3753	5767	20.2	194	15.0	89.3	546
2360*4		NI-OF26-SDB7-COMP (D)	121	103	1.90	23.6	5.95	18.9	79.5
2360*8		Field Blank - Filtered	3.36 U	2.66	0.119 U	0.025 U	0.436	0.883 U	11.9

MSL		Sponsor	As (µg/L)	Se (µg/L)	Ag (µg/L)	Cd (µg/L)	Sn (µg/L)	Pb (µg/L)	Hg (µg/L)
Code	Rep	I.D.	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	CVAF
2360*10		NI-OF23A-SDB7-FF (T)	0.648	1.47 U	0.109	1.26	2.45	21.9	0.0164
2360*5		NI-OF23A-SDB7-FF (D)	0.208	1.47 U	0.04 U	0.0564	0.50 U	0.223	0.00404
2360*9		NI-OF26-SDB7-COMP (T)	2.62	1.61	0.311	6.35	0.891	77.5	0.0494
2360*4		NI-OF26-SDB7-COMP (D)	1.15	1.47 U	0.04 U	0.882	0.50 U	1.50	0.00547
2360*8		Field Blank - Filtered	0.158 U	1.47 U	0.04 U	0.054 U	0.50 U	0.0602	0.000871

SAMPLE ID	DISSOLVED COPPER (µg/L)	TOTAL COPPER (µg/L)
NI-BAY23A-SDB7-PRE	2.3	5.0
NI-BAY23A-SDB7-DUR	2.8	5.3
NI-BAY26-SDB7-FF	50	112
NI-BAY26-SDB7-PRE	2.3	4.2
NI-BAY26-SDB7-DUR	1.7	2.7

SAMPLE ID	DISSOLVED ZINC (µg/L)	TOTAL ZINC (µg/L)
NI-BAY23A-SDB7-PRE	16.96	16.47
NI-BAY23A-SDB7-DUR	13.19	18.47
NI-BAY26-SDB7-FF	588.41	917.30
NI-BAY26-SDB7-PRE	15.39	22.72
NI-BAY26-SDB7-DUR	6.22	6.97



## METALS QA/QC

**PROGRAM:** SPAWAR, Task 19, batch 2  
**PARAMETER:** Metals  
**LABORATORY:** Battelle/Marine Sciences Laboratory, Sequim, Washington  
**MATRIX:** Stormwater

### QA/QC DATA QUALITY OBJECTIVES

	Reference Method	Range of Recovery	SRM Accuracy	Relative Precision	Target Detection Limit (µg/L)
Aluminum	ICP/OES	50-150%	±20%	±50%	50.0
Iron	ICP/OES	50-150%	±20%	±50%	10.0
Manganese	ICP/OES	50-150%	±20%	±30%	0.5
Chromium	ICP/MS	50-150%	±20%	±30%	1.0
Nickel	ICP/MS	50-150%	±20%	±30%	0.05
Copper	ICP/MS	50-150%	±20%	±30%	0.05
Zinc	ICP/MS	50-150%	±20%	±30%	0.5
Arsenic	FIAS	50-150%	±20%	±30%	0.5
Selenium	FIAS	50-150%	±20%	±30%	0.2
Silver	GFAA	50-150%	±20%	±30%	0.5
Cadmium	ICP/MS	50-150%	±20%	±30%	0.05
Tin	ICP/MS	50-150%	±20%	±30%	0.5
Lead	ICP/MS	50-150%	±20%	±30%	0.05
Mercury	CVAF	50-150%	±25%	±30%	0.01

### METHOD

Nine (9) samples were analyzed for fourteen (14) metals: nickel (Ni), copper, (Cu), arsenic (As), selenium (Se), silver (Ag), cadmium (Cd), tin (Sn) and lead (Pb) by inductively coupled plasma mass spectroscopy (ICP/MS) following EPA Method 1638m, aluminum (Al), iron (Fe), chromium (Cr), manganese (Mn), and zinc (Zn) by inductively coupled plasma optic emission spectroscopy following EPA Method 200.7 and mercury (Hg) by cold vapor atomic fluorescence (CVAF) following EPA Method 1631e.

Samples were preserved with nitric acid prior to arrival at MSL. Samples analyzed for Hg by CVAF were pre-treated with bromine chloride and stannous chloride to oxidize and convert all Hg compounds to volatile Hg, which is subsequently trapped onto a gold-coated sand trap.

### HOLDING TIMES

Nine (9) samples were received on 5/03/2005 and were logged into Battelle's sample tracking system. The samples were analyzed within the six month holding time for metals and 90 days for Hg. The following list summarizes all analysis dates:

Task	Date Performed
Hg	5/20/05
ICP-MS	5/11/05
ICP-OES	5/23/05

### DETECTION LIMITS

The target detection limit was met for all metals, except Ni, Cu, Se and Cd. The MDL for seawater analysis by dilution is somewhat higher than

our typical MDL's for direct analysis. Sample concentrations were substantially greater than the MDL, except Se. The method detection limit was met for all metals. An MDL is determined by multiplying the standard deviation of the results of a minimum of 7 replicate low level spikes by the Student's t value at the 99th percentile.

**METHOD BLANKS**

One method blank was analyzed with this batch of samples. Results were less than 3 times the MDL for all metals.

**BLANK SPIKES**

One sample of reagent water was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

**MATRIX SPIKES**

One sample was spiked at several levels with metals. Recoveries were within the QC limits of 50-150% for all metals.

**REPLICATES**

One sample was analyzed in duplicate. All results were within the QC limits of  $\pm 30\%$  ( $\pm 50\%$  for Al and Fe).

**SRM**

One matrix-appropriate standard reference material (SRM) was analyzed for each method; 1641d, river water, and 1640, natural water, obtained from the National Institute of Science and Technology.

SRM 1640 has 22 certified and reference metals. Recovery for all metals reported were within the control limit of  $\pm 20\%$  of the certified or reference value. Tin and Hg are not certified in 1640. SRM 1641d is certified for Hg. Recovery for Hg was within the control limit of  $\pm 25\%$  of the certified value.

**REFERENCES**

EPA. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4- 91-010. Environmental Services Division, Monitoring Management Branch.

## METALS QA/QC (CONT.)

MSL	Rep	Sponsor	Al (µg/L)	Fe (µg/L)	Cr (µg/L)	Mn (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As (µg/L)
Code		I.D.	ICP-OES	ICP-OES	ICP-OES	ICP-OES	ICP-MS	ICP-MS	ICP-OES	ICP-MS
<b>PROCEDURAL BLANK</b>										
		Dissolved	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.248 U	0.158 U
		TRM	3.36 U	2.51 U	0.119 U	0.025 U	0.074 U	0.883 U	0.113 U	0.158 U
<b>METHOD DETECTION LIMIT</b>			3.36	2.51	0.119	0.025	0.074	0.883	0.113	0.158
Project Target Detection Limit			50.0	10.0	1.00	0.50	0.05	0.05	0.50	0.50
<b>STANDARD REFERENCE MATERIAL</b>										
1640		Dissolved	56.3	34.0	37.4	119	26.0	78.1	53.7	26.2
1640		TRM	N/A	N/A	N/A	N/A	25.3	81.4	N/A	25.2
1640		certified/reference value	52.0	34.3	38.6	122	27.4	85.2	53.2	26.7
1640		range	±1.5	±1.6	±1.6	±1.1	±0.8	±1.2	±1.1	±0.73
		% difference	8%	1%	3%	2%	5%	8%	1%	2%
		% difference	N/A	N/A	N/A	N/A	8%	4%	N/A	6%
1641d		certified value	NA	NA	NA	NA	NA	NA	NA	NA
1641d		range	NC	NC	NC	NC	NC	NC	NC	NC
1641d		% difference	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>ICV,CCV RESULTS</b>										
ICV			99%	96%	99%	99%	101%	101%	98%	99%
CCV			99%	106%	101%	97%	98%	100%	103%	101%
CCV			100%	107%	98%	99%	98%	96%	102%	97%
CCV			98%	102%	99%	100%	93%	94%	101%	93%
<b>BLANK SPIKE RESULTS</b>										
		Amount Spiked	500	500	100.0	100	10.0	50.0	100.0	10.0
		Blank	3.36 U	2.51 U	0.245 U	0.038 U	0.005 U	0.015 U	0.248 U	0.008 U
		Blank + Spike	587.0	499	99.6	97.3	9.60	49.3	98.0	9.66
		Amount Recovered	587.0	499	99.6	97.3	9.60	49.3	97.8	9.66
<b>MATRIX SPIKE RESULTS</b>										
		Amount Spiked	NS	NS	NS	NS	10.0	50.0	NS	10.0
		NI-OF26-SDB7-COMP (D)	N/A	N/A	N/A	N/A	5.95	18.9	N/A	1.15
		NI-OF26-SDB7-COMP (D) + Spike	NA	NA	NA	NA	15.3	65.2	NA	11.5
		Amount Recovered	N/A	N/A	N/A	N/A	9.35	46.3	N/A	10.4
		Percent Recovery	N/A	N/A	N/A	N/A	94%	93%	N/A	104%
		Amount Spiked	500	500	100	100	NS	NS	100	NS
		NI-OF23A-SDB7-FF (D)	11.1	12.4	0.295	2.57	N/A	N/A	33.4	N/A
		NI-OF23A-SDB7-FF (D) + Spike	583	515	97.8	100	NA	NA	129	NA
		Amount Recovered	572	503	97.5	97.7	N/A	N/A	95.6	N/A
		Percent Recovery	114%	101%	98%	98%	N/A	N/A	96%	N/A
		Amount Spiked	NS	NS	NS	NS	NS	NS	NS	NS
		NI-OF23A-SDB7-FF (T)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		NI-OF23A-SDB7-FF (T) + Spike	NA	NA	NA	NA	NA	NA	NA	NA
		Amount Recovered	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
		Percent Recovery	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
<b>REPLICATE RESULTS</b>										
2360*4	1	NI-OF26-SDB7-COMP (D)	121	103	1.90	23.6	5.95	18.9	79.5	1.15
2360*4	2	NI-OF26-SDB7-COMP (D)	130	107	2.00	23.9	5.94	18.6	81.6	1.14
		RPD	7%	4%	5%	1%	0%	2%	3%	1%
		NAB-OF9-SDB7-COMP (D)								
2360*6	1	NAB-OF9-SDB7-COMP (D)	13.2	14.3	1.60	95.9	8.68	37.8	709	20.2
2360*6	2	NAB-OF9-SDB7-COMP (D)	NA	NA	NA	NA	NA	NA	NA	NA
		RPD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

# PAHs

CLIENT ID	NI- OF23A-SDB7- FF	NI- BAY23A-SDB7- PRE	NI- BAY23A-SDB7- DUR	NI- OF26-SDB7-FF	NI- OF26-SDB7- COMP	NI- BAY26-SDB7- DUR	
Battelle ID	S7470-P	S7471-P	S7472-P	S7467-P	S7468-P	S7469-P	
Sample Type	SA	SA	SA	SA	SA	SA	
Collection Date	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005	4/28/2005	
Extraction Date	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005	5/4/2005	
Analysis Date	5/18/2005	5/18/2005	5/18/2005	5/18/2005	5/19/2005	5/17/2005	
Analytical Instrument	MS	MS	MS	MS	MS	MS	
% Moisture	NA	NA	NA	NA	NA	NA	
% Lipid	NA	NA	NA	NA	NA	NA	
Matrix	WATER	WATER	WATER	WATER	WATER	WATER	
Sample Size	1.63	2.65	2.65	2.65	2.65	2.65	
Size Unit-Basis	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	L LIQUID	
Units	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	
Naphthalene	7.27 J	1.78 J	1.81 J	31.04	23.38	1.08 J	
C1-Naphthalenes	3.97 J	1.8 J	1.45 J	104.31	30.76	0.48 J	
C2-Naphthalenes	0.81 U	0.5 U	0.5 U	596.52	135.99	0.5 U	
C3-Naphthalenes	0.81 U	0.5 U	0.5 U	1768.67	356.54	0.5 U	
C4-Naphthalenes	0.81 U	0.5 U	0.5 U	3442.96	618.61	0.5 U	
2-Methylnaphthalene	3.45 J	1.56 J	1.27 J	71.55	22.19	0.45 J	
1-Methylnaphthalene	2.05 J	0.99 J	0.79 J	91.18	24.49	0.29 J	
Biphenyl	1.74 J	0.74 J	0.97 J	20.27	11.62	0.47 U	
2,6-dimethylnaphthalene	3.32 J	0.62 J	1.38 J	189.35	46.1	0.62 U	
Acenaphthylene	2.8 J	5.99 J	5.09 J	9.48	23.33	0.55 J	
Acenaphthene	1.38 J	2.31 J	3.91 J	45.81	18	1.08 J	
2,3,5-trimethylnaphthalene	0.71 U	0.44 U	0.44 U	324.46	63.78	0.44 U	
Dibenzofuran	2.66 J	5.42 J	8.38	23.65	23.44	0.96 J	
Fluorene	2.32 J	2.18 J	3.48 J	73.86	26.77	0.59 J	
C1-Fluorenes	0.84 U	0.51 U	0.51 U	425.27	86.92	0.51 U	
C2-Fluorenes	0.84 U	0.51 U	0.51 U	2010.84	472.99	0.51 U	
C3-Fluorenes	0.84 U	0.51 U	0.51 U	2810.13	579.32	0.51 U	
Anthracene	3.32 J	13.01	14.29	29.06	70.69	0.49 J	
Phenanthrene	40.71	83.94	104.68	175.36	536.24	1.26 J	
C1-Phenanthrenes/Anthracenes	20.74	13.51	16.21	1037.32	389.54	0.81 U	
C2-Phenanthrenes/Anthracenes	46.63	15.77	18.94	2983.94	772.76	0.81 U	
C3-Phenanthrenes/Anthracenes	26.37	0.81 U	0.81 U	2432.11	703.14	0.81 U	
C4-Phenanthrenes/Anthracenes	1.32 U	0.81 U	0.81 U	1319.2	243.89	0.81 U	
1-Methylphenanthrene	5.19 J	2.75 J	3.51 J	248.61	92.73	0.46 U	
Dibenzothiophene	4.08 J	4.14 J	10.46	125.25	62.99	0.38 U	
C1-Dibenzothiophenes	6.35 J	0.38 U	2.6 J	725.47	184.2	0.38 U	
C2-Dibenzothiophenes	24.16	0.38 U	2.88 J	2136.8	528.37	0.38 U	
C3-Dibenzothiophenes	25.02	0.38 U	2.22 J	2414.49	632.8	0.38 U	
C4-Dibenzothiophenes	17.42	0.38 U	0.38 U	1103.85	361.94	0.38 U	
Fluoranthene	67.87	233.86	274.95	154.05	1578.13	4.3 J	
Pyrene	66.39	134.26	154.19	302.64	1414.83	3.19 J	
C1-Fluoranthenes/Pyrenes	21.84	20.16	19.85	446.97	481.58	1.25 J	
C2-Fluoranthenes/Pyrenes	31.4	0.68 U	0.68 U	489.83	542.98	0.68 U	
C3-Fluoranthenes/Pyrenes	20.02	0.68 U	0.68 U	343.23	352.32	0.68 U	
Benzo(a)anthracene	9.73 J	7.01	7.99	36.69	406.38	0.88 J	
Chrysene	50.53	100.65	95.68	172.27	1215.77	2.25 J	
C1-Chrysenes	37.74	0.44 U	6.97	163.47	359.05	0.44 U	
C2-Chrysenes	44.68	0.44 U	0.44 U	186.11	228.17	0.44 U	
C3-Chrysenes	45.78	0.44 U	0.44 U	174.12	196.87	0.44 U	
C4-Chrysenes	19.66	0.44 U	0.44 U	70	112.59	0.44 U	
Benzo(b)fluoranthene	28.09	45.43	44.35	102.67	1159.48	1.78 J	
Benzo(j,k)fluoranthene	20.9	35.69	33.48	85.78	1174.32	1.98 J	
Benzo(e)pyrene	29.71	24.08	23.93	101.85	883.27	1.36 J	
Benzo(a)pyrene	16.7	7.31	6.5	67.79	805.61	1.4 J	
Perylene	5.31 J	1.46 U	1.46 U	21.74	204.2	1.46 U	
Indeno(1,2,3-cd)pyrene	20.3	9.09	8.74	89.03	1068.22	1.45 J	
Dibenz(a,h)anthracene	3.99 J	1.14 J	1.24 J	17.81	197.81	0.3 J	
Benzo(g,h,i)perylene	63.1	8.16 J	9.08 J	120.13	1044.55	1.79 J	

CLIENT ID	NI- OF23A-SDB7- FF	NI- BAY23A-SDB7- PRE	NI- BAY23A-SDB7- DUR	NI- OF26-SDB7-FF	NI- OF26-SDB7- COMP	NI- BAY26-SDB7- DUR	
<b>Surrogate Recoveries (%)</b>							
Naphthalene-d8	49	44	40	45	38 N	58	
Phenanthrene-d10	76	69	65	70	73	70	
Chrysene-d12	92	90	87	84	86	87	

## PAHs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PAH  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PAH	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD plus variance (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.50 – 1.93

**METHOD:** Water samples were extracted for PAH following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for PAH were analyzed using gas chromatography/mass spectrometry (GC/MS), following general NS&T methods. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0129	5/04/05	5/17/05 – 5/19/05

**BLANK:** A procedural blank (PB) sample was prepared with the analytical batch. Procedural blank samples are analyzed to ensure the sample extraction and analysis methods are free of contamination.

**05-0129** – No exceedences noted.

**Comments** – No target analytes were detected above the laboratory control limit (>5 x MDL), however naphthalene and 2-Methylnaphthalene were detected in the procedural blank at a concentration less than the reporting limit (RL). The data was qualified with a “J” in the procedural blank. All authentic field sample concentrations for these compounds were either greater than five times the

**LABORATORY  
CONTROL  
SAMPLE:**

concentration in the associated blank, or less than the RL.

A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PAH were calculated to measure data quality in terms of accuracy.

**05-0129** – All target analytes were recovered within the laboratory control limits (40-120%).

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

**Comments** – None.

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target PAH and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit ( $\leq 30\%$ ).

**SRM:**

**Comments** – None

A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.

**05-0129** – All target analytes were recovered within the laboratory control limits specified by the client ( $\leq 30$  PD).

**SURROGATES:**

**Comments** – None.

Three surrogate compounds were added prior to extraction, including naphthalene-d8, phenanthrene-d10, and chrysene-d12. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0129** – One exceedence noted.

**CALIBRATIONS:**

**Comments** – Percent recoveries for all surrogate compounds were within the laboratory control limits specified by the method (40 – 120% recovery), except for naphthalene-d8 in sample S7468 (OF-NI26-SDB7-FF). The recovery for this compound was calculated to be 38%. Chromatography and calculations were reviewed. No discrepancies were found. The sample prep records indicate an emulsion formed during the extraction of this sample, and that this extract had difficulty passing through the alumina cleanup column. The exceedences were qualified with an “N”. No further corrective action taken.

The GC/MS is calibrated with a minimum of a 6 level curve. The RSD between response factors for the individual target analytes must be  $<25\%$ , the mean RSD  $< 15\%$ . Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of minimally every 10 samples. This PD between the initial calibration RF and the check should be  $<25\%$  for individual analytes, and again the mean PD should be  $<15\%$ .

**05-0129** – No calibration exceedences.

**Comments** – None.

# PAHs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MARTIX SPIKE- NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE- NI-OF23A-SDB7-FF					PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION				
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P					BG247PB-P	BG275PB-P	BG276SRM-P				
Sample Type	LCS			MS			MSD					PB	PB	SRM				
Collection Date	5/4/2005			4/28/2005			4/28/2005					5/4/2005	5/4/2005	5/4/2005				
Extraction Date	5/4/2005			5/4/2005			5/4/2005					5/4/2005	5/4/2005	5/4/2005				
Analysis Date	5/17/2005			5/18/2005			5/18/2005					5/17/2005	5/17/2005	5/17/2005				
Analytical Instrument	MS			MS			MS					MS	MS	MS				
% Moisture	NA			NA			NA					NA	NA	NA				
% Lipid	NA			NA			NA					NA	NA	NA				
Matrix	LIQUID			WATER			WATER					LIQUID	LIQUID	LIQUID				
Sample Size	2.00			0.5			0.5					2.00	2	2.00				
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID					L LIQUID	L LIQUID	L LIQUID				
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Certified Value	+/-	Passing %Difference	Actual %Difference
Naphthalene	686.93	1000.60	69	2051.39	4002.40	51	1973.11	4002.40	49	4.0	1.22	4.35	J	1022.26	1000.6			2.2
C1-Naphthalenes	0.66 U			2801.42	NA		2651.74	NA			0.66 U	2.28	J	1353.64				
C2-Naphthalenes	0.66 U			2.65	UNA		1236.05	UNA			0.66 U	0.66	U	0.66 U				
C3-Naphthalenes	0.66 U			2.65	UNA		2.65	UNA			0.66 U	0.66	U	0.66 U				
C4-Naphthalenes	0.66 U			2.65	UNA		2.65	UNA			0.66 U	0.66	U	0.66 U				
2-Methylnaphthalene	699.17	1002.00	70	2138.17	4008.00	53	2035.88	4008.00	51	3.8	0.6 J	1.92	J	938.81	1002			6.3
1-Methylnaphthalene	701.45	1001.20	70	2124.31	4004.80	53	2032.5	4004.80	51	3.8	0.5 U	1.35	J	940.5	1001.2			6.1
Biphenyl	883.83	1000.20	69	2186.57	4000.80	55	2056.84	4000.80	51	7.5	0.63 U	0.63	U	927.81	1000.2			7.2
2,6-dimethylnaphthalene	871.72	1001.00	67	2149.41	4004.00	54	2025.97	4004.00	51	5.7	0.83 U	0.83	U	898.7	1001			10.2
Acenaphthylene	696.61	1000.65	70	2330.15	4002.60	58	2230.88	4002.60	56	3.5	0.7 U	0.7 U	U	965.76	1000.65			3.5
Acenaphthene	705.01	1000.75	70	2351.79	4003.00	59	2236.53	4003.00	56	5.2	0.75 U	0.75	U	972.35	1000.75			2.8
2,3,5-trimethylnaphthalene	696.21	1000.30	70	2463.11	4001.20	62	2320.61	4001.20	58	6.7	0.58 U	0.58	U	953.76	1000.3			4.7
Dibenzofuran	688.85	1002.20	69	2360.31	4008.80	59	2254.7	4008.80	56	5.2	0.3 U	0.65	J	953.67	1002.2			4.8
Fluorene	716.57	1000.70	72	2582.59	4002.80	64	2455.24	4002.80	61	4.8	0.68 U	0.57	J	985.56	1000.7			1.5
C1-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
C2-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
C3-Fluorenes	0.68 U			2.72	UNA		2.72	UNA			0.68 U	0.68	U	0.68 U				
Anthracene	764.04	1000.65	76	2991.32	4002.60	75	2868.53	4002.60	72	4.1	0.51 U	0.51	U	1024.04	1000.65			2.3
Phenanthrene	739.01	1000.65	74	2909.16	4002.60	72	2772.41	4002.60	68	5.7	1.08 U	1.67	J	1001.33	1000.65			0.1
C1-Phenanthrenes/Anthracenes	1.08 U			2310.61	NA		2235.23	NA			1.08 U	1.08	U	1.08 U				
C2-Phenanthrenes/Anthracenes	1.08 U			88.37	NA		88.37	NA			1.08 U	1.08	U	1.08 U				
C3-Phenanthrenes/Anthracenes	1.08 U			58.53	NA		51.04	NA			1.08 U	1.08	U	1.08 U				
C4-Phenanthrenes/Anthracenes	1.08 U			4.32	UNA		4.32	UNA			1.08 U	1.08	U	1.08 U				
1-Methylphenanthrene	769.45	1000.30	77	3032.32	4001.20	76	2916.84	4001.20	73	4.0	0.61 U	0.61	U	1029.72	1000.3			2.9
Dibenzothiophene	727.14	1001.00	73	2828.38	4004.00	71	2702.91	4004.00	67	5.8	0.5 U	0.5 U	U	991.17	1001			1
C1-Dibenzothiophenes	0.5 U			138.06	NA		130.53	NA			0.5 U	0.5 U	U	0.5 U				
C2-Dibenzothiophenes	0.5 U			29.62	JNA		33.61	NA			0.5 U	0.5 U	U	0.5 U				
C3-Dibenzothiophenes	0.5 U			31.49	JNA		36.17	NA			0.5 U	0.5 U	U	0.5 U				
C4-Dibenzothiophenes	0.5 U			24.27	JNA		22.05	JNA			0.5 U	0.5 U	U	0.5 U				
Fluoranthene	821.94	1000.50	82	3251.87	4002.00	80	3170.94	4002.00	78	2.5	0.77 U	1.55	J	1104.38	1000.5			10.4
Pyrene	824.66	1000.50	82	3271.32	4002.00	80	3176.64	4002.00	78	2.5	0.9 U	1.01	J	1107.39	1000.5			10.7
C1-Fluoranthenes/Pyrenes	0.9 U			29.03	JNA		31.31	JNA			0.9 U	0.9 U	U	0.9 U				
C2-Fluoranthenes/Pyrenes	0.9 U			23.18	JNA		25.07	JNA			0.9 U	0.9 U	U	0.9 U				
C3-Fluoranthenes/Pyrenes	0.9 U			24.42	JNA		30.07	JNA			0.9 U	0.9 U	U	0.9 U				
Benzo(a)anthracene	829.99	1000.60	83	3342.41	4002.40	83	3185.28	4002.40	79	4.9	1.36 U	0.31	J	876.32	1000.6			12.4
Chrysene	823.75	1000.75	82	3181.59	4003.00	78	3113.69	4003.00	77	1.3	0.59 U	0.72	J	857.67	1000.75			14.3
C1-Chysenes	0.59 U			34.57	NA		38.44	NA			0.59 U	0.59	U	0.59 U				
C2-Chysenes	0.59 U			51.96	NA		58.75	NA			0.59 U	0.59	U	0.59 U				
C3-Chysenes	0.59 U			38.83	NA		44.77	NA			0.59 U	0.59	U	0.59 U				
C4-Chysenes	0.59 U			2.36	UNA		2.36	UNA			0.59 U	0.59	U	0.59 U				
Benzo(b)fluoranthene	851.64	1000.75	85	3402.73	4003.00	84	3290.1	4003.00	81	3.6	1.16 U	1.16	U	893.46	1000.75			10.7
Benzo(k)fluoranthene	881.56	1000.65	88	3353.44	4002.60	83	3254.85	4002.60	81	2.4	1.31 U	1.31	U	921.45	1000.65			7.9
Benzo(e)pyrene	776.8	1001.80	78	3028.88	4007.20	75	2982.69	4007.20	74	1.3	0.51 U	0.51	U	815.6	1001.8			18.6
Benzo(a)pyrene	839.45	1000.65	84	3257.28	4002.60	81	3122.06	4002.60	78	3.8	1 U	1	U	882.23	1000.65			11.8
Perylene	819.83	1000.20	82	3320.82	4000.80	83	3226.69	4000.80	81	2.4	1.93 U	1.93	U	866.73	1000.2			13.3
Indeno(1,2,3-cd)pyrene	812.86	1000.60	81	3339.86	4002.40	83	3224.82	4002.40	80	3.7	0.99 U	0.99	U	853.56	1000.6			14.7
Dibenz(a,h)anthracene	882.52	1000.55	88	3440.18	4002.20	86	3281.85	4002.20	82	4.8	0.84 U	0.84	U	924.45	1000.55			7.6
Benzo(g,h,i)perylene	814.87	1000.70	81	3214.16	4002.80	79	3128.86	4002.80	77	2.6	0.99 U	0.99	U	854.95	1000.7			14.6

CLIENT ID	LABORATORY CONTROL SAMPLE			MARTIX SPIKE- NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE- NI-OF23A-SDB7-FF					PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION				
Surrogate Recoveries (%)																		
Naphthalene-d8	83			51			43					83	52	68				
Phenanthrene-d10	80			72			68					78	71	75				
Chrysene-d12	102			89			86					96	87	95				

# PCBs

CLIENT ID	NI- OF23A-SDB7- FF		NI- OF26-SDB7- COMP	
Battelle ID	S7470-P		S7468-P	
Sample Type	SA		SA	
Collection Date	4/28/2005		4/28/2005	
Extraction Date	5/4/2005		5/4/2005	
Analysis Date	5/29/2005		5/30/2005	
Analytical Instrument	MS		MS	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	1.63		2.65	
Size Unit-Basis	L LIQUID		L LIQUID	
Units	NG/L LIQUID		NG/L LIQUID	
C12(8)	0.11	U	0.07	U
C13(18)	0.13	U	0.08	U
C13(28)	0.13	U	0.08	U
C14(44)	0.24	U	0.14	U
C14(49)	0.24	U	0.14	U
C14(52)	0.24	U	4.31	
C14(66)	0.24	U	3.9	
C14(77)	0.23	U	0.14	U
C15(87)	0.38	U	5.13	
C15(101)	0.38	U	29.3	
C15(105)	0.17	U	3.34	
C15(114)	0.38	U	0.23	U
C15(118)	0.12	U	7.05	
C15(123)	0.13	U	0.08	U
C15(126)	0.19	U	0.12	U
C16(128)	0.43	U	5.89	
C16(138)	0.43	U	74.73	
C16(153)	0.43	U	164.58	
C16(156)	0.12	U	7.02	
C16(157)	0.23	U	0.14	U
C16(167)	0.43	U	3.92	
C16(169)	0.18	U	0.11	U
C17(170)	0.3	U	55.33	
C17(180)	0.17	U	228.53	E
C17(183)	0.3	U	38.24	
C17(184)	0.3	U	0.18	U
C17(187)	0.3	U	84.98	
C17(189)	0.13	U	3.89	
C18(195)	0.59	U	11.77	
C19(206)	0.54	U	8.3	
C110(209)	0.66	U	1.5	J
<b>Surrogate Recoveries (%)</b>				
C12(14)	71		82	
C13(34)	76		84	



## PCBs QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** PCB  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PCB	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery  (target spike must be >5 x native conc.)	≤30% PD on average  (for analytes >5x MDL)	≤30% RPD  (calculated between the MS and MSD samples)	MDL: ~0.09 – 0.53

**METHOD:** Water samples were extracted for PCB following general NS&T methods. Approximately 1 liter of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate and concentrated. The extract was then fortified with RIS and split quantitatively for the required analyses. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS). The method is based on key components of the PCB congener analysis approach described in EPA Method 1668A. Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

	<u>Batch</u>	<u>Extraction Date</u>	<u>Analysis Date</u>
	05-0129	5/4/05	5/28/05 – 5/30/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0129** – No exceedences noted.

**LABORATORY CONTROL SAMPLE:** **Comments** – No target analytes were detected in the procedural blank. A laboratory control sample (LCS) was prepared with each analytical batch. The percent recoveries of target PCB were calculated to measure data quality in terms of accuracy.

**05-0129** – One exceedence noted.

**Comments** – All target analytes were recovered within the specified laboratory control limits (40-120%), except for PCB 169. This analyte was over-recovered at

**MATRIX  
SPIKE/MATRIX  
SPIKE  
DUPLICATE:**

141%. It was also over-recovered in both the MS and MSD samples. Chromatography and calculations were reviewed. No discrepancies were found. The exceedence has been qualified with an "N". Since PCB 169 was not detected in any field samples, the affect of this exceedence on the data is minimal. No further corrective action is necessary.

A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair was prepared with each analytical batch. The percent recoveries of target PCB and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.

**05-0129** – Three percent recovery exceedences noted.  
No RPD exceedences noted.

**Comments** – All target analytes were recovered within the specified laboratory control limits (40-120%), except for PCB 169 in samples S7470MS and S7470MSD (background OF-NI23A-SDB7-FF) and PCB 209 in sample S7470MS. All exceedences were due to over-recoveries. Chromatography and calculations were reviewed, no discrepancies were found. The exceedences were qualified with an "N". Since PCB 169 was not detected in any field samples, and PCB 209 was not detected above the RL, the affect of these exceedences on the data is minimal. No further corrective action is necessary.

**SRM:**

A standard reference material was prepared with each analytical batch. The percent difference (PD) between the measured value and the certified range was calculated to measure data quality in terms of accuracy. The MQO criteria of 30% PD was added to the variance of each analyte. The variance of each analyte is determined by dividing the range value by the target.

**05-0129** – All PDs were within the specified laboratory control limits.

**Comments** – None.

**SURROGATES:**

Two surrogate compounds were added prior to extraction, including PCB 14 and PCB 34. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).

**05-0129** – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).

**CALIBRATION:**

**Comments** – None.

The GC/MS is calibrated with a minimum of a 6-point curve. The co-efficient of determination must be  $\geq 0.995$  for each target analyte. Each batch of samples analyzed is bracketed by a calibration check sample, run at a frequency of every 12 hours (minimally). This PD between the initial calibration RF and the check should be <20% for individual analytes; 15% on average. Additionally an ICC check was run with the initial calibration. The PD for the ICC should be < 15%, for each analyte.

**05-0129** – One exceedence noted.

**Comments** – In mid C1466.d PCB 105 was over-recovered and had a PD of 31%. Two samples S7468 and S7478 (Samples OF-NI26-SDB7-Comp and OF-NAB18-SDB7-Comp, respectively) had PCB 105 detected in them. Chromatography and calculations were reviewed. No discrepancies were found. The deviation has been documented and the data reviewed. No further corrective action was taken.

# PCBs QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE- NI-OF23A-SDB7-FF				PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION						
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P				BG247PB-P	BG275PB-P	BG276SRM-P						
Sample Type	LCS			MS			MSD				PB	PB	SRM						
Collection Date	5/4/2005			4/28/2005			4/28/2005				5/4/2005	5/4/2005	5/4/2005						
Extraction Date	5/4/2005			5/4/2005			5/4/2005				5/4/2005	5/4/2005	5/4/2005						
Analysis Date	5/28/2005			5/29/2005			5/29/2005				5/28/2005	5/28/2005	5/28/2005						
Analytical Instrument	MS			MS			MS				MS	MS	MS						
% Moisture	NA			NA			NA				NA	NA	NA						
% Lipid	NA			NA			NA				NA	NA	NA						
Matrix	LIQUID			WATER			WATER				LIQUID	LIQUID	LIQUID						
Sample Size	2.00			0.5			0.5				2.00	2	2.00						
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	L LIQUID	L LIQUID						
Units	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	NG/L LIQUID	Target	% Recovery	RPD (%)	NG/L LIQUID	NG/L LIQUID	NG/L LIQUID	Certified Value	+/-	Passing %Difference	Actual %Difference		
C12(8)	27.49	40.12	69	98.76	160.48	62	111.42	160.48	69	10.7	0.09 U	0.09 U	0.09 U	27.52	34.24	2.88	38.41	19.6	
C13(18)	32.94	40.12	82	117.38	160.48	73	123.26	160.48	77	5.3	0.11 U	0.11 U	0.11 U	31.47	32.93	0.30	30.92	4.4	
C13(28)	29.26	40.04	73	118.72	160.16	74	114.24	160.16	71	4.1	0.11 U	0.11 U	0.11 U	30.54					
C14(44)	34.28	40.08	86	134.47	160.32	84	124.95	160.32	78	7.4	0.19 U	0.19 U	0.19 U	30.39	32.86	0.59	31.8	7.5	
C14(49)	40.18	40.16	100	150.87	160.64	94	145.68	160.64	91	3.2	0.19 U	0.19 U	0.19 U	0.19 U					
C14(52)	31.65	40.00	79	122.5	160.00	77	119.2	160.00	75	2.6	0.19 U	0.19 U	0.19 U	30.03	33.07	0.38	31.16	9.2	
C14(66)	31.54	40.04	79	141.85	160.16	89	118.9	160.16	74	18.4	0.19 U	0.19 U	0.19 U	30.09	32.82	0.62	31.9	8.3	
C14(77)	31.71	40.00	79	160.6	160.00	100	131.34	160.00	82	19.8	0.18 U	0.18 U	0.18 U	31.48	33.55	1.10	33.29	6.2	
C15(87)	35.98	40.00	90	165.64	160.00	104	136.48	160.00	85	20.1	0.31 U	0.31 U	0.31 U	34.88	33.1	0.27	30.82	5.4	
C15(101)	34.94	40.08	87	155.41	160.32	97	124.41	160.32	78	21.7	0.31 U	0.31 U	0.31 U	31.45	32.56	0.47	31.43	3.4	
C15(105)	32.22	40.04	80	187.32	160.16	117	144.07	160.16	90	26.1	0.14 U	0.14 U	0.14 U	33.85	32.67	1.01	33.09	3.6	
C15(114)	0.31 U			1.23 U			1.23 U				0.31 U	0.31 U	0.31 U	0.31 U					
C15(118)	32.35	40.04	81	163.33	160.16	102	126.35	160.16	79	25.4	0.1 U	0.1 U	0.1 U	29.41	32.74	1.06	33.23	10.2	
C15(123)	0.11 U			0.43 U			0.43 U				0.11 U	0.11 U	0.11 U	0.11 U					
C15(126)	29.27	40.24	73	166.74	160.96	104	130.52	160.96	81	24.9	0.16 U	0.16 U	0.16 U	32.45	33.22	1.38	34.14	2.3	
C15(128)	29.39	40.24	73	149.58	160.96	93	117.39	160.96	73	24.1	0.35 U	0.35 U	0.35 U	27.53	32.94	0.27	30.83	16.4	
C15(138)	33.24	40.08	83	176.99	160.32	110	139.78	160.32	87	23.4	0.35 U	0.35 U	0.35 U	31.99	32.43	0.38	31.18	1.4	
C15(153)	34.07	40.04	85	168.47	160.16	105	131.73	160.16	82	24.6	0.35 U	0.35 U	0.35 U	30.86	32.64	0.62	31.91	5.5	
C15(156)	0.1 U			0.4 U			0.4 U				0.1 U	0.1 U	0.1 U	0.1 U					
C15(157)	0.19 U			0.76 U			0.76 U				0.19 U	0.19 U	0.19 U	0.19 U					
C15(167)	0.35 U			1.42 U			1.42 U				0.35 U	0.35 U	0.35 U	0.35 U					
C15(169)	56.68	40.16	141	309.8	160.64	193	248.63	160.64	155	21.8	0.15 U	0.15 U	0.15 U	0.15 U					
C17(170)	29.13	40.20	72	163.63	160.80	102	131.34	160.80	82	21.7	0.25 U	0.25 U	0.25 U	27.28	32.72	0.54	31.66	16.6	
C17(180)	29.47	40.16	73	175.36	160.64	109	146.13	160.64	91	18.0	0.14 U	0.14 U	0.14 U	29.53	32.96	0.32	30.97	10.4	
C17(183)	32.99	40.16	82	169.17	160.64	105	137.46	160.64	86	19.9	0.25 U	0.25 U	0.25 U	0.25 U					
C17(184)	34.92	40.16	87	163.2	160.64	102	132	160.64	82	21.7	0.25 U	0.25 U	0.25 U	0.25 U					
C17(187)	30.23	40.12	75	152.19	160.48	95	127.03	160.48	79	18.4	0.25 U	0.25 U	0.25 U	30.46	32.75	0.30	30.93	7	
C17(189)	0.11 U			0.42 U			0.42 U				0.11 U	0.11 U	0.11 U	0.11 U					
C18(195)	29.27	40.12	73	148.26	160.48	92	120.19	160.48	75	20.4	0.48 U	0.48 U	0.48 U	27.7	32.83	0.66	32	15.6	
C19(206)	33.76	40.12	84	172.85	160.48	108	143.4	160.48	89	19.3	0.44 U	0.44 U	0.44 U	32.46	32.02	0.59	31.85	1.4	
C110(209)	46.77	40.04	117	223.66	160.16	140	182.47	160.16	114	20.5	0.53 U	0.53 U	0.53 U	42.96	32.99	0.45	31.36	30.2	
Surrogate Recoveries (%)																			
C12(14)	87			74			77				77	68	80						
C13(34)	94			79			82				80	70	82						

# PESTICIDES

CLIENT ID	NI-OF23A-SDB7-FF		NI-OF26-SDB7-COMP	
Battelle ID	S7470-P		S7468-P	
Sample Type	SA		SA	
Collection Date	4/28/2005		4/28/2005	
Extraction Date	5/4/2005		5/4/2005	
Analysis Date	5/14/2005		5/14/2005	
Analytical Instrument	ECD		ECD	
% Moisture	NA		NA	
% Lipid	NA		NA	
Matrix	WATER		WATER	
Sample Size	1.63		2.65	
Size Unit-Basis	L LIQUID		L LIQUID	
Units	NG/L LIQUID		NG/L LIQUID	
2,4'-DDD	1	U	7.52	
2,4'-DDE	0.11	J	0.52	U
2,4'-DDT	0.59	U	5.98	
4,4'-DDD	1.17	U	6.55	
4,4'-DDE	0.3	J	9.29	
4,4'-DDT	0.74	J	16.1	
aldrin	0.49	U	0.3	U
a-chlordane	0.51	J	8.56	
g-chlordane	1.35		14.36	
a-BHC	0.42	U	0.26	U
b-BHC	0.58	U	0.36	U
d-BHC	0.48	U	1.62	
Lindane	0.61	U	0.37	U
cis-nonachlor	0.79	U	3.16	
trans-nonachlor	0.3	J	6.48	
Chlorpyrifos	0.63	U	0.39	U
oxychlordane	0.48	U	0.3	U
dieldrin	0.94	U	2.53	
endosulfan I	0.09	J	0.21	U
endosulfan II	0.85	U	5.98	
endosulfan sulfate	0.8	U	33.23	
endrin	0.92	U	0.57	U
endrin aldehyde	1.04	U	6.25	
endrin ketone	1.09	U	0.67	U
heptachlor	0.72	U	0.44	U
heptachlor epoxide	1.93	U	1.19	U
Hexachlorobenzene	1.01	U	0.62	U
methoxychlor	2.41		15.05	
Mirex	0.76	U	0.47	U
<b>Surrogate Recoveries (%)</b>				
CI2(14)	91		89	
CI3(34)	88		95	
CI5(104)	85		90	
CI5(112)	90		92	

## PESTICIDES QA/QC

**PROJECT:** Task Order TO0015/TO0019 – Contaminant Analysis of Stormwater  
**PARAMETER:** Pesticides  
**LABORATORY:** Battelle, Duxbury, MA  
**MATRIX:** Water  
**SAMPLE CUSTODY:** Water samples were collected 4/28/05. The samples were received at Battelle Duxbury on 5/3/05. Upon arrival, the cooler temperatures ranged from 2.2°C – 3.2°C. One sample, BAY-NI26-SDB7-Pr, was broken upon receipt. The project manager was informed of this issue, and relayed it to the client. The lab was instructed to proceed with the remaining samples. No other custody issues were noted. Samples were logged into the Battelle LIMS and received unique IDs. Samples were stored in the access-controlled upper cold room refrigerator at 4.0°C until sample preparation could begin. Samples were extracted as one analytical batch, 05-0129, along with the appropriate quality control samples.

	Reference Method	Method Blank	Surrogate Recovery	LCS/MS Recovery	SRM % Diff.	Sample Replicate Relative Precision	Detection Limits (ng/L)
PESTICIDE	General NS&T	<5xMDL	40-120% Recovery	40-120% Recovery (target spike must be >5 x native conc.)	≤30% PD plus variance (for analytes >5x MDL)	≤30% RPD (calculated between the MS and MSD samples)	MDL: ~0.27 – 1.58

**METHOD:** Water samples were extracted for pesticide following general NS&T methods. Approximately 2 liters of water was spiked with surrogates and extracted three times with dichloromethane using separatory funnel techniques. The combined extract was dried over anhydrous sodium sulfate, concentrated, processed through alumina cleanup column, concentrated, copper cleaned, and further purified by GPC/HPLC. The post-HPLC extract was concentrated, fortified with RIS and split quantitatively for the required analyses. Extracts intended for pesticide analysis were solvent exchanged into hexane and analyzed using a gas chromatography/electron capture detector (GC/ECD). Sample data were quantified by the method of internal standards, using the Recovery Internal Standard (RIS) compounds.

**HOLDING TIMES:** Samples were prepared for analysis in one analytical batch and were extracted within 7 days of sample collection and analyzed within 40 days of extraction.

Batch	Extraction Date	Analysis Date
05-0129	5/04/05	5/14/05 – 5/16/05

**BLANK:** A procedural blank (PB) was prepared with the analytical batch. Blanks are analyzed to ensure the sample extraction and analysis methods were free of contamination.

**05-0129** – No exceedences noted.

**Comments** – No target analytes were detected in the procedural blank.

**LABORATORY CONTROL** A laboratory control sample (LCS) was prepared with the analytical batch. The percent recoveries of target pesticides were calculated to measure data quality in

<b>SAMPLE:</b>	<p>terms of accuracy.</p> <p><b>05-0129</b> – All target analytes were recovered within the laboratory control limits specified by the client (40-120%).</p> <p><b>Comments</b> – None.</p>
<b>MATRIX SPIKE/MATRIX SPIKE DUPLICATE:</b>	<p>A matrix spike (MS) and a matrix spike duplicate (MSD) sample pair were prepared with each analytical batch. The percent recoveries of target pesticides and the relative percent difference between the two samples were calculated to measure data quality in terms of accuracy and precision.</p> <p><b>05-0129</b> – All target analytes were recovered within the laboratory control limits specified by the client (40-120%). All calculated RPDs were within the laboratory control limit (<math>\leq 30\%</math>).</p> <p><b>Comments</b> – None</p>
<b>SRM:</b>	<p>A standard reference material (SRM, a certified second source standard was spiked into a natural seawater as an SRM) was prepared with each analytical batch. Surrogate corrected data has been reported for the SRM only.</p> <p><b>05-0129</b> – All percent differences for reported target analytes were within the laboratory control limits (<math>&lt;30\%</math> difference plus variance).</p> <p><b>Comments</b> – None.</p>
<b>SURROGATES</b>	<p>Four surrogate compounds were added prior to extraction, including PCB 14, PCB 34, PCB 104, and PCB 112. The recovery of each surrogate compound was calculated to measure data quality in terms of accuracy (extraction efficiency).</p> <p><b>05-0129</b> – Percent recoveries for all surrogate compounds were within the laboratory control limits (40 – 120% recovery).</p> <p><b>Comments</b> – None.</p>
<b>CALIBRATIONS:</b>	<p>The instrument is calibrated with a 6-level (minimum) calibration, ranging in concentration from <math>\sim 0.001</math> ng/uL to <math>\sim 0.125</math> ng/uL. The initial correlation coefficient must be <math>&gt; 0.995</math>. Calibration checks are analyzed minimally every 12 hours. The samples must be bracketed by passing calibrations. Calibration checks must have a percent difference <math>\leq 25\%</math>.</p> <p><b>05-0129</b> – No exceedences noted.</p> <p><b>Comments</b> – None.</p>

## PESTICIDES QA/QC (CONT.)

CLIENT ID	LABORATORY CONTROL SAMPLE			MATRIX SPIKE- NI-OF23A-SDB7-FF			MATRIX SPIKE DUPLICATE-NI-OF23A-SDB7-FF				PROCEDURAL BLANK	050504-01: DUXBURY SEAWATER	GG73: PCB/PESTICIDE SRM SOLUTION						
Battelle ID	BG248LCS-P			S7470MS-P			S7470MSD-P				BG247PB-P	BG275PB-P	BG276SRM-P						
Sample Type	LCS			MS			MDS				PB	PB	SRM						
Collection Date	5/4/2005			4/28/2005			4/28/2005				5/4/2005	5/4/2005	5/4/2005						
Extraction Date	5/4/2005			5/4/2005			5/4/2005				5/4/2005	5/4/2005	5/4/2005						
Analysis Date	5/16/2005			5/14/2005			5/14/2005				5/16/2005	5/16/2005	5/16/2005						
Analytical Instrument	ECD			ECD			ECD				ECD	ECD	ECD						
% Moisture	NA			NA			NA				NA	NA	NA						
% Lipid	NA			NA			NA				NA	NA	NA						
Matrix	LIQUID			WATER			WATER				LIQUID	LIQUID	LIQUID						
Sample Size	2.00			0.5			0.5				2.00	2	2.00						
Size Unit-Basis	L LIQUID			L LIQUID			L LIQUID				L LIQUID	L LIQUID	L LIQUID				Certified Value	Passing +/-	Actual %Difference
Units	NG/L	Target	% Recovery	NG/L	Target	% Recovery	NG/L	Target	% Recovery	RPD (%)	NG/L	NG/L	NG/L						
2,4'-DDD	33.25	40.12	83	126.17	160.48	79	121.46	160.48	76	3.9	0.81 U	0.81 U	65.74						
2,4'-DDE	29.51	40.01	74	116.42	160.05	73	110.03	160.05	69	5.6	0.69 U	0.69 U	22.4	31.62	0.27	30.86		29.2	
2,4'-DDT	26.38	40.23	66	110.77	160.93	69	104.02	160.93	65	6.0	0.48 U	0.48 U	27.15	31.34	0.14	30.46		13.4	
4,4'-DDD	33.01	40.01	83	128.85	160.02	81	123.46	160.02	77	5.1	0.95 U	0.95 U	24.85	31.87	0.43	31.36		22	
4,4'-DDE	32.85	40.01	82	125.33	160.02	78	118.75	160.02	74	5.3	0.68 U	0.68 U	28.26	31.62	0.16	30.51		10.6	
4,4'-DDT	32.99	40.02	82	130.94	160.09	81	124.55	160.09	77	5.1	0.59 U	0.59 U	27.74	31.47	0.19	30.61		11.9	
dieldrin	27.61	40.01	69	105.56	160.06	66	97.41	160.06	61	7.9	0.4 U	0.4 U	21.28						
a-chlordane	29.84	40.03	75	113.71	160.11	71	108.08	160.11	67	5.8	0.38 U	0.38 U	28.85	31.55	0.19	30.61		14.9	
a-chlordane	28.59	40.06	71	107.53	160.26	66	103.45	160.26	64	3.1	0.4 U	0.4 U	0.4 U						
a-BHC	23.22	40.02	58	84.2	160.06	53	72.71	160.06	45	16.3	0.34 U	0.28 J	0.32 J						
b-BHC	26.75	40.01	67	100.77	160.02	63	93.5	160.02	58	8.3	0.47 U	0.47 U	0.47 U						
b-BHC	31.05	40.02	78	123.12	160.07	77	113.38	160.07	71	8.1	0.39 U	0.39 U	0.39 U						
lindane	26.45	40.01	66	103.5	160.04	65	92.08	160.04	58	11.4	0.49 U	0.49 U	22.74			31.55	0.16	30.51	27.9
cis-nonachlor	33.3	40.03	83	124.09	160.11	77	119.47	160.11	75	2.6	0.65 U	0.65 U	0.65 U						
trans-nonachlor	30.91	40.06	77	117.4	160.22	73	112.61	160.22	70	4.2	0.4 U	0.4 U	27.72	31.78	0.22	30.7		12.8	
Chlorpyrifos	32.53	40.10	81	127.35	160.40	79	121.06	160.40	75	5.2	0.51 U	0.51 U	0.51 U						
oxychlordane	28.88	40.03	72	108.92	160.11	68	102.68	160.11	64	6.1	0.39 U	0.39 U	0.39 U						
dieldrin	32.5	40.01	81	119.69	160.03	75	115.7	160.03	72	4.1	0.76 U	0.76 U	27.43	31.55	0.21	30.66		13.1	
endosulfan I	31.23	40.03	78	114.7	160.11	72	110.45	160.11	69	4.3	0.27 U	0.27 U	0.27 U						
endosulfan II	31.53	40.02	79	121.66	160.08	76	115.01	160.08	72	6.9	0.69 U	0.69 U	0.69 U						
endosulfan sulfate	35.11	40.02	88	133.4	160.07	83	127.81	160.07	80	3.7	0.65 U	0.65 U	0.65 U						
endrin	34.35	40.01	86	136.19	160.05	85	128.49	160.05	80	6.1	0.75 U	0.75 U	0.75 U						
endrin aldehyde	27.27	40.01	68	105.84	160.03	66	95.74	160.03	62	6.3	0.85 U	0.85 U	0.85 U						
endrin ketone	35.14	40.02	88	132.66	160.06	83	129.21	160.06	81	2.4	0.89 U	0.89 U	0.89 U						
heptachlor	29.47	40.00	74	114.63	160.02	72	104.8	160.02	65	10.2	0.59 U	0.59 U	25.28	31.63	0.24	30.76		20.1	
heptachlor epoxide	28.54	40.01	71	102.62	160.02	64	98.63	160.02	62	3.2	1.58 U	1.58 U	23.46	31.63	0.27	30.86		25.8	
hexachlorobenzene	30.22	40.06	75	114.74	160.24	72	107.22	160.24	67	0.83 U	0.83 U	0.83 U	27.24	31.49	0.14	30.46		13.5	
methoxychlor	33.31	40.01	83	133.39	160.05	82	127.62	160.05	78	5.0	0.98 U	0.98 U	0.98 U						
Mirex	34	40.03	85	124.94	160.13	78	121.75	160.13	76	2.6	0.62 U	0.62 U	29.34	31.86	0.45	31.41		7.9	
Surrogate Recoveries (%)																			
C12(14)	93			83			76				85		79						
C13(34)	97			87			76				86		84						
C15(104)	91			80			77				86		75						
C15(112)	98			82			79				96		88						

## TSS

SAMPLE LABEL	TSS (mg/L)
NI-OF23A-SDB7-FF	63.571
NI-BAY23A-SDB7-PRE	5.536
NI-BAY23A-SDB7-DUR	6.232
NI-OF26-SDB7-FF	145.558
NI-OF26-SDB7-COMP	162.415
NI-BAY26-SDB7-PRE	4.519
NI-BAY26-SDB7-DUR	4.165

## DOC

SAMPLE LABEL	DOC (mg/L)
NI-OF-23A-SDB7-FF	3.796
NI-OF-23A-SDB7-FF	3.748
NI-OF-23A-SDB7-FF	3.810
NI-BAY23A-SDB7-PRE	2.144
NI-BAY23A-SDB7-PRE	2.074
NI-BAY23A-SDB7-PRE	2.059
NI-BAY23A-SDB7-DUR	3.111
NI-BAY23A-SDB7-DUR	3.243
NI-BAY23A-SDB7-DUR	3.284
NI-OF26-SDB7-FF	47.653
NI-OF26-SDB7-FF	49.174
NI-OF26-SDB7-FF	49.197
NI-OF26-SDB7-COMP	1.089
NI-OF26-SDB7-COMP	0.798
NI-OF26-SDB7-COMP	0.841
NI-BAY26-SDB7-PRE	1.789
NI-BAY26-SDB7-PRE	1.695
NI-BAY26-SDB7-PRE	1.643
NI-BAY26-SDB7-DUR	2.874
NI-BAY26-SDB7-DUR	3.120
NI-BAY26-SDB7-DUR	3.047



## **APPENDIX E**

### **TIE1 Report**

Please note that the report in this appendix was generated with slightly different acronyms from those used throughout the body of the report and other appendices. The differences are as follows:

MAIN REPORT	THIS APPENDIX
NAV	NAVSTA
SUB	SUBASE

Additionally, one outfall identified as OF23CE in the report and other appendices is identified as OF23C+e in this appendix.



# Toxicity Identification Evaluation (TIE) Study of San Diego Bay Stormwater

## *February 18, 2004 Sampling Event* **FINAL REPORT** Response to External Comments Included

**Prepared for:** Computer Sciences Corporation  
4045 Hancock Street  
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San Diego (SPAWAR)  
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**Prepared by** Nautilus Environmental  
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**Submitted:** April 26, 2006

### Data Quality Assurance:

- Nautilus Environmental is a certified laboratory under the State of California Department of Health Services Environmental Laboratory Accreditation Program (ELAP), Certificate No. 1802.
- All test results included in this report have met internal Quality Assurance/Quality Control (QA/QC) requirements, as well as minimum acceptability criteria as outlined in their respective protocols.
- All data have been reviewed and verified.
- Any test data discrepancies or protocol deviations have been noted in the summary report pages.

Results verified by: **Chris Stransky, Laboratory Manager**      Date: **April 26, 2006**

## **1.0 INTRODUCTION**

From February through July 2004, preliminary screening and Toxicity Identification Evaluation (TIE) studies were performed on stormwater samples collected from six storm drain outfalls (NAVSTA: OF 9; OF 11; and OF 14; SUBASE: OF 11B; OF 23c+e; and OF 26) discharging into San Diego Bay, San Diego, California. Stormwater toxicity to several marine species, including *Mytilus galloprovincialis* (blue mussel), *Atherinops affinis* (topsmelt), and *Americamysis bahia* (opossum shrimp) has been documented in previous monitoring surveys. Confirmation studies using the blue mussel, opossum shrimp, and *Menidia beryllina* (inland silverside) were performed at the AMEC Earth & Environmental Aquatic & Terrestrial Toxicology Laboratory (AMEC) located in San Diego, California. Inland silversides were used in place of topsmelt due to lack of availability. Toxicity to mussel larvae was confirmed for all six samples. One sample (SUBASE OF 23 c+e) also exhibited marked toxicity to the opossum shrimp. No toxicity to the silversides was observed in any of the samples tested. Subsequently, Phase I TIEs using the blue mussel were initiated for all six sites, and a single Phase I TIE was initiated with opossum shrimp on SUBASE OF 23 c+e. Metals, particularly zinc and copper, were largely responsible for toxicity in all six samples tested. Results from the SUBASE OF 11B Phase I TIE also identified the presence of an organic toxicant. TIE sample manipulations were performed using methods outlined by the U.S. Environmental Protection Agency (EPA). All biological testing was conducted at AMEC. Supporting analytical testing was conducted in partnership with Calscience Environmental Laboratories (CEL), located in Garden Grove, California. Results of the screening studies, Phase I TIEs, and Phase II/III TIEs are presented in this report. Screening studies were initiated on 19 February 2004. Phase I testing was initiated on 27 February 2004. Phase II/III TIEs were initiated between 3 April and 15 July 2004, and identification of the organic constituent found in SUBASE OF 11B is ongoing.

## **2.0 MATERIALS AND METHODS**

### **2.1 Test Material**

Stormwater samples were collected on 18 February 2004 between 4:25 and 6:30 PM under the supervision of SPAWAR personnel. The samples were collected using peristaltic pumps and contained in plastic bags lining 19-L plastic buckets. As soon as sampling was completed, the buckets were placed in a 4°C cold room and stored overnight. AMEC personnel picked up the samples the following morning and transported them to AMEC for testing. Upon arrival at the laboratory, each sample was assigned a tracking number, and water quality measurements of

temperature, pH, dissolved oxygen (DO), conductivity, alkalinity, and hardness were recorded (Table 1).

**Table 1. Water Quality Parameter Measurements upon Sample Receipt.**

Site ID	Date Collected	Date Received	Temp. (°C)	pH (units )	DO (mg/L)	Cond. (µmhos/cm)	Alkalinity (mg/L CaCO <sub>3</sub> )	Hardness (mg/L CaCO <sub>3</sub> )
<b>NAVSTA OF 9</b>	2/18/04	2/19/04	15.0	7.38	10.7	1316	20	132
<b>NAVSTA OF 11</b>	2/18/04	2/19/04	14.7	7.34	9.8	142	18	24
<b>NAVSTA OF 14</b>	2/18/04	2/19/04	14.4	7.48	10.0	1956	20	192
<b>SUBASE OF 11B</b>	2/18/04	2/19/04	14.4	7.45	10.1	299	27	125
<b>SUBASE OF 23c+e</b>	2/18/04	2/19/04	14.9	7.12	9.8	156	16	26
<b>SUBASE OF 26</b>	2/18/04	2/19/04	15.6	7.58	10.2	317	27	61

Temperature and conductivity were measured with an Orion 130 meter. DO was measured using a YSI 55 meter, and an Orion 250A+ meter was used to measure pH. Alkalinity (Hach Method 8203) and hardness (Hach Method 8213) were checked using Hach digital titrators (Model 16900). The samples were held at 4°C in the dark at AMEC. Appropriate chain-of-

custody (COC) procedures were followed during all phases of this study. Copies of the COC forms for this study are attached in Appendix F.

## **2.2 Test Design and Bioassay Procedures**

The overall experimental design incorporated a number of features to facilitate comparisons of sensitivity between species, and identifying the presence and degree of both acute and chronic toxicity. The Navy's stormwater permit requires evaluation of acute toxicity with both opossum shrimp (*Americamysis bahia*) and topsmelt (*Atherinops affinis*) (inland silversides, *Menidia beryllina*, were substituted for topsmelt during this study). However, in case the samples were not sufficiently toxic to elicit acute responses, the test design incorporated the 7-day chronic test procedures. Thus, if the samples exhibited acute toxicity within the first 96 hours of exposure, the tests could be terminated and TIEs initiated. However, if no acute toxicity was observed, it would still be possible to default to the sublethal growth endpoint to evaluate differences between samples and species. Similarly, the 48-hour mussel embryo development using *Mytilus galloprovincialis* test was incorporated into the study design because of its known sensitivity to copper, and its comparatively short exposure duration. Thus, if results for the mussels appeared correlated with those obtained with opossum shrimp and/or inland silversides, subsequent TIE characterization could be conducted in a more cost-effective manner and with less sample volume than could be achieved using 96-hour or 7-day exposure durations.

The results of the screening tests were used to select samples that would be amenable to follow-up investigation of the cause of toxicity. In general, TIEs have the highest probability of success if conducted on samples that produce well-defined toxic responses that do not dissipate quickly over time. Consequently, a degree of response that can be clearly separated from the control is highly desirable. While this ultimately depends on the number of replicates used and the reproducibility of the test methods, our experience suggests that a 30-percent difference from the control usually provides sufficient resolution against which to judge the effectiveness of the various treatments used to determine the general characteristics of the toxicant and, ultimately, to identify and confirm the cause of toxicity.

The blue mussel embryo development assay was performed in accordance with "Conducting Static Acute Toxicity Tests Starting with Embryos of Four Species of Saltwater Bivalve Molluscs (E724-94)" (ASTM 1994). Procedures for testing stormwater using the opossum shrimp and inland silverside survival and growth tests followed "Short-Term Methods for Estimating the

Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition (EPA/821/R-02/014),” (EPA 2002).

Procedures for performing Phase I TIEs are outlined in “Methods for Aquatic Toxicity Identification Evaluations – Phase I Toxicity Characterization Procedures, Second Edition (EPA/600/6-91/003)” (EPA 1991), “Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I (EPA/600/6-91/005F)” (EPA 1992), and “Marine Toxicity Identification Evaluation (TIE) – Phase I Guidance Document” (EPA 1996). Procedures for performing Phase II and III TIEs are outlined in “Methods for Aquatic Toxicity Identification Evaluations – Phase II Toxicity Identification Procedures for Samples Exhibiting Acute and Chronic Toxicity (EPA/600/R-92/080)” (EPA 1993a), and “Methods for Aquatic Toxicity Identification Evaluations – Phase III Toxicity Confirmation Procedures for Samples Exhibiting Acute and Chronic Toxicity (EPA/600/R-92/081)” (EPA 1993b), respectively.

### **2.2.1 Screening Bioassays**

#### **Blue Mussel Embryo Development Test**

Carlsbad Aquafarms in Carlsbad, CA supplied the blue mussel *Mytilus galloprovincialis*. The mussels were transported to AMEC in ice chests via same-day courier service. In the laboratory, the organism receipt date and arrival condition were recorded in a logbook. The mussels were then acclimated to test temperature and salinity, and observed each day prior to test initiation for any indications of significant mortality (>10%).

Mussel embryos were exposed to stormwater for a period of 48 hours to evaluate effects on percent-normal embryo development. Sample concentrations of 12.5, 25, 50, and 68 (the highest testable concentration) percent were tested concurrently with a negative control. Due to the low salinities of the samples, hypersaline brine was added to each sample to raise the salinity to 32 ppt. The volume of hypersaline brine required to adjust the salinity determined the highest testable concentration for each sample. An additional control composed of hypersaline brine and deionized water was also tested to ensure any observed toxic effects were not due to the brine.

Test solutions were prepared using graduated cylinders and pipettes. Measurements of pH, DO, temperature, and salinity were recorded for each test concentration and control. Five replicate test chambers were prepared for each test concentration and control. Replicates

consisted of 30-ml shell vials containing 10 ml of test solution. Test solutions were acclimated to 15°C in temperature-controlled environmental chambers prior to initiation.

In order to spawn the mussels, brood stock were exposed to heated ultraviolet (UV) treated seawater (27-29°C) in shallow plastic trays. Within 30-60 minutes, the mussels began to spawn. Spawning individuals were removed and isolated in individual 250-ml beakers containing 20°C seawater. After allowing individuals to continue to spawn for 30 minutes, eggs were examined under a compound microscope in order to determine egg quality. The three “best” egg stocks (as defined by microscopic observations of egg shape, color, and opacity) were poured into 1-L Erlenmeyer flasks and each was fertilized with sperm from at least three different males. Fertilization was allowed to continue for twenty minutes. Each sperm-egg stock mixture was then poured through a 20-µm screen allowing sperm to pass through while retaining fertilized eggs. The three embryo stocks were allowed to develop for approximately two hours in a 15°C environmental chamber. A 1-ml aliquot was then removed from each embryo stock and examined under a compound microscope. The embryo stock that exhibited the furthest development (i.e., most number of cleavages per cell) was diluted to a concentration of 200 embryos/ml, and 1 ml of this stock was added to each vial to initiate testing. A 16:8 hour light:dark illumination cycle was provided for the duration of the test. Test chambers were covered with a clear plexiglass sheet to reduce evaporation and prevent test solution contamination.

Temperature, pH, DO, and salinity were measured daily in surrogate test chambers for each concentration and control. At test termination, larvae in each test chamber were preserved with 1 ml of seawater-buffered Formalin prior to evaluation. A subsample of 100 bivalve embryos from each test chamber was counted under a compound microscope at 400x magnification. The embryos were classified as normal or abnormal. Normally developed embryos have a distinct D-shape with complete formation of the shell.

A concurrent reference toxicant test (positive control) using copper (II) chloride (CuCl<sub>2</sub>) was conducted in conjunction with the stormwater tests.

### **Opossum Shrimp and Inland Silverside 7-Day Survival and Growth Tests**

Juvenile opossum shrimp were purchased from Aquatic Biosystems of Fort Collins, CO. The organisms were placed in plastic bags containing oxygenated culture water, packed in insulated containers, and transported to AMEC via overnight delivery service. Upon arrival at AMEC, water quality parameters of temperature, pH, DO, and salinity were measured and recorded in a

logbook. The condition of the organisms was also noted. The mysids were then acclimated to test salinity and temperature, and observed prior to test initiation for any indications of stress (e.g. abnormal swimming behavior) or significant mortality (>10%). The mysids were fed *Artemia* nauplii to satiation during holding. Mysids were 6 days old upon arrival at AMEC and 7 days old upon test initiation.

Juvenile silversides were purchased from Aquatic Biosystems of Fort Collins, CO. The organisms were placed in plastic bags containing oxygenated culture water, packed in insulated containers, and transported to AMEC via overnight delivery service. Upon arrival at AMEC, their condition was noted, and water quality measurements of temperature, pH, DO, and salinity were recorded in a logbook. The fish were then acclimated to test salinity and temperature, and observed prior to test initiation for any indications of stress (e.g. abnormal swimming behavior) or significant mortality (>10%). The silversides were 9 days old upon arrival at AMEC and 10 days old upon test initiation; they were fed *Artemia* nauplii to satiation during holding.

These tests estimate chronic toxicity by evaluating survival and growth of opossum shrimp or inland silversides over a 7-day exposure period. Sample concentrations of 25, 50, and 100 percent were tested along with a negative control. Due to the low salinities of the samples, Forty Fathoms™ sea salt was added to each sample to raise the salinity to 32 ppt. An additional control composed of Forty Fathoms™ sea salt and deionized water was also tested to ensure observed mortality was not due to the addition of artificial salt rather than other toxic constituents.

Test solutions were prepared using graduated cylinders and pipettes. Measurements of pH, DO, temperature, and salinity were recorded for each test concentration and control. Eight (mysids) or five (silversides) replicate test chambers were prepared for each test concentration and control. Replicates for the mysid test consisted of 400-ml plastic cups containing 250 ml of test solution. Replicates for the silverside test consisted of 1-L glass jars containing 500 ml of test solution. Test solutions were acclimated to 25°C in temperature-controlled environmental chambers prior to initiation, for both the shrimp and silverside tests.

Five organisms were counted and transferred from holding bowls into individual plastic soufflé cups. A second technician verified counts and condition of all test organisms prior to addition of the organisms to the test chambers, and again when test initiation was complete. A 16:8 hour light:dark illumination cycle was provided for the duration of the test. Test chambers were covered with a clear plexiglass sheet to prevent evaporation and cross-contamination of the test



solutions.

Test solutions were renewed once per day, and organisms were fed two times per day. Temperature, pH, DO, and salinity were measured daily in both freshly prepared test solutions, and test solutions collected from the test chambers for each concentration and control. Survival status was recorded for each test chamber once per day. At test termination, final observations were made and test animals were prepared for weight determination.

Dry weights were determined by placing organisms from each test chamber into individual tared aluminum pans and drying them in an oven at 60°C for 24 hours. After drying, pans were weighed on a Mettler 240AE balance to the nearest 0.01 mg.

Acute CuCl<sub>2</sub> reference toxicant tests (positive control) were conducted within the same week of these chronic tests.

### **2.2.2 Phase I TIE Treatments**

Phase I treatments are designed to remove, inhibit, or potentiate a particular classes of compounds that may be present in the sample, thereby isolating the toxic signal. Selected treatments were applied in this study; detailed descriptions of each treatment are provided below, and a general schematic of Phase I TIE characterization procedures is shown in Figure 1.

Filtered, natural seawater (mussel larvae) or artificial seawater (opossum shrimp) was used as dilution and control water for these studies. Untreated control water was tested concurrently with the “Baseline” (untreated) stormwater tests for each site and species. Aliquots of the appropriate control water underwent each of the Phase I manipulations (method controls) and were tested alongside the treated stormwater samples. The method controls are used to assess whether the sample manipulations resulted in adverse effects due to the procedures themselves.

### **Baseline Tests**

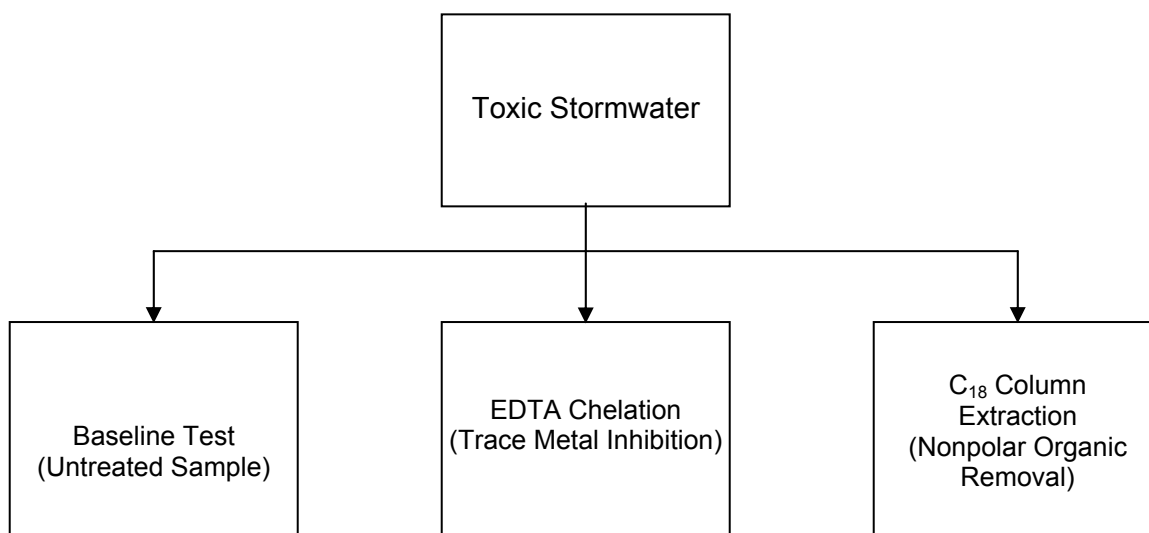
Baseline tests were performed concurrently with the Phase I TIE treatments to compare the response in untreated stormwater to responses obtained after the manipulations. Treatments that altered the toxicity compared with the toxicity of the baseline test were used to identify classes of toxic compounds present in the sample.

### **EDTA Metal Chelation**

The addition of ethylenediaminetetraacetic acid (EDTA) was used to determine the extent of toxicity attributable to divalent cationic trace metals (EPA 1991). EDTA chelates divalent cationic trace metals, thereby reducing their bioavailability. EDTA was added to the method controls and all stormwater dilutions at exposure concentrations of 30 and 60 mg/L.

### **Solid-Phase Extraction**

Solid-phase extraction (SPE) with a C<sub>18</sub> column was used to determine the extent of toxicity associated with nonpolar organic compounds. It has been found that C<sub>18</sub> columns also have the ability to remove some metals as well (EPA 1991). A 5-ml capacity Baker brand column was used for this procedure. Post-filtered SPE columns were labeled, wrapped in airtight resealable bags, and held at 4°C for potential subsequent Phase II testing.



**Figure 1. Schematic diagram of Phase I TIE sample treatments used for San Diego Bay stormwater samples.**

### **2.2.3 Phase I TIE Bioassays**

#### **Blue Mussel Embryo Development Test**

A dilution series was prepared for each treatment to evaluate its effectiveness at different concentrations. Bioassays were conducted following the same methods for organism procurement, test initiation, monitoring and termination previously described for screening tests. The experimental design, including number of replicates, concurrent controls and test concentrations, is summarized in Table 2.

**Table 2. Phase I TIE Toxicity Test Experimental Design – Blue Mussel**

<b>Test Procedure</b>	<b>Replicates</b>	<b>Test Solutions</b>
<b>Baseline Tests</b> (NAVSTA OF 9, OF 11, OF 14, SUBASE OF 11B, OF 23 c+e, and OF 26)	2	Lab Control, Brine Control, 25, and 50% <sup>a</sup>
<b>Phase I Manipulations</b> (EDTA addition <sup>b</sup> and C <sub>18</sub> column extraction)	2	Method Control, 25, and 50% <sup>a</sup>
<b>Reference Toxicant Test</b>	5	0, 2.5, 5, 10, 20, and 40 µg/L Cu

<sup>a</sup> Toxicity to blue mussels observed in all six screening bioassays was sufficient to test a 50% dilution as the highest concentration for all sites.

<sup>b</sup> EDTA was added to test solutions for final concentrations of 30 and 60 mg/L across concentrations.

### **Opossum Shrimp 7-Day Survival and Growth Test**

Because the opossum shrimp test requires daily renewal of test solutions, the remaining sample volume was insufficient to test multiple concentrations. Consequently, the TIE treatments were performed only on 100% sample. Fresh aliquots of SUBASE OF 23 c+e stormwater were treated with EDTA each day three hours prior to test solution renewal. However, due to the time associated with C<sub>18</sub> column extraction, a sample volume adequate for the test initiation and all of the daily renewals was prepared the day prior to test initiation. All remaining aspects of the tests pertaining to organism procurement, test initiation, monitoring and termination were conducted following the same methods as previously described for the screening tests. Experimental design, including number of replicates, concurrent controls, and test concentrations is summarized in Table 3.

**Table 3. Phase I TIE Toxicity Test Experimental Design – Opossum Shrimp**

<b>Test Procedure</b>	<b>Replicates</b>	<b>Test Solutions</b>
<b>Baseline Test</b> (SUBASE 23 c+e)	5	Lab Control, Salt Control, and 100%
<b>Phase I Manipulations</b>		

<b>(Round One)</b> (EDTA addition <sup>a</sup> and C <sub>18</sub> column extraction)	5	Method Control and 100%
<b>Reference Toxicant Test</b>	8	0, 25, 50, 100, 200, and 400 µg/L Cu

<sup>a</sup> EDTA was added to test solutions for final concentrations of 30 and 60 mg/L.

## **2.2.4 Phase II/III TIEs**

During Phase II TIE procedures, additional manipulations and measurements are performed in an effort to identify and confirm the contaminants that are responsible for toxicity. Specific Phase II methods depend on the results obtained during Phase I testing. Confirmation of suspected toxicants is performed during Phase III of the TIE, which uses a combination of statistical and experimental procedures to provide additional evidence that supports the identification process. The Phase II and III TIE procedures were conducted using the mussel embryo development test because the treatments could be completed more rapidly (48-hour end-point) and cost-effectively than with opossum shrimp, which require a 7-day exposure period to achieve the sub-lethal endpoint. Conclusions regarding the cause(s) of toxicity to opossum shrimp were based on inferential comparisons to the mussel data, and known sensitivities to the contaminants identified.

### **C<sub>18</sub> Column Methanol Elutions- SUBASE OF 11B**

Non-polar organic compounds bound to C<sub>18</sub> columns can be removed from the columns using methanol. Two types of methanol elutions were performed for this study: one used only 100 percent methanol, and the other used a concentration gradient of methanol. The first elution method was used with C<sub>18</sub> columns from Phase I in order to confirm that non-polar organic toxicants had been retained on the columns. After recovery of toxicity was successful, six L of the remaining SUBASE OF 11B stormwater were filtered through six additional C<sub>18</sub> columns. Following a confirmatory elution of one column with 100 percent methanol to ensure that toxicity had not dissipated in the sample over time, the remaining columns were subsequently eluted sequentially with the following series of methanol/water fractions to elute compounds based on their polarity: 0 (Control), 50, 75, 80, 85, 90, 95, and 100 percent methanol. This step not only isolates the toxic constituent in one fraction, it also eliminates all of the organic constituents found in the other fractions. This makes it easier to detect the toxicant using analytical techniques such as GC/MS, since there are fewer peaks in the sample to cause interferences.

For each set of elutions, 2 ml of the appropriate methanol concentration was pumped through the columns using a peristaltic pump set at an approximate rate of 1 ml per minute. For elutions conducted using methanol/water fractions, care was taken to ensure that the columns did not dry out between fractions. Extracts were collected into 2-ml amber glass Voa<sup>®</sup> vials.

The extracts were added to clean dilution water at concentrations that were 2X (3 April and 8 May) and/or 4X (3 April, 8 May, and 15 July) the concentration of that in the original stormwater sample. Concurrent method controls consisted of: 1) clean dilution water passed through the C<sub>18</sub> column; 2) a methanol control equivalent to the highest concentration achieved in the tested fractions. Bioassays were conducted following the same methods for organism procurement, test initiation, monitoring and termination as previously described for the screening and Phase I tests. The experimental design, including number of replicates, concurrent controls and test concentrations, for these tests is summarized in Table 4.

**Table 4. Phase II TIE Toxicity Test Experimental Design – Blue Mussel**

<b>Test Procedure</b>	<b>Replicates</b>	<b>Dilution Series</b>
<b>Baseline Test</b> (SUBASE OF 11B)	2	Lab Control, Brine Control, 25, and 50% <sup>a</sup>
<b>C<sub>18</sub> Column Elutions</b>		
3 April	5	Method Controls, 25, 50, and 100% <sup>b</sup>
8 May	5	Method Controls, and 100%
15 July	5	Method Controls, 50, 75, 80, 85, 90, 95, and 100% <sup>c</sup>
<b>Reference Toxicant Tests</b>	5	0, 2.5, 5, 10, 20, and 40 µg/L Cu

<sup>a</sup> The highest testable concentration due to the addition of hypersaline brine was 59%.

<sup>b</sup> Dilution series was created after the 100% methanol eluted fraction was added back to dilution water at 2X the original concentration.

<sup>c</sup> Dilution series refers to the concentration of methanol filtered through the column. All extracts were added back to dilution water at 4X the original concentration.

### **Copper and Zinc Mixture Studies**

Based on Phase I TIE and analytical chemistry results, studies were conducted to evaluate the toxicity of copper and zinc to mussel larvae. Four bioassays were conducted using clean laboratory seawater and analytically verified trace metal stock solutions: 1) a mixture of copper and zinc at concentrations based on the ratio of the two metals in the stormwater samples (excluding SUBASE 23 c+e); 2) a mixture of copper and zinc at concentrations based on the ratio of their individual Median Effect (EC<sub>50</sub>) Concentrations; 3) a copper reference toxicant test;

and 4) a zinc reference toxicant test. Results from these studies were used to evaluate the extent to which each of the two metals contributed to toxicity in the stormwater samples, and if the two metals exhibited additive or synergistic toxicity. All aspects of these bioassays were conducted similarly to screening tests.

## **2.3 Statistical Analyses**

Proportional data (e.g., percent normal embryos, percent survival) were arcsine square-root transformed prior to analysis. Growth data were analyzed without transformation. To determine if parametric or non-parametric statistical methods could be applied to the data, the data were evaluated for normality (Shapiro-Wilks Test) and homogeneity of variance (Bartlett's Test). Depending on the results of these tests, Steel's Many One Rank Test (non-parametric) or Dunnett's Test (parametric) was used to identify significant differences between each concentration and the appropriate control (brine or salt). Minimum Significant Differences (MSDs) were calculated as a percentage of the control response for each test, based on Dunnett's t-statistic. Note that this procedure likely overestimates test sensitivity in cases where the test endpoints were determined with non-parametric methods.

Median Lethal ( $LC_{50}$ ), and/or  $EC_{50}$  values were also calculated for all tests that exhibited a dose-response curve. These endpoints were calculated with Maximum Likelihood Probit, or Trimmed Spearman-Kärber methods. ToxCalc Comprehensive Toxicity Data Analysis and Database Software, Version 5.0, or the Comprehensive Environmental Toxicity Information System (CETIS), version 1.0, was used for these analyses.

## **2.4 Analytical Chemistry**

Based on historical chemical and toxicological data available for the six stormwater outfalls, subsamples from each site were analyzed for a suite of total trace metals, including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc. Because  $C_{18}$  columns can bind some trace metals in addition to non-polar organic substances, subsamples were also collected following  $C_{18}$  column extraction and analyzed for the same suite of trace metals to determine if a reduction in toxicity following  $C_{18}$  extraction was due to removal of trace metals. Finally, due to the possibility of anionic surfactants in the samples, each sample was analyzed for methylene-blue active substances (MBAS), a colorimetric method that detects anionic surfactants. Analytical measurements were performed by CEL.

## **2.5 Quality Assurance**

AMEC implements quality assurance (QA) procedures in accordance with our internal QA Plan, which is based on applicable protocols and guidance documents. These procedures encompass all aspects of testing, including the source, handling, condition, receipt, and storage of samples and test organisms, and the calibration and maintenance of instruments and equipment. All data generated by the laboratory are monitored for completeness and accuracy at the end of each day, and at the end of each individual test period. Laboratory controls are conducted concurrently with every assay. In addition, reference toxicant tests are performed concurrently with every assay, or on a monthly basis, to confirm that test organism quality, and laboratory conditions and procedures, remain consistent over time.

## **3.0 RESULTS AND DISCUSSION**

Detailed descriptions of the results from screening tests, as well as the Phase I and Phase II/III TIEs are presented in the following sections. Tables and figures summarizing the toxicity data are presented in Appendix A. Statistical summaries and raw bench datasheets are presented in Appendix B. Appendix C contains reference toxicant test results, as well as a laboratory quality control chart for each species. The analytical chemistry report from CEL is in Appendix D, and the sample receipt information and COC forms, are contained in Appendices E and F, respectively.

### **3.1 Screening Bioassays**

#### **3.1.1 Blue Mussel Embryo Development Tests**

All six stormwater samples exhibited appreciable toxicity to blue mussel embryos; no normal development was observed in the highest testable concentration (68 percent) of each sample, and the EC<sub>50</sub>s ranged from 16 to 38 percent stormwater (Table 5). SUBASE OF 26 was the most toxic sample tested and NAVSTA OF 9 was the least toxic. Based on these data, all of these samples exhibited sufficient toxicity to trigger a Phase I TIE.

#### **3.1.2 Opossum Shrimp Survival and Growth Tests**

At 96 hours, survival in all six undiluted stormwater samples ranged between 55 and 90 percent, compared with 95 to 100 percent in the controls. However, only one of the samples (SUBASE OF 23 c+e) exhibited at least a 30 percent reduction in survival relative to the controls; this effect was also statistically significant. These data are included in Table 6.

At the end of the 7-day exposure period, mean survival in the undiluted stormwater samples ranged from 50 to 88 percent. NAVSTA OF 11, OF 14, and SUBASE OF 23 c+e were the sites exhibiting statistically significant decreases in survival. Of these, only SUBASE OF 23 c+e exhibited a response in excess of 30 percent (Table 6). By way of comparison, laboratory seawater controls exhibited a mean survival of 93 percent, and survival among the artificial salt controls ranged from 93 to 95 percent. With respect to test organism growth, all six sites exhibited significantly reduced biomass compared to the artificial salt controls (Table 6). Mean values for biomass in undiluted stormwater ranged from 0.06 mg per shrimp (SUBASE OF 23 c+e) to 0.20 mg per shrimp (NAVSTA OF 9). In contrast, control biomass ranged from 0.25 to 0.30 mg per shrimp in laboratory seawater, and 0.22 to 0.28 mg per shrimp in solutions of artificial sea salts. Although sublethal responses were apparent to varying degrees in all six of the samples tested, budget constraints did not allow for conducting chronic Phase I TIEs on all samples. Consequently, a single Phase I chronic TIE was conducted on SUBASE OF 23 c+e, the sample that exhibited the greatest toxicity to opossum shrimp.

### **3.1.3 Inland Silverside Survival and Growth Tests**

Silversides exhibited markedly less sensitivity to the stormwater samples than mussels or mysids. None of the samples tested resulted in any statistically significant reductions in survival or growth. The lowest survival was associated with SUBASE OF 23 c+e; in undiluted sample, mean survival was 88 percent at 96 hours, and mean survival and biomass were 84 percent and 0.49 mg per fish, respectively, after 7 days of exposure. All of these values were within 10 percent of the same endpoints exhibited by the artificial salt control and were not statistically significant. These data are shown in Table 7.

**Table 5. Pre-TIE screening test results using the blue mussel for 48-hour embryo development.**

Site ID	Mean Normal Development (%)					NOEC <sup>a</sup>	EC <sub>25</sub> (% Sample)	EC <sub>50</sub>
	0%	12.5%	25%	50%	68%			
Lab Control 1	81	NA	NA	NA	NA	NA	NA	NA
Brine Control 1	80	NA	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	82	81	5.4	0.00	25	32	38
NAVSTA OF 11	NA	77	79	0.27	0.32	25	31	34
NAVSTA OF 14	NA	77	62	0.00	0.00	25	25	27
Lab Control 2	81	NA	NA	NA	NA	NA	NA	NA
Brine Control 2	75	NA	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	81	69	1.0	0.00	25	28	32
SUBASE OF 23c+e	NA	73	0.00	0.00	0.00	12.5	15	19
SUBASE OF 26	NA	70	0.20	0.00	0.00	12.5	14	17



**Table 6. Pre-TIE screen test results using the opossum shrimp for a) 96-hour survival, b) 7-day survival, and c) 7-day growth.**

**a)**

Site ID	Mean Survival (%)				NOEC <sup>a</sup>	LC <sub>25</sub> (% Sample)	LC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	95	NA	NA	NA	NA	NA	NA
Salt Control 1	100	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	100	93	90	100	>100	>100
NAVSTA OF 11	NA	100	98	85	100	>100	>100
NAVSTA OF 14	NA	93	98	85	100	>100	>100
Lab Control 2	95	NA	NA	NA	NA	NA	NA
Salt Control 2	98	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	98	100	85	100	>100	>100
SUBASE OF 23c+e	NA	93	93	55	50	83	>100
SUBASE OF 26	NA	95	95	88	100	>100	>100

**b)**

Site ID	Mean Survival (%)				NOEC <sup>a</sup>	LC <sub>25</sub> (% Sample)	LC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	93	NA	NA	NA	NA	NA	NA
Salt Control 1	95	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	98	93	88	100	>100	>100
NAVSTA OF 11	NA	100	95	78	50	>100	>100
NAVSTA OF 14	NA	93	95	75	50	>100	>100
Lab Control 2	93	NA	NA	NA	NA	NA	NA
Salt Control 2	93	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	95	100	83	100	>100	>100
SUBASE OF 23c+e	NA	83	80	50	50	63	>100
SUBASE OF 26	NA	95	95	85	100	>100	>100

**c)**

Site ID	Mean Biomass (mg)				NOEC <sup>a</sup>	EC <sub>25</sub> (% Sample)	EC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	0.30	NA	NA	NA	NA	NA	NA
Salt Control 1	0.28	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	0.28	0.25	0.20	50	88	>100
NAVSTA OF 11	NA	0.25	0.21	0.10	25	50	81
NAVSTA OF 14	NA	0.21	0.19	0.18	25	24	>100
Lab Control 2	0.25	NA	NA	NA	NA	NA	NA
Salt Control 2	0.22	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	0.24	0.22	0.16	50	90	>100
SUBASE OF 23c+e	NA	0.13	0.12	0.06	<25	16	59
SUBASE OF 26	NA	0.31	0.22	0.17	50	74	>100

<sup>a</sup> NOEC statistical comparisons based on the salt control

NA - Not applicable

**Table 7. Pre-TIE screen test results using the inland silverside for a) 96-hour survival, b) 7-day survival, and c) 7-day growth.**

**a)**

Site ID	Mean Survival (%)				NOEC <sup>a</sup>	LC <sub>25</sub> (% Sample)	LC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	100	NA	NA	NA	NA	NA	NA
Salt Control 1	96	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	100	100	96	100	>100	>100
NAVSTA OF 11	NA	100	96	100	100	>100	>100
NAVSTA OF 14	NA	100	100	100	100	>100	>100
Lab Control 2	100	NA	NA	NA	NA	NA	NA
Salt Control 2	100	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	100	96	96	100	>100	>100
SUBASE OF 23c+e	NA	100	96	88	100	>100	>100
SUBASE OF 26	NA	100	96	96	100	>100	>100

**b)**

Site ID	Mean Survival (%)				NOEC <sup>a</sup>	LC <sub>25</sub> (% Sample)	LC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	92	NA	NA	NA	NA	NA	NA
Salt Control 1	92	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	100	100	88	100	>100	>100
NAVSTA OF 11	NA	100	96	100	100	>100	>100
NAVSTA OF 14	NA	100	100	100	100	>100	>100
Lab Control 2	100	NA	NA	NA	NA	NA	NA
Salt Control 2	100	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	100	96	96	100	>100	>100
SUBASE OF 23c+e	NA	96	92	84	100	>100	>100
SUBASE OF 26	NA	96	96	96	100	>100	>100

**c)**

Site ID	Mean Biomass (mg)				NOEC <sup>a</sup>	EC <sub>25</sub> (% Sample)	EC <sub>50</sub>
	0%	25%	50%	100%			
Lab Control 1	0.46	NA	NA	NA	NA	NA	NA
Salt Control 1	0.50	NA	NA	NA	NA	NA	NA
NAVSTA OF 9	NA	0.47	0.57	0.46	100	>100	>100
NAVSTA OF 11	NA	0.48	0.48	0.48	100	>100	>100
NAVSTA OF 14	NA	0.49	0.49	0.53	100	>100	>100
Lab Control 2	0.50	NA	NA	NA	NA	NA	NA
Salt Control 2	0.55	NA	NA	NA	NA	NA	NA
SUBASE OF 11B	NA	0.50	0.49	0.54	100	>100	>100
SUBASE OF 23c+e	NA	0.52	0.50	0.49	100	>100	>100
SUBASE OF 26	NA	0.55	0.51	0.51	100	>100	>100

<sup>a</sup> NOEC statistical comparisons based on the salt control

NA - Not applicable

## **3.2 Phase I TIE**

Phase I TIEs were initiated on samples that exhibited clear evidence of toxicity during the screening tests. On this basis, all of the samples tested with mussels qualified for a TIE. Conversely, no TIEs were pursued with silversides because none of the samples resulted in any adverse effects. While adverse effects on growth were observed in all of the samples tested with opossum shrimp, generally only limited effects were observed with the survival endpoint. Since it was not feasible to perform TIEs on all six samples with 7-day opossum shrimp chronic toxicity tests, the TIE investigation with this species was limited to the sample that produced the greatest level of toxicity; i.e., SUBASE OF 23 c+e.

### **3.2.1 Blue Mussel**

#### **Baseline Tests**

Although all of the test samples exhibited toxicity during the initial toxicity tests conducted 19 February 2004, toxicity had diminished in most of the samples when re-tested on 27 February concurrently with the Phase I TIE manipulations. Toxicity dissipated completely in NAVSTA OF 9, and decreased to less than a 30-percent effect in the 50-percent solutions of NAVSTA OF 11, and OF 14, and in SUBASE OF 11B. All three of these samples had previously exhibited 99 to 100 percent abnormal larvae at this concentration when first tested. SUBASE OF 26 and SUBASE OF 23 c+e still retained most of their original toxicity. These data are shown in Figure 2.

#### **Toxicant Characterization**

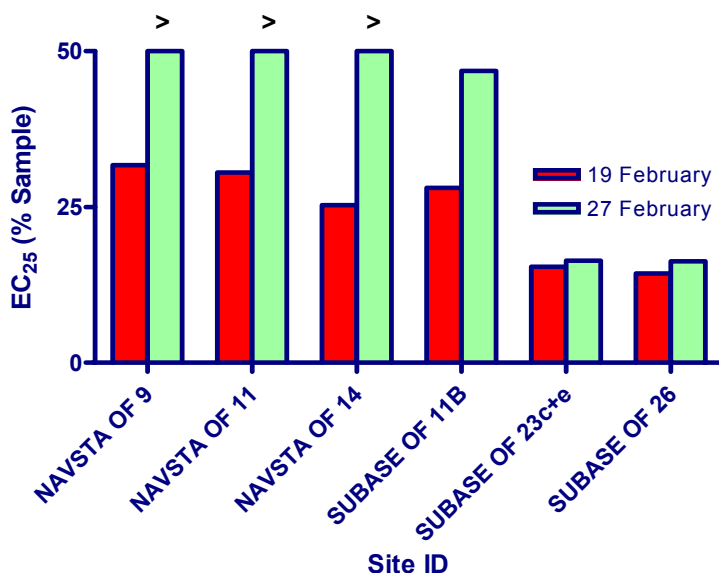
The results of the Phase I TIE treatments are summarized in Table 8. EDTA treatments essentially eliminated the remaining toxicity in samples NAVSTA OF 11 and OF 14, as well as SUBASE OF 23 c+e and OF 26. While EDTA increased the proportion of normal larvae in SUBASE OF 11B, it did not completely eliminate toxicity.

Extraction through SPE columns eliminated toxicity in NAVSTA OF 11 and OF 14, and in SUBASE OF 11B (Table 8). C<sub>18</sub> extraction did not eliminate toxicity in SUBASE OF 23 c+e or OF 26.

Based on the effectiveness of the EDTA treatments, these data suggest that toxicity in samples NAVSTA OF 11 and OF 14, and SUBASE OF 23 c+e and OF 26 was due to divalent cationic metals. Divalent metals contributed to the toxicity observed in SUBASE OF 11B, but a non-

polar organic constituent also contributed to toxicity in this sample, as indicated by the additional reduction in toxicity in a sub-sample treated with a C<sub>18</sub> column, compared with the EDTA treatment. The presence of a toxic organic constituent in SUBASE OF 11B was verified by testing a methanol elution of the C<sub>18</sub> column; toxicity was recovered at both 2X and 4X add-backs, suggesting relatively good recovery from the column. These data are also shown in Table 8.

Note that the conclusion of divalent cationic metals being the primary cause of toxicity is based on the effectiveness of EDTA in removing toxicity. While reduction of toxicity following extraction with C<sub>18</sub> SPE columns is generally attributed to the presence of non-polar organic toxicants, metals concentrations can also be reduced by C<sub>18</sub> extraction (USEPA 1991). For this study, metals concentrations were measured before and after C<sub>18</sub> treatment to determine the extent to which they were reduced following C<sub>18</sub> extraction. These data are presented in Figure 3 for copper and zinc, and clearly demonstrate that concentrations of these two metals were appreciably reduced by extraction with C<sub>18</sub> columns. Thus, the presence of an organic constituent must be confirmed by: 1) a comparative lack of effect of EDTA; and 2) toxicity in a solvent elution of the SPE column. Conversely, while C<sub>18</sub> columns did reduce copper and zinc concentrations in SUBASE OF 23 c+e and OF 26, there was sufficient metal remaining in these filtered samples to result in toxicity (Figure 3).



**Figure 2. Changes in toxicity of San Diego Bay stormwater samples to blue mussel embryos over time. EC<sub>25</sub> values increased for each sample between the initial screens (19 February) and the Phase I TIE baseline tests (27 February).**

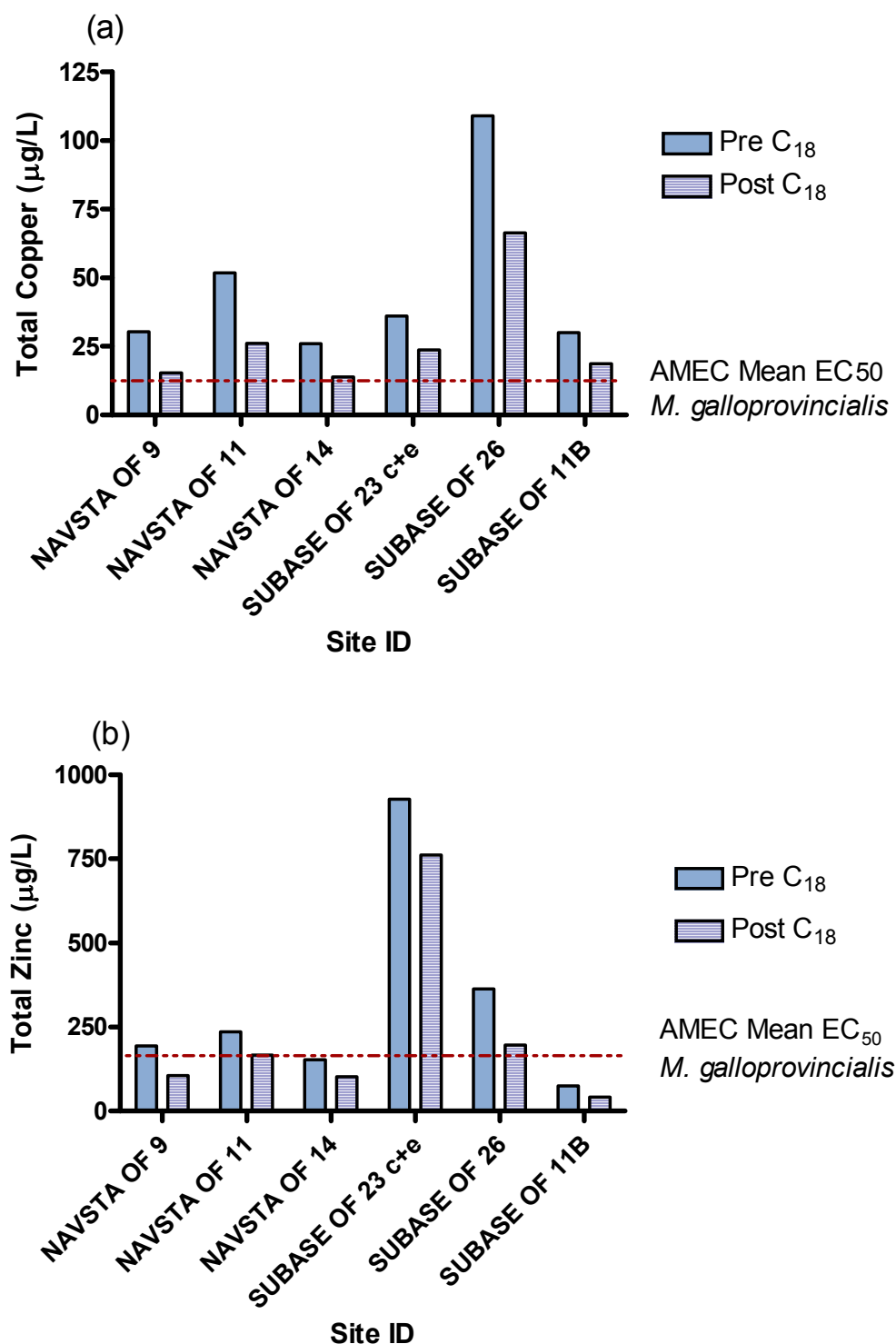


Figure 3. Total Copper (a), and Total Zinc (b) measurements for San Diego Bay stormwater samples before and after  $\text{C}_{18}$  column extraction. Mean  $\text{EC}_{50}$  values for blue mussel embryos are displayed on each figure.

**Table 8. Blue mussel Phase I TIE results.**

Site ID	Conc. (%)	Screen	Phase I Baseline	Mean Normal Development (%)				
				30 mg/L EDTA	60 mg/L EDTA	C <sub>18</sub> Extraction	2x Methanol C <sub>18</sub> Elution	4x Methanol C <sub>18</sub> Elution
NAVSTA OF 9	Method Control <sup>a</sup>	80	96	91	97	92	NT	NT
	50	5.4	92	96	91	97	NT	NT
NAVSTA OF 11	Method Control <sup>a</sup>	80	96	91	97	96	NT	NT
	50	0.0	76	93	96	92	NT	NT
NAVSTA OF 14	Method Control <sup>a</sup>	80	96	91	97	96	NT	NT
	50	0.0	73	96	91	93	NT	NT
SUBASE OF 11B	Method Control <sup>a</sup>	75	96	94	93	93	98	98
	50	1.0	68	73	81	98	0.0	0.0
SUBASE OF 23 c+e	Method Control <sup>a</sup>	75	96	94	93	96	NT	NT
	50	0.0	0.0	88	94	0.0	NT	NT
SUBASE OF 26	Method Control <sup>a</sup>	75	96	94	93	89	NT	NT
	50	0.0	0.0	92	93	1.0	NT	NT

<sup>a</sup> Method controls and C<sub>18</sub> column elutions were prepared using hypersaline brine and deionized water.

NT - Not Tested

### 3.2.2 Opossum Shrimp

#### **Baseline Test**

The results of the baseline test on SUBASE OF 23 c+e initiated 27 February concurrently with the Phase I TIE manipulations were similar to those obtained in the original screening test initiated 19 February, suggesting that toxicity did not dissipate appreciably over this time period. This result is similar to that observed with the mussel larvae test for this sample. At the end of the 7-day exposure period, the baseline test resulted in 44 percent survival, and a mean biomass of 0.10 mg per shrimp. These data are shown in Table 9, which also includes the results of the TIE treatments.

#### **Toxicant Characterization**

Addition of EDTA eliminated adverse effects on both survival and growth of opossum shrimp. In

contrast, extracting the sample with a C<sub>18</sub> column did not improve either of these parameters, compared with the baseline results (Table 9). Overall, these data provide strong evidence that divalent cationic metals were the cause of toxicity to mysids in this sample. These results are consistent with those obtained with the mussel larvae tested with the same sample.

**Table 9. Opossum shrimp Phase I TIE results.**

Treatment	Mean Survival (%)		Mean Biomass (mg)	
	0%	100%	0%	100%
Lab Control	96	NT	0.28	NT
Salt Control	100	NT	0.27	NT
Baseline	NT	44	NT	0.10
30 mg/L EDTA	96	96	0.24	0.29
60 mg/L EDTA	100	96	0.28	0.28
C <sub>18</sub> Column Extraction	96	20	0.42	0.07

<sup>a</sup> NOEC calculations based on comparisons against the brine control.

NT - Not Tested

### **3.3 Phase II/III TIE Bioassays**

#### **3.3.1 Copper and Zinc Mixture Studies**

The results of the Phase I TIE manipulations strongly suggested that divalent cationic metals were the primary cause of toxicity in the samples tested. Metals concentrations in the samples were then compared with available toxicity data to evaluate which of the metals might be contributing to toxicity. Based on a review of metals concentrations in the samples (Table 10), it appeared that copper and zinc were the two most likely causes of toxicity that could be attributed to divalent metals. For example, total copper concentrations in the samples ranged between 26.0 and 109 µg/L; these values exceed our long-term laboratory mean EC<sub>50</sub> value of 13.8 µg/L for mussel larvae exposed to copper by factors of 2 to nearly 8-fold. Similarly, values of zinc in the samples ranged from 75.8 to 927 µg/L; according to the ECOTOX database, concentrations of zinc exceeding 145 µg/L would be expected to result in adverse effects to mussel larvae. Not only were concentrations of these metals sufficiently elevated to be suspected as causes of toxicity, the range and pattern of concentrations also suggested that they could be related to toxicity. Moreover, they were both reduced substantially by extraction with C<sub>18</sub> columns. In contrast, the other metals measured were either: 1) below detection limits;

2) exhibited fairly consistent concentrations across samples; or 3) were not appreciably affected by extraction with C<sub>18</sub> columns.

To help evaluate the extent to which each metal contributed to toxicity and to understand how they interacted when present in solution together, a series of tests were performed to identify the level of toxicity associated with each metal and their degree of interaction. Zinc and copper were tested alone, and as mixtures at two different ratios (4.5:1 and 13.6:1) to evaluate whether the ratios affected the interactive characteristics of the metals.

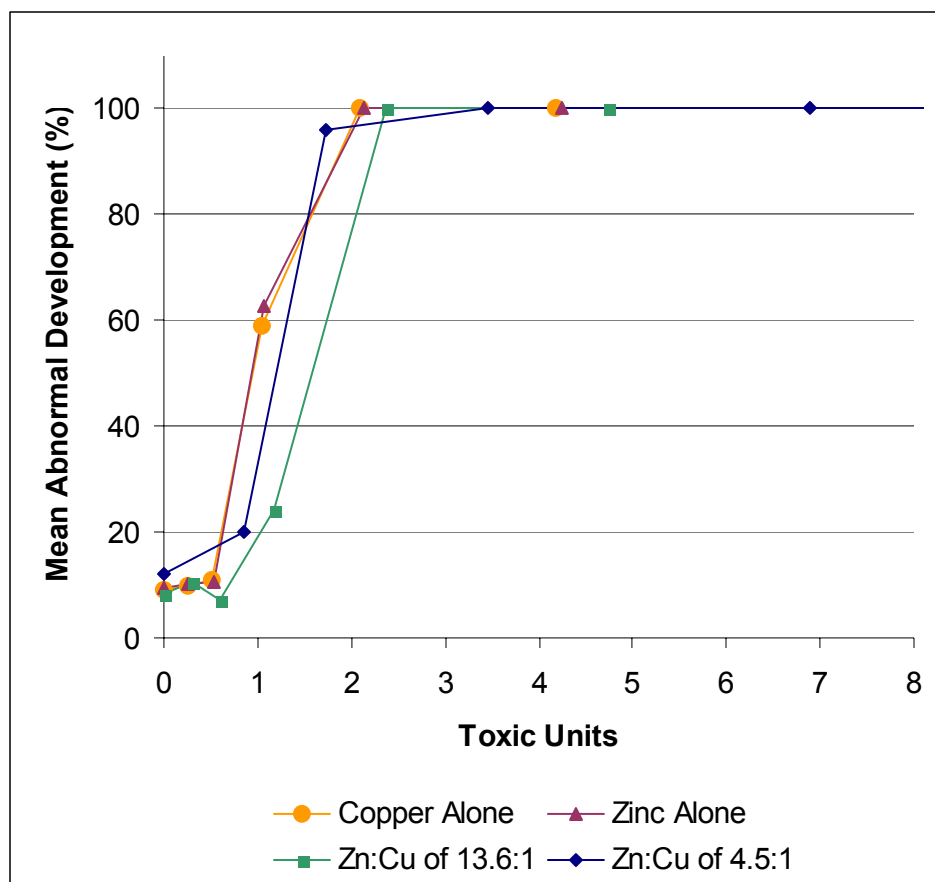
The EC<sub>50</sub> estimates determined for copper and zinc alone were 9.6 and 160 µg/L, respectively. These values are likely conservative as they were obtained in laboratory seawater. Regardless of the ratios tested, toxicity appeared to be additive, in mixtures of the two metals in laboratory seawater, the EC<sub>50</sub>s for the two mixtures were 1.2 and 1.3 total TUs, respectively. Figure 4 shows the response curves for zinc and copper individually, as well as for the two mixtures. Clearly, similar dose-responses were exhibited in all four of the tests, suggesting similar modes of action and additive toxicity. Details of metal concentrations, TUs and observed responses are shown in Appendix Tables A-13 through A-15.

Applying these laboratory-derived EC<sub>50</sub> estimates to metals concentrations measured in the actual samples suggested that, in most cases, the predicted toxicity over-estimated the actual toxicity observed in the original screening tests (Table 11). In other words, there was frequently less toxicity present in the original samples than would have been predicted on the basis of additivity and the concentrations of total metals present. These data suggest that at least some portion of the metals present in the samples was not bioavailable. On average, the actual TUs in the stormwater samples were 64 percent of those that would have been predicted on the basis of the toxicity of copper and zinc in laboratory seawater.

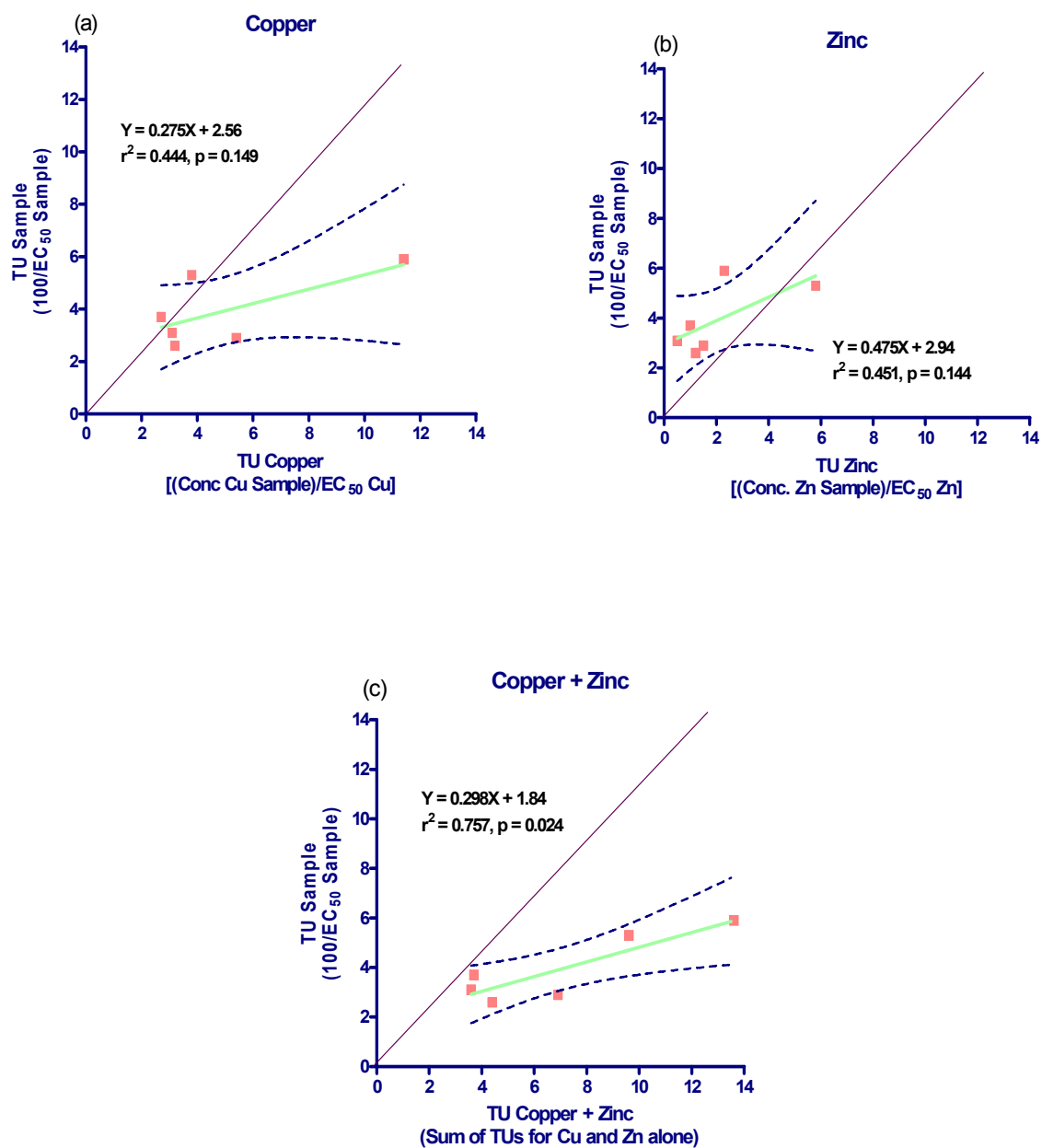
In order to address the relative importance of each of the metals to overall toxicity, predicted TUs for copper and zinc alone and in combination were plotted against the actual TUs determined in screening tests on the original samples (Figure 5). The relationships for copper and zinc alone were not statistically significant ( $p > 0.05$ ); however, the relationship between actual toxicity and the toxicity predicted by the combination of metals was significant ( $p < 0.05$ ). This finding clearly indicated that both metals contributed to the toxicity observed across all samples, which is consistent with the fact that concentrations of each metal varied independently across sites and both exhibited a relatively wide range of concentrations. A linear regression including both zinc and copper as separate variables was then used to predict



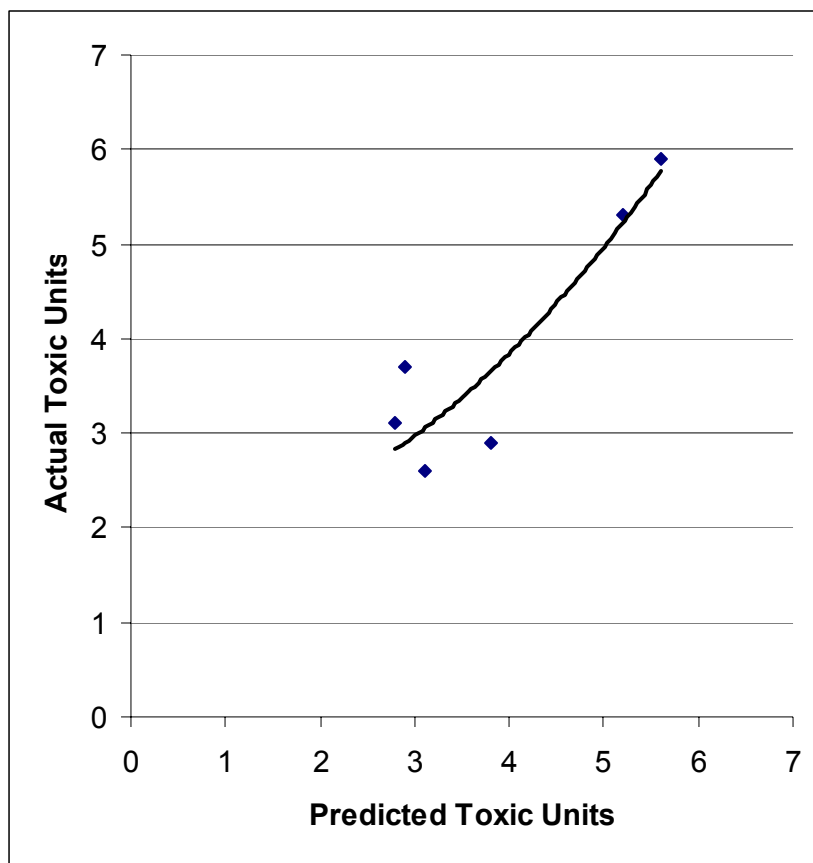
actual toxicity in the samples. A regression between values predicted by this equation and actual TUs observed exhibited an  $R^2$  of 0.80 ( $p < 0.05$ ), suggesting that 80 percent of the variability in toxicity across samples could be explained by the concentrations of these two metals (Figure 6).



**Figure 4. Response of mussel embryos to copper and zinc alone and in combination. Metals are expressed as TUs.**



**Figure 5. Comparisons of predicted TUs, based on copper and zinc, to TUs found in samples when originally tested.**



**Figure 6. Comparison of actual TUs and TUs predicted from a regression incorporating copper and zinc as separate variables:  $TU_{pred} = 1.88 + 0.25TU_{Cu} + 0.41TU_{Zn}$ .**

**Table 10. Total trace metals analysis results for San Diego Bay stormwater samples.**

Trace Metal	Reporting Limit (µg/L)	Measurement	Concentration (µg/L)					
			NAVSTA OF 9	NAVSTA OF 11	NAVSTA OF 14	SUBASE OF 11B	SUBASE OF 23 c+e	SUBASE OF 26
Antimony	15.0	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Arsenic	15.0	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Barium	10.0	Pre-C <sub>18</sub>	12.1	15.3	19.1	12.8	16.4	26.7
		Post-C <sub>18</sub>	13.4	14.7	17.8	11.9	16.5	23.1
Beryllium	1.00	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Cadmium	5.00	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Chromium	5.00	Pre-C <sub>18</sub>	ND	ND	6.32	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	5.88	ND	ND	ND
Cobalt	5.00	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Copper	5.0	Pre-C <sub>18</sub>	30.4	51.8	26.0	30.1	36.1	109
		Post-C <sub>18</sub>	15.4	26.1	13.9	18.7	23.7	66.4
Lead	10.0	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Mercury	0.50	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Molybdenum	5.00	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Nickel	5.00	Pre-C <sub>18</sub>	5.20	5.26	5.23	7.26	9.15	7.02
		Post-C <sub>18</sub>	5.98	ND	ND	5.68	13.3	6.36
Selenium	15.0	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Silver	5.00	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Thallium	15.0	Pre-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
		Post-C <sub>18</sub>	ND	ND	ND	ND	ND	ND
Vanadium	5.00	Pre-C <sub>18</sub>	ND	ND	ND	6.21	ND	6.23
		Post-C <sub>18</sub>	ND	ND	ND	5.15	ND	5.68
Zinc	10	Pre-C <sub>18</sub>	194	236	153	75.8	927	363
		Post-C <sub>18</sub>	106	166	103	42.2	761	196

**Table 11. Comparisons of predicted copper and zinc TUs.**

Site ID	Total Copper (ug/L)	Total Zinc (ug/L)	Screening Test EC <sub>50</sub> (% Sample)	Screening Test TU <sup>a</sup>	Predicted Copper TU <sup>b</sup>	Predicted Zinc TU <sup>b</sup>	Predicted Copper + Zinc TU
NAVSTA OF 9	30.4	194	38	2.6	3.2	1.2	4.4
NAVSTA OF 11	51.8	236	34	2.9	5.4	1.5	6.9
NAVSTA OF 14	26.0	153	27	3.7	2.7	1.0	3.7
SUBASE OF 11B	30.1	75.8	32	3.1	3.1	0.5	3.6
SUBASE OF 23 c+e	36.1	927	19	5.3	3.8	5.8	9.6
SUBASE OF 26	109	363	17	5.9	11	2.3	14

<sup>a</sup> TU is equal to 100 divided by the screening test EC<sub>50</sub>.

<sup>b</sup> TU is equal to the concentration of the trace metal in the stormwater sample divided by the reference toxicant test EC<sub>50</sub>.

### 3.3.1 C<sub>18</sub> Column Methanol Elutions

Eluting a C<sub>18</sub> column used to extract a subsample of SUBASE OF 11B with a methanol gradient resulted in toxicity being recovered in the 95-percent methanol fraction, with no toxicity observed in the adjacent fractions. This suggests that the organic toxicant is relatively non-polar, as it eluted late in the methanol gradient (Table 12). At this point, we believe that the organic toxicant is not likely to be an anionic surfactant because our previous experience suggests that such surfactants typically elute in lower methanol concentrations due to their comparatively high polarity. Moreover, the MBAS measurements ranged from 0.32 to 0.66 mg/L across samples (Table 13), and these concentrations were not related to the level of toxicity observed ( $p > 0.05$ ). However, the level of MBAS measured in the SUBASE OF 11B sample did exceed the 48-hour EC<sub>50</sub> to blue mussels of 0.2 mg/L (unpublished data). Thus, depending on the polarity of the actual surfactant present, it is possible that MBAS contributed to toxicity in this sample. Regardless, the identity of this organic contaminant is being further investigated using GC/MS.

**Table 12. Mean normal development in different methanol fractions used to extract C<sub>18</sub> columns.**

<b>Treatment (% Methanol)</b>	<b>Mean Normal Development (%)</b>
Method Control	86
Methanol Control	90
50	77
75	83
80	84
85	72
90	86
95	34
100	81

**Table 13. Anionic surfactant (as MBAS) analytical results for San Diego Bay stormwater samples.**

<b>Site ID</b>	<b>MBAS (mg/L)<sup>a</sup></b>
NAVSTA OF 9	0.32
NAVSTA OF 11	0.57
NAVSTA OF 14	0.64
SUBASE OF 11B	0.62
SUBASE OF 23 c+e	0.66
SUBASE OF 26	0.52

<sup>a</sup> Reporting limit is 0.10 mg/L.

## **4.0 CONCLUSIONS**

These data provide an indication of the relative sensitivity of three species to the stormwater samples tested, as well as the cause of toxicity in these samples. Mussel larvae were clearly the most sensitive species tested, with adverse effects observed at concentrations as low as 25 percent sample. Based on the survival endpoint, opossum shrimp were less sensitive than mussel larvae; however, the chronic growth endpoint approached the sensitivity exhibited by the mussel larvae for several of the samples tested. Silversides exhibited relatively low sensitivity to the test samples; no statistically significant effects were observed in any of the samples tested.

With respect to mussel larvae, the results of the TIE clearly implicated copper and zinc as the primary causes of toxicity. In addition, an organic toxicant contributed to the toxicity of SUBASE OF 11B.

Metals were also the most likely cause of toxicity to opossum shrimp; although a TIE was only performed on the sample that exhibited the most toxicity (SUBASE OF 23 c+e), the results clearly indicated that metals were the cause of reduced survival and growth in this sample.

Given that the TIE identified copper and zinc as primary causes of toxicity, the differences in sensitivity observed between species can be explained on the basis of these two metals. Mussel larvae are clearly the most sensitive of the three species to copper; our long-term laboratory mean  $EC_{50}$  for this metal ( $n=20$ ) is  $13.8 \mu\text{g/L}$ , which can be compared with long-term average  $LC_{50}$ s of  $125 \mu\text{g/L}$ , and  $243 \mu\text{g/L}$  for silversides and opossum shrimp exposed for 7 days, respectively. Thus, given the range of copper concentrations in the samples ( $26.0$  to  $109 \mu\text{g/L}$ ), mussels would have been the only species expected to exhibit a significant response. Similarly, mussels were the most sensitive species to zinc, with an  $EC_{50}$  of  $160 \mu\text{g/L}$ . Opossum shrimp were less sensitive; during this TIE study, we determined that the 7-day  $LC_{50}$  for this species was  $448 \mu\text{g/L}$ . The ECOTOX database contains 96-hour  $LC_{50}$  estimates for zinc that range from approximately  $300$  to  $550 \mu\text{g/L}$ , with most of the values approaching  $500 \mu\text{g/L}$ . At 96 hours, only SUBASE OF 23 c+e exhibited any significant indication of acute toxicity, and then only to opossum shrimp. Zinc was the most likely constituent responsible for this observed response; the concentration of zinc present in the sample ( $927 \mu\text{g/L}$ ) exceeded literature values for acute toxicity by 2- to 3-fold. Moreover, comparison of the metals concentrations and degree of toxic responses exhibited by the opossum shrimp in the different samples suggests that zinc was the primary cause of toxicity to this species in SUBASE OF 23 c+e (Table 14). This sample exhibited the highest degree of toxicity to opossum shrimp and also contained the highest concentration of zinc ( $927 \mu\text{g/L}$ ), and the only concentration of zinc that clearly exceeded the threshold for acute toxicity. Thus, the range of concentrations in the remaining samples (i.e.,  $75.8$  to  $363 \mu\text{g/L}$ ) were likely at, or below, the threshold for acute toxicity, particularly if bioavailability was reduced due to binding by various ligands (e.g., dissolved organic carbon) possibly present in the samples. Silversides were the least sensitive species tested, which suggests that they are even more tolerant to zinc than opossum shrimp.

**Table 14. Opossum shrimp screening test results with copper and zinc sample concentrations.**

Site ID	Mean Survival (%)		Mean Biomass (mg)		Total Copper	Total Zinc
	100% Sample	Salt Control	100% Sample	Salt Control	(ug/L)	(ug/L)
<b>NAVSTAOF 9</b>	88	95	0.20	0.28	30.4	194
<b>NAVSTA OF 11</b>	78	95	0.10	0.28	51.8	236
<b>NAVSTA OF 14</b>	75	95	0.18	0.28	26.0	153
<b>SUBASE OF 11B</b>	83	93	0.16	0.22	30.1	75.8
<b>SUBASE OF 23 c+e</b>	50	93	0.06	0.22	36.1	927
<b>SUBASE OF 26</b>	85	93	0.17	0.22	109	363

<sup>a</sup> NOEC statistical comparisons based on the salt control

NA - Not applicable

The results for each of the samples are reviewed below in the context of the findings of the TIE investigation. These summaries emphasize the tests conducted with mussel larvae, but mysid results are included where appropriate.

NAVSTA OF 9 – This sample exhibited 2.6 TU when tested originally and contained an estimated 3.2 TU Cu and 1.2 TU Zn. Toxicity dissipated completely when the Phase I TIE was performed, so the contribution of metals to toxicity could not be verified empirically. However, there was sufficient metal present in the sample to account for the original toxicity. Both copper and zinc were present at concentrations in excess of 1 TU, so it is possible that both metals contributed to toxicity, although their relative contributions are not known. The results of the TIE process for this sample are summarized as a flowchart in Figure 7.

NAVSTA OF 11 – This sample exhibited 2.9 TU when tested originally, and contained an estimated 5.4 TU Cu and 1.5 TU Zn. Toxicity dissipated appreciably by the time the Phase I TIE was performed, but there was enough of a response remaining to determine that EDTA removed all of the toxicity, implicating divalent metals as the cause of toxicity. Both copper and zinc were present at concentrations sufficient to result in toxicity, but their relative contributions could not be determined. As with NAVSTA OF 9, copper could have accounted for all of the toxicity, but zinc could only have accounted for partial toxicity. However, without data to document their relative bioavailability, it is not possible to know whether toxicity was due to copper alone or to a combination of copper and zinc. The results of the TIE process for this sample are summarized as a flowchart in Figure 8.



NAVSTA OF 14 – This sample exhibited 3.7 TU when tested originally, and contained an estimated 2.7 TU Cu and 1.0 TU Zn. Toxicity had decreased when the Phase I TIE was performed, but EDTA effectively removed the residual toxicity, implicating metals as the cause of toxicity. Toxicity was due to a combination of copper and zinc, as neither metal alone was present at a concentration sufficiently high enough to account for the original toxicity. These findings are summarized in the flowchart in Figure 9.

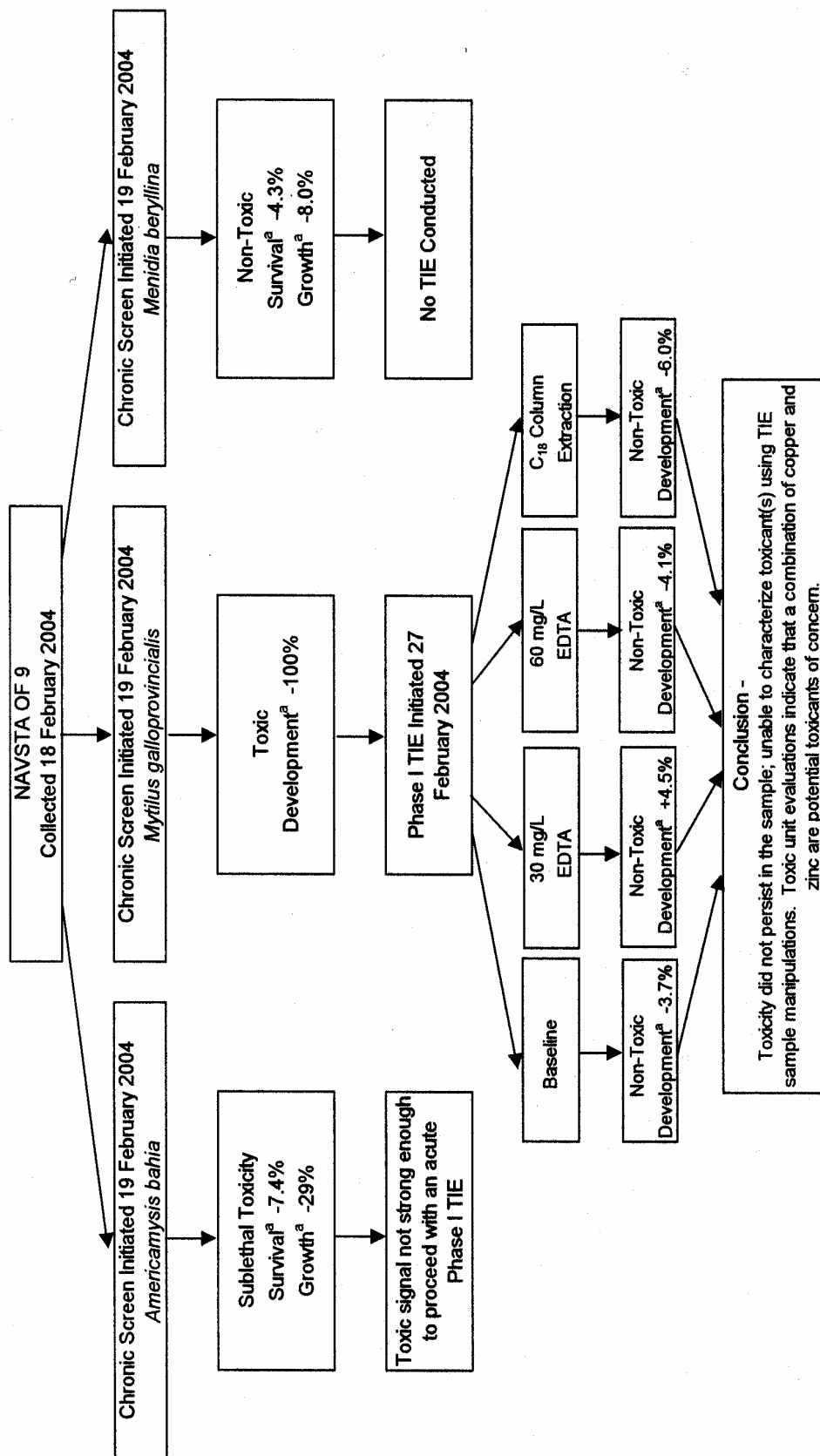
SUBASE OF 11B – This sample exhibited 3.1 TU when tested originally, and contained 3.1 TU Cu and 0.5 TU Zn. While toxicity decreased by the time the Phase I TIE was initiated, there was still sufficient residual toxicity to determine that: 1) EDTA was able to remove some of the remaining toxicity; and 2) C<sub>18</sub> was able to remove all of the residual toxicity. The effectiveness of the C<sub>18</sub> column could be explained on the basis of partial removal of zinc and copper from solution, but a non-polar organic constituent was also implicated as toxicity was recovered in a methanol elution of the C<sub>18</sub> column. Collectively, these data suggest that toxicity was primarily due to copper, but a non-polar organic constituent also contributed to toxicity; the actual contribution of each of these constituents is problematic to determine since the relative dissipation rates are not known. Note that the identity of the non-polar organic is being investigated further. The results of the TIE process for this sample are summarized as a flowchart in Figure 10.

SUBASE OF 23 c+e – This sample exhibited 5.3 TU when tested originally, and contained 3.8 TU Cu and 5.8 TU Zn. Significant toxicity was still present when tested in conjunction with the Phase I TIE. EDTA clearly removed toxicity, implicating divalent cations as the cause of toxicity. Sufficient copper was not present to account for all of the toxicity present. Conversely, there was barely enough Zn to account for all of the toxicity. Under the assumption that not all of the metal present would be bioavailable, it would be reasonable to conclude that both metals contributed to toxicity in this sample, although the exact contribution of each cannot be established. These findings are presented in a flowchart in Figure 11.

Figure 11 also includes the TIE results for mysids. EDTA removed toxicity, indicating that divalent cations were the toxicant involved. Comparison of metals concentrations in the sample with known toxicity benchmarks suggested that zinc was responsible for toxicity.

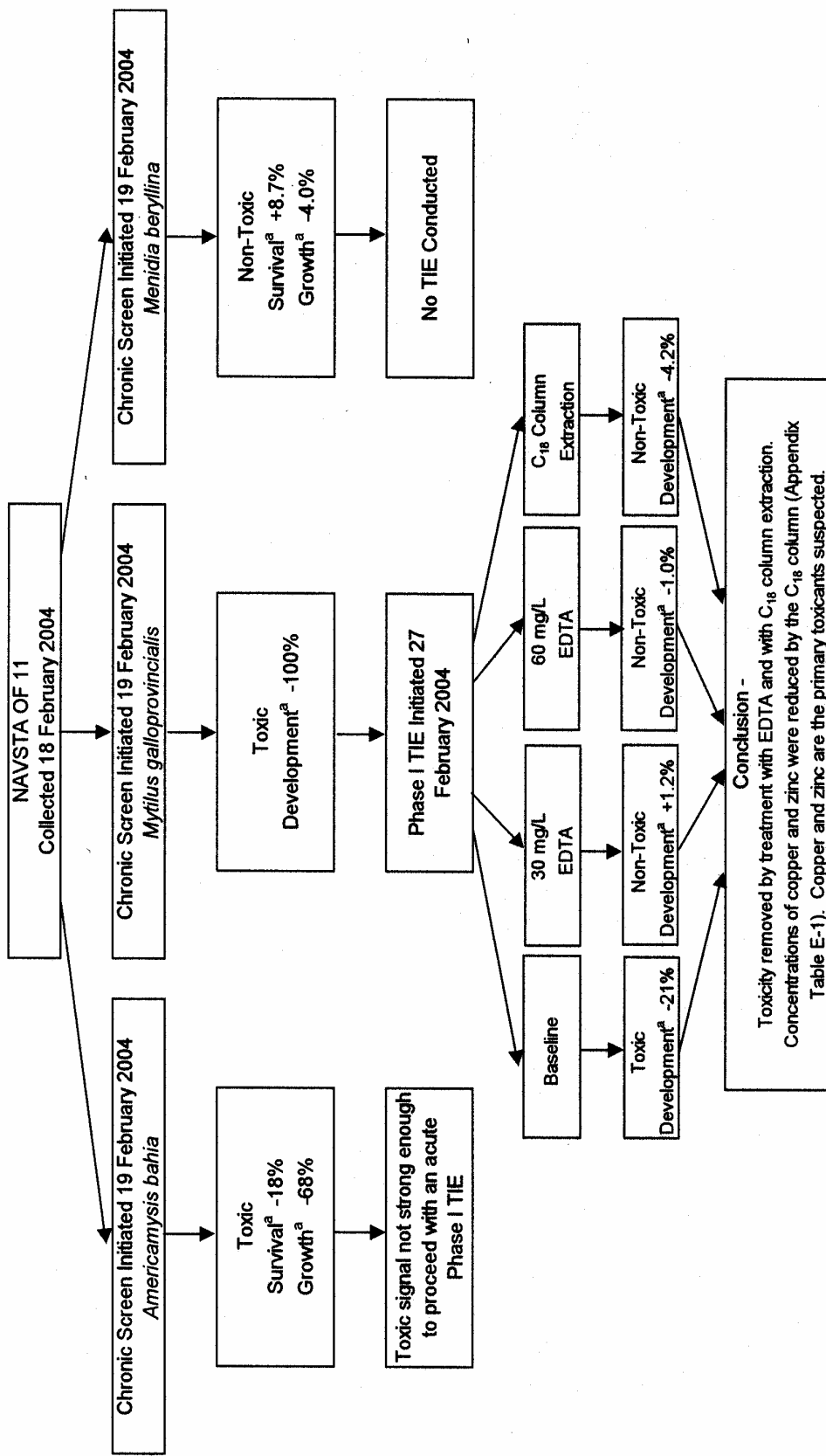
SUBASE OF 26 – This sample exhibited 5.9 TU when tested originally, and contained 11.4 TU Cu and 2.3 TU Zn. Significant toxicity was still present when tested in conjunction with the Phase I TIE. As with SUBASE OF 23 c+e, toxicity was removed by EDTA, indicating that

divalent cationic metals were the cause of toxicity. There was clearly enough copper present to account for all of the toxicity, and sufficient zinc present to account for partial toxicity. Thus, toxicity was due to copper alone, or to a combination of copper and zinc; the exact contribution of each metal would depend on their relative bioavailability. The results of the TIE process for this sample are summarized as a flowchart in Figure 12.



\* Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 7. Summary of Results for NAVSTA OF 9 Stormwater.



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 8. Summary of Results for NAVSTA OF 11 Stormwater.

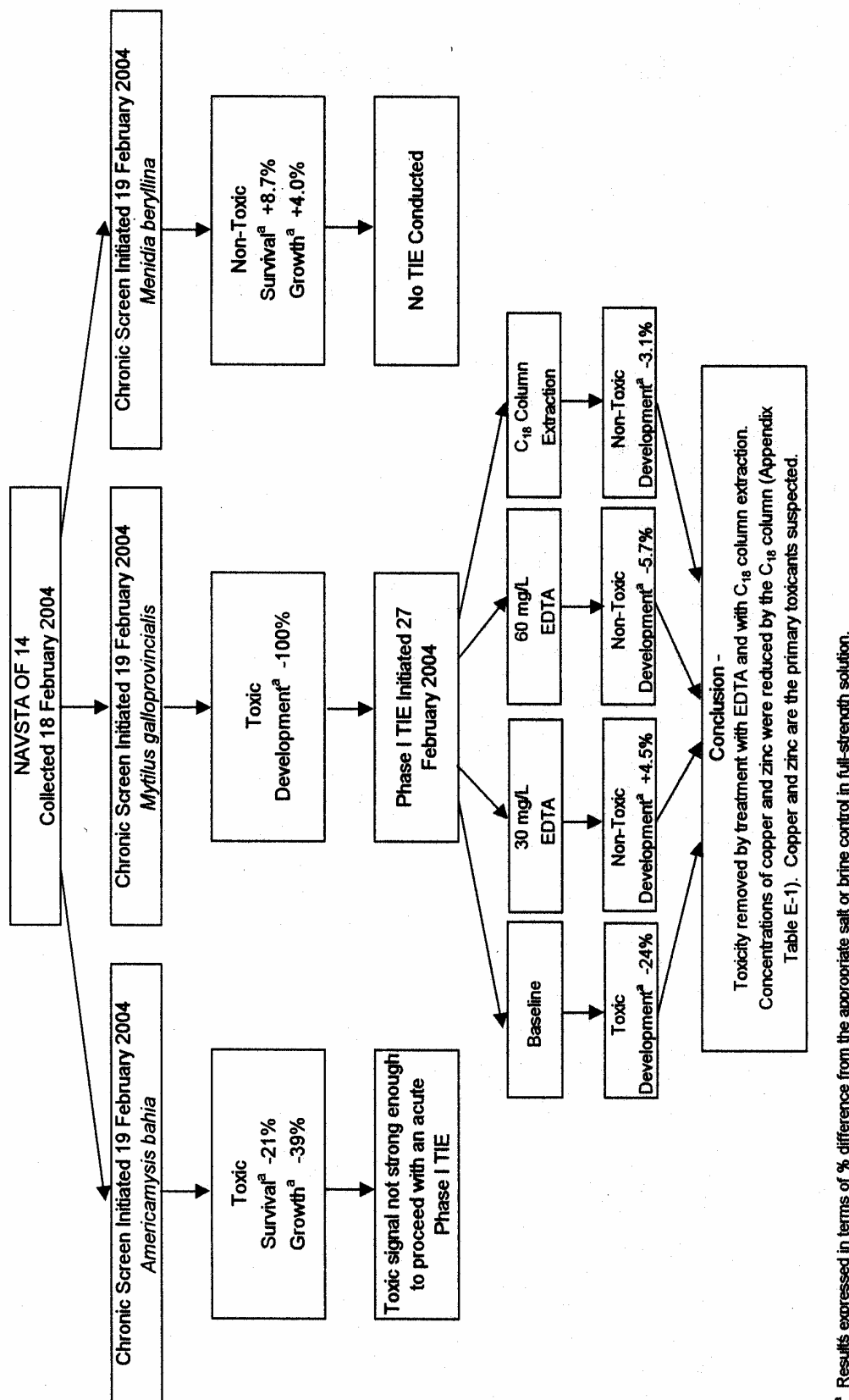
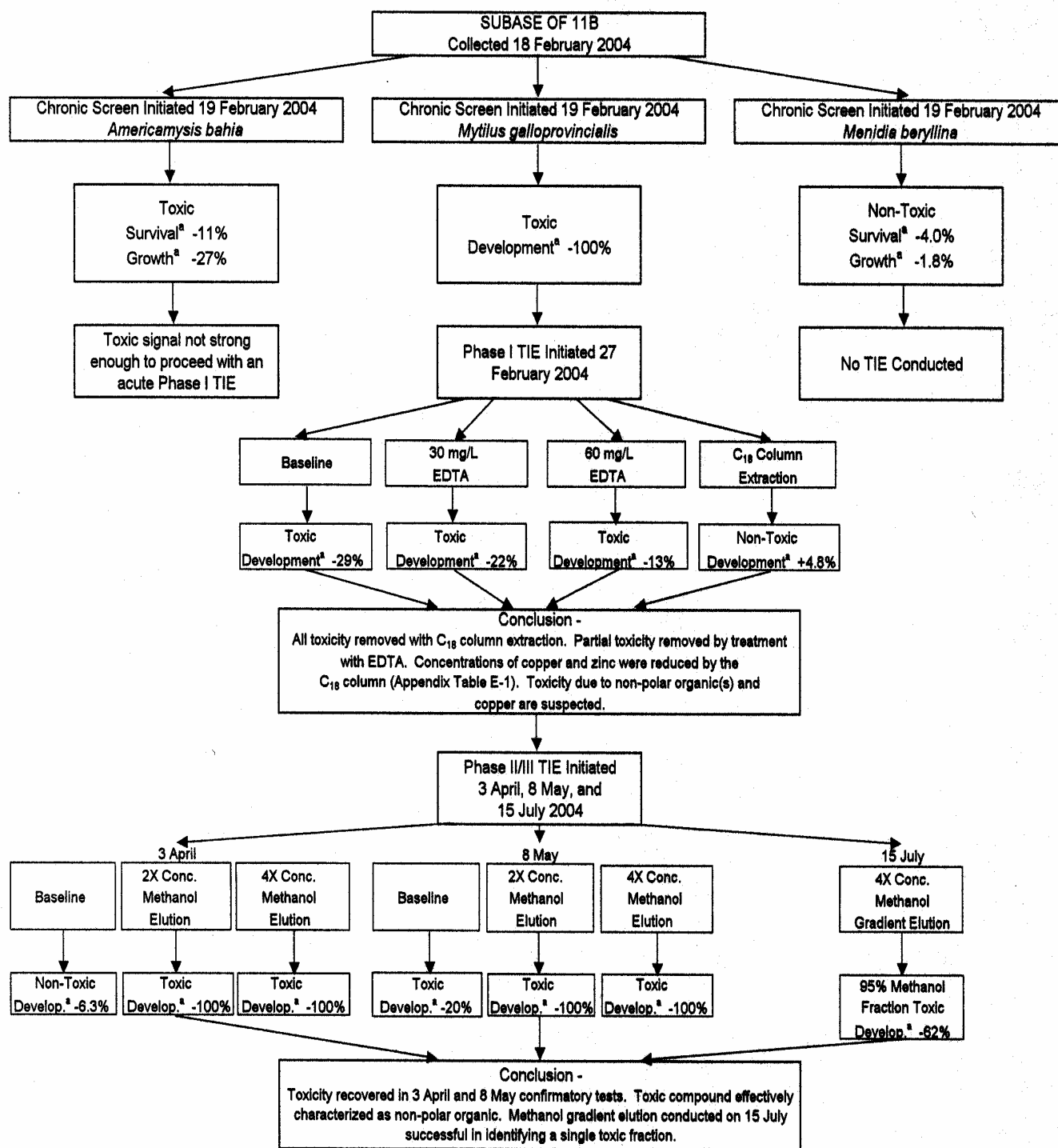
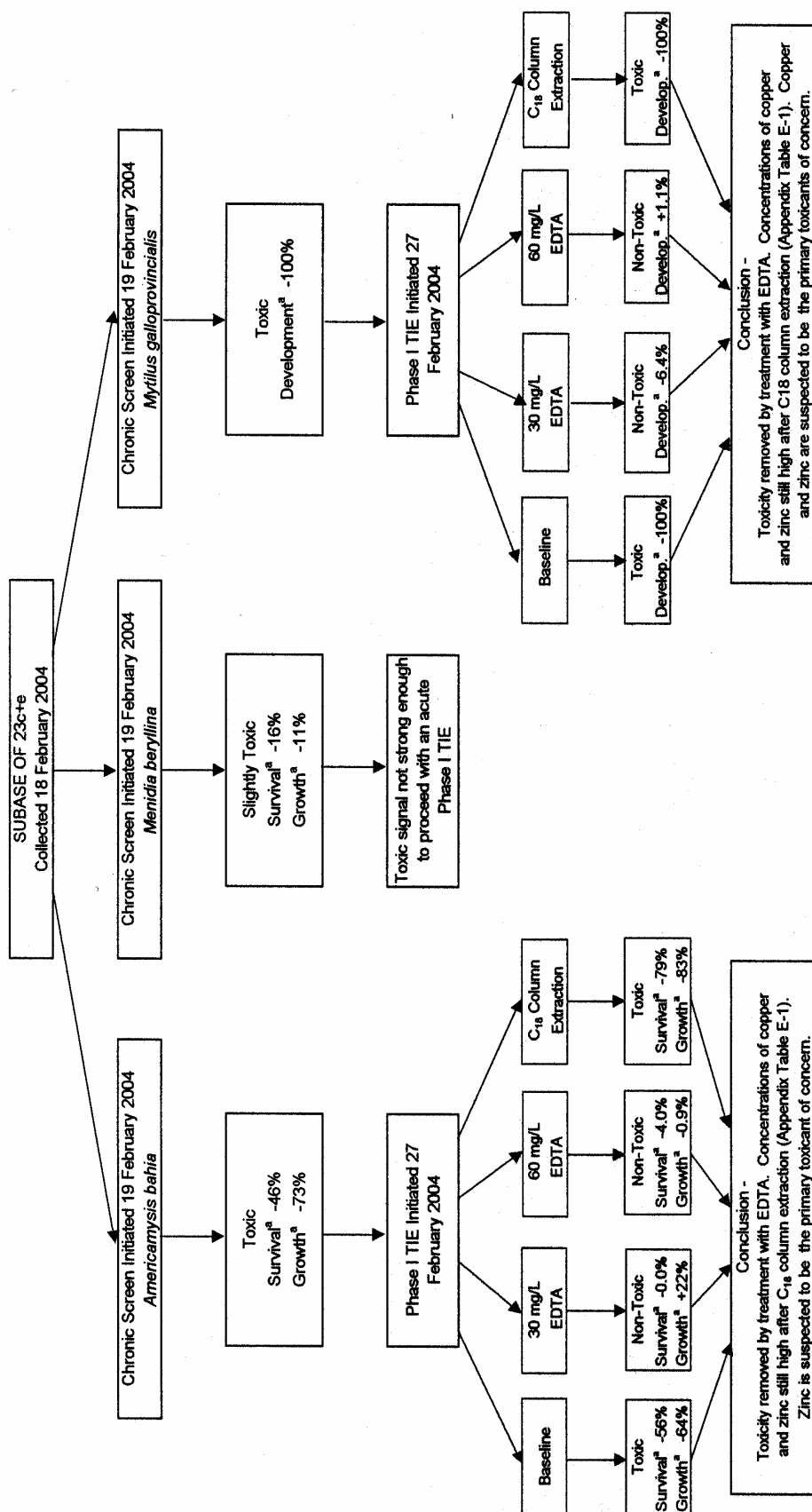


Figure 9. Summary of Results for NAVSTA OF 14 Stormwater.



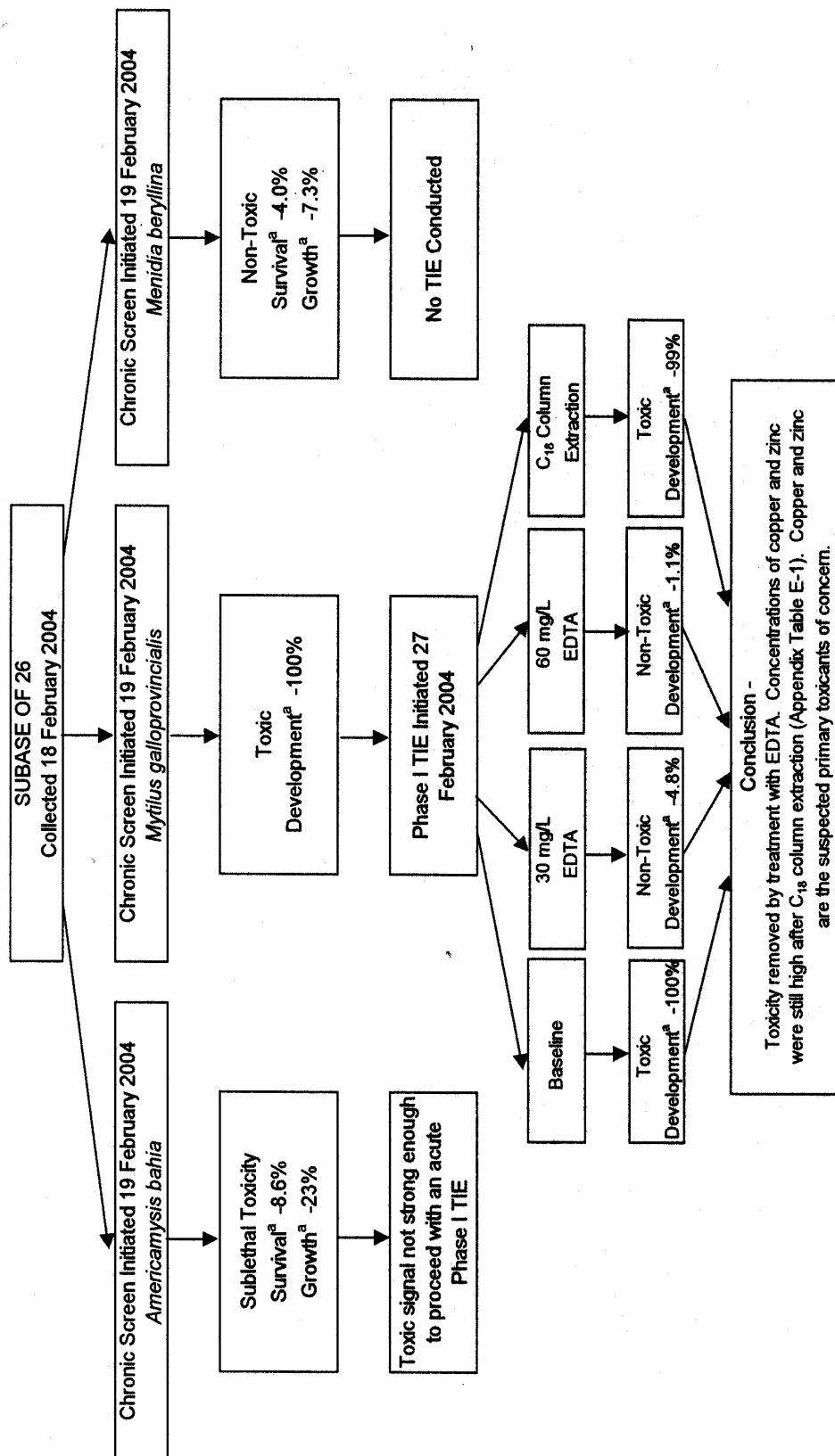
<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

**Figure 10. Summary of Results for SUBASE OF 11B Stormwater.**



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 11. Summary of Results for SUBASE OF 23 c+e Stormwater.



<sup>a</sup> Results expressed in terms of % difference from the appropriate salt or brine control in full-strength solution.

Figure 12. Summary of Results for SUBASE OF 26 Stormwater.



## **5.0 QA/QC**

### **5.1 Screening Bioassays**

#### **5.1.1 Blue Mussel**

Mean normal development of mussel larvae in all laboratory seawater and hypersaline brine controls tested during the screening phase of the study ranged between 75 and 81 percent. MSDs ranged between 10 and 25 percent, indicating test sensitivity was within a suitable range.

#### **5.1.2 Opossum Shrimp**

At 96 hours, control performance met the 90 percent acute criterion in all cases, with mean survival ranging from 95 to 100 percent across laboratory seawater and artificial salt controls. MSDs calculated in comparison with the artificial salt controls ranged from 5 to 11 percent across samples. At 7 days, laboratory seawater controls exhibited mean survival of 93 percent, and survival among artificial salt controls ranged from 93 to 95 percent. MSDs ranged from 6 to 15 percent. Mean control biomass ranged from 0.25 to 0.30 mg per shrimp, and 0.22 to 0.28 mg per shrimp for laboratory seawater and artificial salt controls, respectively. The control criterion for this endpoint is 0.20 mg per shrimp. MSDs calculated for the growth endpoint ranged from 16 to 31 percent, with only one site (SUBASE OF 26) exceeding 25 percent (Appendix A).

#### **5.1.3 Inland Silversides**

Both laboratory seawater and artificial salt controls met survival acceptability criteria. At 96 hours, mean control survival ranged from 96 to 100 percent across controls (> 90 percent acute criterion). MSDs ranged from 5 to 7 percent across samples. At 7-days, mean control survival and biomass ranged from 92 to 100 percent (> 80 percent chronic criterion), and from 0.46 to 0.55 mg per larva, respectively (Appendix A). The criterion for biomass is 0.50 mg per larva. Only one laboratory seawater control fell below this criterion. However, because all statistical comparisons were made using the artificial salt control, results were deemed acceptable for reporting purposes. MSDs for 7-day survival ranged from 6 to 15 percent, and those for growth ranged from 13 to 27 percent. Again, only one sample (NAVSTA OF 9) exceeded 25 percent MSD.

## **5.2 TIEs**

### **5.2.1 Blue Mussel**

EDTA controls exhibited a mean of 91 to 97 percent normal larvae and C<sub>18</sub> controls exhibited 90 to 96 percent normal larvae, indicating that both the addition of EDTA and the C<sub>18</sub> extraction process did not adversely affect the test organisms. Methanol controls in the add-back tests exhibited 94 to 99 percent normal larvae, indicating that the presence of methanol also did not adversely affect the test organisms.

### **5.2.2 Opossum Shrimp**

For the opossum shrimp, survival and growth in the EDTA and C<sub>18</sub> treatment controls were comparable to that observed in the laboratory seawater and artificial salt controls, suggesting that these treatments did not adversely affect the exposed shrimp. Mean survival ranged from 96 to 100 percent, and mean biomass ranged from 0.24 to 0.42 mg per shrimp across controls.

## **5.3 Reference Toxicant Tests**

All reference toxicant test results were within +/- 2 standard deviations of the long-term laboratory control chart averages, suggesting that the sensitivity of the test organisms and the laboratory techniques were consistent throughout the study.

## **6.0 LITERATURE CITED**

- American Society for Testing and Materials (ASTM). 1994. Standard guide for conducting static acute toxicity tests starting with embryos of four species of saltwater bivalve molluscs (E 724-89).
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- U.S. EPA. 2002. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms, Third Edition. U.S. EPA Office of Research and Development, Washington DC. EPA/821/R-02/014.

## **Addendum Report**

### **Evaluation of Toxicity due to Non-polar Organics in Sample NAVSTA OF11B**

A follow-up investigation of toxicity attributable to non-polar organic compounds in NAVSTA Sample OF11B is included in this addendum to a final stormwater toxicity report submitted to SPAWAR August 2, 2004.

This sample exhibited 3.1 TU when originally tested. While overall toxicity decreased by the time the Phase I TIE was initiated, there was still sufficient residual toxicity to determine that: 1) EDTA was able to remove most of the remaining toxicity; and 2) extraction through a C<sub>18</sub> column was able to remove all of the residual toxicity. The effectiveness of the C<sub>18</sub> column in removing all of the toxicity could be partially explained on the basis of removal of zinc and copper from solution but, since EDTA failed to remove all of the toxicity, a non-polar organic constituent was also implicated as contributing some portion of the overall toxicity observed. This hypothesis was confirmed by recovery of toxicity in a methanol elution of the C<sub>18</sub> column. Collectively, these data suggested that toxicity was primarily due to divalent cationic metals (e.g., copper and zinc), but a non-polar organic constituent also contributed to some of the observed toxicity. However, determining the actual contribution of each of these constituents to the toxicity originally observed in the sample is problematic because the relative dissipation rates of each of the contaminants are not known.

In an attempt to identify potential toxicants of concern recovered in the C<sub>18</sub> methanol extract, subsamples of three extracts (90, 95, and 100 percent methanol) were submitted to CRG Marine Laboratories (CRG) for analysis using GCMS, as described in the attached report from CRG. These extracts were selected because toxicity was recovered in the 95-% methanol fraction, but not in either of the adjacent fractions. Thus, comparing relative concentrations in these fractions would help differentiate among constituents present in more than one fraction, in that the fraction exhibiting the highest concentration should also exhibit the greatest toxicity.

The constituents exclusively detected with certainty in only the 95 percent methanol extract were: 1) nonylphenol (NP), and 2) tetramethylbutyl phenol. Phthalate and phthalate esters were detected in all extracts, but were believed to be a result of laboratory contamination. Two additional compounds, 1-nitroso-3-piperidinol and benzoic acid, were also detected in all three extracts, and eluted early in the chromatograms. Consequently, CRG felt they were most likely caused by trace contamination of the methanol solvent. Since toxicity was not present in the 90 and 100 percent methanol extracts, these compounds were not considered to be of toxicological

concern.

Because of the known properties and toxicity of NP, the concentration of this compound was subsequently quantified in the methanol extracts using GCMS. The molecular composition of NP is very similar to tetramethylbutyl phenol and the two compounds may be from a common source.

Analytical results identified five isomer peaks for NP. Total concentrations in the raw methanol extract and within the toxicity test chambers for the methanol add-back study are provided below. Summing the concentrations in the three extracts results in a final estimated concentration of 0.18 µg/L NP in the original sample.

**Nonylphenol Concentrations (µg/L)  
NAVSTA OF 11B**

<b>Sample OF11B</b>	<b>90% Extract</b>	<b>95% Extract</b>	<b>100% Extract</b>
Methanol extract (concentrated 500x)	13.3	57.9	19.6
Toxicity test chambers with methanol extract (concentrated 4X)	0.11	0.46	0.16

A review of toxicity data in EPA's ECOTOX database found a wide range of toxicity values for nonylphenol. On the low end of the curve are NOEC and LOEC values in the range of 5 to 15 µg/L for *Daphnia magna* reproduction, fathead minnow survival, rainbow trout growth, and copepod population effects. Published acute LC50 values for *Americamysis bahia* are in the range of 50 to 100 µg/L for 4-nonylphenol (Lussier et al, 2000). Published nonylphenol LC50 values for *Mytilus edulis* range from 140 µg/L following an 850 hr exposure to 3000 µg/L following a 96-hr exposure (Granmo et al., 1989).

These published values are greater than the concentration of NPE present in the toxic methanol extract at 4X, and calculated for the OF 11B sample based on the totals found in the methanol extracts. Thus, this comparison does not provide a clear indication that there was sufficient NP (and TMBP) present to account for toxicity, although their presence in the toxic fraction is highly suggestive. Alternatively, NP could be a marker for a constituent present in the 95-percent

methanol fraction that was not amenable to analysis with GCMS.

Nonylphenol is a degradation product from a broader class of compounds known as nonylphenol ethoxylates (NPEs). The following information on NPs and NPEs was obtained from a report entitled “Assessment Report - Nonylphenol and its Ethoxylates” by Environment Canada, January 12, 2005. NPEs are common components in detergents, emulsifiers, wetting agents and dispersing agents. Nonylphenol polyethoxylate-containing products are used in many sectors, including textile processing, pulp and paper processing, paints, resins and protective coatings, oil and gas recovery, steel manufacturing, pest control products and power generation. A variety of cleaning products, degreasers and detergents are also available for institutional and domestic use. NPEs are also used in a wide range of consumer products, including cosmetics, and cleaners and paints.

NPEs and their degradation products (including NP) are not produced naturally. The mechanism of degradation is complex but, in general, there is an initial loss of ethoxylate (EO) groups from the original moiety. The intermediate and final products of metabolism are more persistent than the parent NPEs but, ultimately, are expected to undergo biodegradation. Under aerobic and anaerobic treatment conditions, biodegradation to more toxic (and estrogenic) metabolites occurs. These products are NP, nonylphenol ethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), nonylphenoxyacetic acid (NP1EC), and nonylphenoxyethoxyacetic acid (NP2EC). In aquatic environments, primary biodegradation of NPEs is fast, but the resultant products, such as NP1EO, NP2EO, NP1EC, NP2EC and NP, are moderately persistent, especially under anaerobic conditions. Unfortunately, there is currently very limited published toxicity data available for NPEs. No data were available in ECOTOX.

Although we were able to quantify the concentration of NP in the extracts, CRG was not able to quantify the concentration of any of the NP ethoxylates using GCMS. The concentration of NP corresponds well to toxicity in the methanol extract, thus NP and the similar compound recovered, tetramethylbutyl phenol, may serve as good surrogate markers for NPE and its various degradation products. Based on the current weight of evidence, the summed concentrations of the various degradation products may explain the small proportion (approximately 16 percent) of toxicity in the OF11B sample that was unaccounted for after addition of EDTA.

## **References**

- Environment Canada, 2005. Assessment Report – Nonylphenol and its Ethoxylates.  
<http://www.ec.gc.ca/substances/ese/eng/psap/final/npe.cfm>
- Grammo, A., R. Ekelund, K. Magnusson, and M. Berggren. 1989. Lethal and sublethal toxicity of 4-Nonylphenol to the common mussel (*Mytilus edulis* L.). Environ. Pollut. 59(2):115-127.
- Lussier, S.M., D. Champlin, J. LiVolsi, S. Poucher, and R.J. Pruell. 2000. Acute toxicity of para-Nonylphenol to saltwater animals. Environ. Toxicol. Chem 19(3):617-621.

## **APPENDIX F**

### **TIE2 Report**

Please note that the report in this appendix was generated with slightly different acronyms from those used throughout the body of the report and other appendices. The differences are as follows:

MAIN REPORT	THIS APPENDIX
NI	NASNI





# Toxicity Identification Evaluation (TIE) Study of San Diego Bay Stormwater

*March 19, 2005 Sampling Event*

## FINAL REPORT

Response to External Comments Included

**Prepared for:** Computer Sciences Corporation  
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**Submitted:** April 26, 2006

### **Data Quality Assurance:**

- Nautilus Environmental is a certified laboratory under the State of California Department of Health Services Environmental Laboratory Accreditation Program (ELAP), Certificate No. 1802.
- All test results included in this report have met internal Quality Assurance/Quality Control (QA/QC) requirements, as well as minimum acceptability criteria as outlined in their respective protocols.
- All data have been reviewed and verified.
- Any test data discrepancies or protocol deviations have been noted in the summary report pages.

Results verified by: **Chris Stransky, Laboratory Manager**

Date: **April 26, 2006**

## **1.0 INTRODUCTION/ EXECUTIVE SUMMARY**

The toxicity of stormwater samples from four outfall locations (identified as NAB OF 9, NAB OF 18, NASNI OF 23a, and NASNI OF 26) and four receiving water samples from San Diego Bay collected near each of the outfall locations was evaluated using a suite of marine test species including *Mytilus galloprovincialis* (Mediterranean mussel), *Atherinops affinis* (Pacific topsmelt), and *Americamysis bahia* (mysis shrimp). All samples were collected during a light rain event (approximately 0.1 inch), which occurred on March 19, 2005. Mussel embryo development was evaluated following a 48-hour exposure to the samples and survival of mysids and topsmelt was evaluated following an acute 96-hour exposure. Toxicity Identification Evaluation (TIE) studies were performed on samples that exhibited toxicity to any of the test species. Of the eight samples tested, three of the stormwater samples (NAB OF 9, NAB OF 18, and NASNI OF 23a) exhibited toxicity to one or more of the species tested. Two of these samples (NAB OF 18 and NASNI OF 23a) were toxic to all three species tested. Sample NAB OF 9 was toxic to mussels and mysids, but not to topsmelt. The trace metals copper and zinc were wholly responsible for toxicity to mussels in this sample. Zinc, and a possible contribution from copper were responsible for toxicity to mysids in Sample NAB OF 9. A combination of toxicants including copper, zinc, and surfactants were responsible for toxicity to mussels in both NAB OF 18 and NAB OF 23a. Evidence suggests that surfactants were responsible for all toxicity observed in NAB OF 18 and NASNI OF 23a for both mysids and topsmelt. None of the bay receiving water samples were toxic to any of the species tested. All toxicity tests and TIE procedures were performed at Nautilus Environmental's San Diego location (Nautilus). Supporting analytical testing was conducted in partnership with Calscience Environmental Laboratories (CEL), located in Garden Grove, California. Results of the screening studies, Phase I TIEs, and Phase II/III TIEs are presented in this report. Toxicity screening studies were initiated on March 19, 2005 and TIE evaluations were performed between March 24 and May 23, 2005.

## **2.0 MATERIALS AND METHODS**

### **2.1 Test Material**

Stormwater samples were collected on March 19, 2005 between 2:25 and 4:25 AM under the supervision of Chuck Katz at SPAWAR. The samples were collected in plastic-lined, 19-L plastic buckets using peristaltic pumps to fill each container. As soon as sampling was completed, the buckets were transported to Nautilus by SPAWAR personnel. Upon arrival at the laboratory, each sample was assigned a tracking number, and water quality measurements

of temperature, pH, dissolved oxygen (DO), conductivity or salinity, alkalinity, and hardness were recorded (Table 1).

Temperature and conductivity or salinity were measured with an Orion 130 meter. DO was measured using a YSI 55 meter, and an Orion 250A+ meter was used to measure pH. Alkalinity (Hach Method 8203) and hardness (Hach Method 8213) were checked using Hach digital titrators (Model 16900). The samples were held at 4°C in the dark at Nautilus prior to testing. Appropriate chain-of-custody (COC) procedures were followed during all phases of this study. Copies of the COC forms for this study are attached in Appendix F.

## **2.2 Test Design and Bioassay Procedures**

The overall experimental design was built to facilitate comparisons of sensitivity between species and identify the presence and degree of acute toxicity. The Navy's stormwater permit requires evaluation of acute toxicity with both mysid shrimp (*Americamysis bahia*) and topsmelt (*Atherinops affinis*). However, the 48-hour mussel embryo development test (using *Mytilus galloprovincialis*) was also incorporated into this study design because of its known sensitivity to copper, a contaminant known to be historically relevant at these sites. TIEs were then performed using any species exhibiting toxicity to any sample material.

The results of the screening tests were used to select samples that would be amenable to follow-up investigation of the cause of toxicity. In general, TIEs have the highest probability of success if conducted on samples that produce well-defined toxic responses that do not dissipate quickly over time. Consequently, a degree of response that can be clearly separated from the control is highly desirable. While this ultimately depends on the number of replicates used and the variability of the results, our experience suggests that a minimum of a 20-percent difference from the control usually provides sufficient resolution against which to judge the effectiveness of the various treatments. These treatments can then be used to determine the general characteristics of the toxicant, and ultimately to identify and confirm the cause of toxicity.

**Table 1. Water Quality Parameter Measurements upon Sample Receipt.**

Site ID	Date Collected	Date Received	Temp. (°C)	pH (units)	DO (mg/L)	Conductivity (µmhos/cm) or Salinity (ppt)	Alkalinity (mg/L CaCO <sub>3</sub> )	Hardness (mg/L CaCO <sub>3</sub> )
<b>NAB OF 9</b>	3/19/05	3/19/05	15.9	7.54	8.7	8140 <sup>a</sup>	60	794
<b>NAB OF 18</b>	3/19/05	3/19/05	15.9	7.53	8.5	2260 <sup>a</sup>	55	379
<b>NASNI OF 23a</b>	3/19/05	3/19/05	16.6	7.71	10	443 <sup>a</sup>	35	95
<b>NASNI OF 26</b>	3/19/05	3/19/05	18.1	8.07	6.8	21000 <sup>a</sup>	162	>1000
<b>NAB OF 9 Bay</b>	3/19/05	3/19/05	16.0	8.20	8.3	32.1 <sup>b</sup>	94	NA
<b>NAB OF 18 Bay</b>	3/19/05	3/19/05	15.3	8.14	8.0	32.1 <sup>b</sup>	115	NA
<b>NASNI OF 23a Bay</b>	3/19/05	3/19/05	16.3	8.19	8.4	32.7 <sup>b</sup>	113	NA
<b>NASNI OF 26 Bay</b>	3/19/05	3/19/05	16.3	8.19	8.4	32.7 <sup>b</sup>	113	NA

Note: <sup>a</sup> conductivity or <sup>b</sup> salinity

NA - not applicable, as hardness is not measured in saline samples

The Mediterranean mussel embryo development assay was performed in accordance with “Conducting Static Acute Toxicity Tests Starting with Embryos of Four Species of Saltwater Bivalve Molluscs (E 724-98)” (ASTM 1999). Procedures for testing stormwater using mysid shrimp and Pacific topsmelt acute survival tests followed “Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. Fifth Edition. (EPA-821-R-02-012)” (EPA 2002a).

Procedures for performing Phase I TIEs are outlined in “Methods for Aquatic Toxicity Identification Evaluations – Phase I Toxicity Characterization Procedures, Second Edition (EPA/600/6-91/003)” (EPA 1991), “Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I (EPA/600/6-91/005F)” (EPA 1992), and “Marine Toxicity Identification Evaluation (TIE) – Phase I Guidance Document” (EPA 1996). Procedures for performing Phase II and III TIEs are outlined in “Methods for Aquatic Toxicity Identification Evaluations – Phase II Toxicity Identification Procedures for Samples Exhibiting Acute and Chronic Toxicity (EPA/600/R-92/080)” (EPA 1993a), and “Methods for Aquatic Toxicity Identification Evaluations – Phase III Toxicity Confirmation Procedures for Samples Exhibiting Acute and Chronic Toxicity (EPA/600/R-92/081)” (EPA 1993b), respectively.

### **2.2.1 Screening Bioassays**

#### **Mediterranean Mussel Embryo Development Test**

The Mediterranean mussel, *Mytilus galloprovincialis*, was field collected by Nautilus personnel in Mission Bay, San Diego, California and transported to Nautilus in ice chests containing blue ice. In the laboratory, the organism receipt date and arrival condition were recorded in a logbook. The mussels were then acclimated to test temperature and salinity, and observed each day prior to test initiation for any indications of significant mortality (>10%).

Mussel embryos were exposed to stormwater for a period of 48 hours to evaluate effects on embryo development. Original screening tests were conducted using a sample concentration series of 12.5, 25, 50 percent, and the highest testable concentration (dependent upon the initial salinity of the sample) along with a concurrent negative control. Test solutions were prepared using graduated cylinders and pipettes. TIE testing was conducted on a reduced dilution series to focus resources on the concentrations most likely to express toxicity. Due to the low salinities of the samples, hypersaline brine was added to each sample to raise the salinity to 32 ppt. The volume of hypersaline brine required to adjust the salinity determined the highest testable concentration for each sample. An additional negative control composed of

hypersaline brine and deionized water was also tested to ensure any observed toxic effects were not due to the brine.

Measurements of pH, DO, temperature, and salinity were recorded for each test concentration and control. Five replicate test chambers were prepared for each test concentration and control. Replicates consisted of 30-ml shell vials containing 10 ml of test solution. Test solutions were acclimated to 15°C in temperature-controlled environmental chambers prior to initiation.

In order to spawn the mussels, brood stock were exposed to heated ultraviolet (UV) treated seawater (27-29°C) in shallow plastic trays. Within 60-90 minutes, the mussels began to spawn. Spawning individuals were removed and isolated in individual 250-ml beakers containing 20°C seawater. After allowing individuals to continue to spawn for 30 minutes, the quality of the eggs was examined under a compound microscope. The three “best” egg stocks (as defined by microscopic observations of egg shape, color, and opacity) were poured into 1-L Erlenmeyer flasks and each was fertilized with sperm from at least three different males. Fertilization was allowed to continue for twenty minutes. Each sperm-egg stock mixture was then poured through a 20-µm screen allowing sperm to pass through while retaining fertilized eggs. The three embryo stocks were allowed to develop for approximately two hours in a 15°C environmental chamber. A 1-ml aliquot was then removed from each embryo stock and examined under a compound microscope. The embryo stock that exhibited the furthest development (i.e., most number of cleavages per cell) was diluted to a concentration of 400 embryos/ml, and 0.5 ml of this stock was added to each vial to initiate testing. Mussel embryos were exposed to a 16:8 hour light:dark illumination cycle for the duration of the test. Test chambers were covered with a clear Plexiglas sheet to reduce evaporation and prevent test solution contamination.

Temperature, pH, DO, and salinity were measured daily in surrogate test chambers for each concentration and control. At test termination, larvae in each test chamber were preserved with 1 ml of seawater-buffered Formalin prior to evaluation. A subsample of 100 bivalve embryos from each test chamber was counted under a compound microscope at 400x magnification. The embryos were classified as normal or abnormal. Normally developed embryos have a distinct D-shape with complete formation of the shell.

A concurrent reference toxicant test (positive control) using copper (II) chloride (CuCl<sub>2</sub>) was conducted in conjunction with the stormwater tests.

### **Mysid and Topsmelt 96-Hour Acute Tests**

Juvenile mysids and topsmelt were purchased from Aquatic Biosystems of Fort Collins, Colorado. Prior to shipment, the organisms were placed in plastic bags containing oxygenated culture water, packed in insulated containers, and transported to Nautilus via overnight delivery service. Upon arrival at Nautilus, water quality parameters of temperature, pH, DO, and salinity were measured and recorded in a logbook for each species. The condition of the organisms was also noted. The organisms were then acclimated to test salinity and temperature, and observed prior to test initiation for any indications of stress (e.g. abnormal swimming behavior) or significant mortality (>10%) and were fed *Artemia* nauplii to satiation during holding. Mysids were 3-4 days old upon arrival at Nautilus and 3-4 days old upon test initiation. Topsmelt were 11-12 days old upon arrival at Nautilus and 11-13 days old upon test initiation.

These tests estimate acute toxicity by evaluating survival of mysid shrimp or topsmelt over a 96-hour exposure period. Original screening tests were conducted using a sample concentration series of 25, 50, and 100 percent sample along with a concurrent negative control consisting of 32 ppt natural seawater. TIE manipulations and tests were conducted on the undiluted sample only. Test solutions were prepared using graduated cylinders and pipettes.

Due to the low salinities of the samples, Forty Fathoms™ sea salt was added to each sample to raise the salinity to 32 ppt. An additional control composed of Forty Fathoms™ sea salt and deionized water was also tested to ensure observed mortality was not due to the addition of artificial salt rather than other toxic constituents.

Measurements of pH, DO, temperature, and salinity were recorded for each test concentration and control. Four replicate test chambers were prepared for each test concentration and control. Replicates consisted of 400-ml plastic cups containing 250 ml of test solution. Test solutions were acclimated to 25°C for mysid and 20°C for topsmelt tests in temperature-controlled environmental chambers prior to initiation.

Five mysids were counted and transferred from holding bowls into individual plastic soufflé cups. A second technician verified counts and condition of all test organisms prior to addition of the organisms to the test chambers, and again when test initiation was complete. Due to their size, five topsmelt were counted and transferred from holding bowls directly into their corresponding test chambers. A second technician verified counts and condition of all test organisms when test initiation was complete. A 16:8 hour light:dark illumination cycle was provided for the duration of the test. Test chambers were covered with a clear Plexiglas sheet

to prevent evaporation and cross-contamination of the test solutions.

Test solutions were renewed at 48 hours. Mysids were fed twice per day and topsmelt once per day. Temperature, pH, DO, and salinity were measured daily in the test chambers for each concentration and control and in freshly prepared test solutions at the 48-hour renewal. Survival of organisms was recorded for each test chamber once per day. At test termination, final observations and counts were performed.

All copper chloride reference toxicant tests (positive control) were conducted within a 3-week period of these tests.

### **2.2.2 Phase I TIE Treatments**

Phase I TIE treatments are designed to remove, inhibit, or potentiate a particular class of compounds that may be present in the sample, thereby isolating the toxic signal. Selected treatments were applied in this study; detailed descriptions of each treatment are provided below, and a general summary of Phase I TIE characterization procedures is shown in Tables 2 and 3.

Filtered, natural seawater (mussel larvae) and artificial seawater (mysid and topsmelt) were used as dilution and control water for these studies. Untreated control water was tested concurrently with the “Baseline” (untreated) stormwater tests for each site and species. Aliquots of the appropriate control water underwent each of the Phase I manipulations (method controls) and were tested alongside the treated stormwater samples. The method controls are used to assess whether the sample manipulations resulted in adverse effects due to the procedures themselves.

### **Baseline Tests**

Baseline tests were performed concurrently with the Phase I TIE treatments to compare the organism response in untreated stormwater to responses obtained after manipulations of the sample. Treatments that altered the toxicity compared to the toxicity of the baseline test were used to identify classes of toxic compounds present in the sample.



### **EDTA Metal Chelation**

The addition of ethylenediaminetetraacetic acid (EDTA) was used to determine the extent of toxicity attributable to divalent cationic trace metals (EPA 1991). EDTA chelates divalent cationic trace metals, thereby reducing their bioavailability. EDTA was added to the method controls and all stormwater dilutions at an exposure concentration of 60 mg/L.

### **Solid-Phase Extraction**

Solid-phase extraction (SPE) with a C<sub>18</sub> column was used to determine the extent of toxicity associated with non-polar organic compounds. It has been found that C<sub>18</sub> columns also have the ability to remove some metals as well (EPA 1991). A 5-ml capacity Baker brand column was used for this procedure. Post-filtered SPE columns were labeled, wrapped in airtight re-sealable bags, and held in the dark at 4°C for potential subsequent Phase II testing.

### **Aeration**

Aeration of the sample was used to determine the extent of toxicity associated with volatile or sublutable compounds. Sublutable compounds include surface-active compounds such as resin acids, soaps, detergents, charged stabilization polymers, and coagulation polymers used in chemical manufacturing processes. Samples were heavily aerated in 1-L glass graduated cylinders for 1-hour and any foam created was collected and stored at 4°C for subsequent testing. Samples were then siphoned out of the cylinders and held in the dark at 4°C for testing.

### **Combination Treatments**

A combination of treatments can be used when more than one toxicant is suspected. This can occur when previous testing indicates that a particular treatment or set of treatments remove partial toxicity. By combining treatments, multiple contaminants can be inhibited, and when viewed in the context of results of prior testing, specific contaminants of concern can be isolated. A second round of Phase I TIE testing included two sets of combination treatments: 1) Solid-phase extraction + EDTA metal chelation, and 2) Aeration + EDTA metal chelation. The SPE + EDTA treatment was performed to determine the extent of toxicity related to both non-polar organic compounds and divalent cationic trace metals. EDTA, at a test concentration of 60 mg/L, was added to post-C<sub>18</sub> extracted sample prior to testing. The aeration + EDTA treatment was performed to determine the extent of toxicity related to both volatile or sublutable

compounds and divalent cationic trace metals. EDTA, at a test concentration of 60 mg/L, was added to post-aerated sample prior to testing.

#### **Aeration Foam Add-back**

During the first round of the TIE, any foam produced during the aeration treatment was collected and stored in a glass beaker at 4°C. Any sublutable contaminants removed during the aeration treatment (now contained in the foam extract) were added back to laboratory dilution water at 25 percent of the original sample volume (a 4X concentration).

#### **SPE Methanol Elution Add-back**

Non-polar organic compounds bound to SPE columns can be removed from the columns using methanol. Methanol extractions were performed by pumping 2 ml of 100 percent methanol through the column using a peristaltic pump set at an approximate rate of 1 ml per minute. Extracts were collected into 2-ml amber glass Voa<sup>®</sup> vials. The extracts were then added to clean dilution water at concentrations that were two times that in the original stormwater sample. Because the extraction method is not 100 percent efficient at removing contaminants from the column, concentrating the extract in this way increases the likelihood of recovering the toxicity of a sample. Concurrent method controls consisted of: 1) clean dilution water to which methanol passed through the SPE column was added; and 2) a methanol control equivalent to the highest methanol concentration achieved in the tested fractions.

#### **Anion Extraction of SPE Elution**

Anion columns were used to determine the extent of toxicity associated with anionic compounds, in particular anionic surfactants that may have been removed from solution by the C<sub>18</sub> column. Toxic C<sub>18</sub> methanol extracts were added to laboratory dilution water and then pulled through an anion column. Anionic metals (e.g. aluminum, fluoride, and bromide) will not be recovered in methanol extracts, thus this class of compounds is ruled out at this point. A 3-ml capacity Burdick & Jackson brand column was used for this procedure. Post-filtered columns were labeled, wrapped in airtight re-sealable bags, and held at 4°C for potential subsequent Phase II testing.

### 2.2.3 Phase I TIE Bioassays

#### **Mediterranean Mussel Embryo Development Test**

A dilution series was prepared for each treatment to evaluate its effectiveness at different concentrations. Bioassays were conducted following the same methods for organism procurement, test initiation, monitoring and termination previously described for screening tests. The experimental design, including number of replicates, concurrent controls and test concentrations, is summarized in Table 2.

**Table 2. Phase I TIE Toxicity Test Experimental Design – Blue Mussel**

<b>Test Procedure</b>	<b>Replicates</b>	<b>Test Solutions</b>
<b>Baseline Tests</b> (NAB OF 9, NAB OF 18 NASNI OF 23a)	5	Lab Control, Brine Control, 12.5, 25, 55 or 59% <sup>a</sup>
<b>Phase I Manipulations</b> <b>(Round One - 3/24/05)</b> (EDTA, SPE column, and Aeration)	5	Method Control, 12.5, 25, and 55 or 59% <sup>a</sup>
<b>Phase I Manipulations<sup>b</sup></b> <b>(Round Two – 4/8/05)</b> (EDTA + SPE column, EDTA + Aeration, Aeration foam add-back 4X, SPE column elution 2X, and Anion extraction of SPE elution)	5	Method Control, 61%
<b>Reference Toxicant Test</b>	5	0, 2.5, 5, 10, 20, and 40 µg/L Cu

<sup>a</sup> The highest testable concentration for each of the samples: NAB OF 9 – 59%; NAB OF 18 and NASNI OF 23a - 55%.

<sup>b</sup> Tested only with samples NAB OF 18 and NASNI OF 23a.

#### **Mysid and Topsmelt 96-hour Acute Test**

During the initial screening tests all samples, with the exception of NAB OF18, exhibited a substantial decrease in toxicity when diluted to 50 percent. Consequently, the TIE treatments were performed only on undiluted sample to maximize the likelihood of detecting a toxic signal. Fresh aliquots of samples were treated with EDTA three hours prior to the 48-hour solution renewal. However, due to the time associated with C<sub>18</sub> column extraction, a sample volume adequate for the test initiation and renewal was prepared the day prior to test initiation. All remaining aspects of the tests pertaining to organism procurement, test initiation, monitoring

and termination were conducted following the same methods previously described for the screening tests. Experimental design, including number of replicates, concurrent controls, and test concentrations is summarized in Table 3.

**Table 3. Phase I TIE Toxicity Test Experimental Design – Mysids and Topsmelt**

Test Procedure	Replicates	Test Solutions
<b>Baseline Test</b> (NAB OF 9 <sup>a</sup> , NAB OF 18 NASNI OF 23a)	4	Lab Control, Salt Control, and 100%
<b>Phase I Manipulations (Round One – 3/30/05)</b> (EDTA Chelation, SPE column, and Aeration)	4	Method Control and 100%
<b>Phase I Manipulations<sup>b</sup> (Round Two – 4/21/05)</b> (EDTA + Aeration, Aeration foam add-back 4X, SPE column elution 2X, and Anion extraction of SPE elution)	4	Method Control and 100%
<b>Reference Toxicant Tests</b>		
Mysid	4	0, 37.5, 75, 150, 300, and 600 µg/L Cu
Topsmelt	4	0, 25, 50, 100, 200, and 400 µg/L Cu

<sup>a</sup> Mysid only

<sup>b</sup> Tested only with mysids and sample NAB OF 18

#### **2.2.4 Phase II/III TIEs**

During Phase II/III TIE procedures, additional testing was performed in an effort to identify and confirm specific contaminants responsible for toxicity. Specific Phase II/III methods depended upon the results obtained during Phase I testing in which metals, specifically copper and zinc, were suspected to be a major source of toxicity. Confirmation of these suspected toxicants was performed using a combination of statistical and experimental procedures to provide additional lines of evidence that supported the identification process. The Phase II/III TIE procedures were conducted using the mysid acute survival test due to its permit compliance relevance. For comparison and clarification, results of similar Phase II/III TIE procedures performed and reported during the 2004 storm season using the Mediterranean mussel are also reported.

### **Copper and Zinc Mixture Studies**

Based on Phase I TIE and analytical chemistry results, studies were conducted to evaluate the combined toxicity of copper and zinc to mysids. This same set of experiments and associated results for the Mediterranean mussel were previously provided to SPAWAR in a report submitted in August 2004. Four bioassays were conducted using clean laboratory seawater and analytically verified trace metal stock solutions: 1) a mixture of copper and zinc at concentrations based on the ratio of the two metals in the stormwater samples; 2) a mixture of copper and zinc at concentrations based on the ratio of their individual acute Median Lethal Effect (LC<sub>50</sub>) Concentrations; 3) a copper reference toxicant test; and 4) a zinc reference toxicant test. Results from these studies were used to evaluate the extent to which each of the two metals contributed to overall toxicity in the stormwater samples, and if the two metals exhibited additive or synergistic toxicity. All aspects of these bioassays were conducted similarly to screening tests.

### **2.3 Statistical Analyses**

Proportional data (e.g. percent normal embryos, percent survival) were arcsine square-root transformed prior to analysis. To determine if parametric or non-parametric statistical methods could be applied to the data, the data were evaluated for normality (Shapiro-Wilks Test) and homogeneity of variance (Bartlett's Test). Depending on the results of these tests, Steel's Many One Rank Test (non-parametric) or Dunnett's Test (parametric) was used to identify significant differences between each concentration and the appropriate control (brine or salt). Minimum Significant Differences (MSDs) were calculated as a percentage of the control response for each test, based on Dunnett's t-statistic. For a more detailed analysis of MSD relationships see Appendix G. Note that this procedure likely overestimates test sensitivity in cases where the test endpoints were determined with non-parametric methods.

LC<sub>50</sub> and/or Median-Effect (EC<sub>50</sub>) concentration values were also calculated for all tests that exhibited a dose-response curve. These endpoints were calculated with Maximum Likelihood Probit, or Trimmed Spearman-Kärber methods depending on specific assumptions met by the data. Comprehensive Environmental Toxicity Information System (CETIS), version 1.025b, was used for these analyses.

## **2.4 Analytical Chemistry**

Based on historical chemical and toxicological data available for the four stormwater outfalls, subsamples from each site were analyzed for a suite of total and dissolved trace metals. Samples were filtered through a Gelman 0.45- $\mu$ m glass fiber filter at Nautilus on the day of sample receipt within 24 hours of collection for analysis of the dissolved fraction. Because C<sub>18</sub> SPE columns can bind some trace metals in addition to non-polar organic substances, subsamples were also collected from NAB OF 18 and NASNI OF 23a following C<sub>18</sub> SPE column extraction and analyzed for the same suite of trace metals to determine if a reduction in toxicity following C<sub>18</sub> SPE extraction may be due to removal of trace metals.

Due to their prevalence in stormwater runoff, and observation of some foaming in samples when poured, surfactants were measured by analyzing methylene blue activated substances (MBAS) both prior to and after aeration of the samples. MBAS includes a common group of anionic surfactants known as linear alkyl sulfonates (LAS). Surfactants were analyzed by CEL following EPA Method 425.1.

## **2.5 Quality Assurance**

Nautilus implements quality assurance (QA) procedures in accordance with our internal QA Plan, which is based on applicable protocols and guidance documents. These procedures encompass all aspects of testing, including the source, handling, condition, receipt, and storage of samples and test organisms, and the calibration and maintenance of instruments and equipment. All data generated by the laboratory are monitored for completeness and accuracy at the end of each day, and at the end of each individual test period. Laboratory controls are conducted concurrently with every assay. In addition, reference toxicant tests are performed concurrently with every assay, or on a monthly basis, to confirm that test organism quality, and laboratory conditions and procedures, remain consistent over time.

### **3.0 RESULTS AND DISCUSSION**

Detailed descriptions of the results of screening tests and all TIE procedures are presented in the following sections. Tables summarizing the toxicity data are presented in Appendix A. Statistical summaries and raw bench datasheets are presented in Appendix B. Appendix C contains reference toxicant test results, as well as a laboratory quality control chart for each species. Analytical chemistry reports from CEL are in Appendix D, and sample receipt information and COC forms, are contained in Appendices E and F, respectively.

#### **3.1 Screening Bioassays**

The results of the initial toxicity screening tests performed on March 19, 2005 are summarized in Figures 1 through 6 and Appendix Tables A-1 through A-5.

##### **3.1.1 Stormwater Outfall Samples**

###### **Mussel Embryo Development**

Three stormwater samples (NAB OF 9, NAB OF 18, and NASNI OF 23a) exhibited appreciable toxicity to mussel embryos; no normal development was observed in the highest testable concentration (57 to 69 percent) of each sample, and EC<sub>50</sub> values ranged from 12 to 22 percent stormwater (Figure 1). Based on these data, all of these samples exhibited sufficient toxicity to trigger a Phase I TIE. One sample, NASNI OF 26, was not toxic to mussels with a mean of 89 percent of the embryos exhibiting normal development in the highest concentration tested (69 percent).

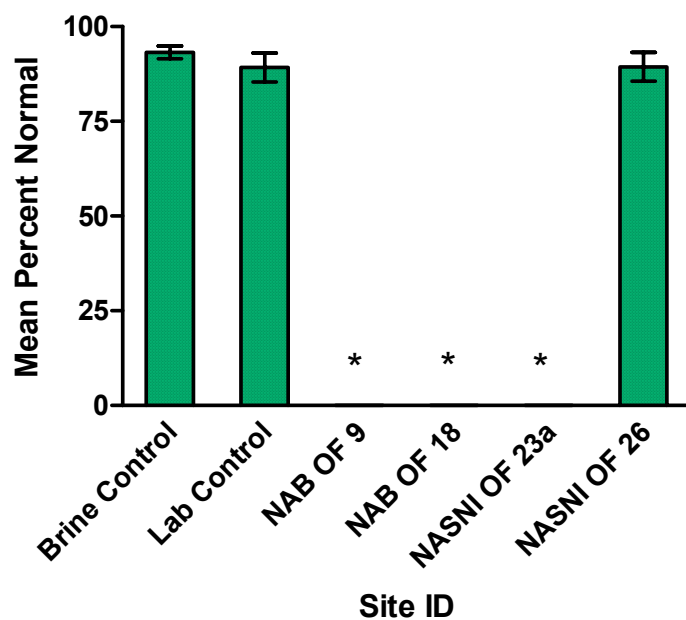
###### **Mysid Shrimp Acute Survival**

At 96 hours, mean survival of mysids among all four undiluted stormwater samples ranged between 5 and 95 percent, compared with 95 to 100 percent in the controls (Figure 2). Three of these samples (NAB OF 9, NAB OF 18, and NASNI OF 23a) exhibited at least a 20 percent reduction in survival relative to the controls; however, only NAB OF 9 and NAB OF 18 were statistically significant. The site with the lowest survival (NAB OF 18) exhibited an LC<sub>50</sub> value of 42 percent. The LC<sub>50</sub> value for NAB OF 9 exceeded 100 percent.

###### **Pacific Topsmelt Acute Survival**

Mean acute survival in the four undiluted stormwater samples ranged between 0 and 100 percent, compared with 100 percent in both controls (Figure 3). Two of these samples (NAB OF

18 and NASNI OF 23a) exhibited at least a 20 percent reduction in survival relative to the controls, and both were statistically significant. Similar to mysids, the site with the lowest survival (NAB OF 18) had an LC<sub>50</sub> value of 38 percent, while LC<sub>50</sub> values for all other samples exceeded 100 percent.



**Figure 1. Stormwater Toxicity Screening Test Results for Mussel Embryo Development (100 percent sample). Mean values are presented  $\pm$  1 standard deviation. Asterisks indicate significant differences relative to the brine control.**



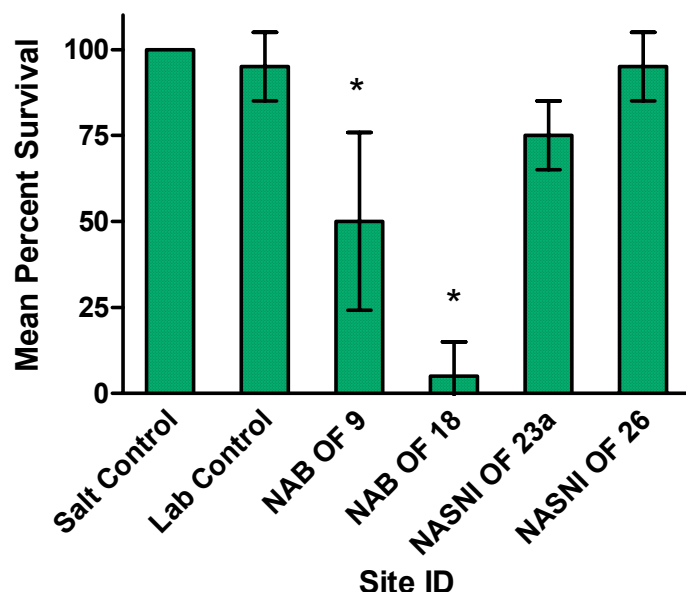


Figure 2. Stormwater Toxicity Screening Test Results for Mysid Shrimp Survival (100 percent sample). Mean values are presented  $\pm$  1 standard deviation. Asterisks indicate significant differences relative to the salt control.

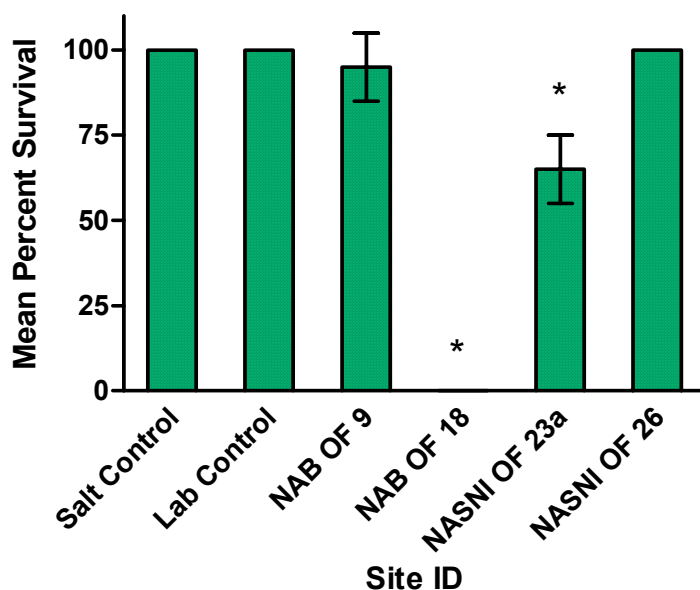
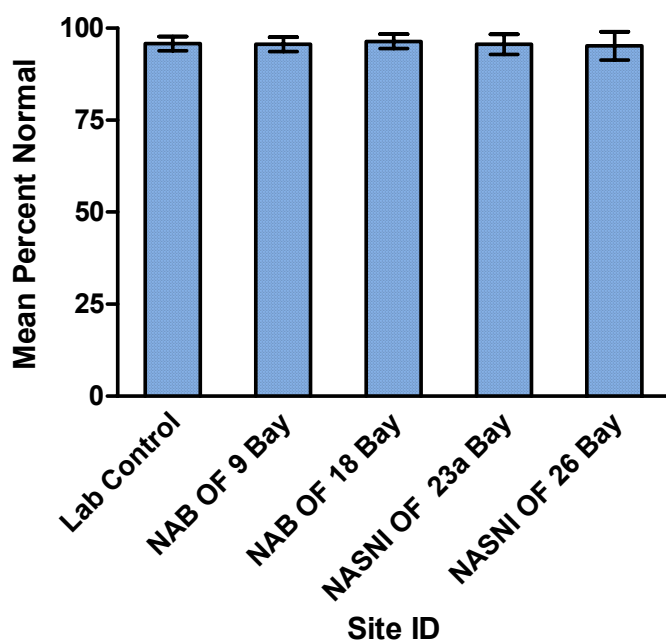


Figure 3. Stormwater Toxicity Screening Test Results for Pacific Topsmelt Survival (100 percent sample). Mean values are presented  $\pm$  1 standard deviation. Asterisks indicate significant differences relative to the salt control.

### 3.1.2 Bay Water Samples

All samples collected from the receiving water of San Diego Bay near each outfall were non-toxic to all three test species. Mean mussel embryo development ranged from 95 to 96 percent and mysid and topsmelt acute survival ranged from 95 to 100 percent among all four samples tested (Figures 4 through 6). Based on salinity, these samples were greater than 50 percent bay water.



**Figure 4. Bay Water Toxicity Screening Test Results for Mussel Embryo Development (100 percent sample). Mean values are presented  $\pm$  1 standard deviation.**

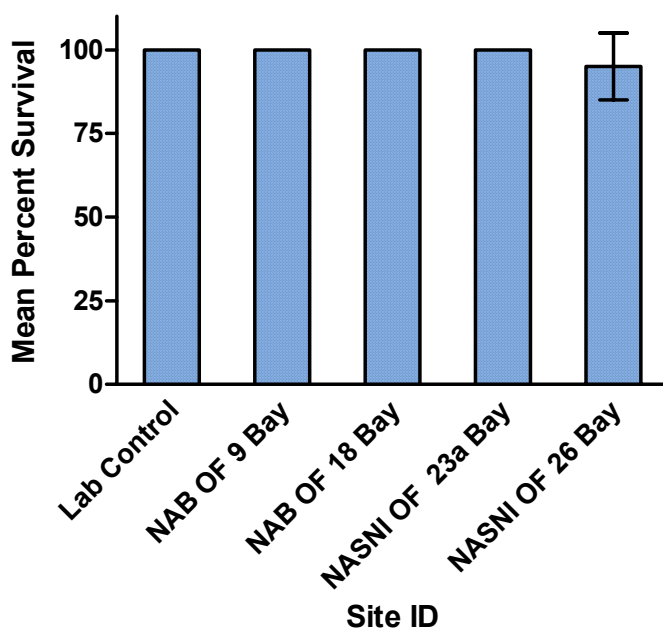


Figure 5. Bay Water Toxicity Screening Test Results for Mysid Shrimp Survival (100 percent sample). Mean values are presented  $\pm$  1 standard deviation.

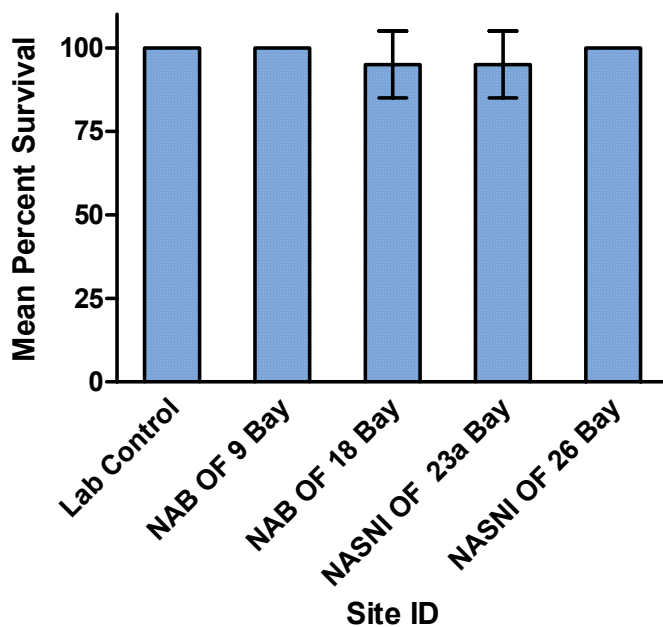


Figure 6. Bay Water Toxicity Screening Test Results for Pacific Topsmelt Survival (100 percent sample). Mean values are presented  $\pm$  1 standard deviation.

### **3.2 Phase I TIEs**

Phase I TIEs were initiated on samples that exhibited clear evidence of toxicity during the screening tests (statistically significant and/or at least a 20 percent difference from the control). On this basis, three of the samples tested with both mussels and mysids qualified for a TIE (NAB OF 9, NAB OF 18, and NASNI OF 23a) and two of these samples (NAB OF 18 and NASNI OF 23a) qualified for a TIE using Pacific topsmelt.

#### **3.2.1 Mediterranean Mussel**

##### **Baseline Tests**

The magnitude of toxicity was similar between the screening tests conducted on March 19, 2005 and Baseline tests conducted five days later with the TIE on March 24, 2005 (Figure 7). There was, however, a slight decrease in toxicity for NASNI OF 23a, with normal development between the two test dates increasing from 24 to 88 percent in the 25 percent dilution. A second round of Baseline tests conducted on April 8, 2005 for NAB OF 18 and NASNI OF 23a remained toxic, with mean normal development of zero and one percent, respectively in a 61 percent dilution (Figure 8). Normal development in Baseline controls ranged from 90 to 98 percent.

##### **Toxicant Characterization**

###### ***Round One Test Series***

Results of the initial Phase I TIE treatments performed on March 24, 2005 are shown in Figure 7 and summarized in Appendix Table A-6. The EDTA treatment essentially eliminated toxicity in NAB OF 9. While EDTA increased the proportion of normal larvae in NAB OF 18 and NASNI OF 23a, it did not completely eliminate toxicity in these samples.

Extraction through a SPE C<sub>18</sub> column eliminated toxicity in NASNI OF 23a. Aeration also eliminated most of the toxicity observed in this sample. Both aeration and C<sub>18</sub> treatments removed a portion but not all of the toxicity in NAB OF 18, and no toxicity was removed following these treatments in NAB OF 9.

Based on the effectiveness and specificity of the EDTA treatment, these data suggest that toxicity in sample NAB OF 9 was due largely to divalent cationic metals. Subsequent Phase I testing was, therefore, not performed for this sample.

Mean normal development in the treatment controls ranged from 92 to 98 percent, with the exception of the aeration treatment, which had slightly lower normal development between 84 and 91 percent.

### ***Round Two Test Series***

TIE results for Samples NAB OF 18 and NASNI OF 23a were investigated further on April 8, 2005 by performing a combination of characterization treatments shown in Figure 8 and summarized in Appendix Table A-7.

#### **NAB OF 18**

Addition of EDTA following both extraction through a C<sub>18</sub> column and aeration treatments successfully eliminated toxicity in NAB OF 18. These treatments suggest that all observed toxicity is due to a combination of cationic trace metals and an organic that is removed or detoxified by both the C<sub>18</sub> and aeration treatments. The presence of a toxic organic constituent in NAB OF 18 was verified by testing a methanol elution of the C<sub>18</sub> column; toxicity was recovered in this elution at a 2X add-back, suggesting relatively good recovery from the column. Foam collected during the aeration process was also toxic when added back to dilution water at a 4X concentration. Based on prior experience, these results, in combination with the degree of foaming observed during the aeration test, are consistent with characteristics exhibited by surfactants. To further investigate this hypothesis, the toxic 2X methanol elution was pulled through an anion exchange column and retested. Toxicity of the methanol extract was eliminated following this procedure indicating that the organic toxicant in the extract is anionic, thus providing further supporting evidence that the organic toxicant of concern is an anionic surfactant.

#### **NASNI OF 23a**

Results for NASNI OF 23a were also investigated further by performing a similar combination of characterization treatments as shown in Figure 8. Addition of EDTA following the aeration treatment removed all observed toxicity in this sample. Similar to NAB OF 18, the foam add-back procedure also elicited a strong toxic response. Unlike NAB OF 18, however, the C<sub>18</sub> methanol elution add-back was not toxic at 2X add-back. Although evaluation of anion toxicity in the C<sub>18</sub> elution was not possible due to the lack of toxicity in the methanol extract, the results for this sample also suggest that toxicity is due to a surfactant in addition to cationic trace metals. All treatment method controls for this series of tests exceeded 90 percent normal development.

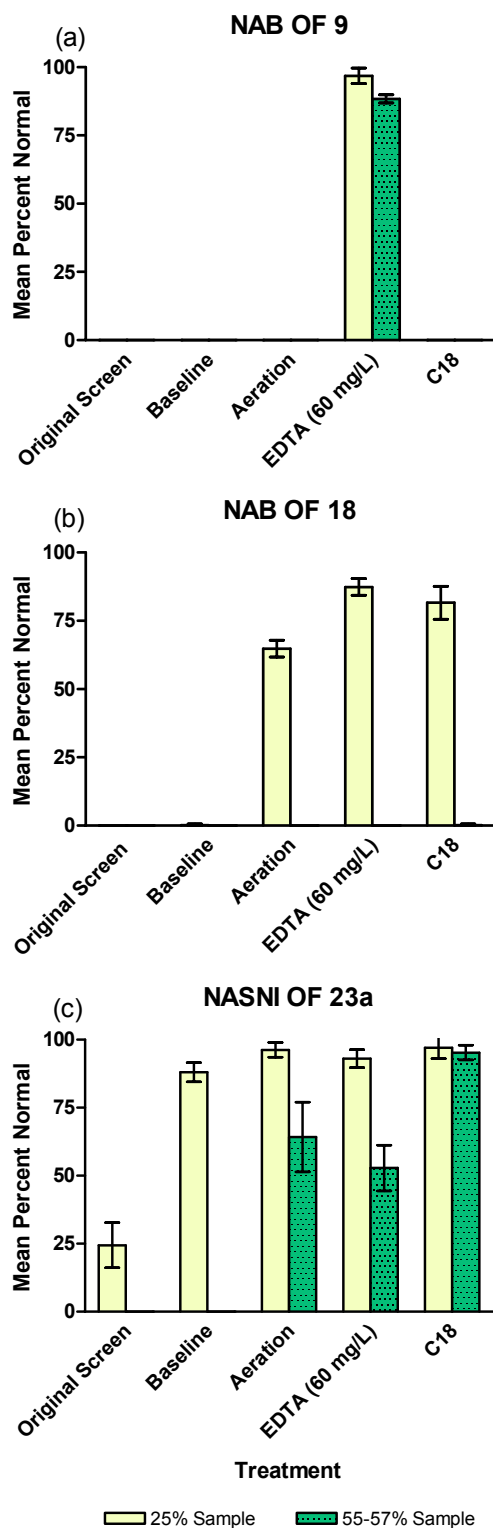
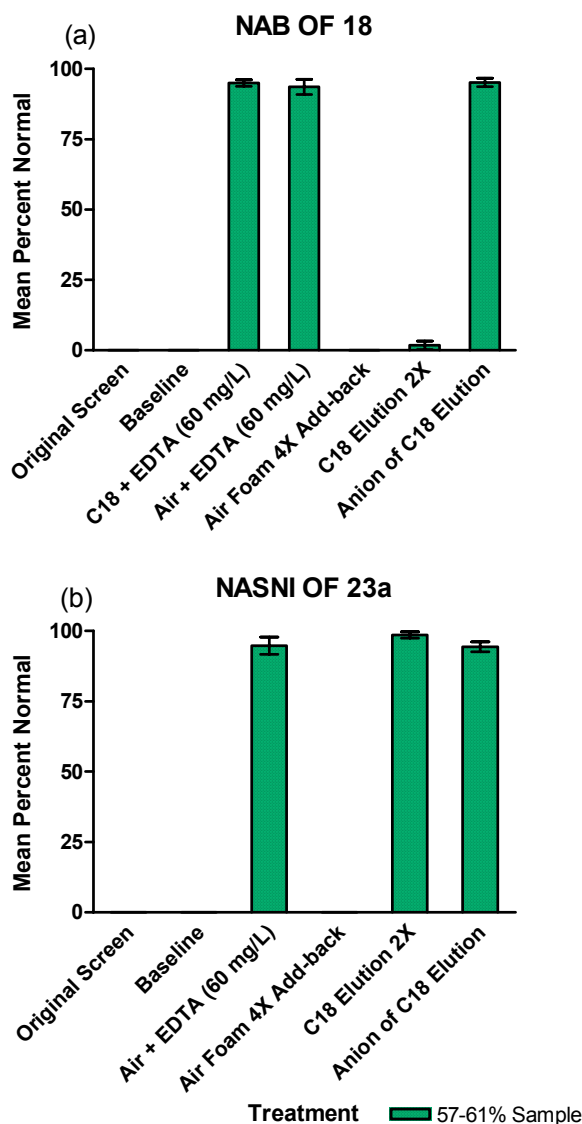


Figure 7. Mussel Phase I, Round 1 TIE results (March 24, 2005). Mean results are presented  $\pm 1$  standard deviation for: (a) NAB OF 9; (b) NAB OF 18; and (c) NASNI OF 23a. Mean normal development in the treatment controls ranged from 92 to 98 percent, with the exception of the aeration treatment at 84 to 91 percent.



**Figure 8. Mussel Phase I, Round 2 TIE results (April 8, 2005). Mean results are presented  $\pm 1$  standard deviation for: (a) NAB OF 18; and (b) NASNI OF 23a. Mean normal development in the treatment method controls ranged from 93 to 100 percent.**

### 3.2.2 Mysid Shrimp

#### Baseline Test

The results of the Baseline tests for NAB OF 9 and NAB OF 18 conducted on March 30, 2005 concurrently with the Phase I TIE manipulations were similar to those obtained in the original screening test initiated eleven days prior on March 19, 2005, suggesting that toxicity did not

dissipate appreciably over this time period (Figure 9). Toxicity of NAB OF 9 actually appeared to increase slightly. Toxicity was no longer present in sample NASNI OF 23a when the first round of TIE treatments were initiated; however, the initial toxic response in the screening test was much less than that observed for NAB OF 9 and NAB OF 18. Toxicity dissipated completely in Sample NAB OF 18 by the time a second round of TIE treatments was initiated on April 21, 2005.

Mean survival of mysids was 100 percent in the Baseline control.

### **Toxicant Characterization**

#### ***Round One Test Series***

The results of initial Phase I TIE treatments performed on March 30, 2005 are shown in Figure 9 and summarized in Appendix Table A-8.

The EDTA treatment eliminated toxicity in sample NAB OF 9, but had no observable effect on toxicity of NAB OF 18.

Extraction through a SPE C<sub>18</sub> column eliminated toxicity of NAB OF 18. Aeration also eliminated most of the toxicity observed in this sample. Aeration and C<sub>18</sub> treatments had no effect on the toxicity of NAB OF 9.

Toxicity completely dissipated in NASNI OF 23a, eliminating any meaningful comparisons between TIE manipulations and the Baseline test for this sample.

Based on the effectiveness and specificity of the EDTA treatment, these data suggest that, like mussels, toxicity to mysids in sample NAB OF 9 was due primarily to divalent cationic metals. Subsequent Phase I testing was, therefore, not performed for this sample.

Mean survival in all method controls ranged from 90 to 100 percent.

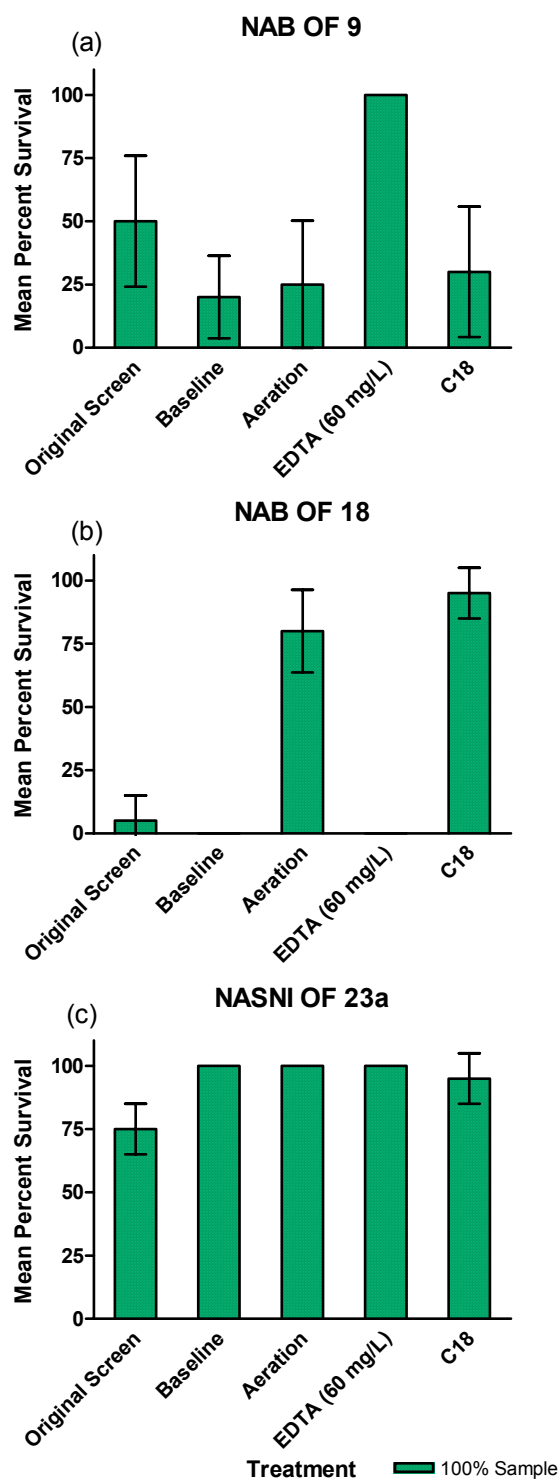
#### ***Round Two Test Series***

Results for NAB OF 18 were investigated further by performing a combination of characterization treatments on April 21, 2005. These data are shown in Figure 10 and summarized in Appendix Table A-9.

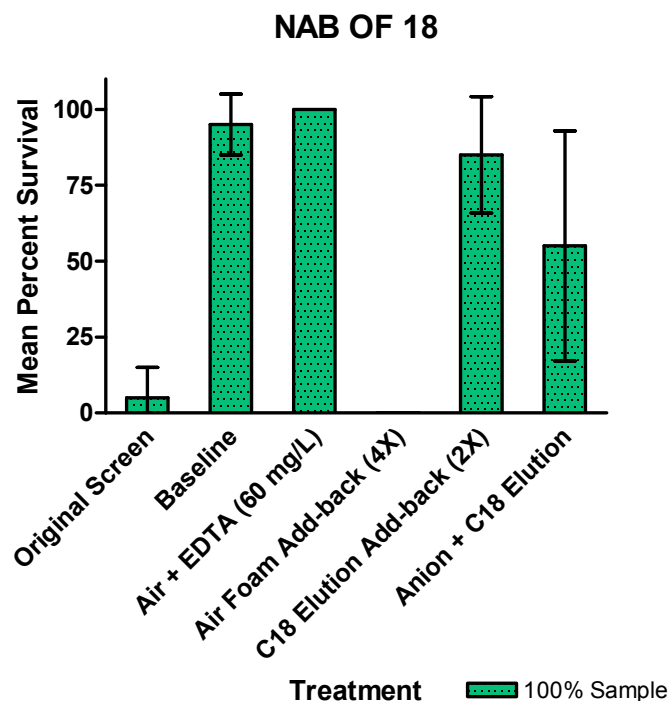
Baseline toxicity of this sample completely dissipated by the time this round of tests was



initiated almost 4 weeks post-collection. This loss of toxicity eliminates any meaningful comparisons between TIE manipulations (e.g. aeration + EDTA) and the baseline sample. Extraction of methanol through the C<sub>18</sub> column tested at a 2X add-back concentration, although successful for the mussel, failed to exhibit toxicity to mysids. This observation suggests that the organic toxicant of concern is more toxic to mussels than mysids if reduced toxicity following C<sub>18</sub> extraction was due to the same compound for both species. Foam collected during the aeration process, however, was toxic when added back to dilution water at a 4X concentration. This treatment provides strong evidence that the primary toxic constituent of concern for mysids in NAB OF18 may also be a surfactant. Mean survival of mysids in all controls ranged from 90 to 100 percent during this series of tests.



**Figure 9. Mysid shrimp Phase I, Round 1 TIE results (March 30, 2005). Mean results are presented  $\pm$  1 standard deviation for: (a) NAB OF 9; (b) NAB OF 18; and (c) NASNI OF 23a. Mean survival in all controls ranged from 90 to 100 percent.**



**Figure 10. Mysid shrimp Phase I, Round 2 TIE results (April 21, 2005). Mean results are presented  $\pm$  1 standard deviation for NAB OF 18. Mean survival in all controls ranged from 90 to 100 percent.**

### 3.2.2 Pacific Topsmelt

#### Baseline Test

Results of the Baseline test for NAB OF 18 conducted on March 30, 2005 concurrent to Phase I TIE manipulations were similar to those obtained in the original screening test initiated eleven days prior on March 19, 2005, demonstrating that toxicity did not dissipate appreciably over this time period. As with mysids, toxicity was no longer present in sample NASNI OF 23a when the first round of TIE treatments was initiated, however, the initial toxic response in the screening test was much lower than that observed for NAB OF 9 and NAB OF 18.

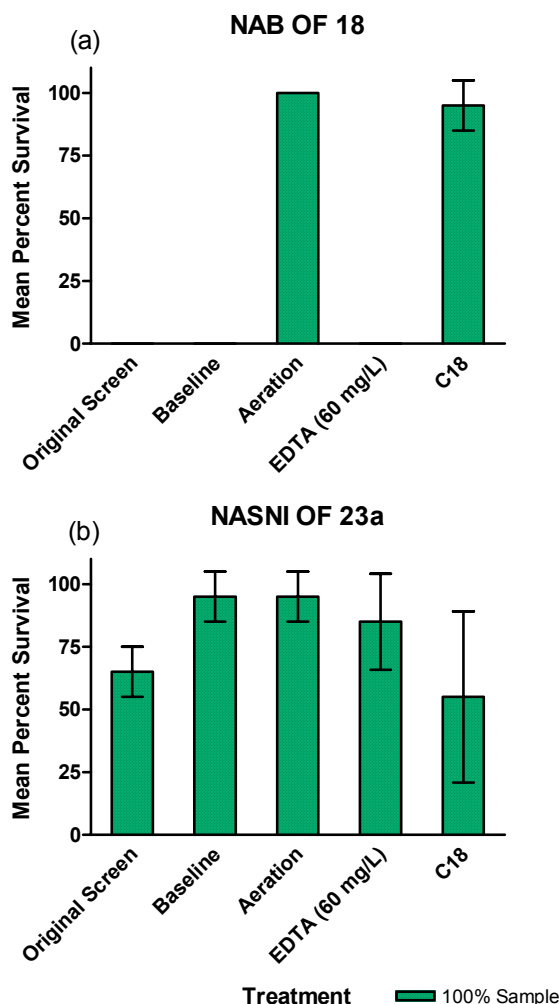
Mean survival of topsmelt in Baseline control was 100 percent.

#### Toxicant Characterization

The results of Phase I TIE treatments performed on March 30, 2005 are summarized in Figure 11 and Appendix Table A-10. Because toxicity dissipated completely in NASNI OF 23a, only results for NAB OF 18 are described.

The EDTA treatment had no observable effect on toxicity of NAB OF 18, however, both extraction through a SPE C<sub>18</sub> column and aeration eliminated toxicity in this sample. These results suggest that surfactants were the primary toxicant of concern to Pacific topsmelt in this sample. Additional TIE testing was not performed using this species due to the similarity of results observed in tests with the mysids and mussels.

Mean survival of topsmelt in all method controls ranged from 90 to 100 percent.



**Figure 11. Pacific topsmelt Phase I TIE results (March 30, 2005). Mean results are presented  $\pm$  1 standard deviation for: (a) NAB OF 18; and (b) NASNI OF 23a. Mean survival in all controls ranged from 90 to 100 percent.**

### **3.3 Phase II/III TIE Evaluation**

#### **3.3.1 Species Sensitivity to Toxicants Identified**

The absolute and relative sensitivity of the three species tested to various constituents of concern based on classes of compounds identified during the Phase I TIE characterization phase provides further evidence as to the causes of toxicity in the stormwater samples. Mussel larvae were clearly the most sensitive species tested, with adverse effects observed at concentrations as low as 12 percent sample. Based on the survival endpoint, mysid shrimp and topsmelt were similar in sensitivity, but both were less sensitive than mussel larvae.

Cationic trace metals and surfactants were identified as the classes of compounds responsible for observed toxicity during Phase I TIE testing. A summary of analytical results for total and dissolved trace metals in stormwater outfall samples is provided in Table 4. A review of metal concentrations in the samples and available toxicity data identified only copper and zinc as the most likely causes of toxicity attributable to divalent metals in any of the stormwater samples tested. Copper and zinc are the only two metals that exceeded EPA water quality criteria for the protection of aquatic marine life in any of the samples tested (EPA 2002b). For comparison, concentrations of copper and zinc (both pre- and post-C<sub>18</sub> extraction) and toxicity values for each of the three species tested in laboratory dilution water at Nautilus are shown in Figure 12. For both metals, mussels were clearly more sensitive; mysids and topsmelt were similar.

Surfactant concentrations in screening samples over time and post aeration are shown in Figure 13.

A summary of available EC<sub>50</sub>/LC<sub>50</sub> point estimate values for the primary toxicants of concern identified is provided in Table 5 for all species tested. Due to the limited zinc and surfactant data available for mussels and topsmelt, a summary of EC<sub>50</sub>/LC<sub>50</sub> point estimate values for a few closely related species is also provided in Table 6.

The following results for trace metals focus on the dissolved fraction, as it is well-documented that this fraction, rather than total, is much more closely associated with biological effects (Bergman and Dorward-King 1997)

## **Copper**

Mussel larvae are clearly the most sensitive of the three species to copper; our long-term mean EC<sub>50</sub> for this metal (n=20) is 9.5 µg/L, which can be compared with long-term average LC<sub>50</sub> values of 163 µg/L and 233 µg/L for 96-hour topsmelt and mysid shrimp exposures, respectively. Published mean 48- to 96-hour EC<sub>50</sub> literature values for *M. galloprovincialis* are similar to values obtained at Nautilus, ranging from 5.8 µg/L (Martin et al. 1981) to 7.9 (EPA 1998). Published acute 96-hour LC<sub>50</sub> values for mysids are slightly less than those derived at Nautilus at 153 to 181 µg/L copper (Lussier et al. 1985 and Cripes 1994), while published values for topsmelt are slightly greater at 288 to 365 µg/L (Anderson et al. 1991 and McNulty et al. 1994). Thus, given the range of dissolved copper concentrations in the samples (83 to 212 µg/L), mussels would have exhibited the greatest response to copper, with much lower responses exhibited by mysids or topsmelt. Topsmelt, however, exhibited no toxicity in Sample NAB OF 9, which had the highest copper concentration among the stormwater samples tested, but mysids showed improvement in survival when this sample was treated with EDTA.

Based on the amount of data generated at Nautilus for copper, and because TIE procedures performed during this study using the same dilution water with methods that are consistent with our standard reference toxicant procedures, the following toxic unit (TU) values were calculated using sensitivity data derived at Nautilus.

In order to apply these general sensitivity guidelines more directly to the samples tested, predicted TUs based on metal concentrations in the samples were calculated (TU = metal concentration in the sample/ EC or LC<sub>50</sub> values derived at Nautilus)

Predicted TU values based on copper concentrations range from 6.4 to 16.3 among the three toxic samples for the bivalve embryo development test (Table 7). Predicted TU values based on copper for mysids and topsmelt range from 0.3 to 0.7 and 0.5 to 1.3, respectively among the three toxic samples (Tables 8 and 9). Based on these TU values, and the observation that topsmelt exhibited no toxicity in the sample with the highest copper concentration (NAB OF 9), copper does not appear to be primarily responsible for observed toxicity to either mysids or topsmelt in any of the samples tested. It is possible, however, that copper may still contribute to zinc toxicity through additivity.

## **Zinc**

Similar to copper, mussels were again the most sensitive species to zinc, with an EC<sub>50</sub> of 159 µg/L determined previously at Nautilus. This is similar to values published in the literature for this species and endpoint; 175 µg/L by Martin et al. (1981) and 178 µg/L by Phillips (2000). Mysid shrimp and topsmelt are both much less sensitive; we determined that the 96-hour LC<sub>50</sub> values for *Americamysis bahia* and *Atherinops affinis* were 647 and 880 µg/L, respectively. A previous mysid test at Nautilus resulted in an acute LC<sub>50</sub> value of 448 µg/L. Published mysid 96-hour LC<sub>50</sub> estimates for zinc range from approximately 303 to 547 µg/L, with most of the values approaching 500 µg/L (Lussier et al. 1985 and Cripe 1994). Zinc toxicity data was not found in the literature for topsmelt. For similar reasons mentioned in the prior section for copper (dilution water and test method consistency), the following TU values were performed using values derived at Nautilus for all three test species.

The concentration of zinc in NASNI OF 23a, at 297 µg/L, is enough to potentially cause toxicity to bivalve larvae (TU = 1.7), but not great enough to cause toxicity to either mysids or topsmelt (Table 7). Concentrations of zinc, at 985 and 742 µg/L in and NAB OF 18 and NAB OF 9, respectively, are greater than those expected to cause toxicity to all three test species with zinc TU values of 4.2 and 5.6 for bivalves, 1.2 and 1.5 for mysids, and 0.8 to 1.1 for topsmelt (Tables 7 through 9). Zinc TUs for mussels, although elevated, were two to four times less than those for copper, thus indicating that zinc appears to contribute a lesser proportion of toxicity to bivalves than copper. The additivity of these two metals, however, suggests that both could be contributing to observed toxicity to bivalve larvae in all three toxic samples. On the contrary, TU data indicate that zinc, rather than copper, is more likely to be responsible for toxicity to mysids in Sample NAB OF 9. Despite zinc TU values of 1.1 to 1.5 in NAB OF 18 for topsmelt and mysids, EDTA failed to reduce toxicity, indicating that cationic trace metals were not responsible for toxicity to these two species in this sample.

## **Trace Metal Reduction by C<sub>18</sub> Extraction**

The conclusion that divalent cationic metals are contributing to toxicity is based on the effectiveness of EDTA in removing toxicity. While reduction of toxicity following extraction with SPE C<sub>18</sub> columns is generally attributed to the presence of non-polar organic toxicants, metals concentrations can also be reduced by C<sub>18</sub> extraction (USEPA 1991). Therefore, the ability of SPE columns to remove some metals requires that the presence of an organic constituent be further confirmed by: 1) a comparative lack of effect of EDTA; and/ or 2) toxicity in the solvent

elution of the SPE column.

To evaluate the potential reduction in trace metal toxicity in this study due to the C<sub>18</sub> extraction procedure, the concentration of trace metals was measured both prior to and after C<sub>18</sub> treatment in Samples NAB OF 18 and NASNI OF23a. These data are presented in Figure 12 for copper and zinc. Copper was reduced 34 percent in NAB OF 18 and 38 percent in NASNI OF 23a by the SPE C<sub>18</sub> procedure. Zinc was reduced 17 percent in NAB OF 18, but not reduced in sample NASNI OF 23a by the SPE C<sub>18</sub> procedure. These results indicate that while the C<sub>18</sub> extraction may have reduced toxicity due to cationic metals, however, the degree of reduction likely had little bearing on the overall Phase I TIE results and interpretation as confirmation of additional toxicity due to organics was performed by 1) testing methanol elutions from the columns, and 2) performing combined EDTA + C<sub>18</sub> treatments.

### **Surfactants**

Concentrations of surfactants, measured as MBAS, were 1.0, 1.9 and 1.1 mg/L in NAB OF 9, NAB OF 18, and NASNI OF 23a, respectively. Non-toxic NASNI OF 26 had an MBAS concentration of 0.47 mg/L.

Published surfactant toxicity values for all three test species is very limited. Surfactants, measured as MBAS, include anionic forms; nonionic surfactants, such as ethoxylates and nonyl phenol, are not captured by this method. Due to the limited data currently available, and the wide range of chemicals with surfactant properties, a summary of available toxicity data for both anionic and nonionic surfactants is presented in Table 7 for the three species tested. A search for closely related fish and bivalve species was also performed, with published toxicity values summarized in Table 6.

Published anionic surfactant values for *Mytilus galloprovincialis* range from 0.3 to 50 mg/L (Grammo 1972, Grammo et al. 1989, and Swedmark et al. 1971), and a single LAS surfactant EC<sub>50</sub> value of 0.46 mg/L was published by Cardwell et al. (1979) for embryo development of the Pacific oyster. Published anionic surfactant toxicity data, however, was not found for *Americamysis bahia*, *Atherinops affinis*, or closely related species.

In summary, the range of published toxicity values for surfactants (anionic and nonionic) varies widely depending on both the specific type of surfactant tested and species. Sufficient side-by-side testing has not been performed to determine whether there are general sensitivity trends for the three marine species tested in this study. Some anionic surfactant toxicity values for the



bivalves *M. galloprovincialis* and *C. gigas*, are below MBAS concentrations measured in all stormwater outfall samples, thus providing evidence that surfactants may be of concern based on concentration alone. Prior experience at Nautilus has frequently identified toxicity due to anionic surfactants at MBAS concentrations above approximately 1.0 mg/L for a variety of marine and freshwater species.

**Table 4. Trace Metal Analysis Results for San Diego Bay Stormwater Samples.**

Trace Metal	Reporting Limit (µg/L)	Measurement	Concentration (µg/L)			
			NAB OF 9	NAB OF 18	NASNI OF 23a	NASNI OF 26
Aluminum	50	Dissolved	ND	ND	ND	ND
		Total	405	659	224	241
Antimony	15	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Arsenic	15	Dissolved	23.0 <sup>a</sup>	ND	ND	ND
		Total	ND	ND	ND	ND
Barium	10	Dissolved	143	94.4	29.6	27.0
		Total	169	110	39.7	29.0
Beryllium	1	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Cadmium	5	Dissolved	ND	8.00	ND	ND
		Total	ND	9.3	ND	ND
Chromium	5	Dissolved	7.00 <sup>a</sup>	ND	ND	5.0
		Total	ND	7.00	ND	6.0
Cobalt	5	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Copper	5	Dissolved	<b>212</b>	<b>144</b>	<b>83.3</b>	<b>9.0</b>
		Total	<b>278</b>	<b>178</b>	<b>93.6</b>	<b>24.0</b>
Iron	100	Dissolved	ND	ND	ND	ND
		Total	1190	1050	346	337
Lead	10	Dissolved	10.0	ND	ND	ND
		Total	11.0	13.5	ND	13.0
Manganese	5	Dissolved	250	179	ND	21.0
		Total	311	209	42.9	35.0

<sup>a</sup> Dissolved metal was reported at a higher concentration than total metal. However, concentrations were near the reporting limit where true differences in concentration are difficult to detect.

Bold values in red exceed published US EPA national recommended water quality criteria for acute exposures to aquatic marine life (criteria maximum concentration), (EPA 2002b)

ND - Not Detected

**Table 4 (cont'd). Trace Metal Analysis Results for San Diego Bay Stormwater Samples.**

Trace Metal	Reporting Limit (µg/L)	Measurement	Concentration (µg/L)			
			NAB OF 9	NAB OF 18	NASNI OF 23a	NASNI OF 26
Molybdenum	5	Dissolved	ND	6.70	ND	ND
		Total	ND	6.90	ND	ND
Nickel	5	Dissolved	14.0 <sup>a</sup>	13.9	8.1	ND
		Total	12.0	16.2	9.00	ND
Phosphorus	100	Dissolved	ND	319	2190	ND
		Total	166	455	2280	130
Silver	5	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Silicon	50	Dissolved	1600	2140	2310	3650
		Total	2380	3490	2790	4120
Strontium	30	Dissolved	ND	554	86.6	2960
		Total	892	570	93.4	3050
Thallium	15	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Tin	50	Dissolved	ND	ND	ND	ND
		Total	ND	ND	ND	ND
Titanium	15	Dissolved	ND	ND	ND	ND
		Total	69.0	36.5	16.7	ND
Vanadium	5	Dissolved	ND	ND	ND	21.0
		Total	ND	ND	5.40	23.0
Zinc	10	Dissolved	<b>742</b>	<b>985</b>	<b>297</b>	<b>80.0</b>
		Total	<b>1540</b>	<b>1220</b>	<b>398</b>	<b>121</b>

<sup>a</sup> Dissolved metal was reported at a higher concentration than total metal. However, concentrations were near the reporting limit where true differences in concentration are difficult to detect.

Bold values in red exceed published US EPA national recommended water quality criteria for acute exposures to aquatic marine life (criteria maximum concentration), (EPA 2002b)

ND - Not Detected

**Table 5. Toxicity Values for Selected Metals and Surfactants of Potential Concern for *Mytilus galloprovincialis* Embryo Development and Acute Survival of *Americamysis bahia* and *Atherinops affinis***

Species	Chemical of Concern	Test Duration	Endpoint	NOEC (µg/L)	LOEC (µg/L)	Mean LC <sub>50</sub> (µg/L)	Reference
<i>A. bahia</i>	Cu	96 hr	Survival	nr	nr	233	Nautilus (2005)
	Cu	96 hr	Survival	77	140	181	Lussier et al (1985)
	Cu	96 hr	Survival	nr	nr	153	Cripe (1994)
	Zn	96 hr	Survival	nt	nt	499	Lussier et al (1985)
	Zn	96 hr	Survival	nr	nr	303	Cripe (1994)
	Zn	96 hr	Survival	nr	nr	547	Lussier and Gentile (1985)
	Zn	96 hr	Survival	nr	nr	448	Nautilus (2005)
	Surfactants <sup>a</sup>	96 hr	Survival	nr	nr	<1000 to >4 x 10 <sup>6</sup>	Hall et al (1989)
	4-Nonyl Phenol	96 hr	Survival	nr	nr	>50 - <150	Lussier et al (2000)
<i>A. affinis</i>	Cu	96 hr	Survival	nr	nr	288	Anderson et al (1991)
	Cu	96 hr	Survival	nr	nr	365	McNulty et al (1994)
	Cu	96 hr	Survival	160	nr	nr	Isensee et al (1973)
	Cu	96 hr	Survival	nr	nr	163	Nautilus (2005)
	Zn	96 hr	Survival	nr	nr	880	Nautilus (2005)
<i>M. galloprovincialis</i>	Cu	48 hr	Develop.	nr	nr	5.8	Martin et al (1981)
	Cu	48 hr	Develop.	nr	nr	9.5	Nautilus (2005)
	Cu	96 hr	Develop.	nr	nr	7.9	EPA (1998)
	Zn	96hr	Develop.	nr	nr	178	Phillips (2000)
	Zn	48hr	Develop.	nr	nr	175	Martin et al (1981)
	Zn	48hr	Develop.	nr	nr	159	Nautilus (2005)
	Surfactants	96hr	Mortality	nr	nr	50,000	Swedmark et al (1971)
	Nonyl Phenol	96hr	Mortality	nr	nr	3000	Granmo et al (1989)
	LAS	96hr	Develop.	nr	nr	300	Granmo (1972)
	LAS	96hr	Mortality	nr	nr	1.66 (mg/kg)	Bressan et al (1989)

<sup>a</sup> - includes Alkyl Phenol Ethoxylate, Nonyl Phenol Ethoxylate, Octyl Phenol Ethoxylate, Decyl Alcohol Ethoxylate, Tridecyl Alcohol Ethoxylate, and Tripropylene

nr – not reported

**Table 6. Selected Toxicity Data for Selected Metals and Surfactants of Potential Concern for Closely Related Species (The inland silverside minnow *Menidia beryllina*, the Pacific oyster *Crassostrea gigas*, and the Sheepshead minnow *Cyprinodon variegatus*)**

Species	Chemical of Concern	Test Duration	Endpoint	NOEC (µg/L)	LOEC (µg/L)	Mean LC <sub>50</sub> (µg/L)	Reference
<i>M. beryllina</i>	Zn	96hr	Survival	nr	nr	1000 - 10,000	Lewis (1993)
	Nonyl Phenol	96hr	Survival	nr	nr	70	Lussier et al (2000)
<i>C. gigas</i>	Zn	48hr	Development	100	nr	200	Chapman et al (1993)
	Zn	48hr	Development	nr	nr	206	Dinnel et al (1983)
	LAS	48hr	Development	nr	nr	460	Cardwell et al (1979)
<i>C. variegatus</i>	Nonyl Phenol	96hr	Survival	nr	nr	460	Sappington et al (2001)
	Nonyl Phenol	96hr	Survival	nr	nr	142	Lussier et al (2000)

nr – not reported

**Table 7. Comparisons of Predicted Copper and Zinc TUs for Mussel Embryos (Dissolved Concentrations).**

Site ID	Dissolved Cu (µg/L)	Dissolved Zn (µg/L)	Screening Test EC <sub>50</sub> (% Sample)	Screening Test TU <sup>a</sup>	Predicted Cu TU <sup>b</sup>	Predicted Zn TU <sup>b</sup>	Predicted Cu + Zn TU
<b>NAB OF 9</b>	212	742	12.5	<b>8.00</b>	<b>16.3</b>	<b>4.24</b>	<b>20.5</b>
<b>NAB OF 18</b>	144	985	13.7	<b>7.30</b>	<b>11.1</b>	<b>5.63</b>	<b>16.7</b>
<b>NASNI OF 23a</b>	83.3	297	22.1	<b>4.52</b>	<b>6.41</b>	<b>1.70</b>	<b>8.10</b>
<b>NASNI OF 26</b>	9.00	80.0	>69.0	<b>&lt;1.00</b>	<b>0.69</b>	<b>0.46</b>	<b>1.15</b>

<sup>a</sup> TU is equal to 100 divided by the screening test EC<sub>50</sub>.

<sup>b</sup> TU is equal to the concentration of the trace metal in the stormwater sample divided by the concurrent reference toxicant test EC<sub>50</sub> (13 µg/L Cu, and 175 µg/L Zn).

**Table 8. Comparisons of Predicted Copper and Zinc TUs for Mysid Shrimp (Dissolved Concentrations).**

Site ID	Total Copper (µg/L)	Total Zinc (µg/L)	Screening Test EC <sub>50</sub> (% Sample)	Screening Test TU <sup>a</sup>	Predicted Copper TU <sup>b</sup>	Predicted Zinc TU <sup>b</sup>	Predicted Copper + Zinc TU
NAB OF9	212	742	>100	<1.00	0.731	1.40	2.13
NAB OF18	144	985	42.4	2.36	0.497	1.86	2.36
NASNI OF23a	83.3	297	>100	<1.00	0.287	0.560	0.848
NASNI OF26	9.00	80.0	>100	<1.00	0.031	0.151	0.182

<sup>a</sup> TU is equal to 100 divided by the screening test EC<sub>50</sub>.

<sup>b</sup> TU is equal to the concentration of the trace metal in the stormwater sample divided by the reference toxicant test EC<sub>50</sub> (290 µg/L Cu, and 530 µg/L Zn).

**Table 9. Comparisons of Predicted Copper and Zinc TUs for Pacific Topsmelt (Dissolved Concentrations).**

Site ID	Total Copper (µg/L)	Total Zinc (µg/L)	Screening Test EC <sub>50</sub> (% Sample)	Screening Test TU <sup>a</sup>	Predicted Copper TU <sup>b</sup>	Predicted Zinc TU <sup>b</sup>	Predicted Copper + Zinc TU
NAB OF9	212	742	>100	<1.00	1.30	0.843	2.14
NAB OF18	144	985	38.2	2.62	0.883	1.12	2.00
NASNI OF23a	83.3	297	>100	<1.00	0.511	0.338	0.849
NASNI OF26	9.00	80	>100	<1.00	0.055	0.091	0.146

<sup>a</sup> TU is equal to 100 divided by the screening test EC<sub>50</sub>.

<sup>b</sup> TU is equal to the concentration of the trace metal in the stormwater sample divided by the reference toxicant test EC<sub>50</sub> (163 µg/L Cu, and 880 µg/L Zn).

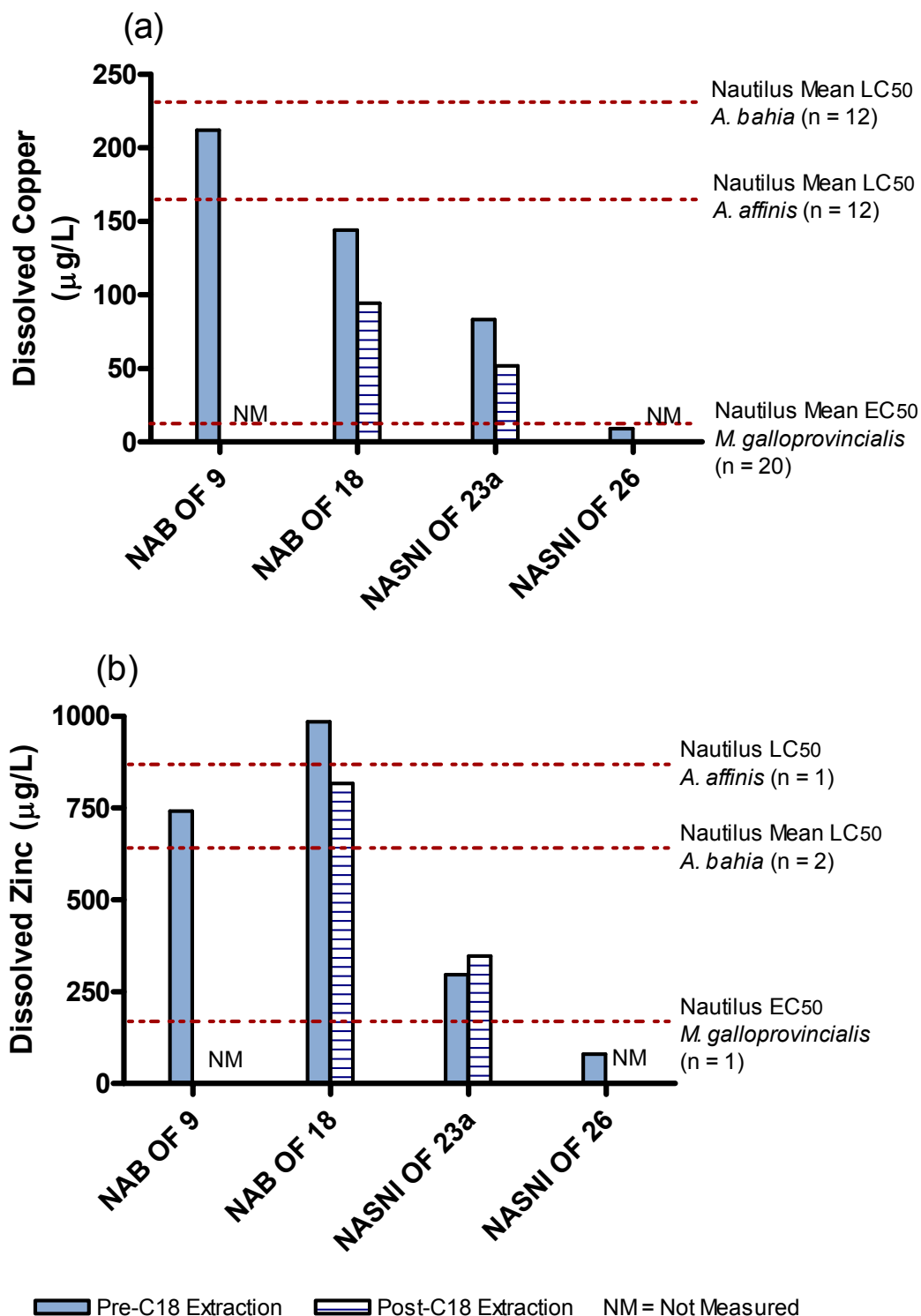
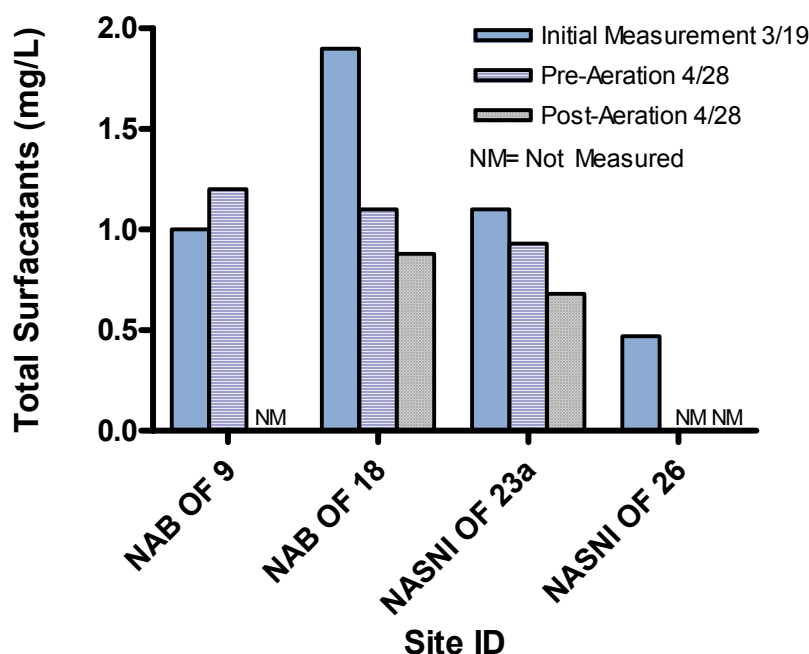


Figure 12. Dissolved copper (a), and dissolved zinc (b) measurements for San Diego Bay stormwater samples before and after C<sub>18</sub> column extraction. Mean EC<sub>50</sub> values (mussel embryos) and acute LC<sub>50</sub> values for mysids and topsmelt are displayed on each figure.



**Figure 13. Anionic surfactant (as MBAS) analytical results for San Diego Bay stormwater samples.**

### 3.3.2 Copper and Zinc Mixture Studies

The results of the Phase I TIE manipulations strongly suggest that divalent cationic metals were the primary cause of toxicity to mussel embryos and mysids in NAB OF 9 and a significant contributor to mussel toxicity in NAB OF 18 and NASNI OF 23a. A comparison of concentrations with available toxicity data further supports these conclusions in that sufficient metal is present to account for the presence of toxicity.

To help evaluate the extent to which each metal contributed to toxicity to both bivalve embryos and mysids, and to understand how they interacted when present in solution together, a series of tests were performed to identify the level of toxicity associated with each metal and their degree of interaction. Zinc and copper were tested alone, and as a mixture at two different ratios to evaluate whether the ratios affected the interactive characteristics of the metals. Mysids were tested May 19, 2005 at ratios of 2.2:1 and 5.4:1. The 5.4 to 1 ratio was the mean ratio of the four stormwater outfall samples analyzed, with ratios ranging from 3.8 to 8.9. The 2.2 value is equal to the  $LC_{50}$  ratio between zinc and copper for mysids. Mediterranean mussels were tested in a prior study (May 2004) at ratios of 4.5:1 and 13.6:1, corresponding to ratios obtained for stormwater samples collected February 19, 2004 (4.5:1) and the  $LC_{50}$  ratio (13.6:1)



between zinc and copper for this species. The metal mixture studies with the mussel are included here, but were previously reported and submitted to SPAWAR as a part of TIE stormwater evaluations conducted in May 2004.

### **Mediterranean Mussel**

The EC<sub>50</sub> estimates determined in May 2004 for copper and zinc individually during this test series was 9.6 and 160 µg/L, respectively. These values are likely conservative as they were obtained in laboratory seawater. Irrespective of the ratios tested, toxicity appeared to be additive; in mixtures of the two metals in laboratory seawater toxic units of 1.2 to 1.3 were calculated. Figure 14 shows the response curves for zinc and copper individually, as well as for the two mixtures. Clearly, similar dose-responses were exhibited in all four of the tests, suggesting similar modes of action and additive toxicity.

Applying these laboratory-derived EC<sub>50</sub> estimates to metals concentrations measured in the actual samples collected March 18, 2005 suggested that, in all cases, the predicted toxicity over-estimated the actual toxicity observed in the original screening tests (Table 7). In other words, there was frequently less toxicity present in the original samples than would have been predicted on the basis the concentrations of total metals present and their additivity. Thus, these data suggest that some portion of the metals present in the samples was not bioavailable. Reduced bioavailability of trace metals due to binding by various ligands (e.g., dissolved organic carbon) is well-documented in the literature (Bergman and Dorward-King 1997). On average, the actual bivalve TUs in the stormwater samples were 46 percent of those that would have been predicted on the basis of the joint toxicity of copper and zinc in laboratory seawater.

In order to address the relative importance of each of the metals to overall toxicity, predicted TUs for copper and zinc alone and in combination were plotted against the actual TUs determined in the screening tests on the original samples (Figure 15). The relationships for copper alone and in combination with zinc were statistically significant ( $p \leq 0.05$ ). A positive relationship was also observed for zinc; however, it was not statistically significant. The relationship between actual toxicity and the toxicity predicted by the combination of metals, however, was the strongest, with an  $r^2$  value of 0.98. This finding suggests that both metals contributed to toxicity in all three toxic samples.

### **Mysid Shrimp**

Mysid acute LC<sub>50</sub> estimates determined concurrently during this study for copper and zinc alone

were 291 and 647 µg/L, respectively. As with bivalves, these values are likely conservative as they were obtained in laboratory seawater. Regardless of the ratios tested, toxicity appeared to be somewhat less than additive, in mixtures of the two metals in laboratory seawater, toxic units for the two mixtures were 1.45 and 1.62 compared with a predicted TU of 1. Figure 16 shows the response curves for zinc and copper individually, as well as for the two mixtures. Clearly, similar dose-responses were exhibited in all four of the tests, suggesting similar modes of action and additive toxicity. Interestingly, however, the two mixture studies appeared to actually be less than additive in toxicity. Not only were the actual TUs required to elicit a response greater than predicted, the slope of the response curves appeared to diverge from those associated with the individual metals.

Applying these laboratory-derived EC<sub>50</sub> estimates to metals concentrations measured in the actual samples collected March 18, 2005 found that the predicted toxicity for the sum of copper and zinc concentrations over-estimated the actual toxicity observed in the original screening test for Sample NAB OF 9 (Table 8). These data suggests that at least some portion of the metals present in Sample OF 9 was not bioavailable. Predicted toxicity based on copper and zinc concentrations in NAB OF 18 was identical to the actual toxicity observed; despite this observation, toxicity in sample NAB OF 18 was clearly attributable to an organic compound, and not to trace metals. Again, this result indicates that a substantial fraction of copper and zinc is not bioavailable. The sum of predicted copper and zinc toxic units for NASNI OF 23a and NASNI OF 26 was less than 1, which corresponds to the actual toxic units of less than 1 that were found for both of these samples.

Unfortunately, due to a lack of mysid data with sufficient toxic responses in this study, predicted versus actual TU plots for copper and zinc alone and in combination were not meaningful for this species and are, therefore, not included.

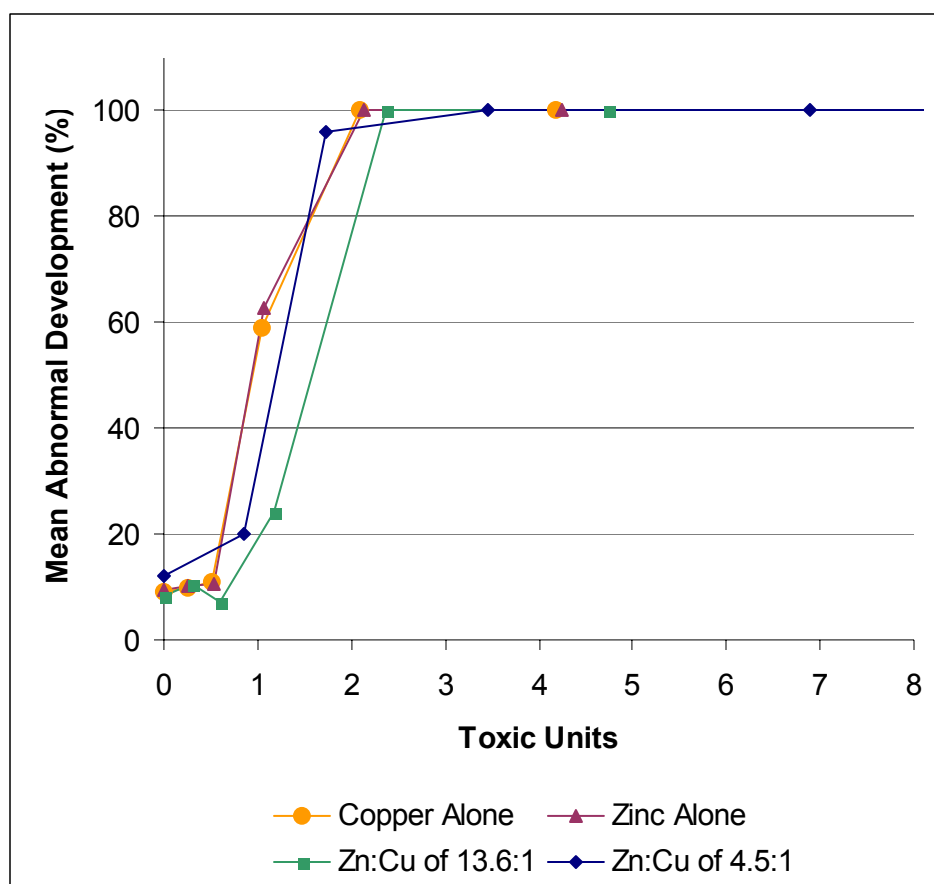
### **Pacific Topsmelt**

A copper and zinc mixture study was not performed for topsmelt; however an evaluation of predicted versus actual toxicity units is provided below.

Topsmelt acute LC<sub>50</sub> estimates determined for copper and zinc based on internal data collected at Nautilus are 163 (n=12) and 880 µg/L (n=1), respectively. As with bivalves and mysids, these values are likely conservative as they were obtained in laboratory seawater.

Applying laboratory-derived EC<sub>50</sub> estimates to copper and zinc concentrations measured in the

actual samples collected March 18, 2005 found that the predicted toxicity over-estimated the actual toxicity observed in the original screening test for Sample NAB OF 9 (Table 9). Sample NAB OF 9 was not toxic to topsmelt, therefore, this data further suggests that a substantial fraction of the metals present in Sample OF 9 were not bioavailable. In contrast to the data for mussels and mysids, the predicted summed copper and zinc toxic units for topsmelt exposed to Sample NAB OF 18 were less than the actual toxicity observed. This observation supports the finding that an organic constituent, and not a trace metal, was responsible for toxicity in this sample. The sum of predicted copper and zinc toxic units for NASNI OF 23a and NASNI OF 26 was less than 1, which corresponds to actual toxic units of less than 1 for both of these samples.



**Figure 14. Response of mussel embryos to copper and zinc alone and in combination. Metals are expressed as TUs. February 2004 study.**

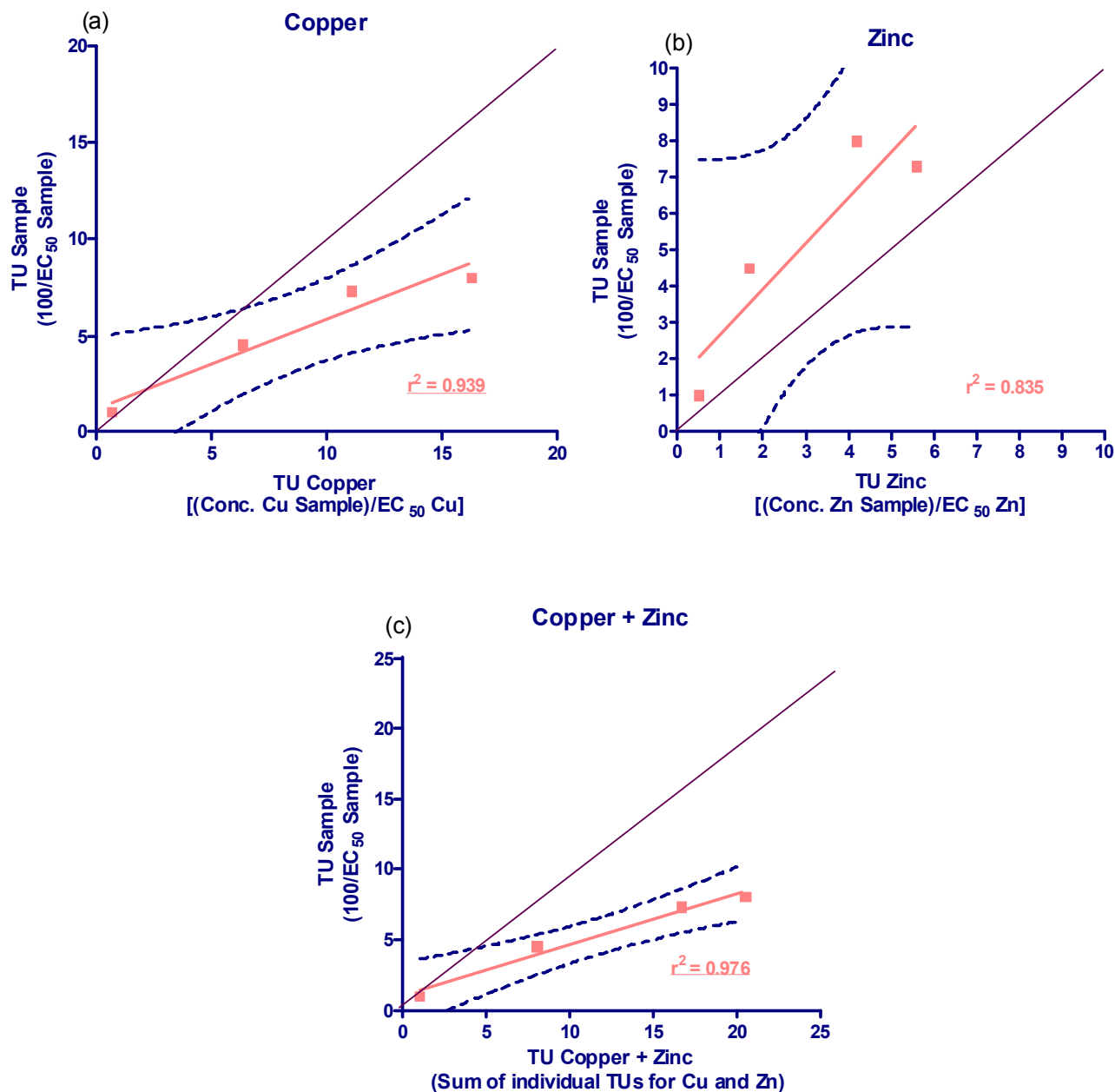
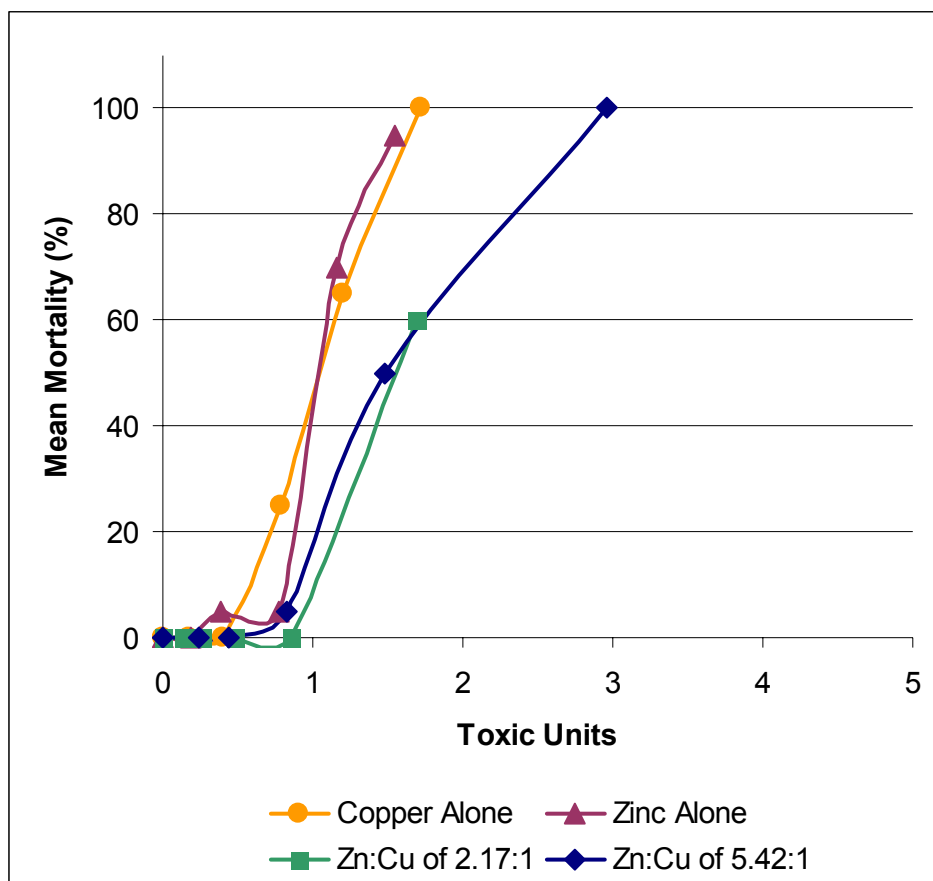


Figure 15. Comparisons of predicted and actual copper and zinc TU values. February 2004 study. Underlined  $r^2$  values are statistically significant ( $p \leq 0.05$ ).



**Figure 16. Response of mysid shrimp to copper and zinc alone and in combination. Metals are expressed as TUs.**

### 3.3.3 Toxicity Relationships to Identified Toxicants of Concern

Relationships between toxicity and concentrations of chemicals of concern across samples provide additional lines of supporting evidence, depending the amount of data available. Relationships alone, however, must be evaluated with caution as chemical constituents are often correlated and interactions between chemical and physical parameters may also effect such relationships.

#### Copper and Zinc

Linear regression relationships between toxicity and concentrations of dissolved copper and zinc to the three species tested are provided in Figures 17 though 19. Despite the limited number of data points available for analysis (n=4), strong relationships were observed between

mussel embryo development and concentrations of both copper and zinc with  $r^2$  values of 0.98 and 0.90, respectively. The relationship between zinc and mysid survival was also reasonably strong with an  $r^2$  value of 0.76. Relationships between mysid survival and copper ( $r^2 = 0.49$ ), and both copper and zinc for topsmelt ( $r^2 = 0.23$  and 0.44, respectively) were relatively weak.

These relationships support conclusions that: 1) copper and zinc contributed toxicity to mussel embryos in all three toxic samples; 2) toxicity to mysids was attributed to zinc in one sample (NAB OF 9); and 3) toxicity to topsmelt was not attributed to copper or zinc in any of the stormwater samples tested.

### **Surfactants**

Multiple lines of evidence from Phase I TIE tests indicated that anionic surfactants are a contributing toxic class of compounds in Samples NAB OF 18 and NASNI OF 23a for both mussels and mysids. Linear regression relationships between concentrations of MBAS and initial screening test responses for all test organisms are provided in Figures 20 through 22. In summary, despite the limited number of data points available for analysis, strong relationships were obtained for mysids and topsmelt with  $r^2$  values of 0.91 and 0.92, respectively. The relationships between bivalve embryo development and MBAS was less compelling, with an  $r^2$  value of 0.57.

These relationships are consistent with the results of the TIE manipulations that suggest that: 1) surfactants contributed some toxicity to mussel embryos in two samples (NAB OF 18 and NASNI OF 23a); and 2) surfactants appear to be primarily responsible for observed toxicity to mysids in these two samples. Evidence suggests that surfactants may also be primarily responsible for toxicity to topsmelt in these two samples, however, additional Phase II/III TIE procedures are required to confirm this hypothesis for the species.

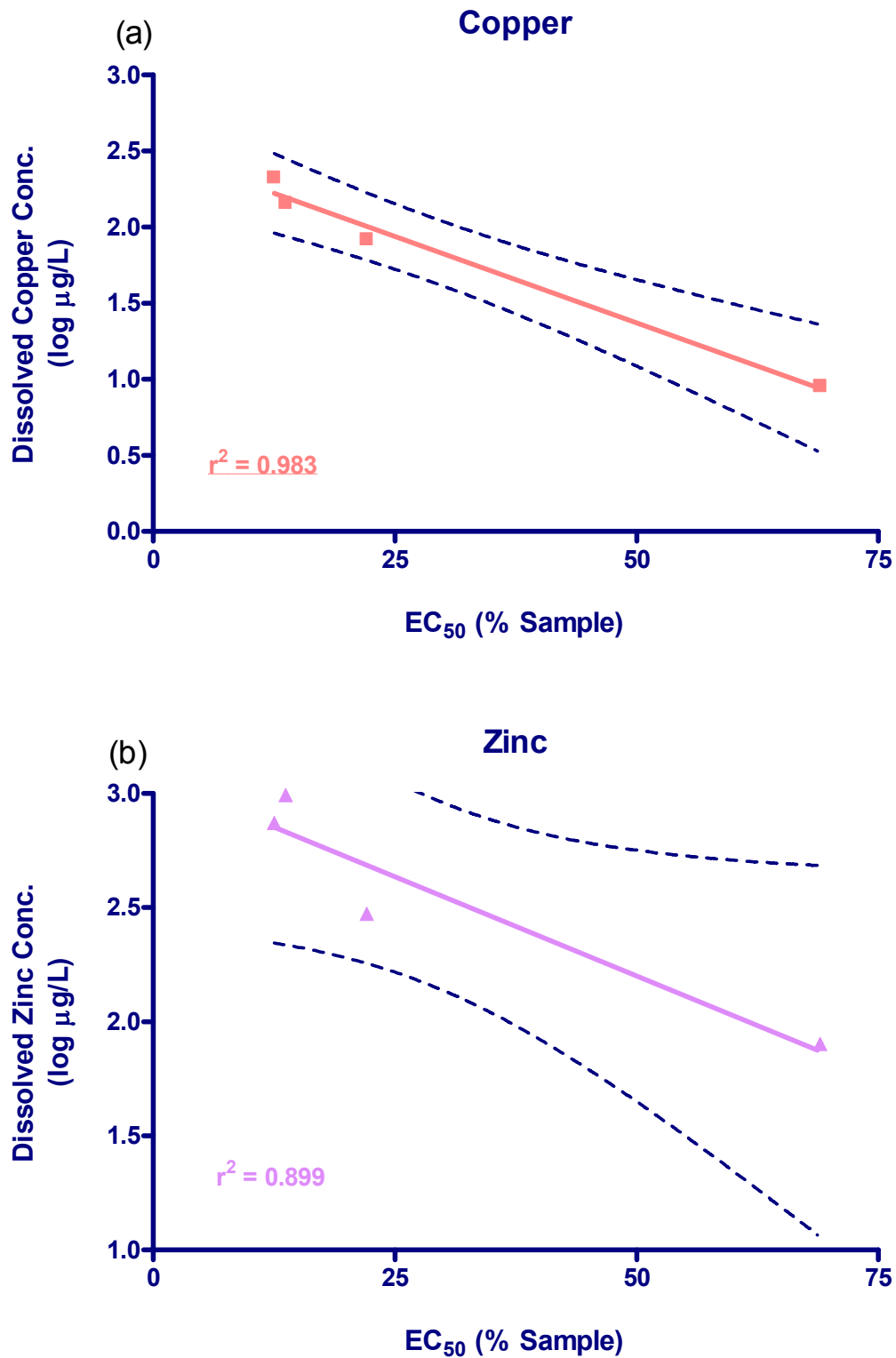


Figure 17. Relationship between mussel embryo development and (a) dissolved copper and (b) dissolved zinc. Underlined  $r^2$  values are statistically significant ( $p \leq 0.05$ )

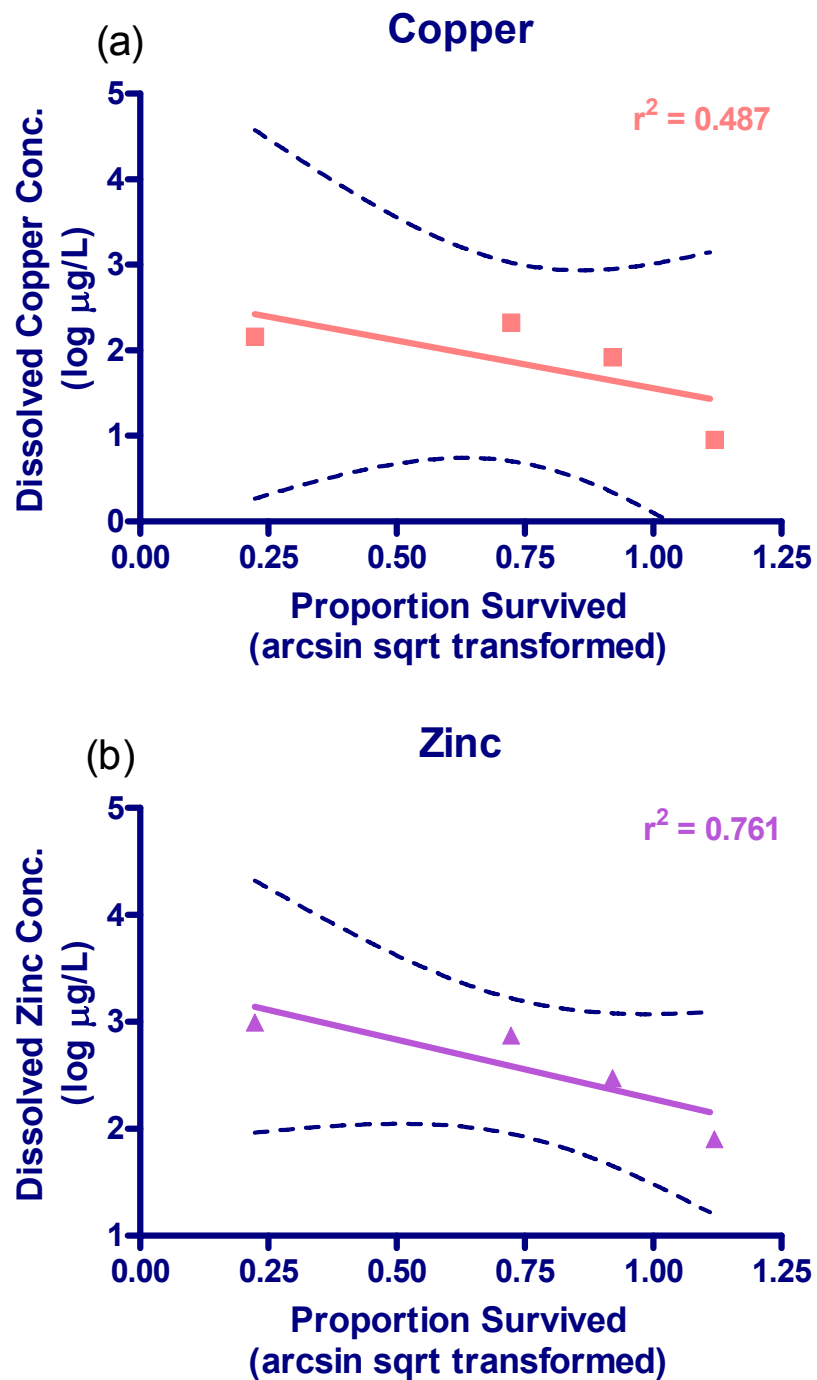


Figure 18. Relationship between acute mysid survival in undiluted sample and (a) dissolved copper and (b) dissolved zinc.



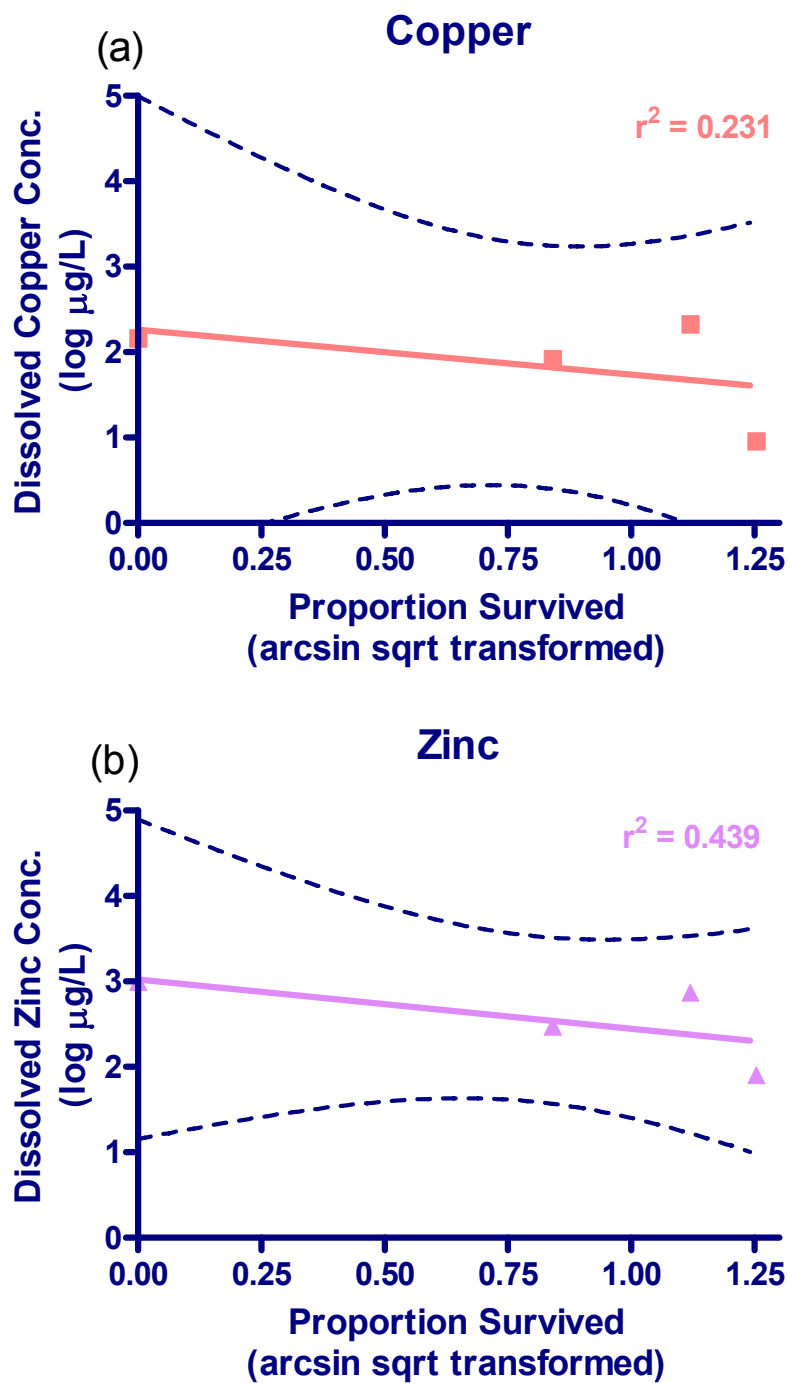


Figure 19. Relationship between acute topsmelt survival in undiluted sample and (a) dissolved copper and (b) dissolved zinc.

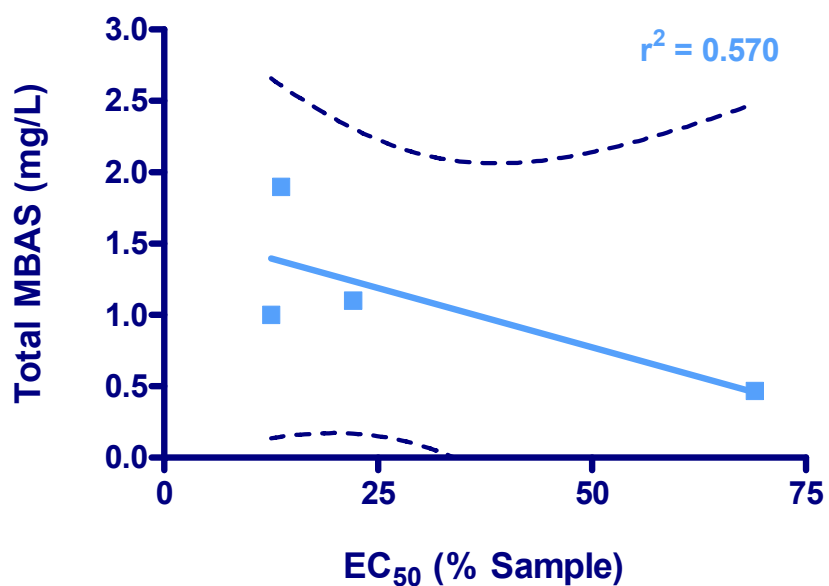


Figure 20. Relationship between mussel embryo development and MBAS concentrations. The EC<sub>50</sub> was plotted on the X axis for this species due to zero percent normal in the highest concentrations tested in all three toxic samples.

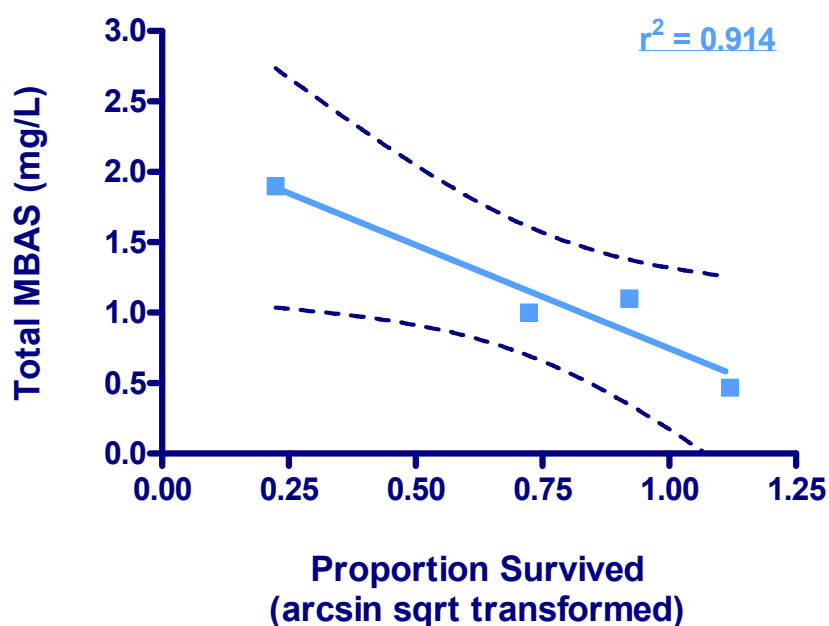


Figure 21. Relationship between acute mysid survival and MBAS concentrations in undiluted sample.

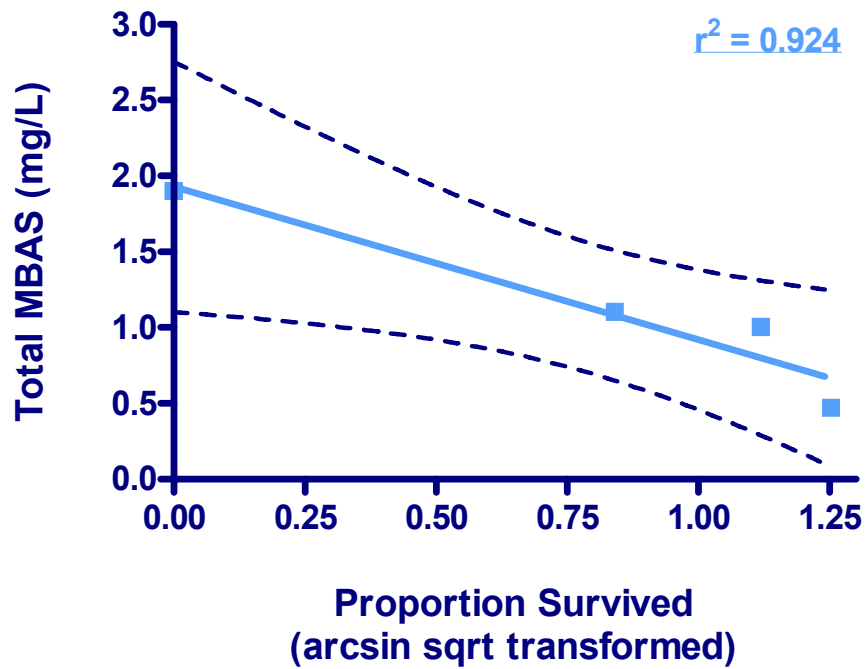


Figure 22. Relationship between acute topsmelt survival and MBAS concentrations in undiluted sample.

## 4.0 CONCLUSIONS

Results for each of the toxic samples are summarized below in the context of the findings of the TIE investigation. A final summary of results is provided in Table 10.

**Table 10. Summary of Identified Toxicants of Concern**

Sample ID	Species/ Endpoint	Primary Toxicant(s)
<b>NAB OF 9</b>	Bivalve embryo development	Copper and zinc
	Mysid acute survival	Zinc and copper
	Topsmelt acute survival	Not toxic
<b>NAB OF 18</b>	Bivalve embryo development	Copper and zinc (50%), Anionic surfactants (50%)
	Mysid acute survival	Surfactants <sup>a</sup>
	Topsmelt acute survival	Surfactants <sup>a</sup>
<b>NASNI OF 23a</b>	Bivalve embryo development	Copper and zinc (50%), Anionic surfactants (50%)
	Mysid acute survival	Surfactants <sup>b</sup>
	Topsmelt acute survival	Surfactants <sup>b</sup>

<sup>a</sup> Weight of evidence suggests surfactants despite the lack of confirmatory TIE data available for interpretation due to loss of toxicity in the sample. The type of surfactant (e.g. anionic vs nonionic) was not confirmed.

## **4.1 NAB OF 9**

### **4.1.1 Mediterranean Mussel**

TIE results clearly identified both copper and zinc as potential causes of toxicity in Sample NAB OF 9 based on 1) the success and specificity of the EDTA treatment, 2) toxic unit calculations for these two metals; and 3) the strong relationship between actual and predicted TU values across all outfall samples for these two metals. Copper, with a predicted TU value of 16.3, potentially contributes a greater proportion of toxicity than zinc, with a much lower predicted TU value of 4.2. The actual proportion of toxicity contributed by each metal, however, is not possible to derive at this point due to unknown differences in bioavailability at the time of sample collection.

### **4.1.2 Mysid**

Zinc and copper were identified as the primary toxicants of concern in Sample NAB OF 9 based on 1) the success and specificity of the EDTA treatment; 2) toxic unit calculations for these two metals; and 3) documented additivity of these two metals. The TU value for zinc (1.2) is greater than that derived during this study for copper (0.7). Based on the range of mysid sensitivity data collected over time at Nautilus, a copper TU value as high as 1.3 may be derived based on its concentration in NAB OF 9. Without data to document their relative bioavailability in the sample, it is not possible to know whether toxicity was due to zinc alone, copper alone, or to a combination of copper and zinc.

## **4.2 NAB OF 18**

### **4.2.1 Mussel**

Toxicity to mussels in Sample NAB OF 18 was attributed to a combination of copper, zinc, and anionic surfactants. Addition of EDTA removed approximately 50 percent of the observed toxicity in the Phase I TIE. Results of this treatment and an evaluation of toxic units indicate that copper and zinc are the only cationic trace metals of concern. Copper, with a predicted TU value of 11.1, potentially contributes a greater proportion of toxicity than zinc, with a predicted TU value of 5.6. Toxicity not removed by EDTA (the remaining 50 percent) may be attributable to anionic surfactants based on the following observations, in concert: 1) reduction in toxicity following extraction of the sample through a C<sub>18</sub> column; 2) a similar reduction in toxicity following aeration; 3) recovery of toxicity in both C<sub>18</sub> methanol extracts and foam collected

during aeration tests; 4) complete removal of toxicity in the C<sub>18</sub> methanol extract following anion exchange; 5) a concentration of surfactants, as MBAS, greater than documented levels of potential concern for some surfactants; and 6) a reduction in surfactant concentrations following aeration. Combined treatments (C<sub>18</sub> + EDTA and aeration + EDTA) completely removed toxicity in the sample, thus providing additional evidence that a combination of trace metals and anionic surfactants may explain all of the toxicity observed in the sample for this species.

#### **4.2.2 Mysid**

Toxicity to mysids in Sample NAB OF 18 was attributed to surfactants based on the following combination of observations: 1) removal of toxicity following both extraction of the sample through a C<sub>18</sub> column and aeration; 2) recovery of toxicity in foam collected during aeration tests; 3) a concentration of surfactants greater than that found to cause toxicity to mysids in prior studies at Nautilus; 4) a reduction in surfactant concentrations following aeration, 5) a strong correlation between surfactant concentrations (i.e. MBAS) and survival of mysids across all samples tested; and 6) anionic surfactants were identified as a cause of toxicity to mussels in this sample. Unlike mussels, trace metals were not identified as a toxicant of concern to mysids in this sample due to the lack of toxicity reduction following addition of EDTA. The loss of toxicity between the screening test and round two TIE Baseline test limited the ability to make interpretations based on most of the TIE treatments performed during this round. Rapid loss of toxicity, however, is another characteristic routinely observed for surfactants as they break down over time and adhere to the sides of sample containers (EPA 1991). In support of this observation, a decrease in surfactant concentrations over time was measured in this study for this sample.

#### **4.2.3 Topsmelt**

Toxicity to topsmelt in Sample NAB OF 18 was attributed to surfactants based on the following combined observations: 1) complete removal of toxicity following both extraction of the sample through a C<sub>18</sub> column and aeration; 2) a concentration of surfactants greater than that found to cause toxicity to other marine species; 3) a reduction in surfactant concentrations following aeration; 4) a strong correlation between surfactant concentrations and survival of topsmelt across all samples tested; and 5) anionic surfactants were identified as a cause of toxicity to mussels in this sample. Trace metals were not identified as a toxicant of concern to topsmelt in this sample due to the lack of toxicity reduction following addition of EDTA.

### **4.3 NASNI OF 23a**

#### **4.3.1 Mussel**

Toxicity to mussels in Sample NASNI OF 23a, like that for NAB OF 18, was attributed to a combination of copper, zinc, and surfactants. Addition of EDTA removed approximately ½ of observed toxicity in the screening test. Results of this treatment and an evaluation of toxic units indicate that copper and zinc are the only cationic trace metals of concern. Copper, with a predicted TU value of 6.4, potentially contributes a much greater proportion of toxicity than zinc, with a predicted TU value of 1.7. Toxicity not removed by EDTA may be attributable to surfactants based on these observations in concert: 1) complete removal of toxicity following extraction of the sample through a C<sub>18</sub> column; 2) a reduction in toxicity following aeration; 3) recovery of toxicity in foam collected during aeration tests; 4) a concentration of surfactants greater than documented levels of potential concern depending on the specific type of surfactant; and 5) a reduction in surfactant (MBAS) concentrations following aeration. The combined aeration and EDTA treatment completely removed toxicity in the sample, thus providing additional evidence that a combination of trace metals and surfactants may explain all of the toxicity observed in the sample for this species.

#### **4.3.2 Mysid**

Toxicity to mysids in Sample NASNI OF 23a, like that in NAB OF 18, appears to also be attributed to surfactants based on the following combined observations: 1) a strong correlation between surfactant (MBAS) concentrations and survival of mysids in all samples tested; 2) a concentration of surfactants greater than documented levels of potential concern; and 3) surfactants were identified as a cause of toxicity to mussels in this sample. The loss of toxicity between the screening and TIE Baseline tests limited the ability to make any interpretations based on TIE treatments. Rapid loss of toxicity, as above, is a characteristic routinely observed for surfactants (EPA 1991). In support of this observation, a decrease in surfactant concentrations over time was measured in this study for this sample.

#### **4.3.3 Topsmelt**

A loss of toxicity between the screening and TIE Baseline tests limited our ability to make additional interpretations based on TIE treatments. Toxicity to topsmelt in Sample NASNI OF 23a, like that in NAB OF 18, may be attributable to surfactants based on the following combined observations: 1) a strong correlation between surfactant concentrations and survival of topsmelt

in all samples; 2) a concentration of surfactants higher than reported levels of concern for other marine species; and. 3) surfactants were identified as a cause of toxicity to mussels in this sample. Rapid loss of toxicity is a routinely observed characteristic for surfactants as they break down over time and adhere to the sides of sample containers (EPA 1991). In support of this observation, a decrease in surfactant concentrations over time was measured in this study for this sample.

## **5.0 QA/QC**

### **5.1 Screening Bioassays**

#### **5.1.1 Mediterranean Mussel**

Mean normal development of mussel larvae in all laboratory seawater and hypersaline brine controls tested during the screening phase of the study ranged between 89 and 96 percent. MSDs ranged between 3.0 and 4.7 percent, indicating test sensitivity was within a suitable range.

#### **5.1.2 Mysid Shrimp**

At 96-hours, control performance met the 90 percent acute criterion in all cases, with mean survival ranging from 95 to 100 percent across laboratory seawater and artificial salt controls. MSDs calculated in comparison with the artificial salt controls ranged from 12.0 to 28.9 percent across samples.

#### **5.1.3 Pacific Topsmelt**

Both laboratory seawater and artificial salt controls met survival acceptability criteria. At 96-hours, mean control survival was 100 percent across all controls (> 90 percent acute criterion). MSDs ranged from 10 to 12.5 percent across samples.

### **5.2 TIEs**

#### **5.2.1 Mediterranean Mussel**

Baseline controls exhibited a mean of 90 to 98 percent normal larvae across all rounds of testing, indicating that the organisms used were healthy and test conditions were adequate. Method controls among the various treatments utilized exhibited 84 to 99 percent normal larvae,



indicating that the test organisms were not adversely affected by the test methods.

### **5.2.2 Mysid Shrimp**

Survival in the baseline laboratory seawater and artificial salt controls ranged from 90 to 100 percent, indicating that the organisms were healthy and test conditions were adequate. Method controls of the treatments ranged from 90 to 100 percent, suggesting that the treatments themselves had no adverse affect on the test animals.

### **5.2.3 Pacific Topsmelt**

Topsmelt survival in the baseline and method controls ranged from 95 to 100 percent, demonstrating that the organisms were healthy and were not affected by testing conditions.

## **5.3 Reference Toxicant Tests**

All reference toxicant test results were within +/- 2 standard deviations of the long-term laboratory control chart averages, suggesting that the sensitivity of the test organisms and the laboratory techniques were consistent throughout the study.

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# **Appendix G**

## **Plume Mapping Data Plots**

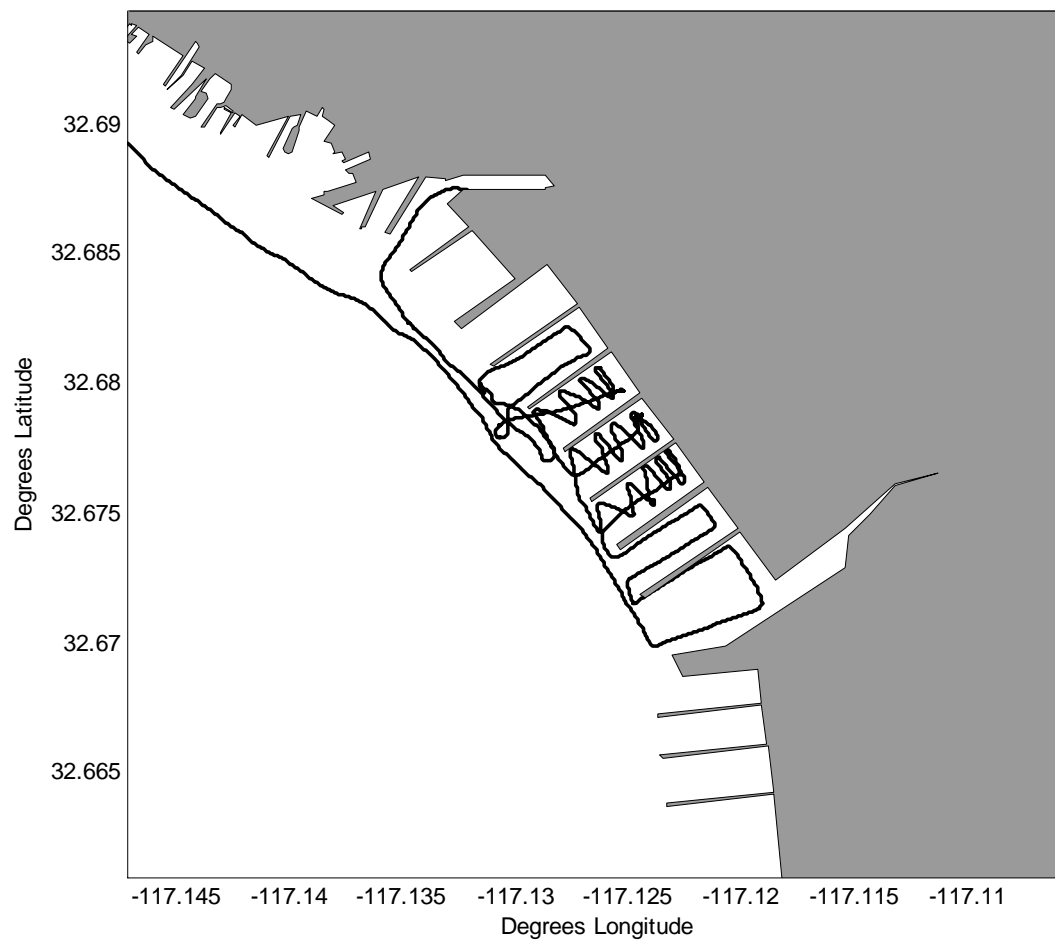
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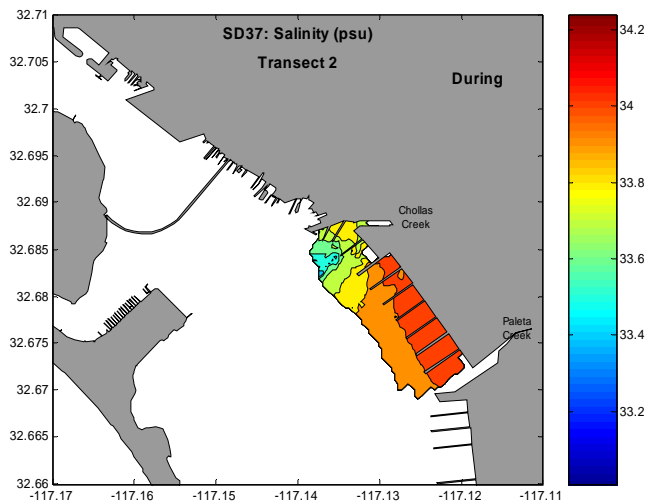
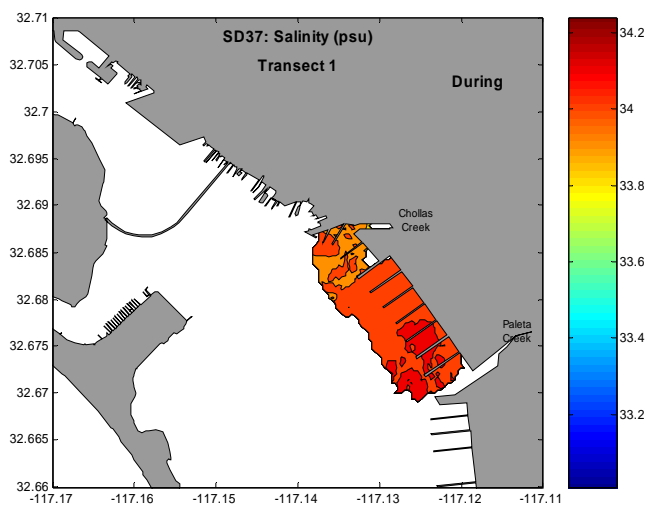
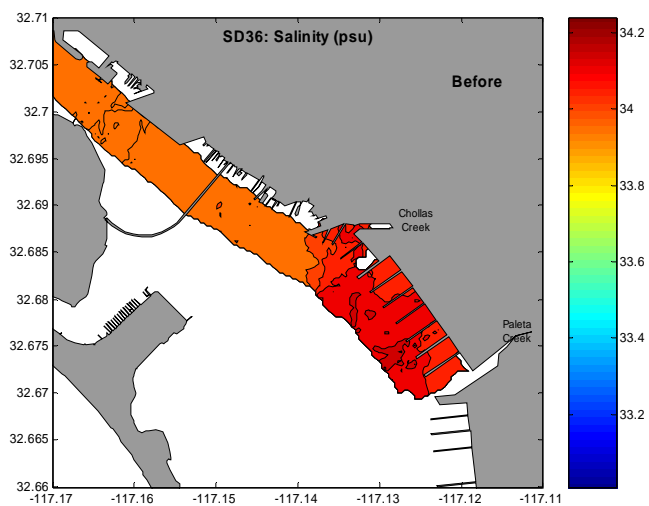
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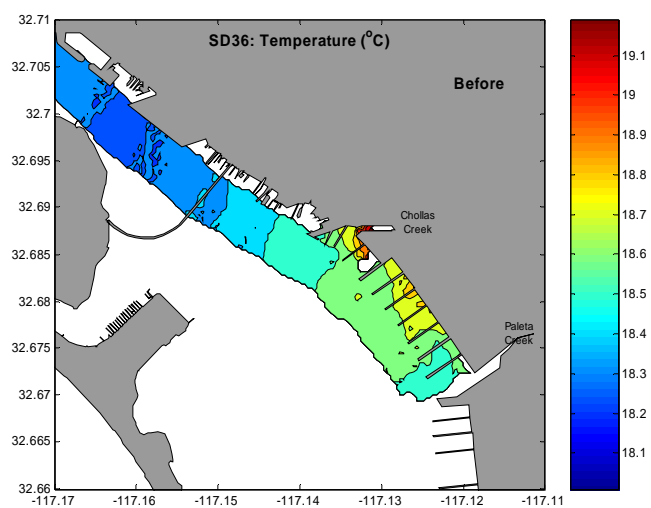
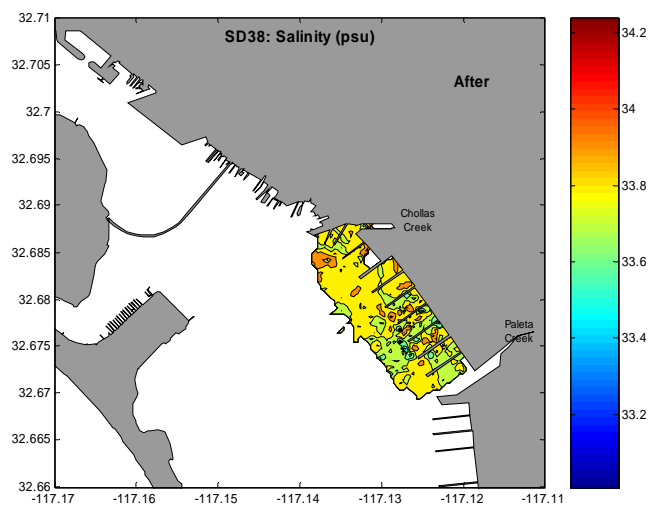
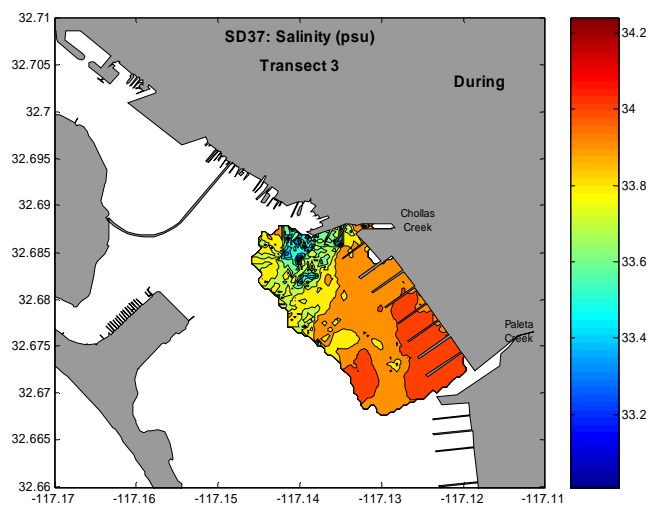
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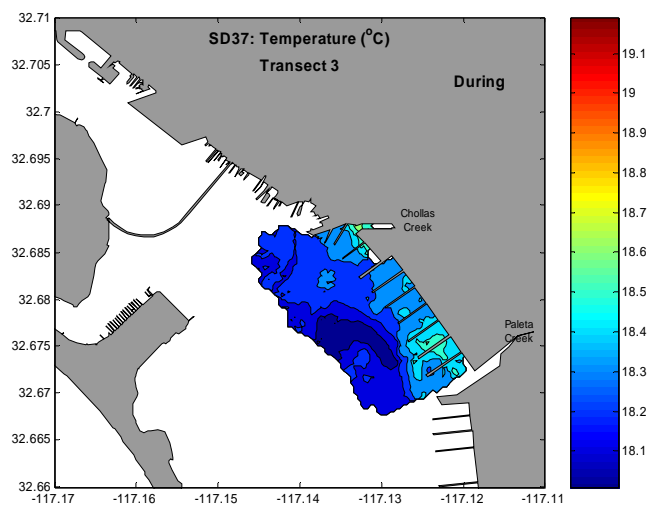
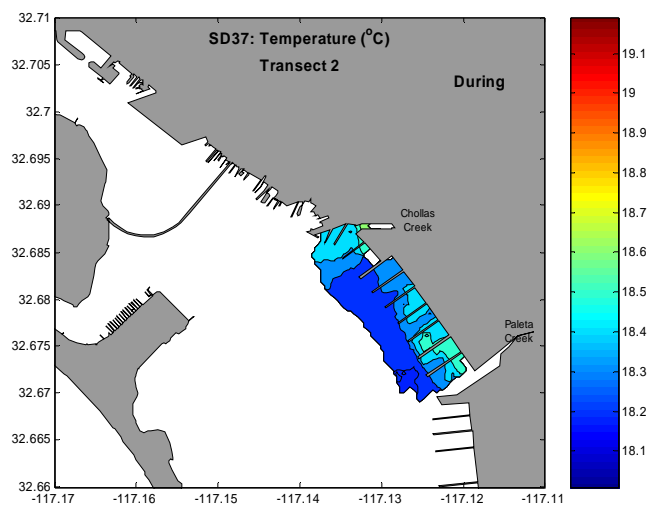
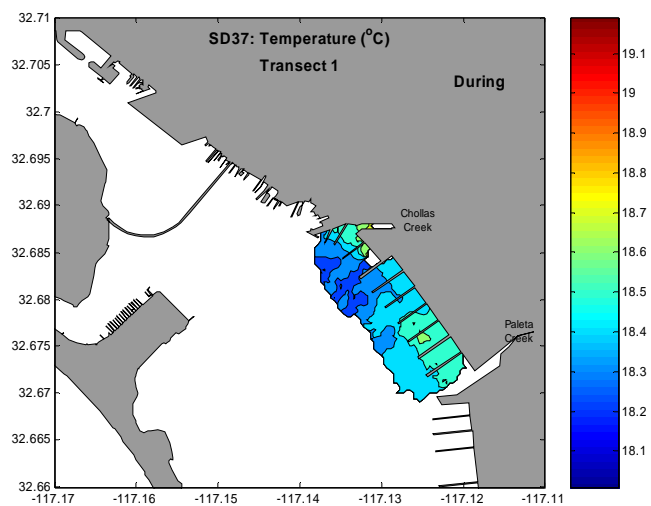
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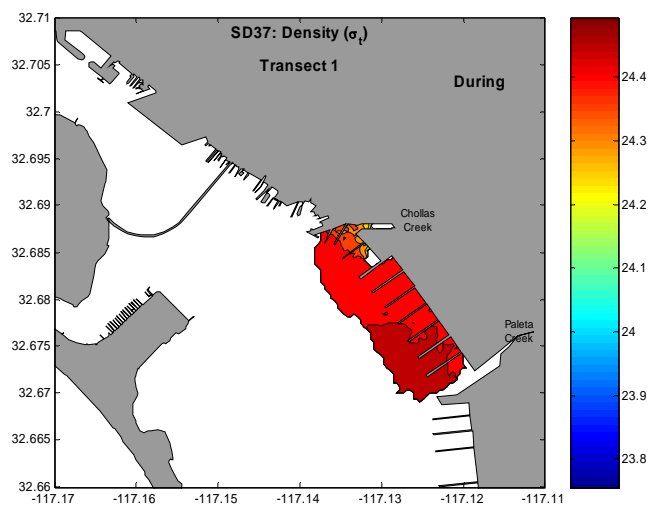
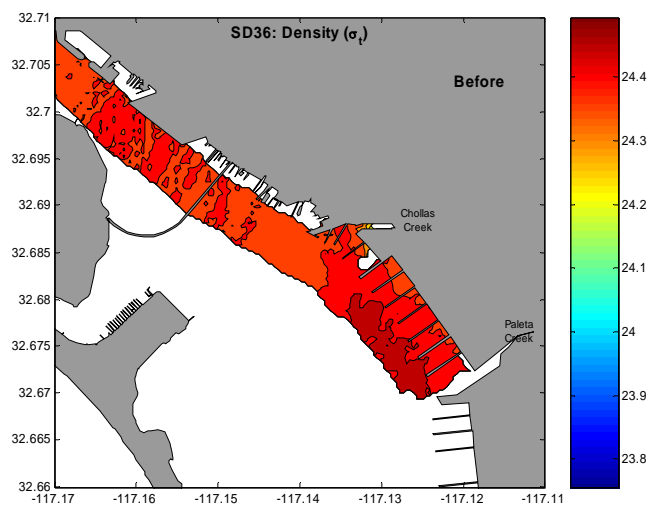
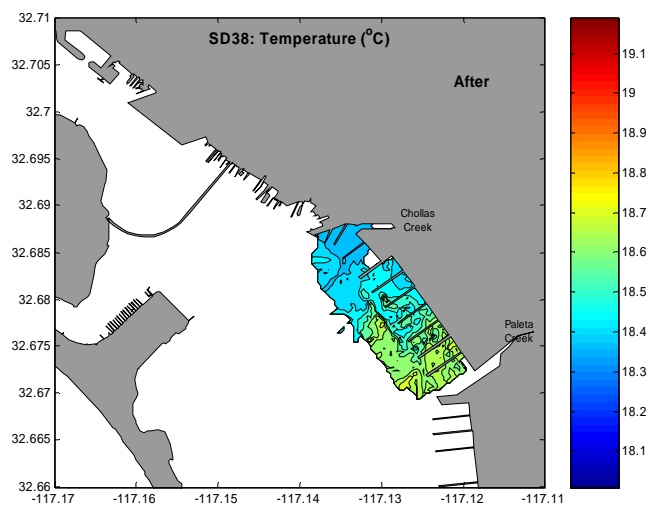


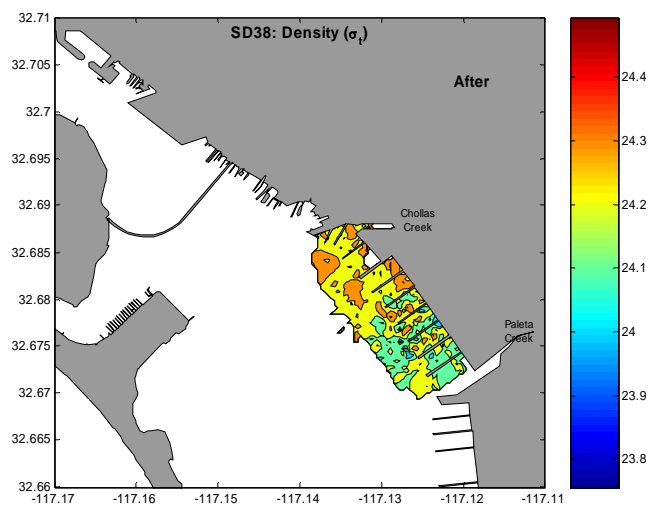
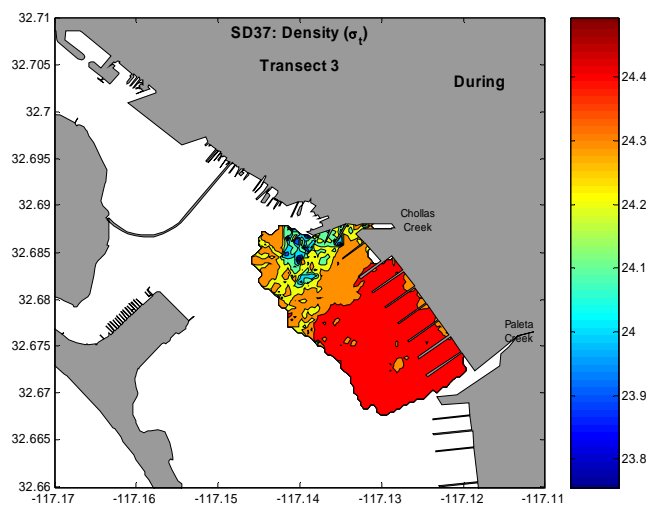
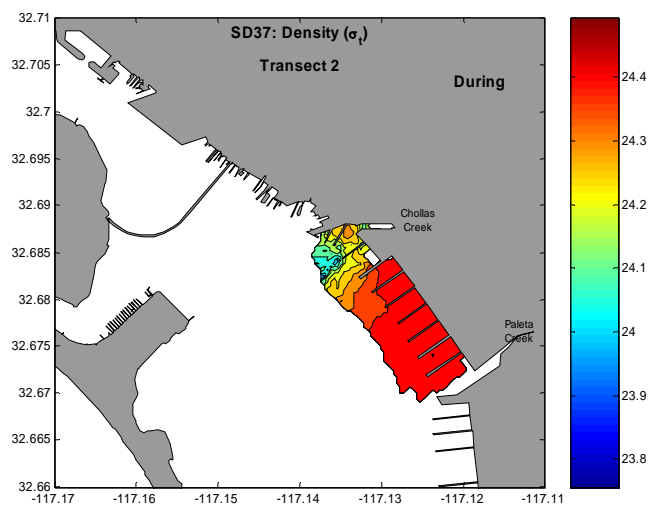


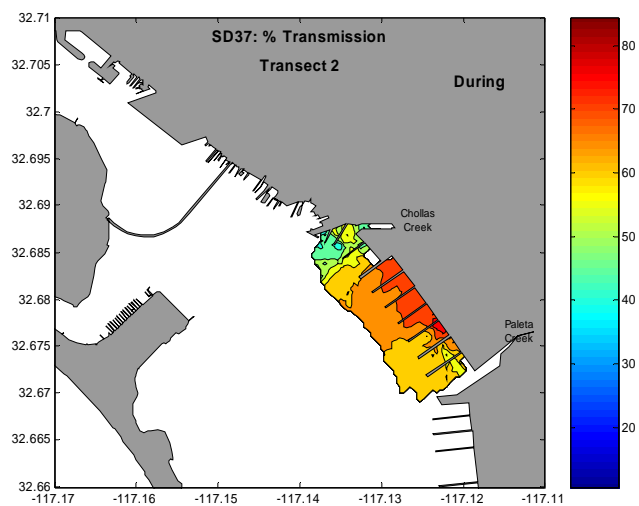
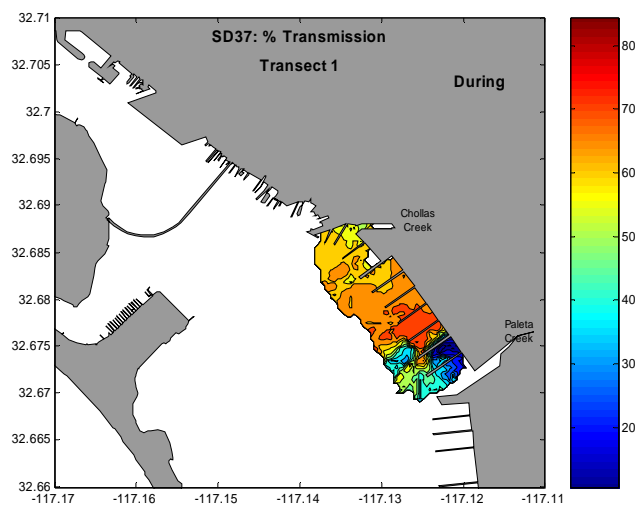
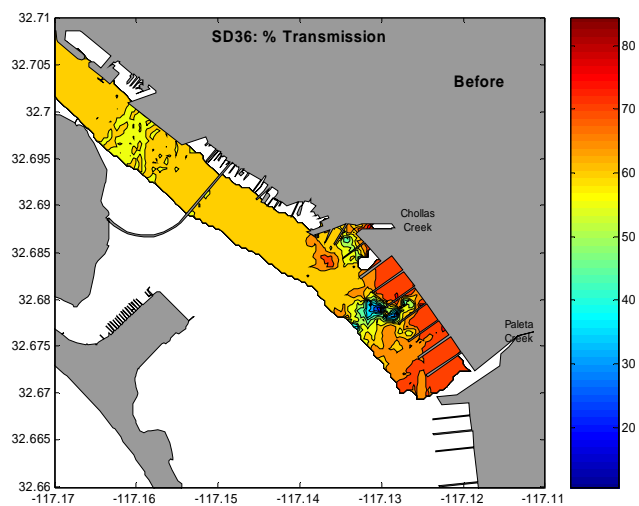


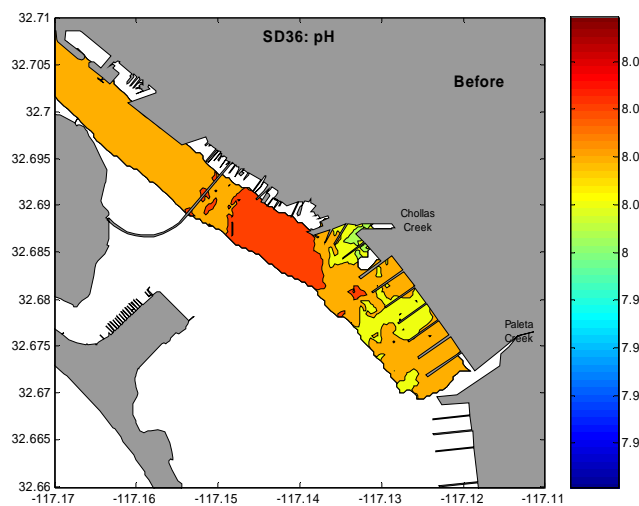
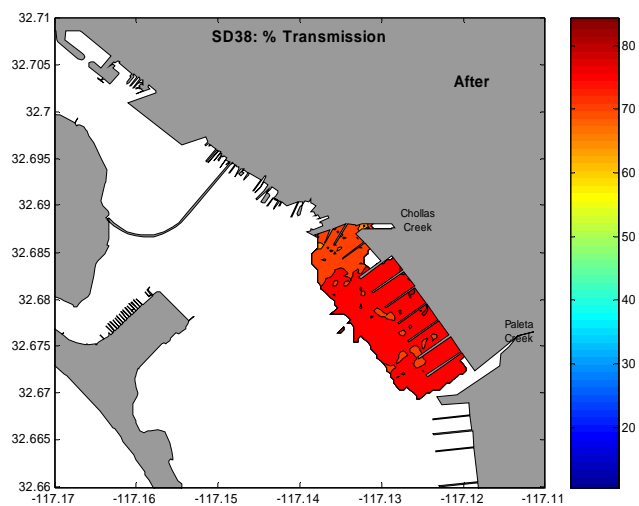
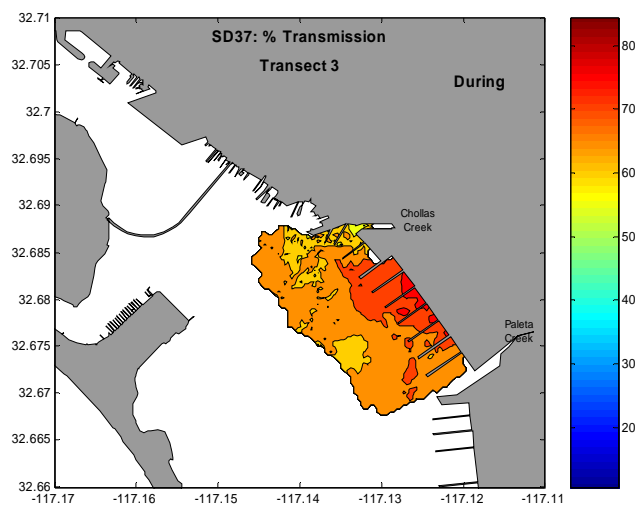


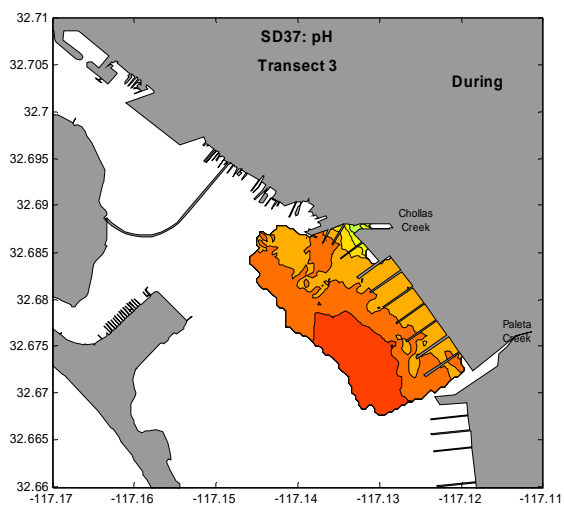
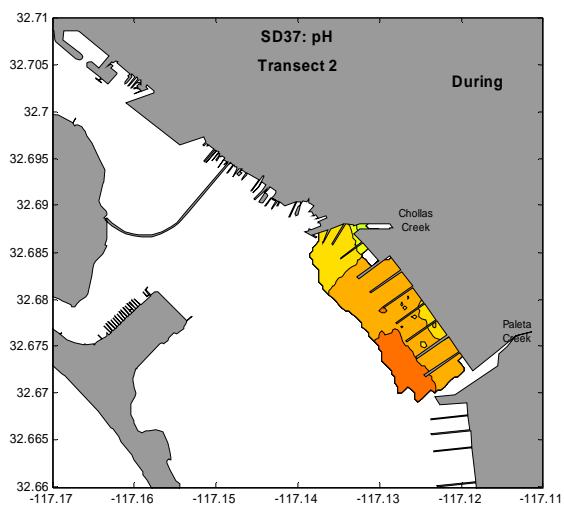
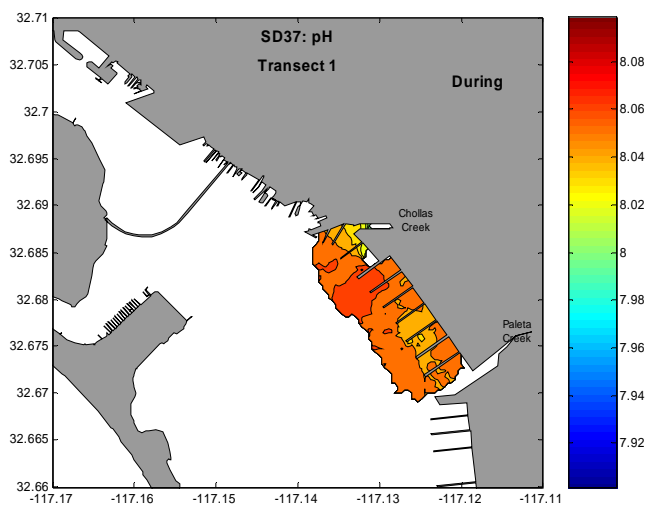


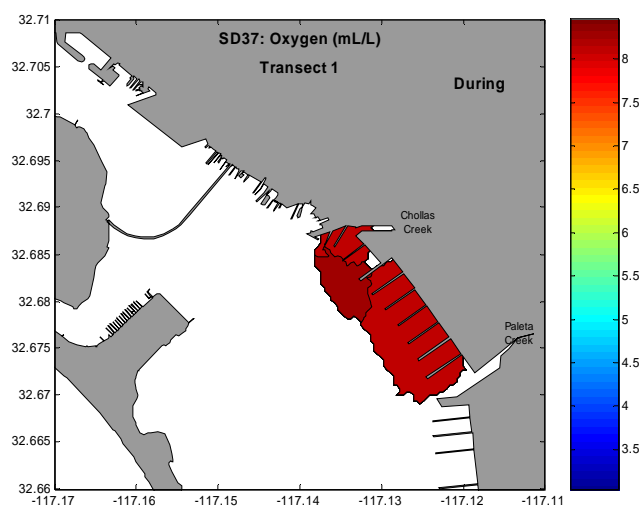
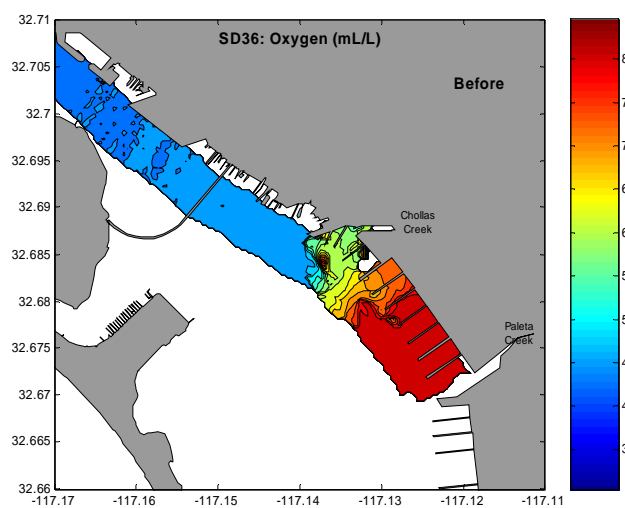
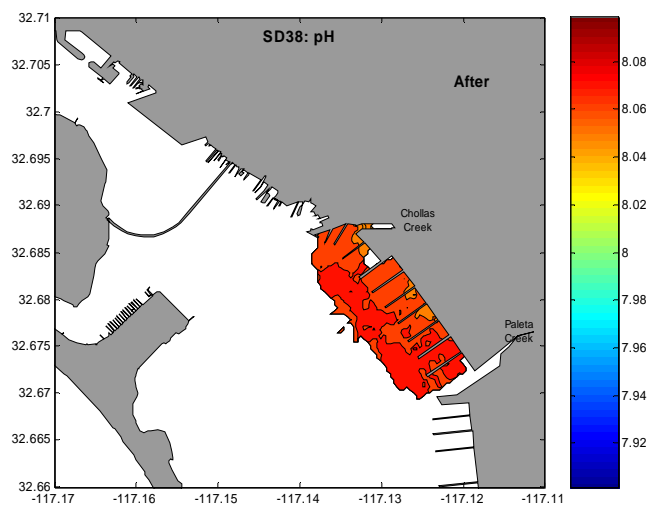




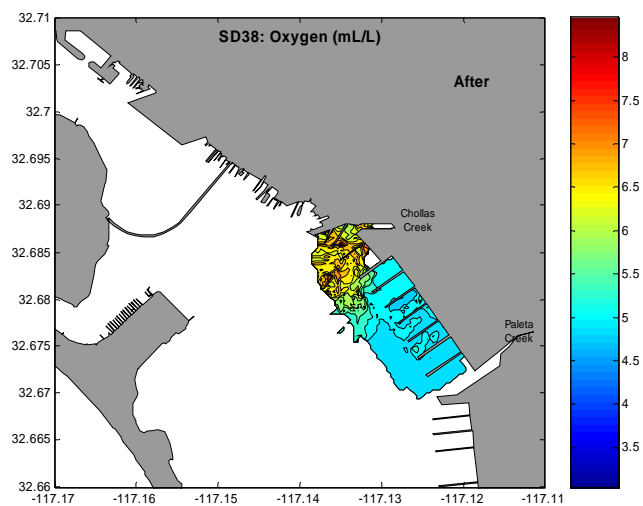
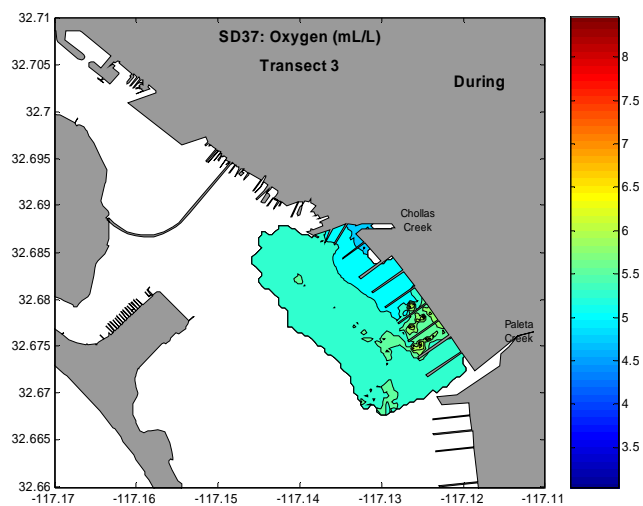
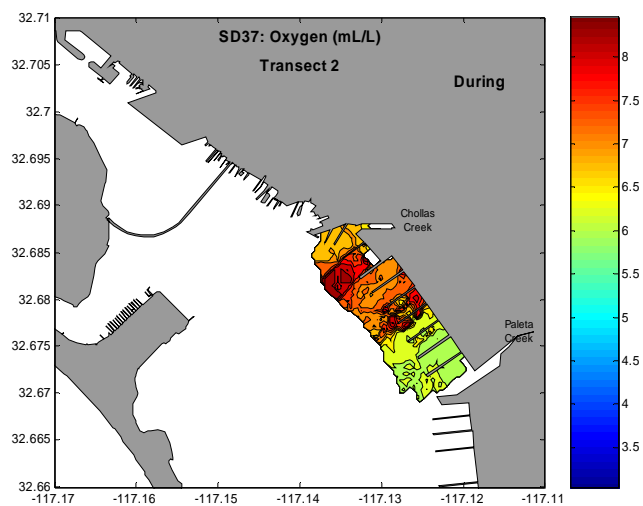


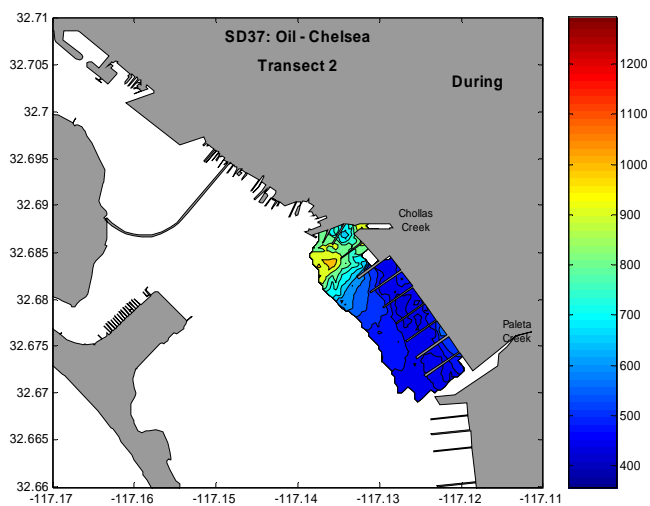
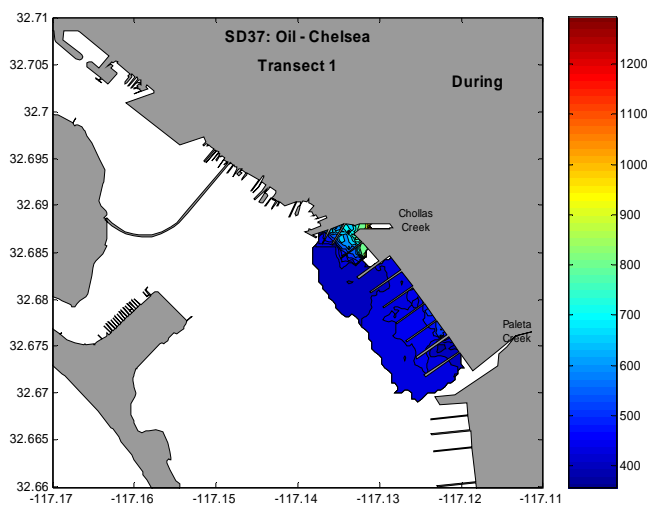
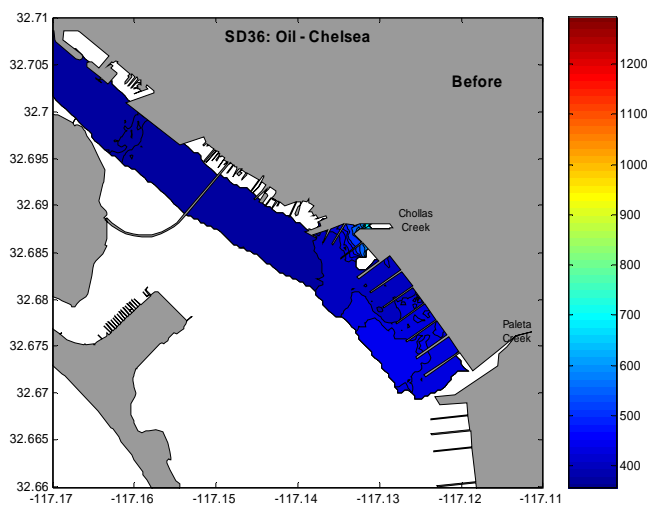


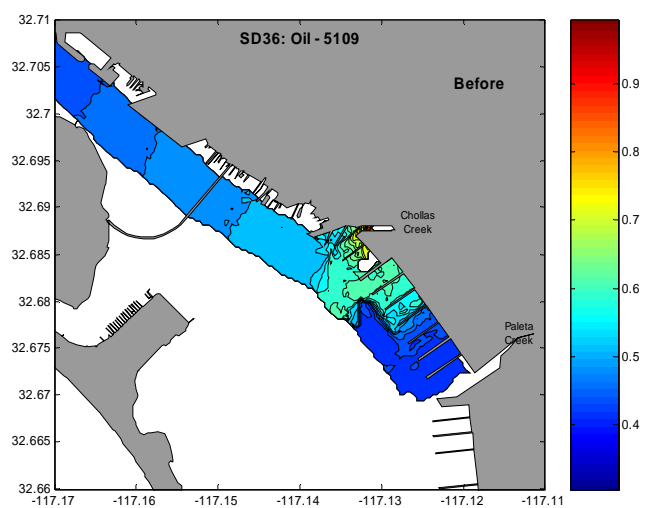
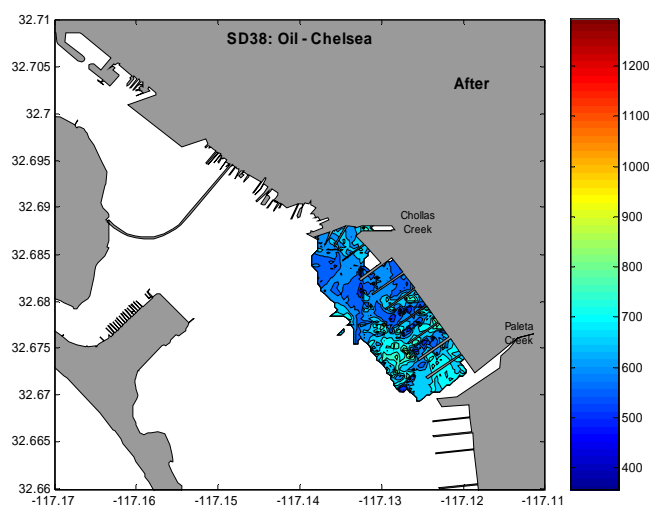
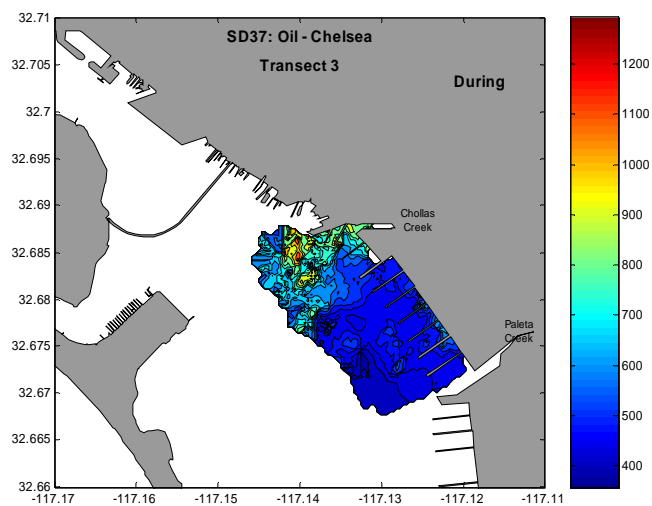


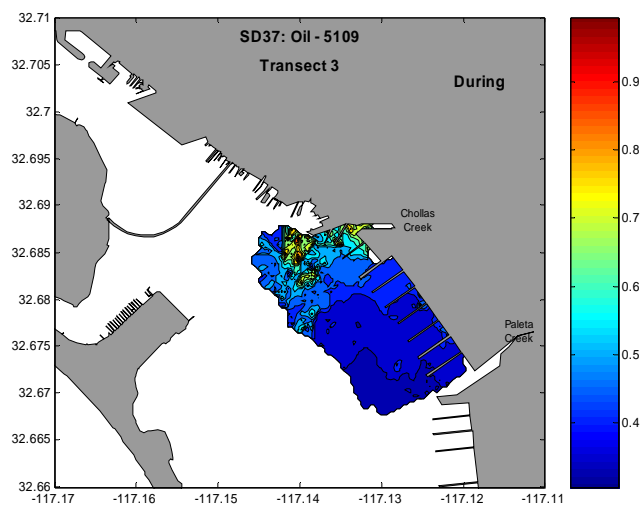
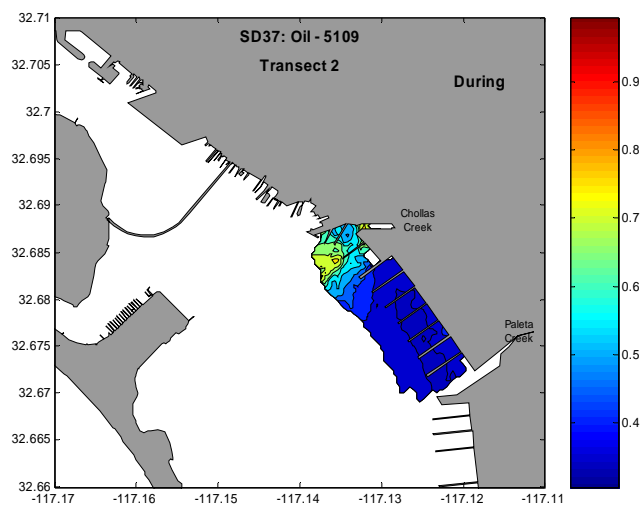
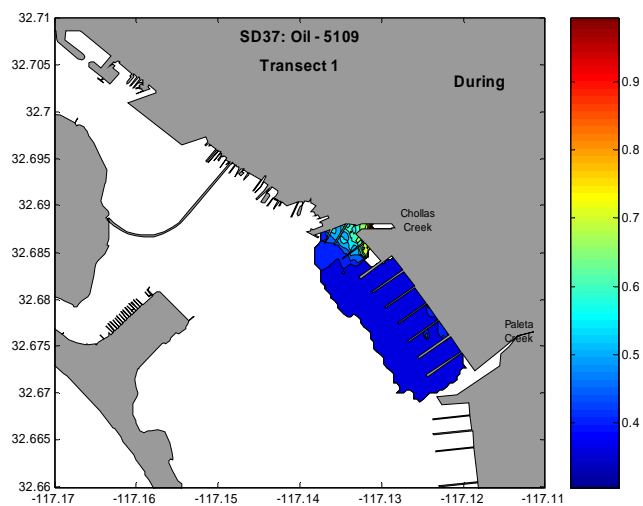


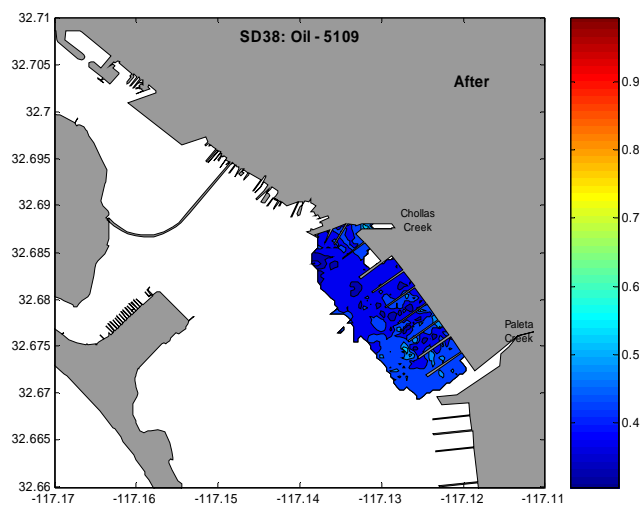


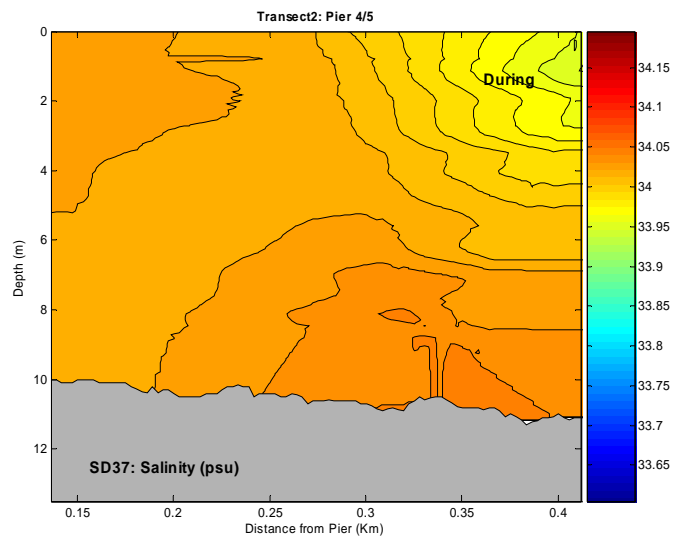
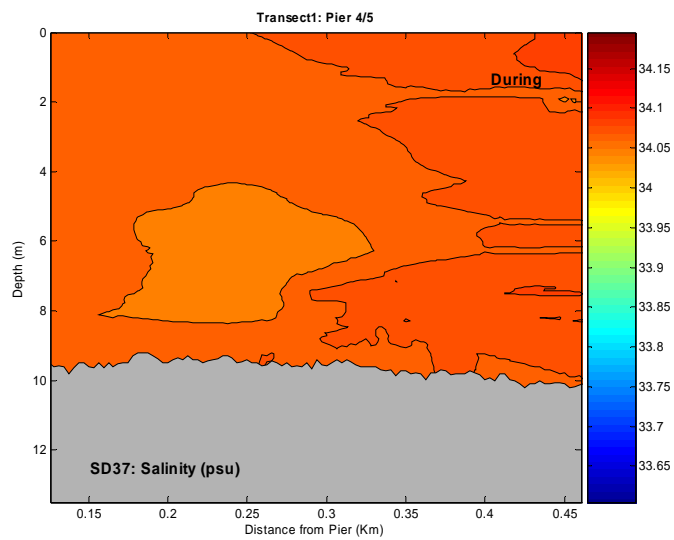
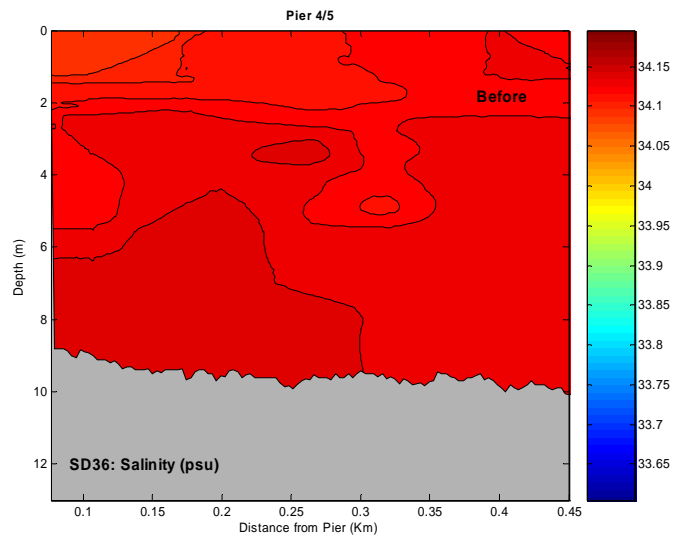


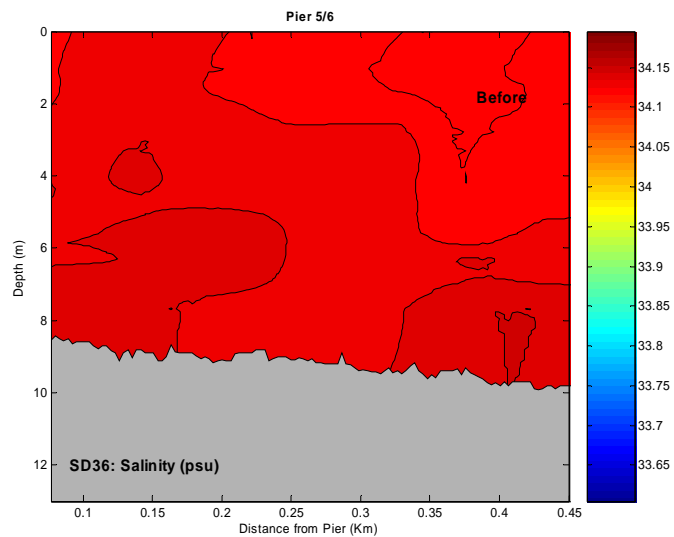
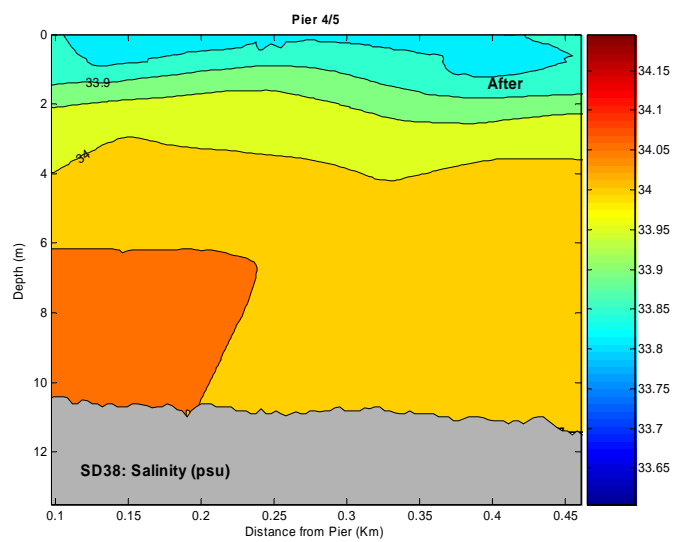
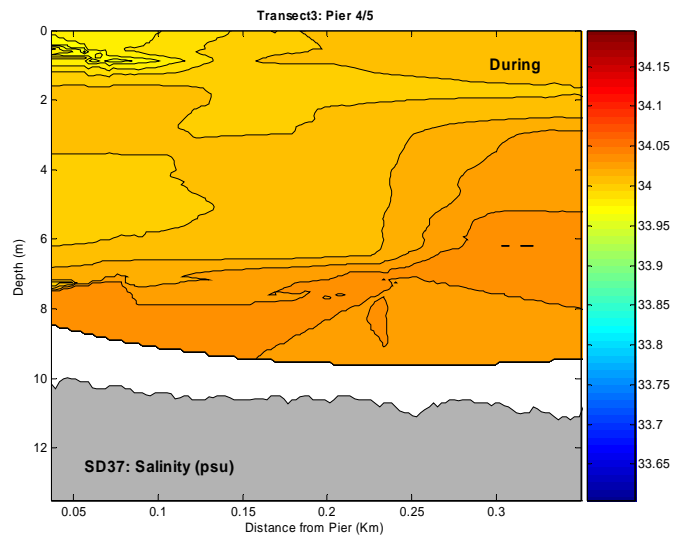


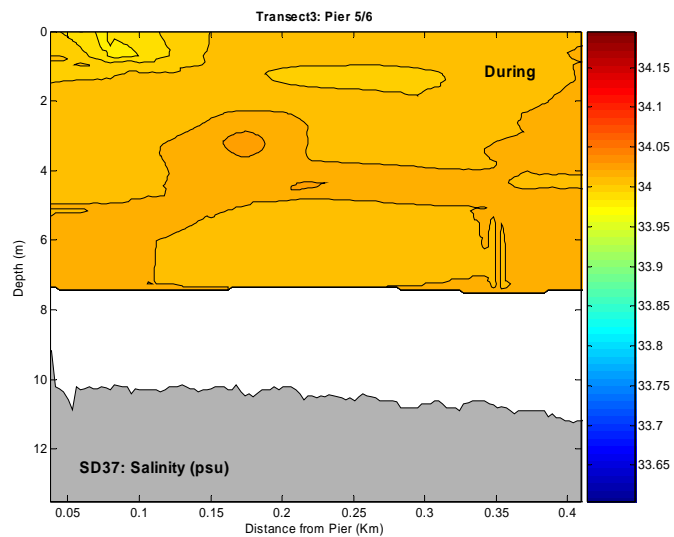
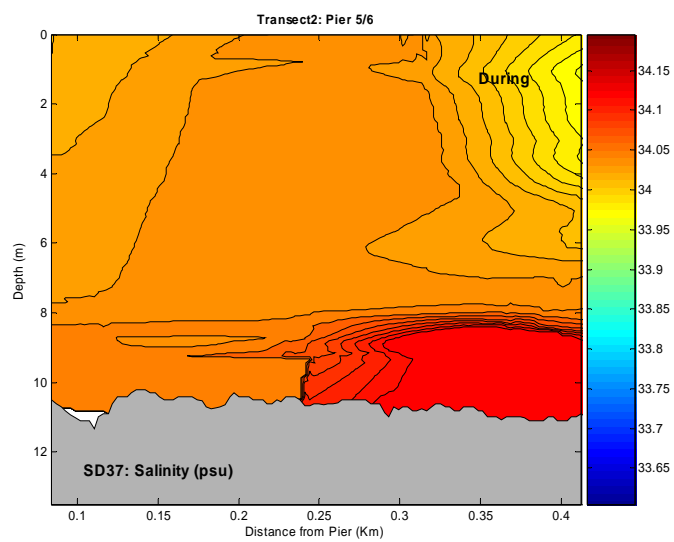
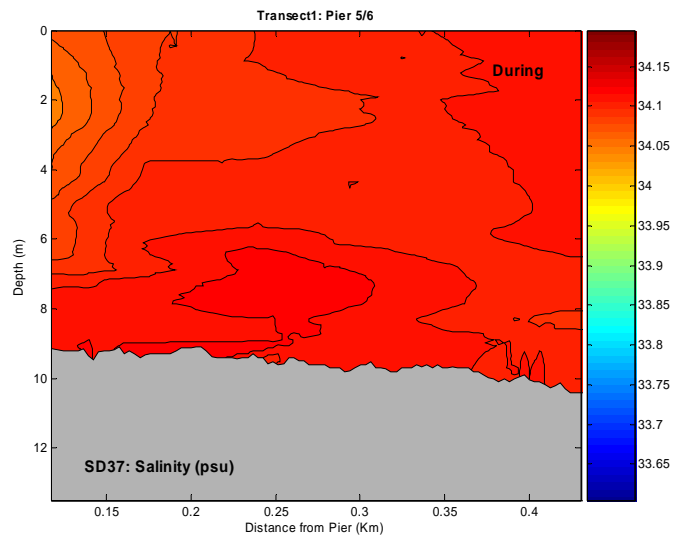




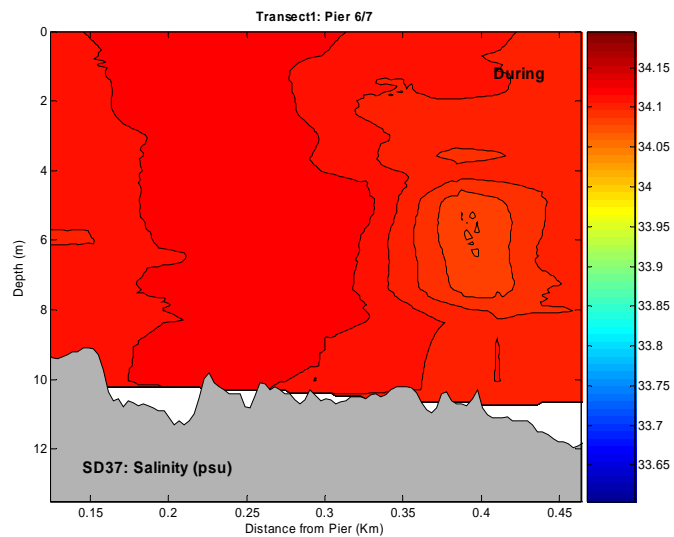
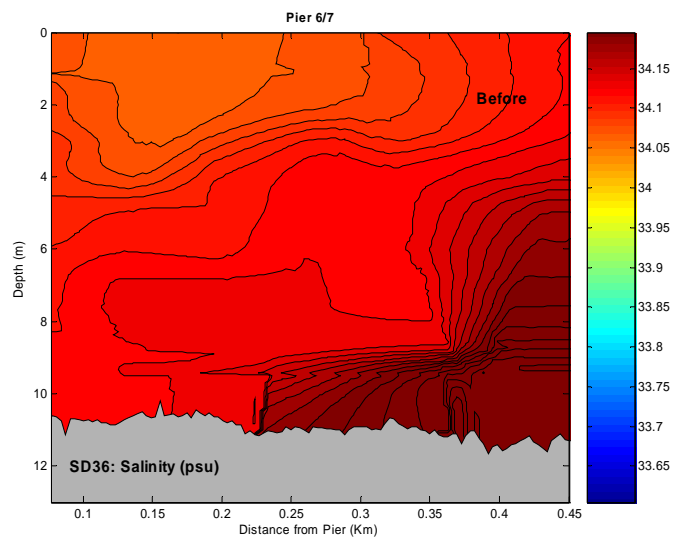
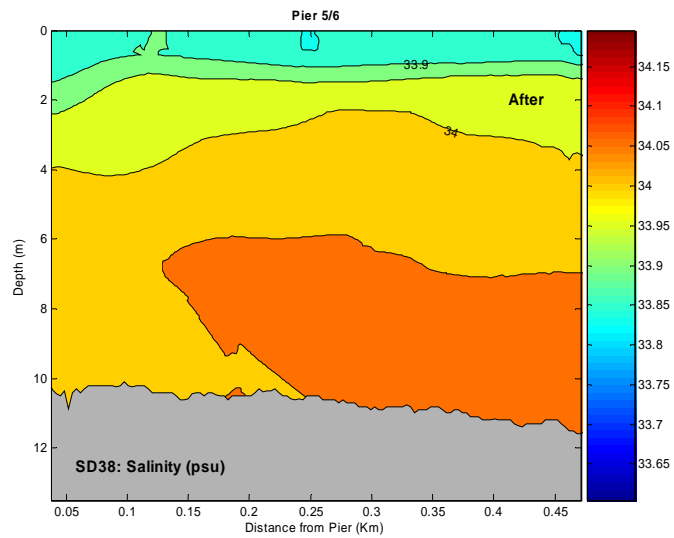


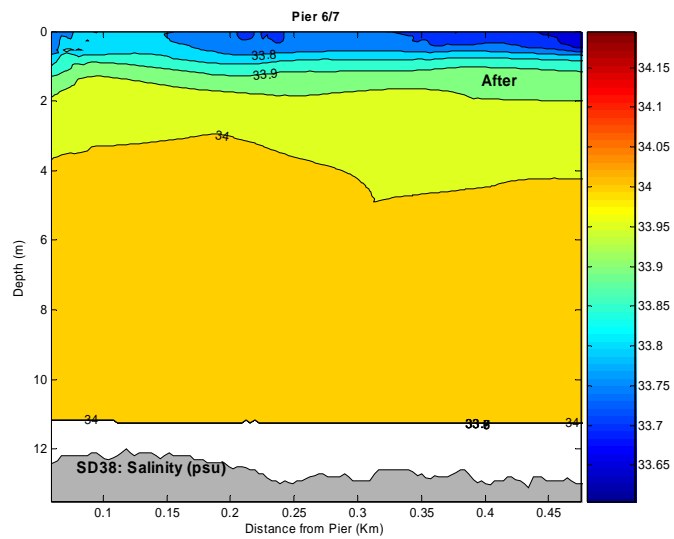
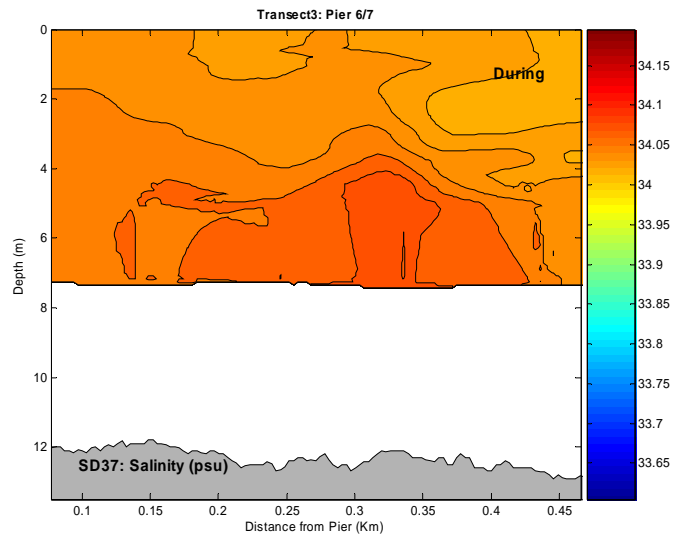
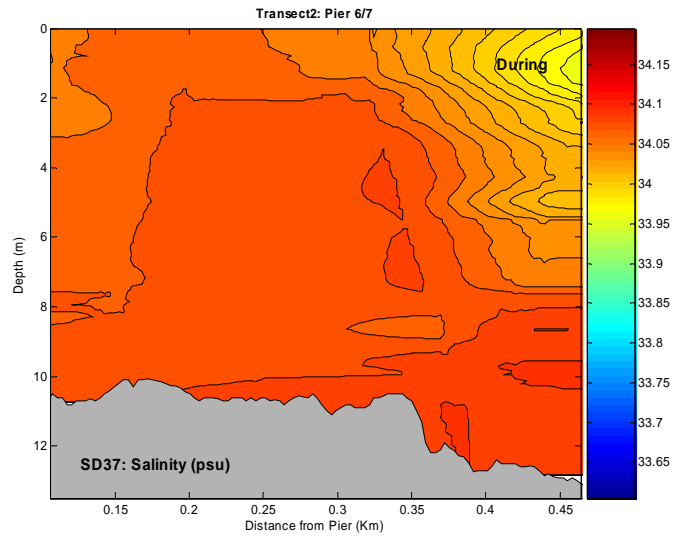




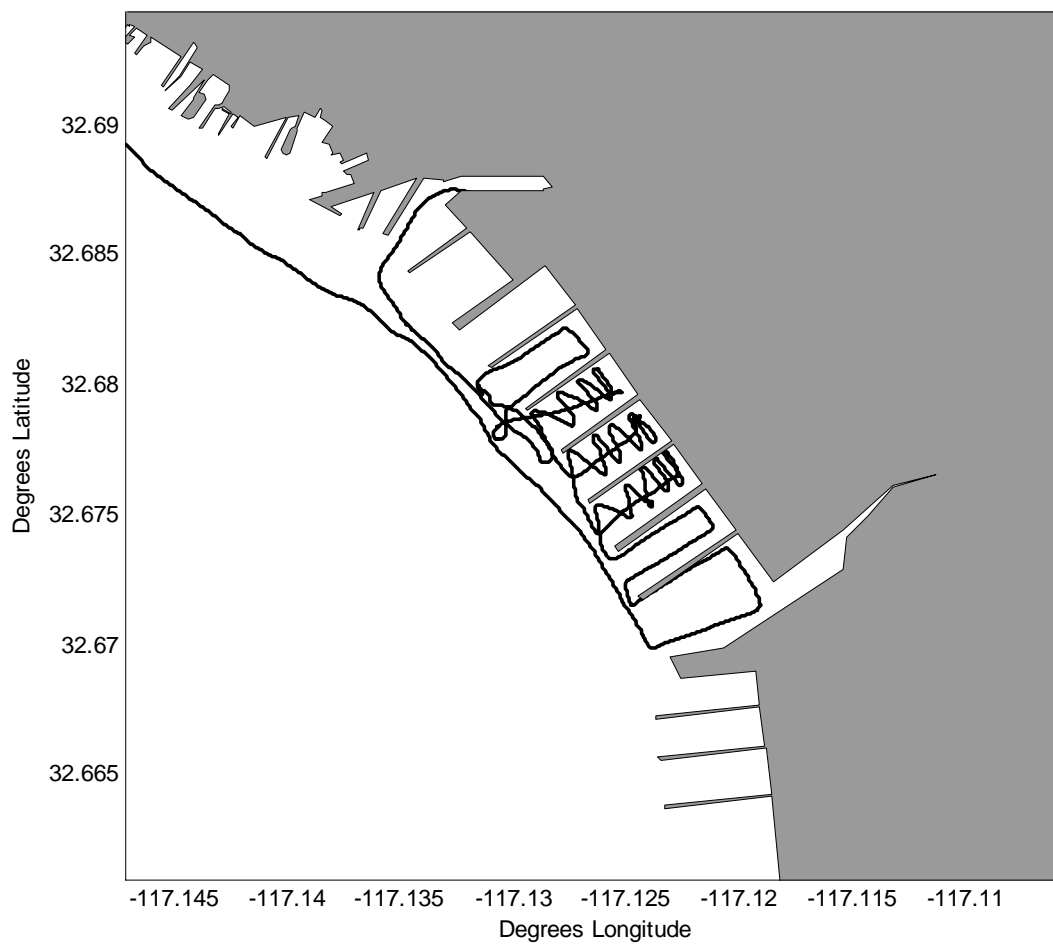


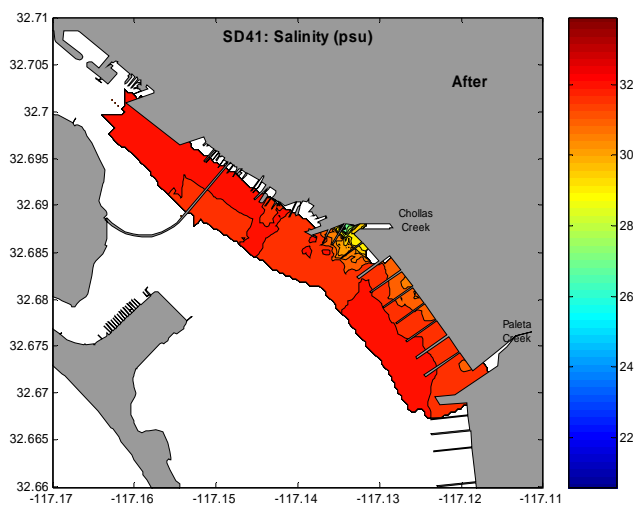
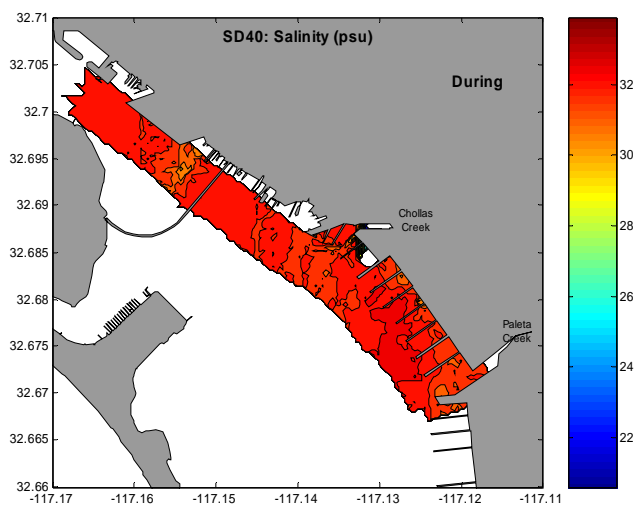
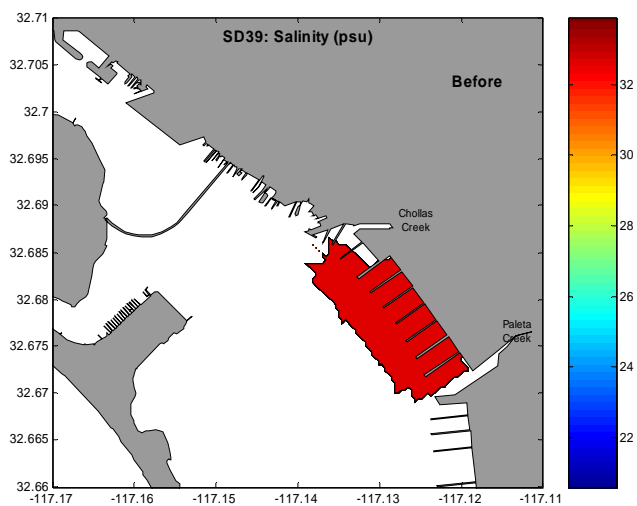


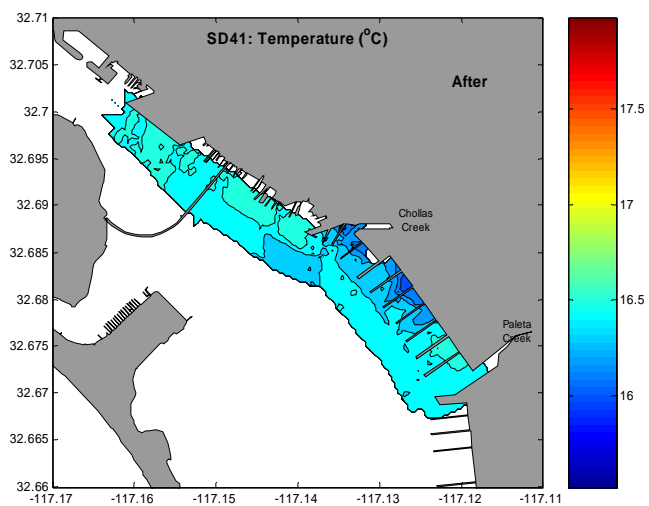
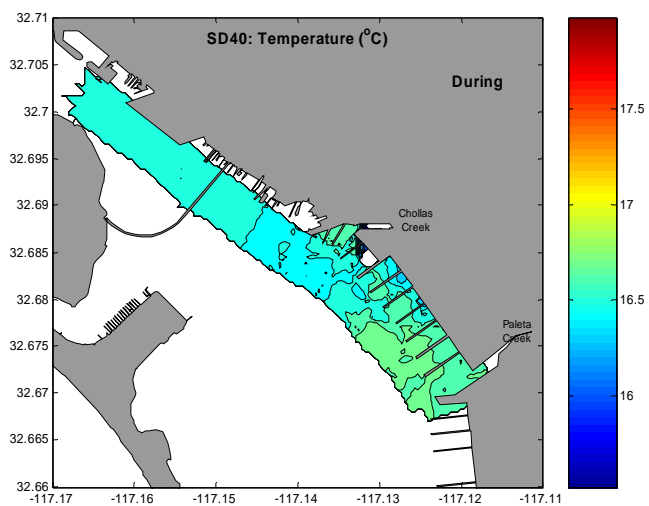
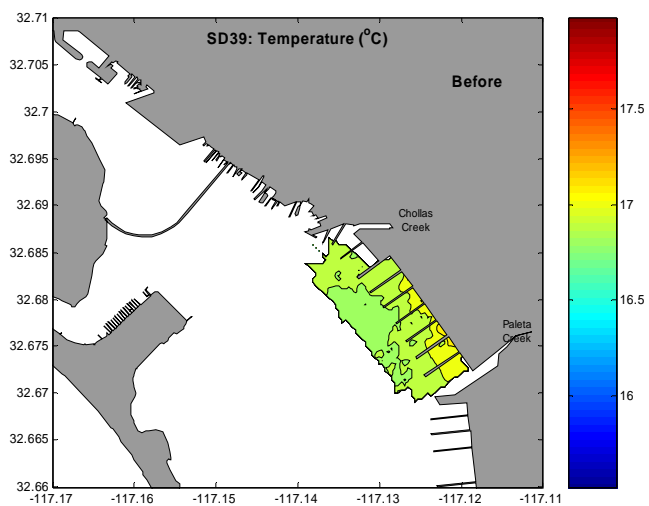


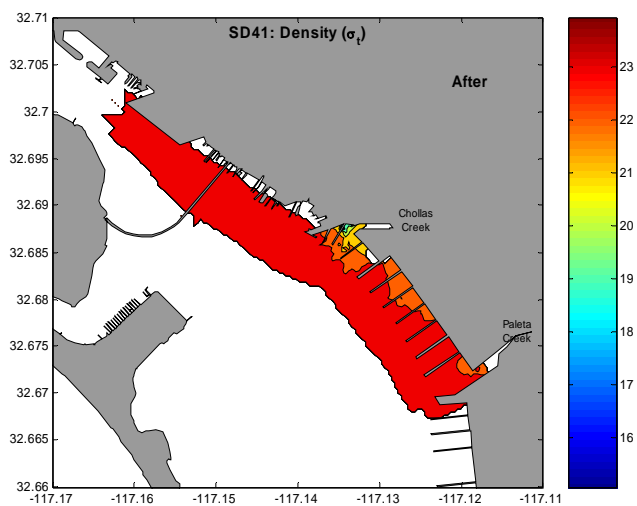
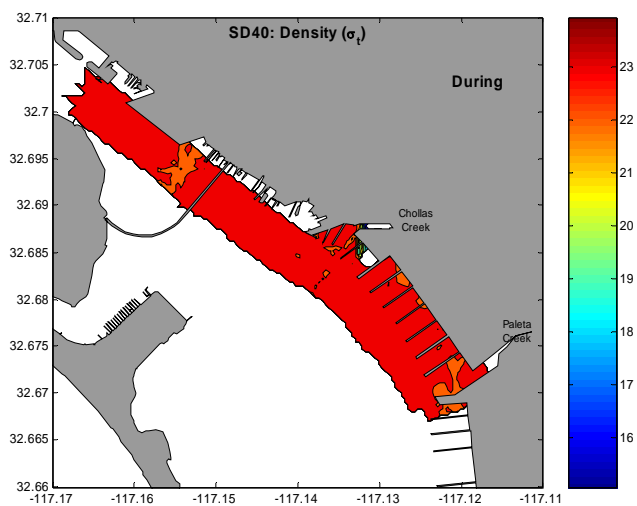
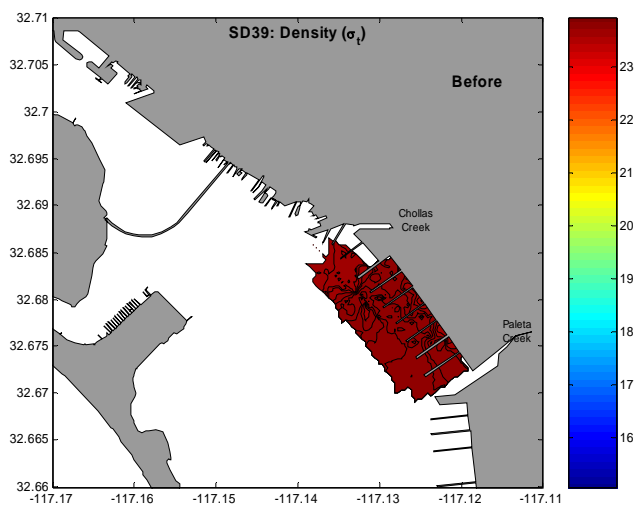


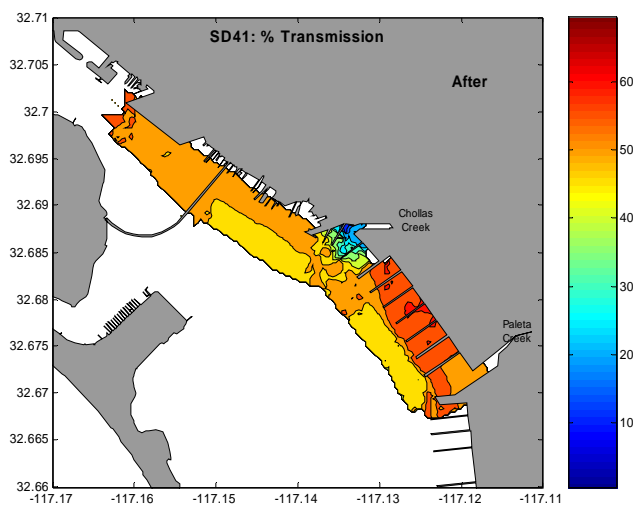
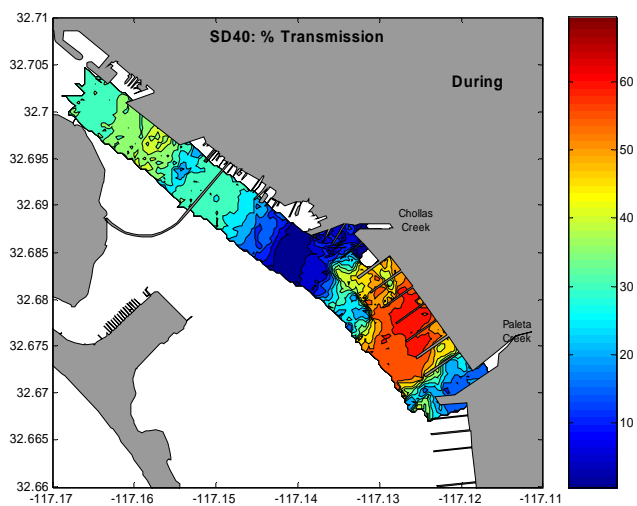
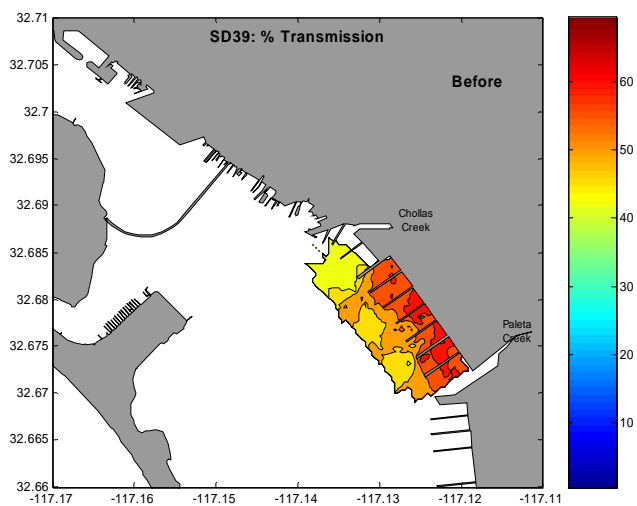
SDB2- 2/24/2004

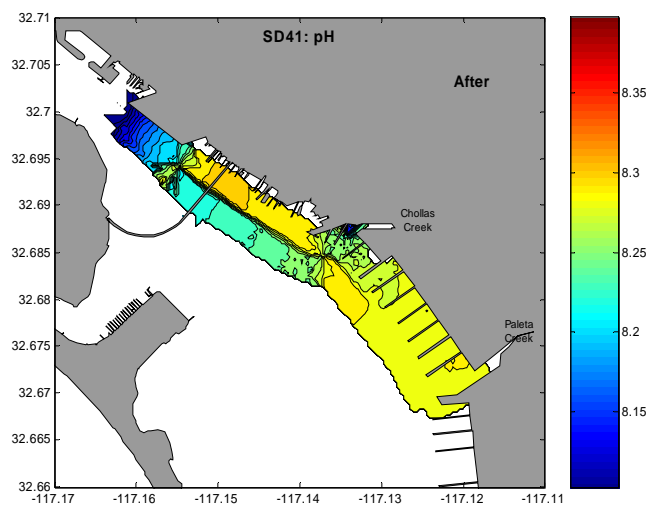
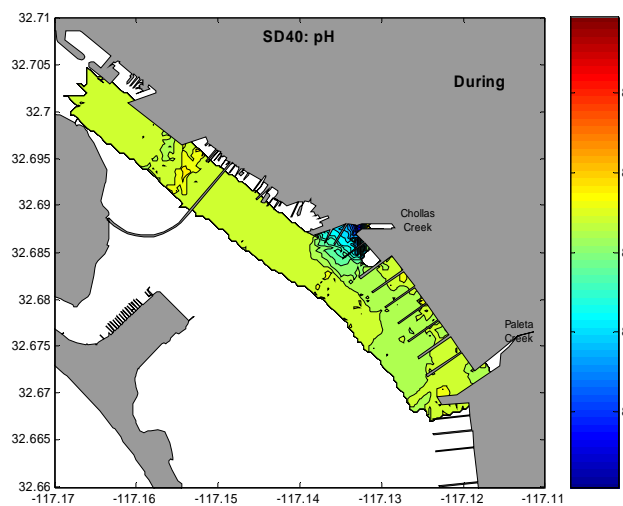
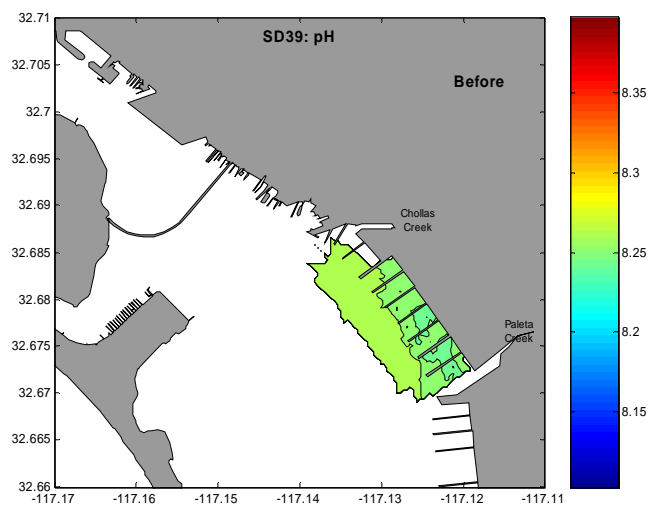




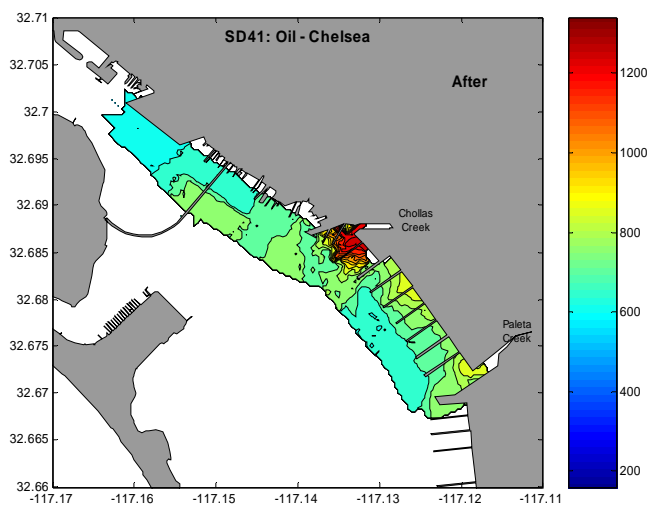
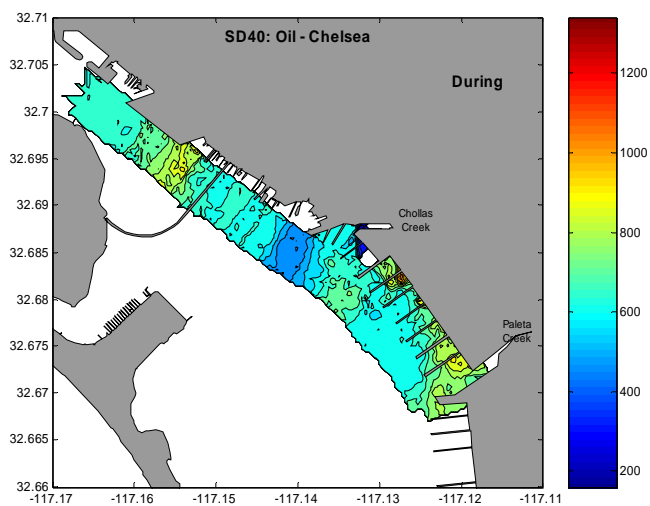
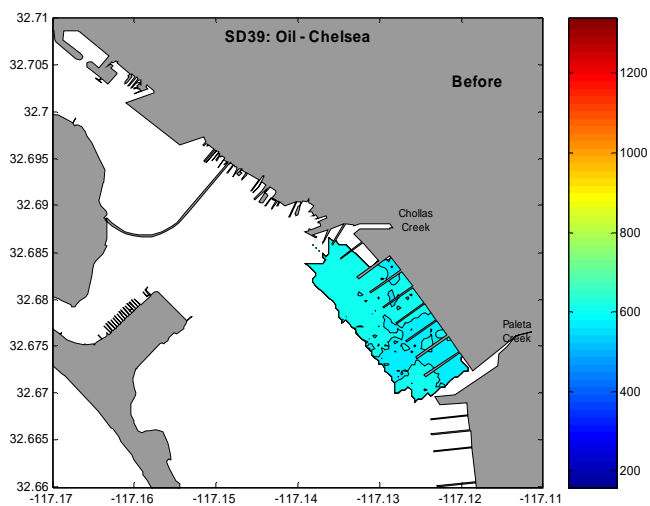


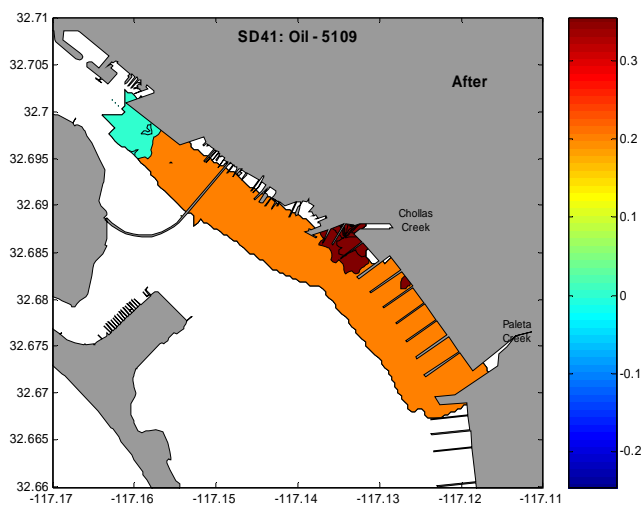
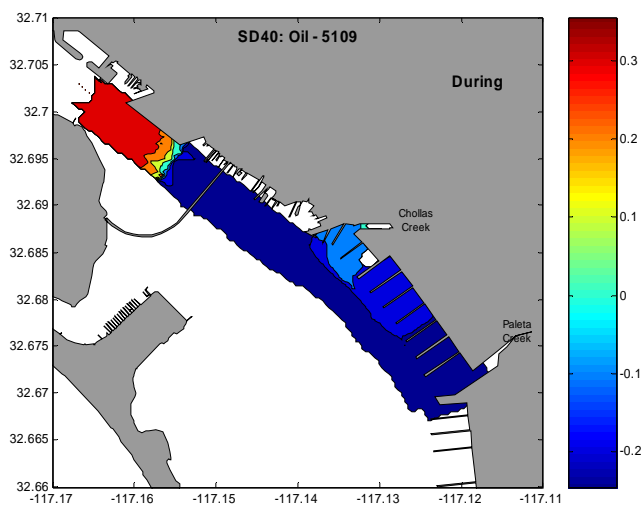
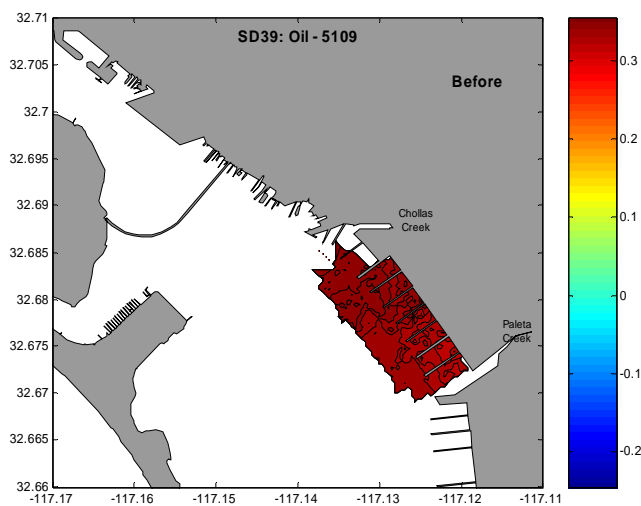


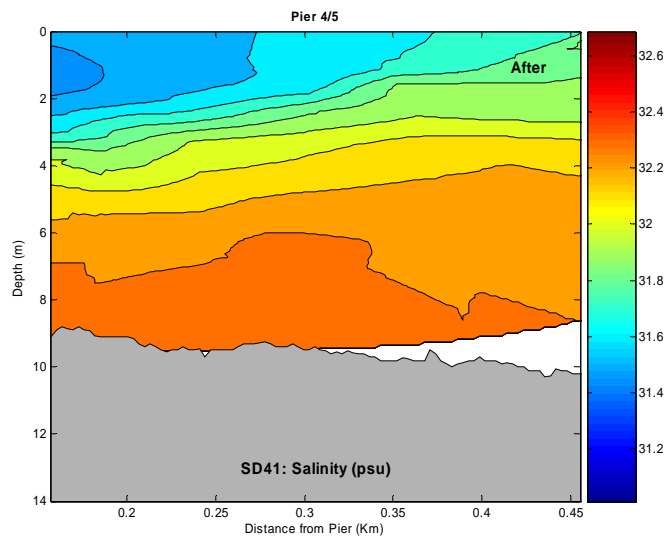
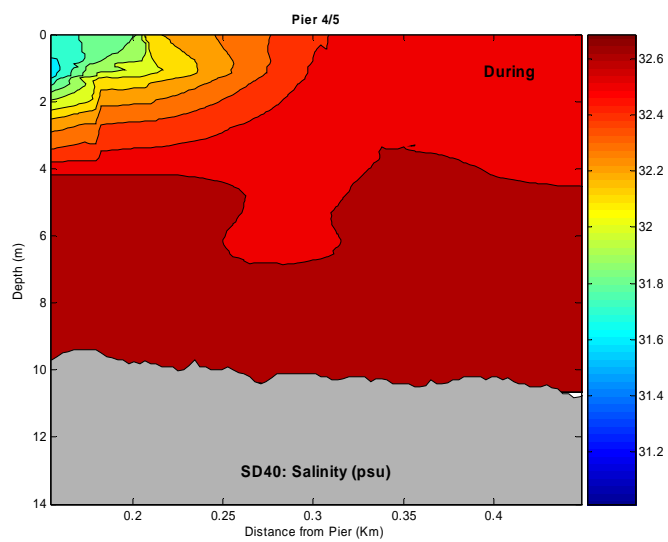
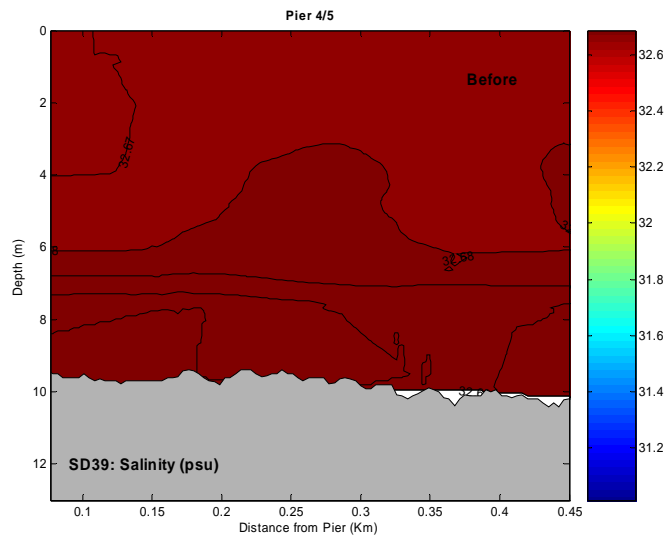


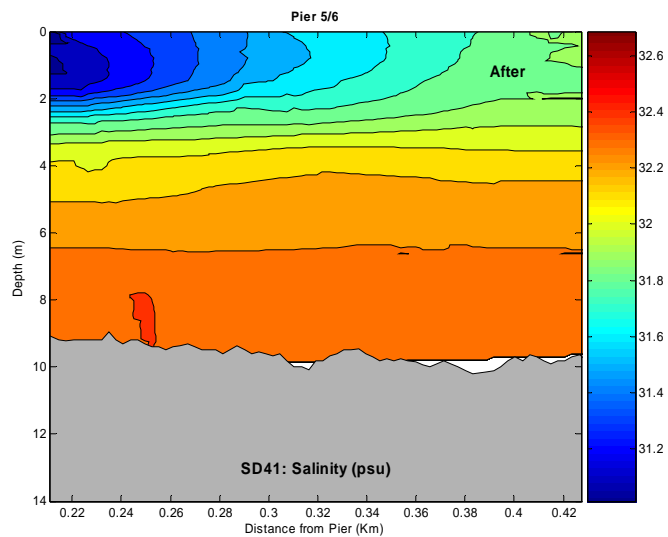
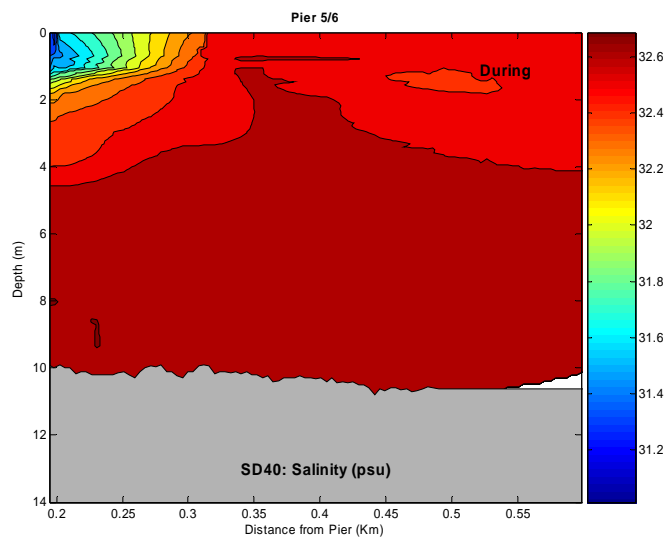
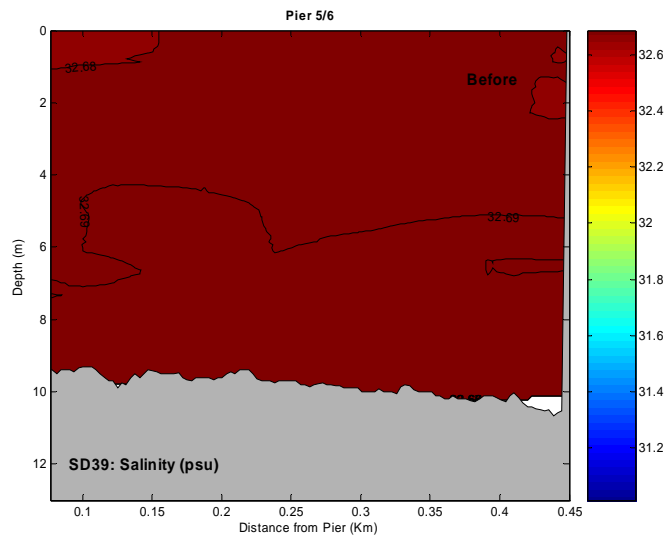


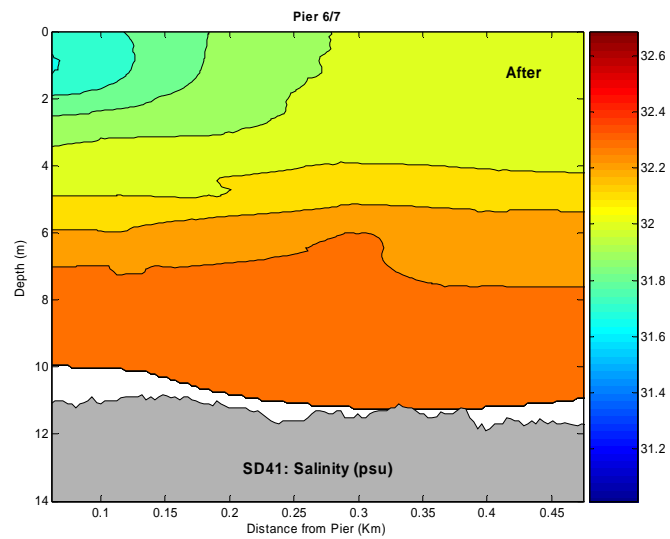
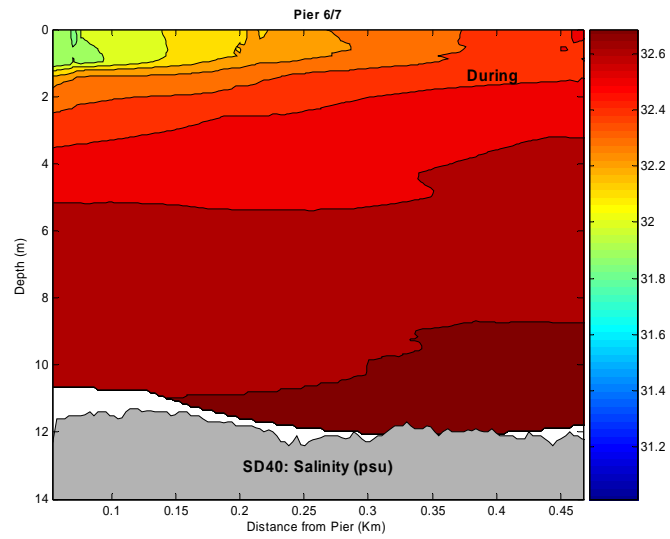
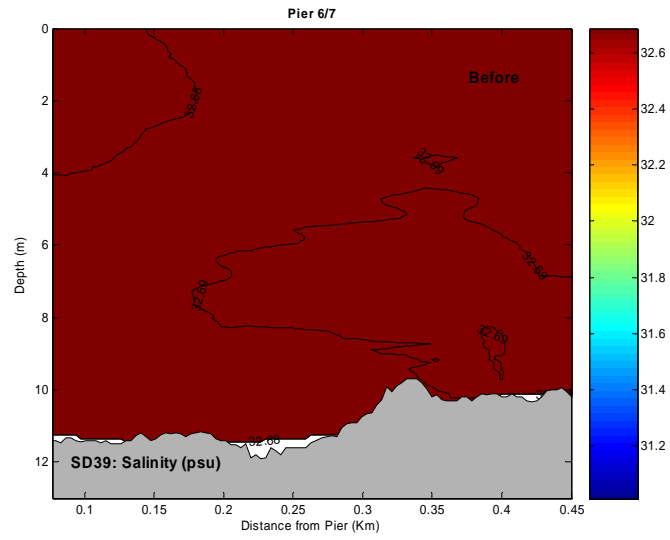










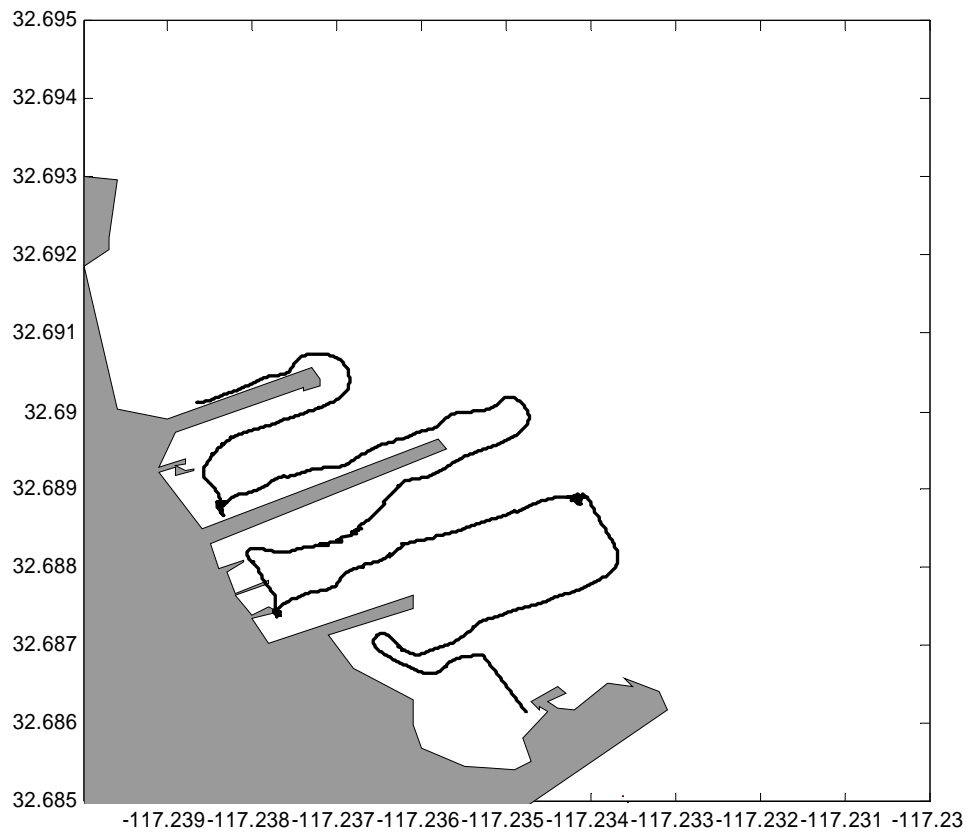


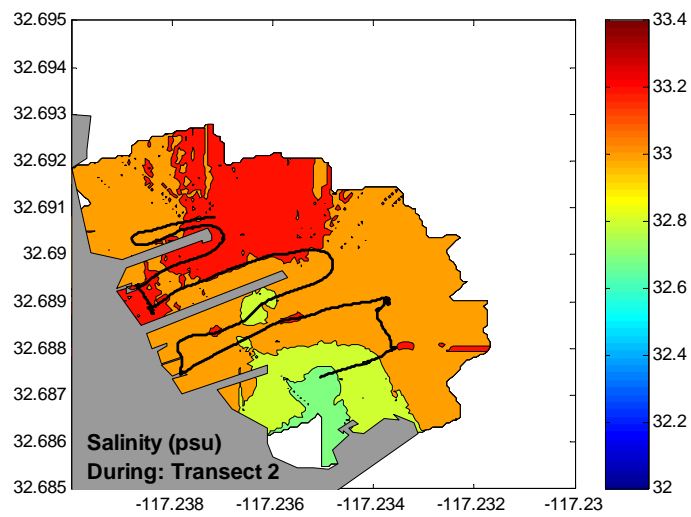
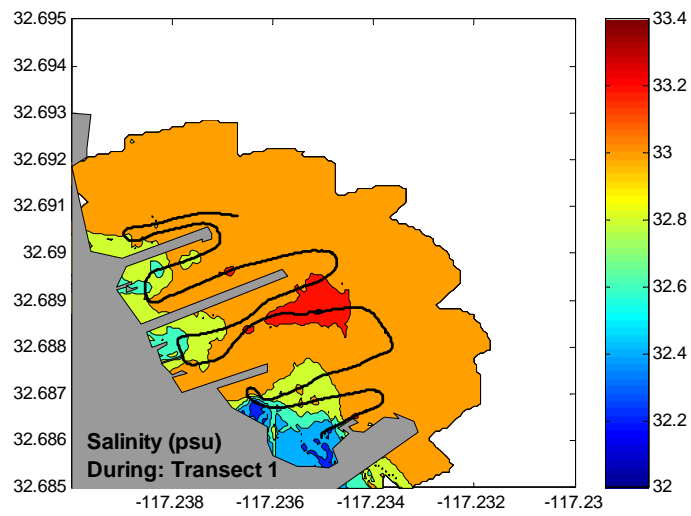
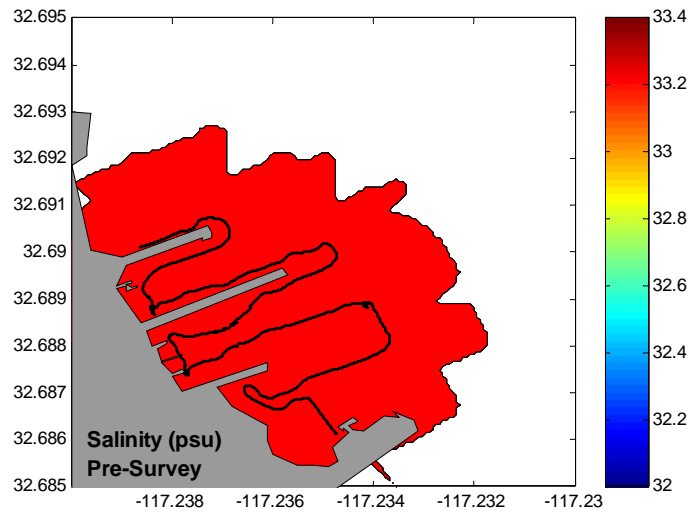
## **Appendix G2**

### ***SUB***

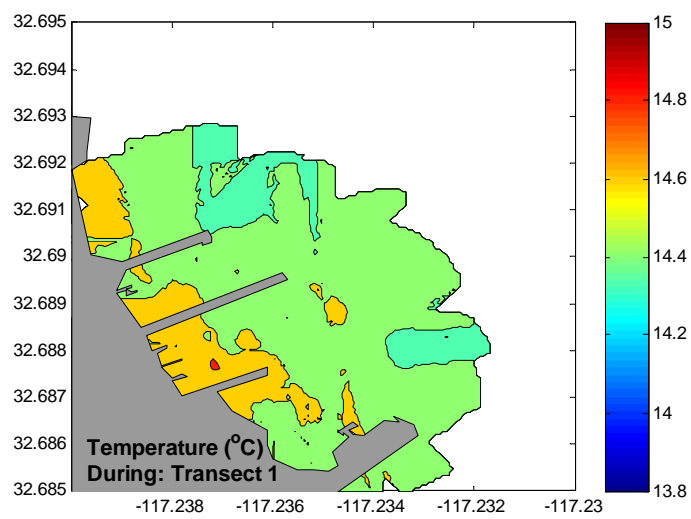
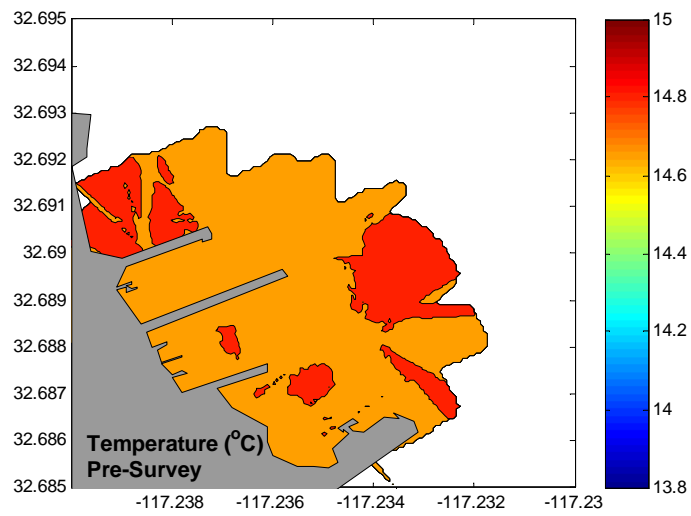
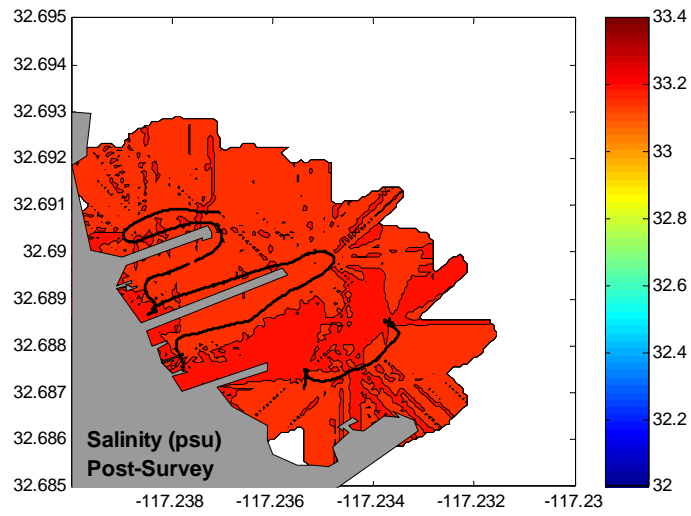
SDB2- 2/24/2003

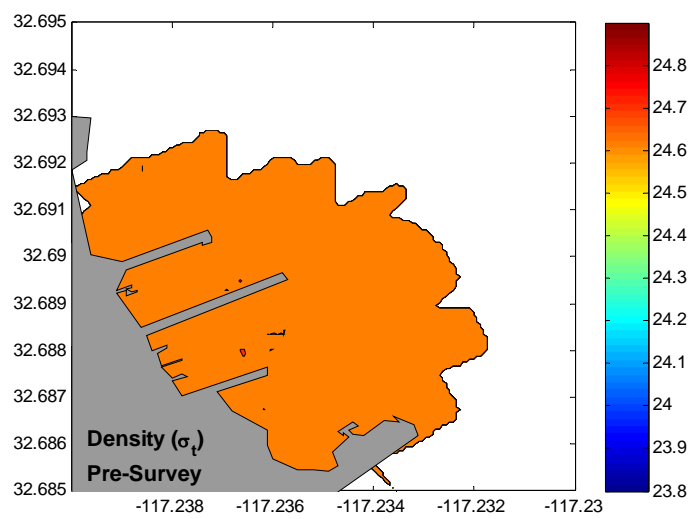
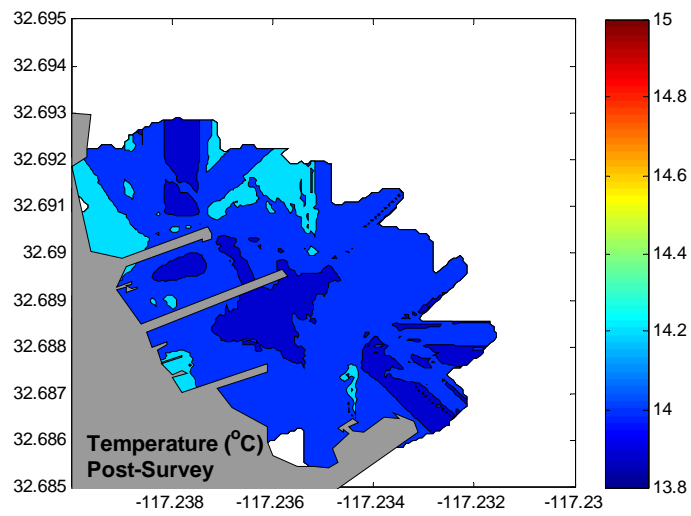
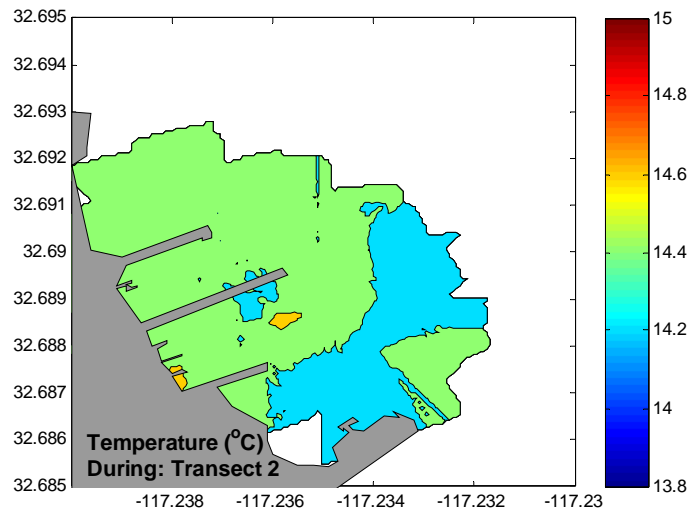
SDB2- 2/24/2004

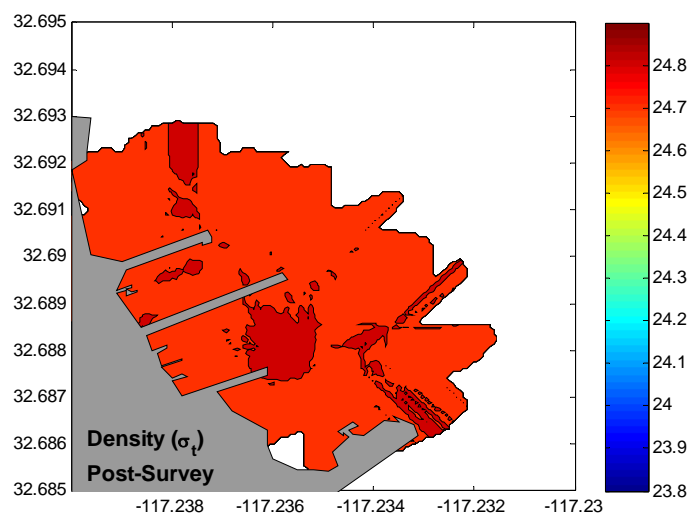
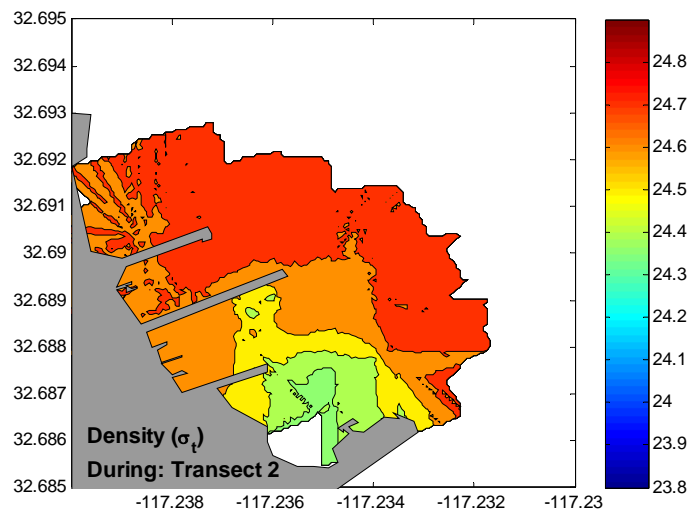
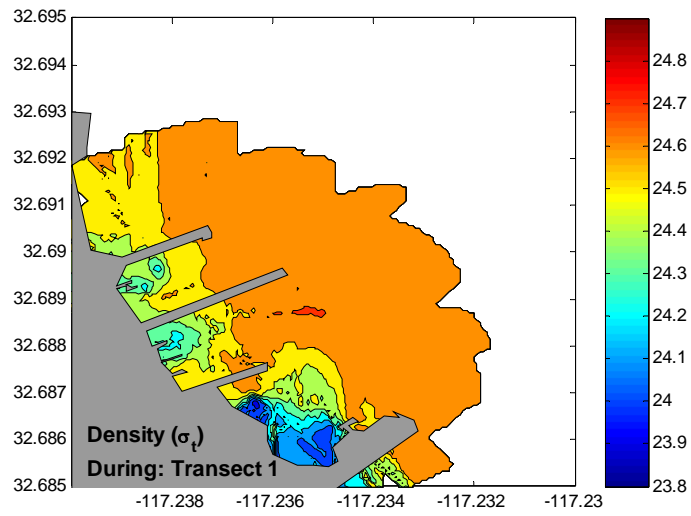


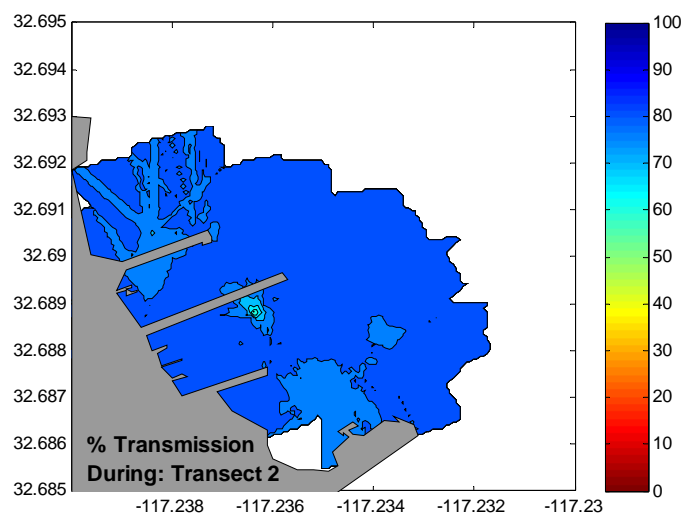
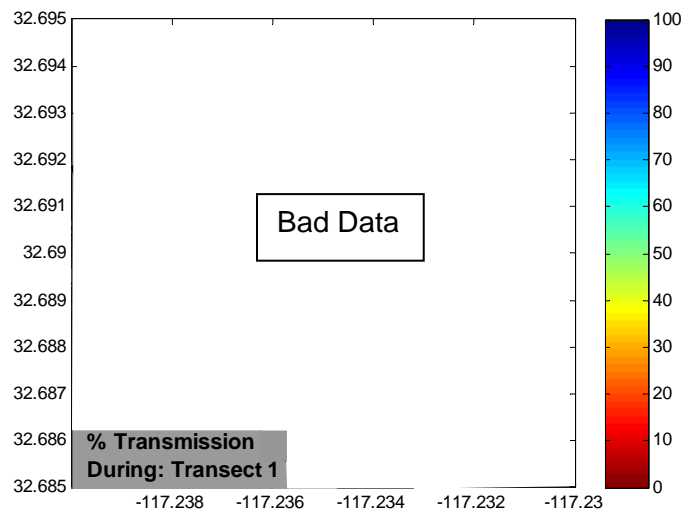
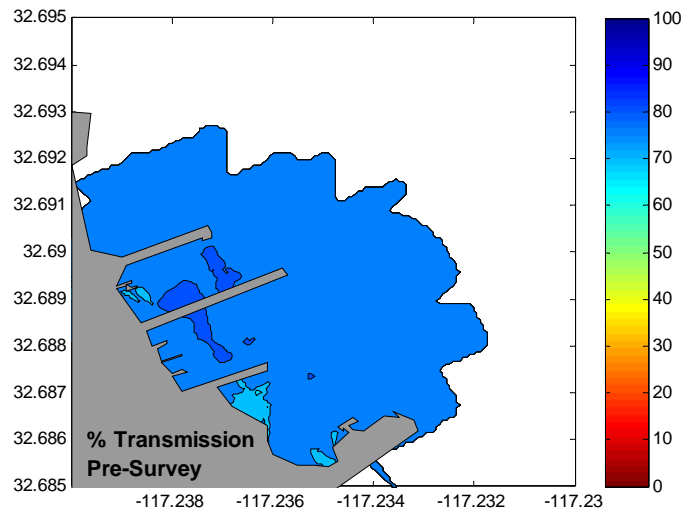


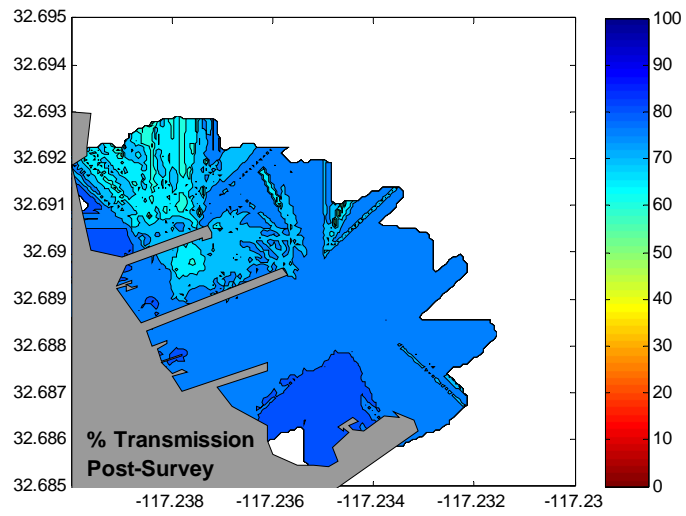








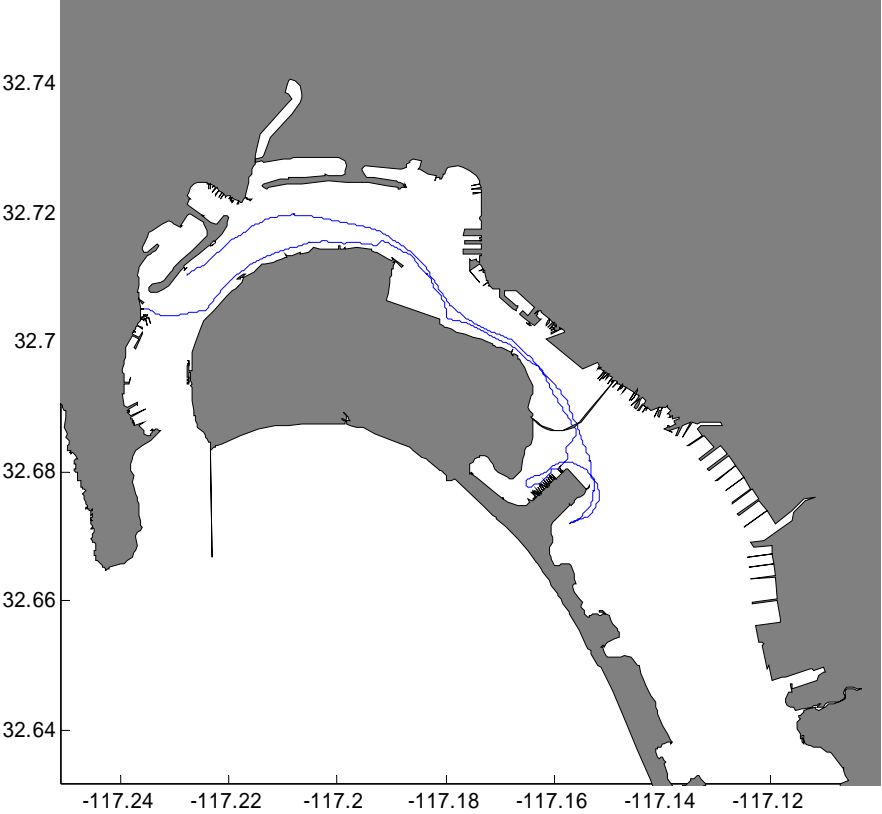


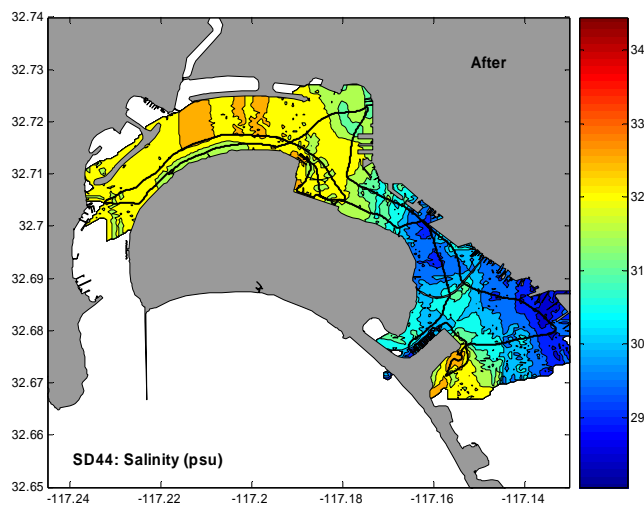
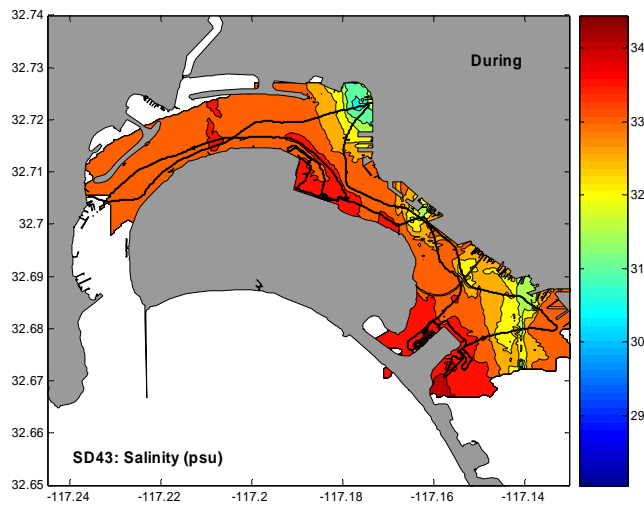
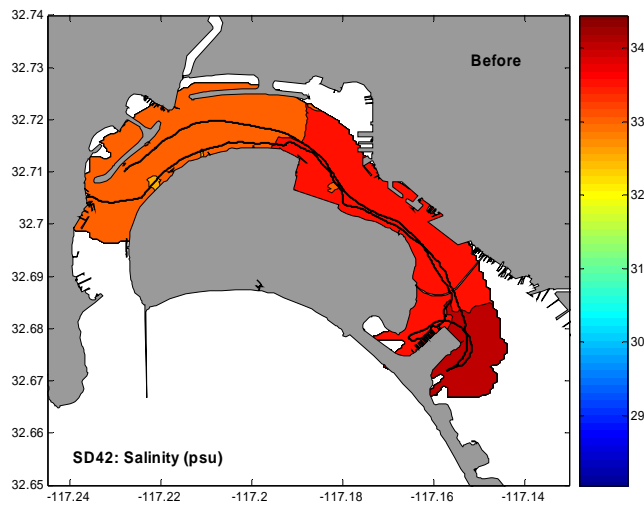


## Appendix G3

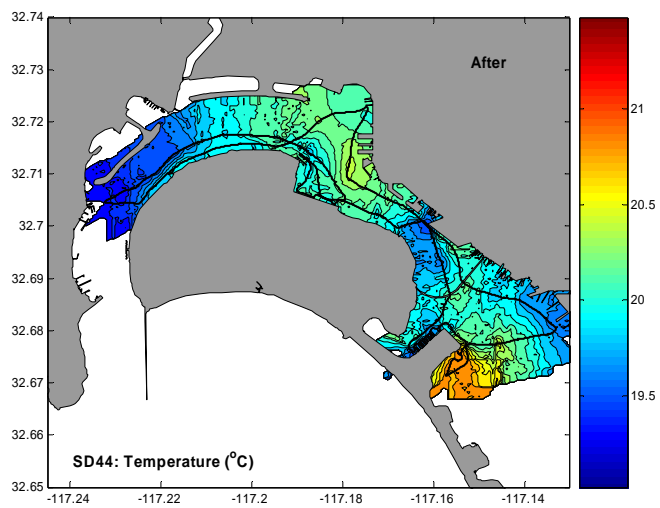
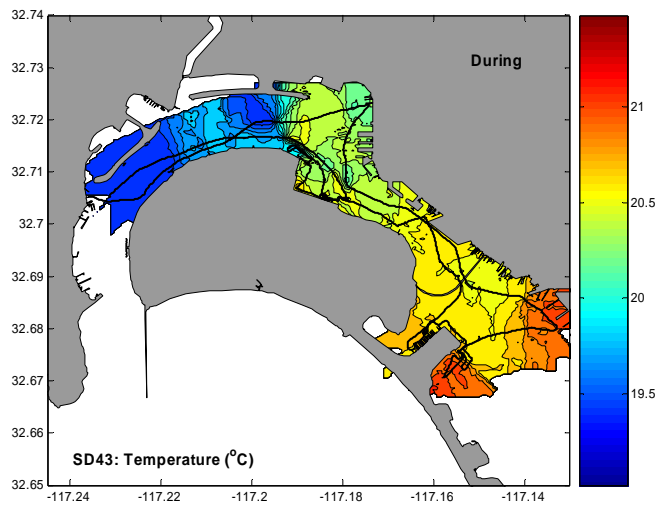
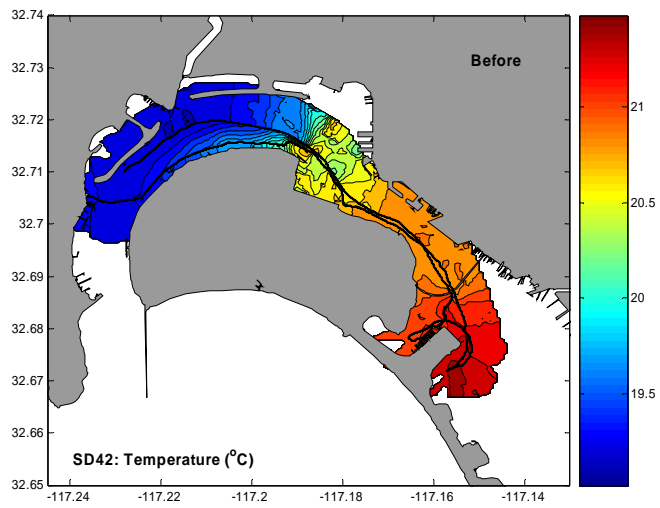
### ***NAB/NI***

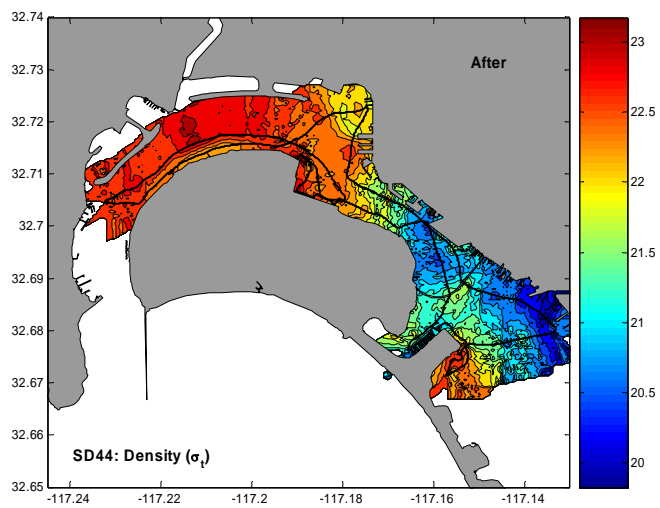
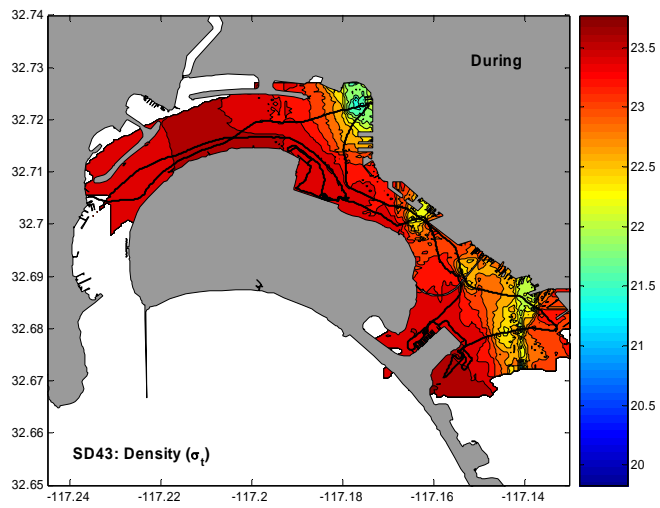
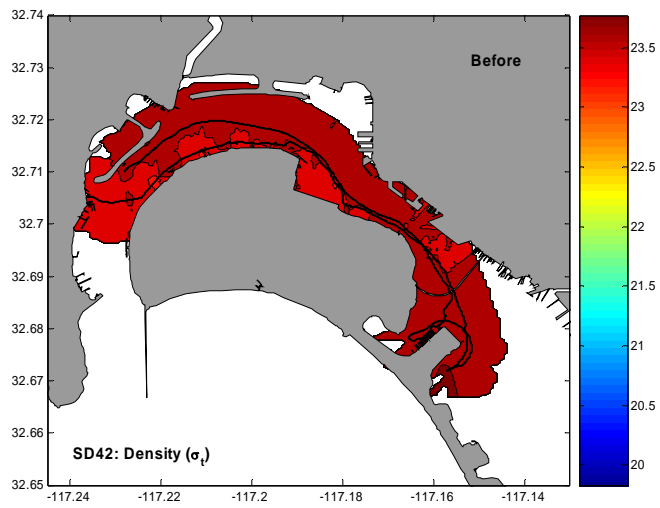
SDB4- 10/17/2004	NAB/NI
SDB6- 2/10/2005	NAB/NI, NAB, NI
SDB7- 4/27/2005	NAB/NI, NAB, NI

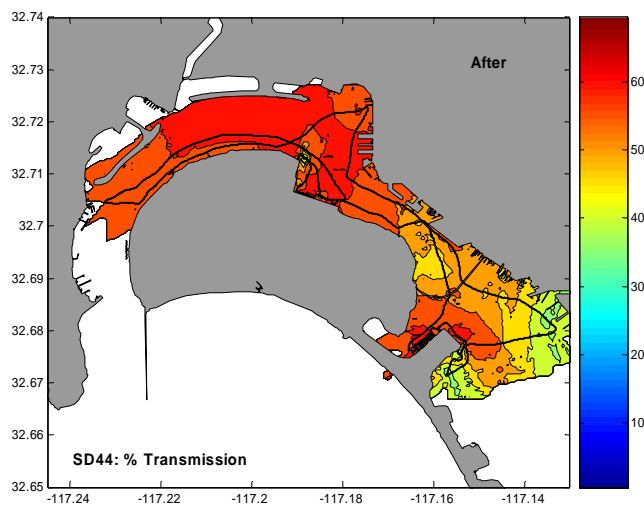
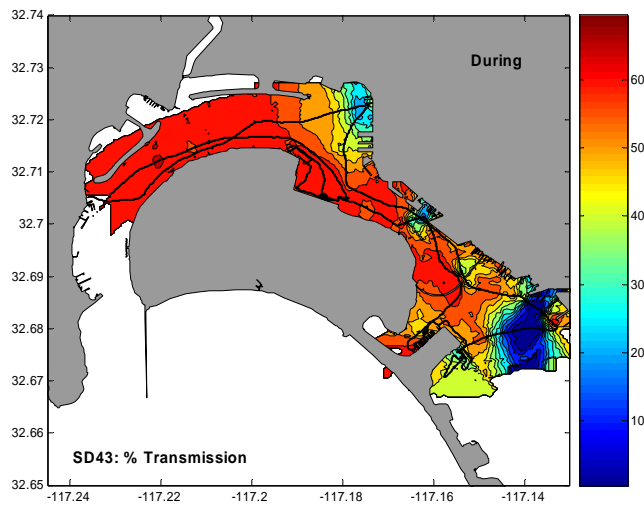
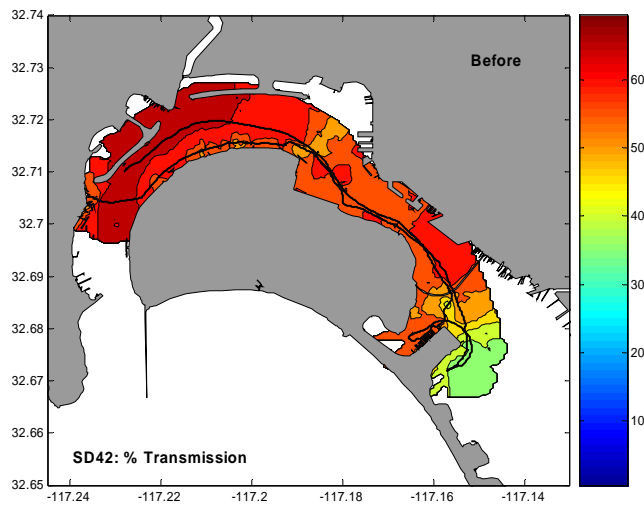




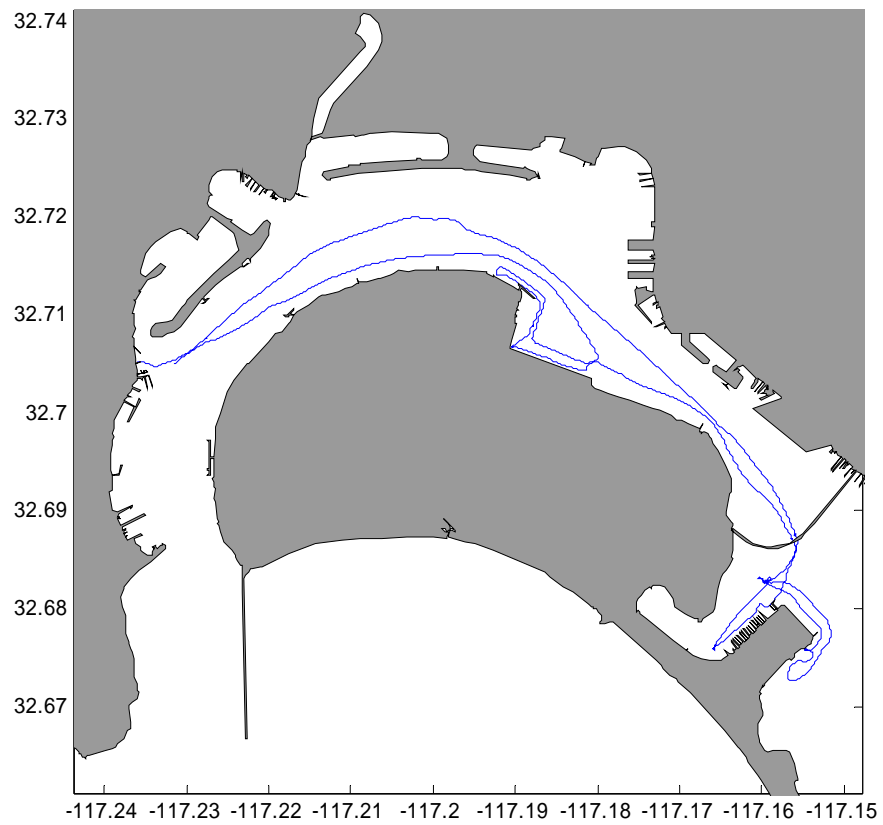


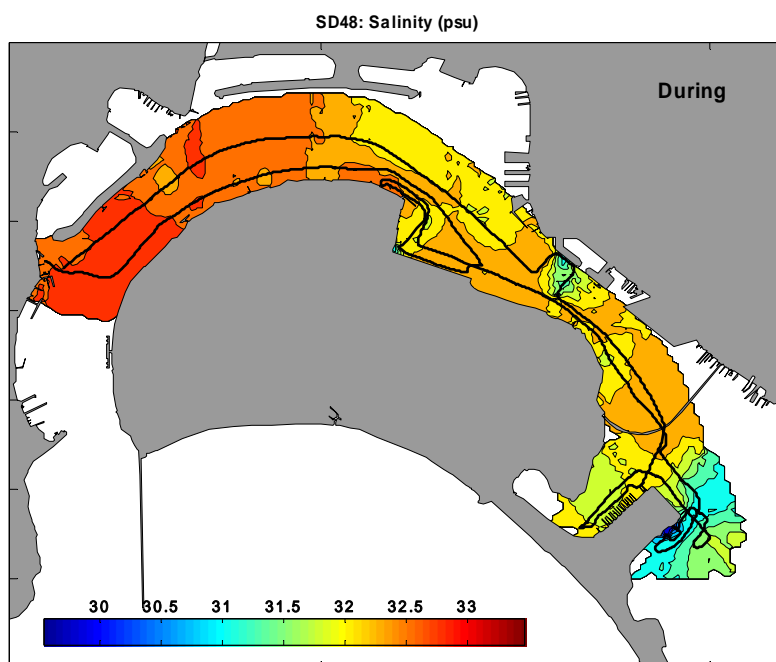
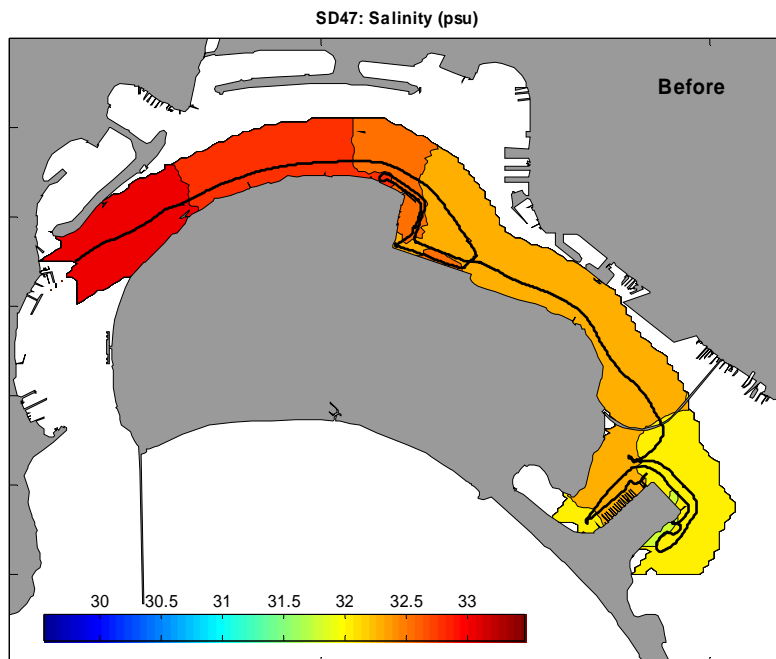


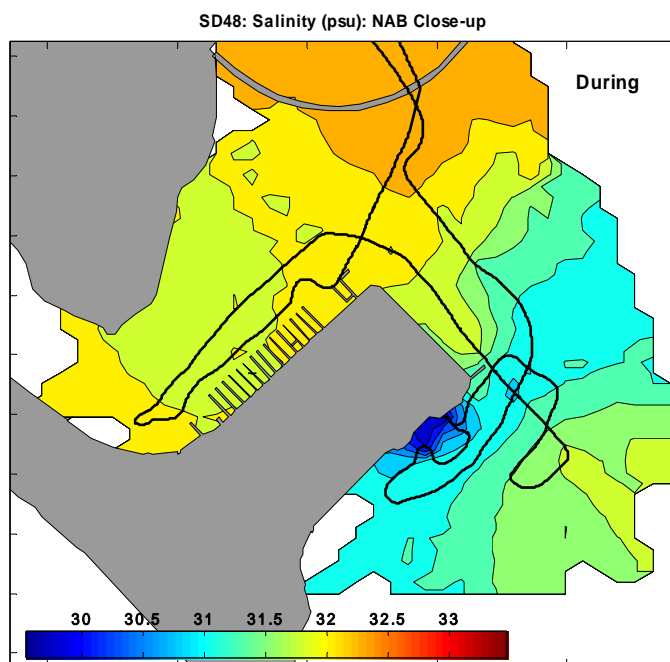
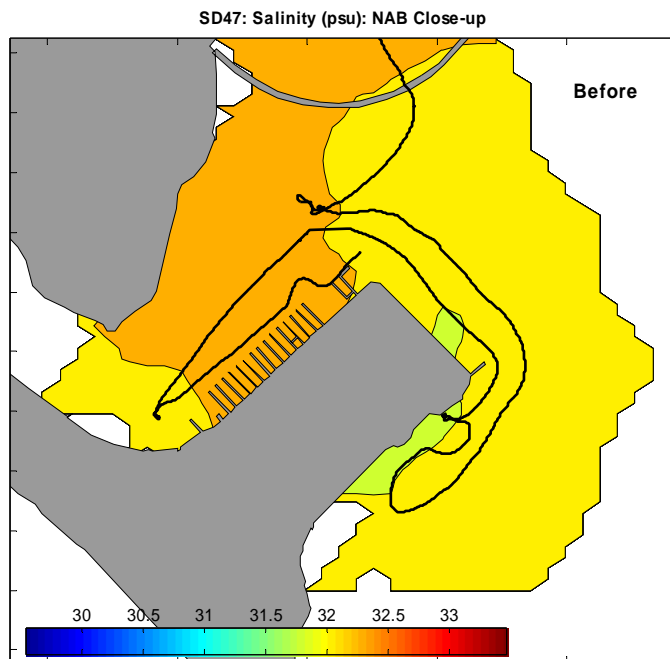




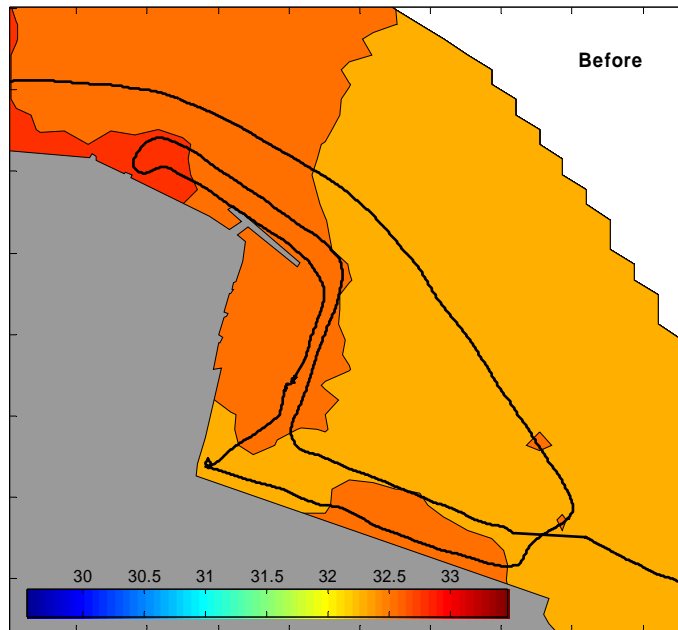
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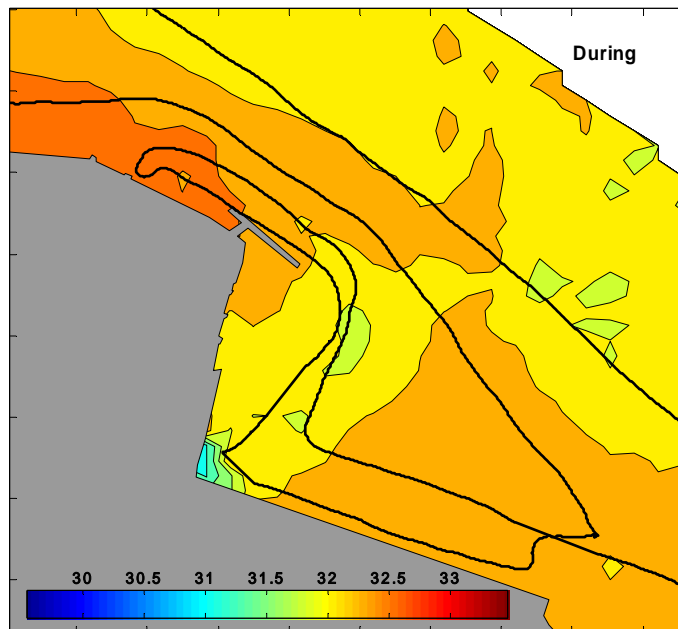


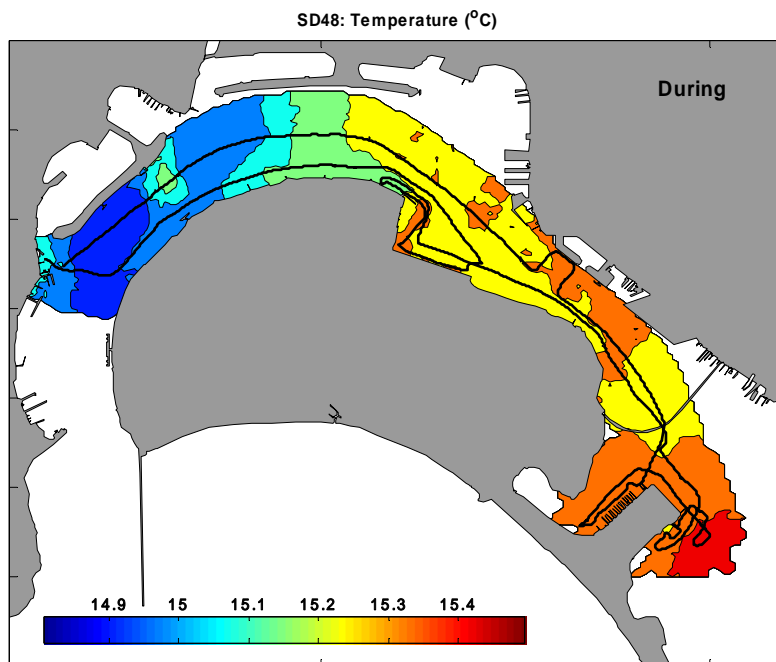
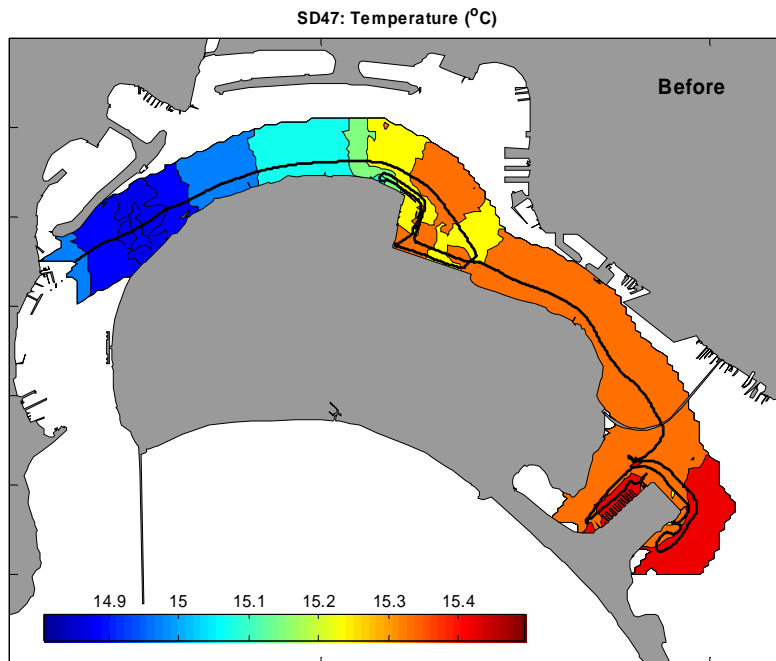


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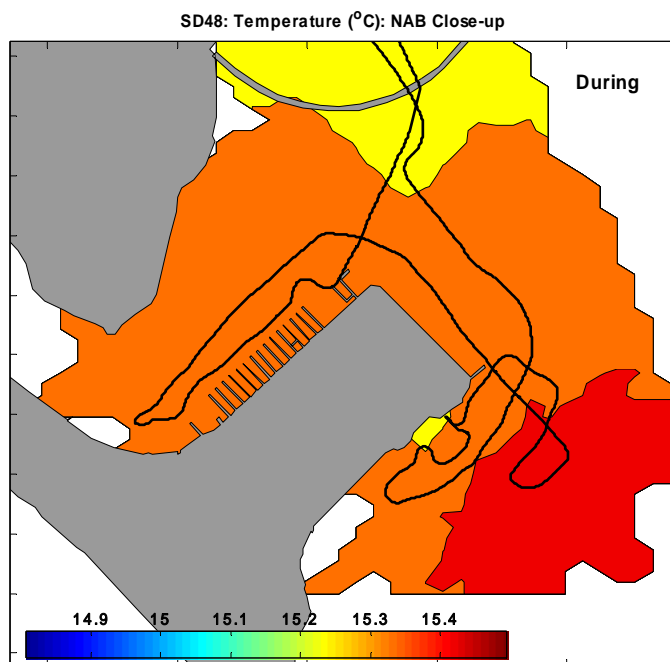
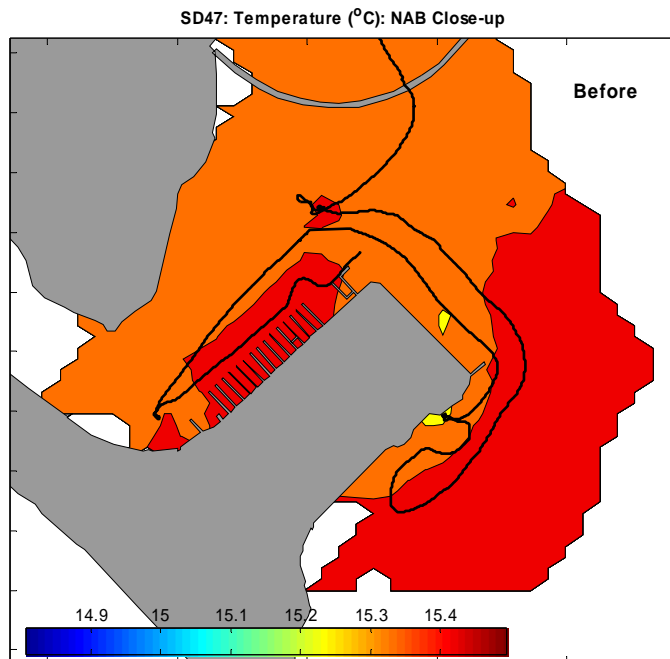


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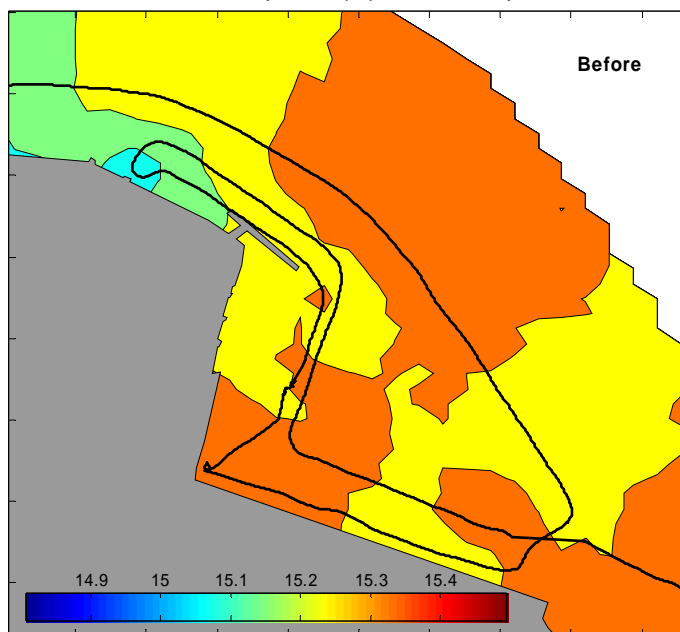




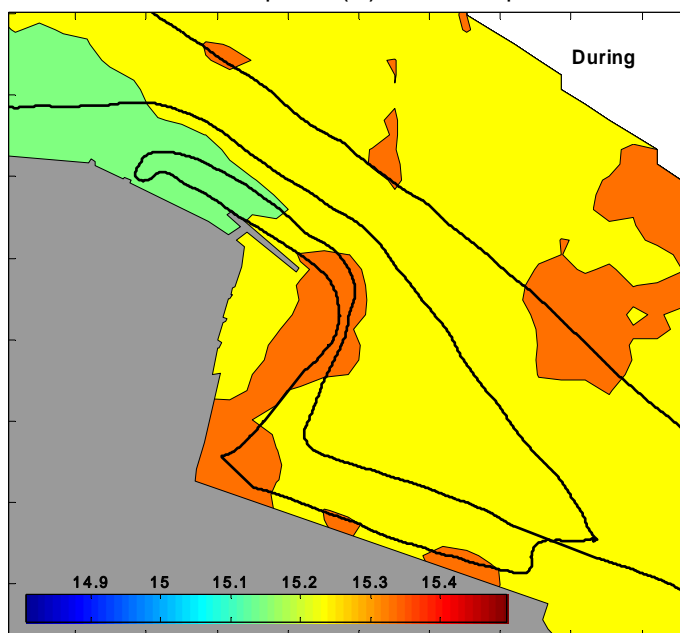




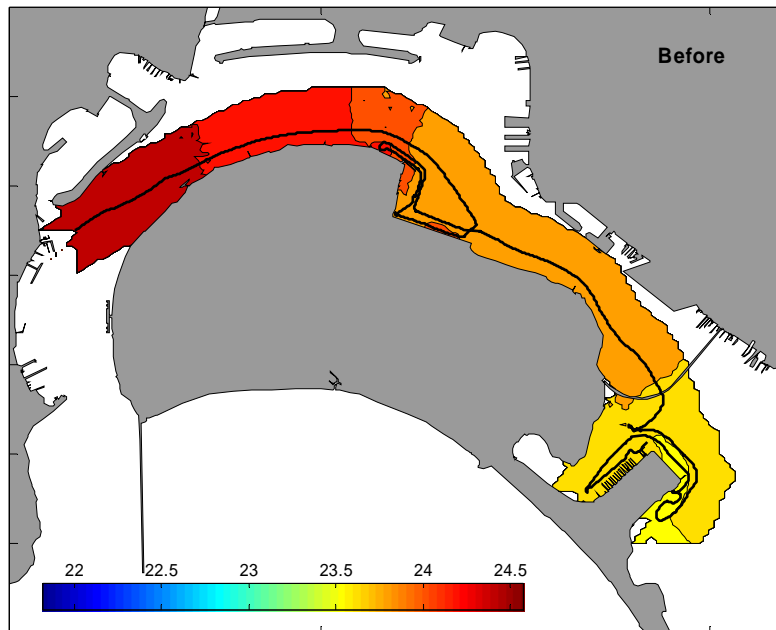
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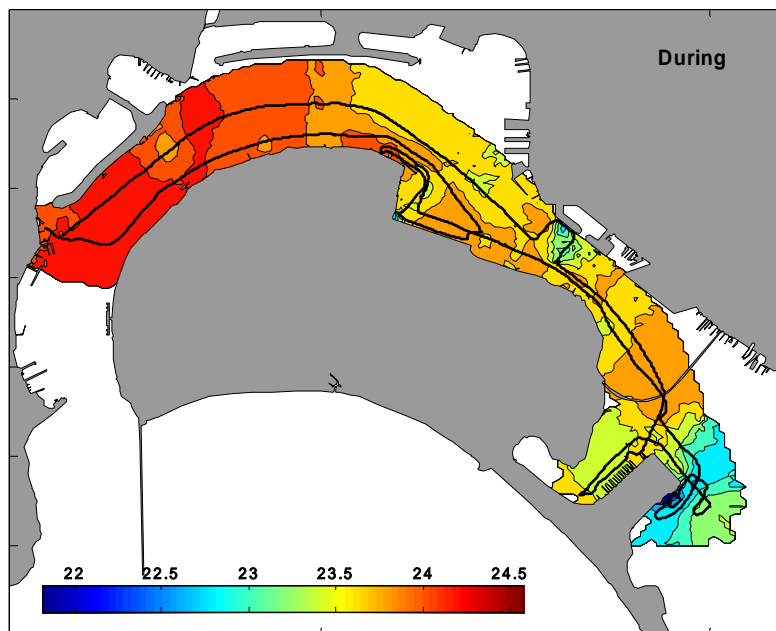
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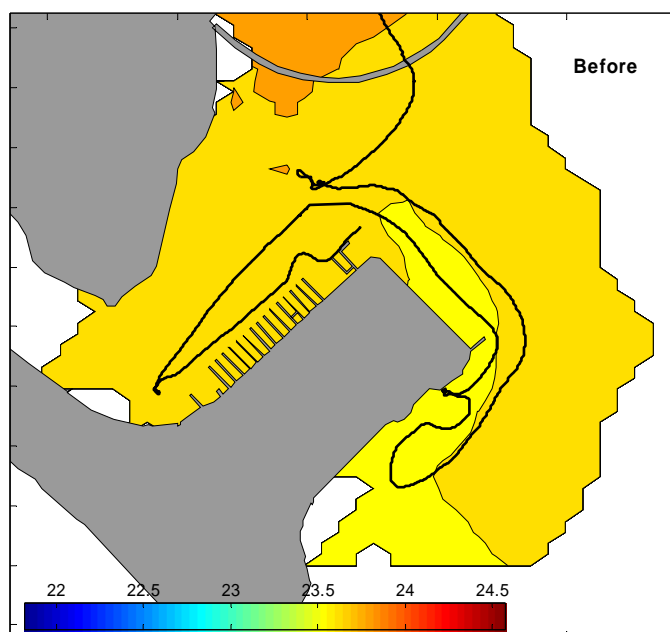
SD47: Density ( $\sigma_t$ )



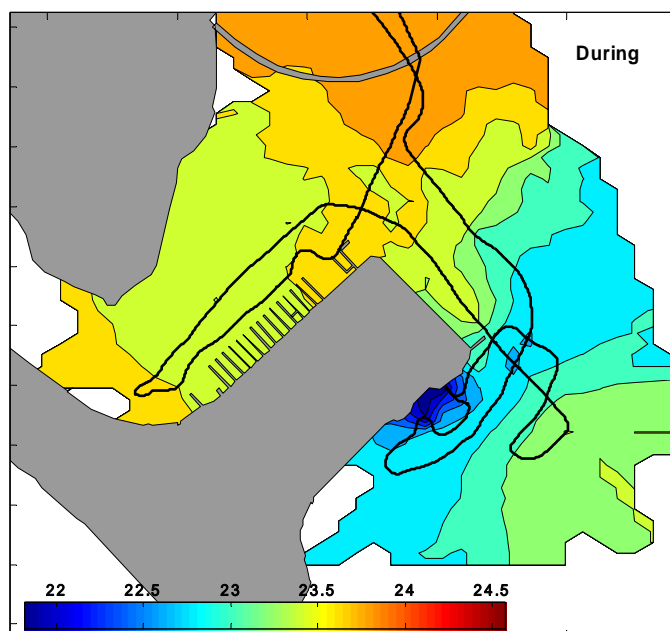
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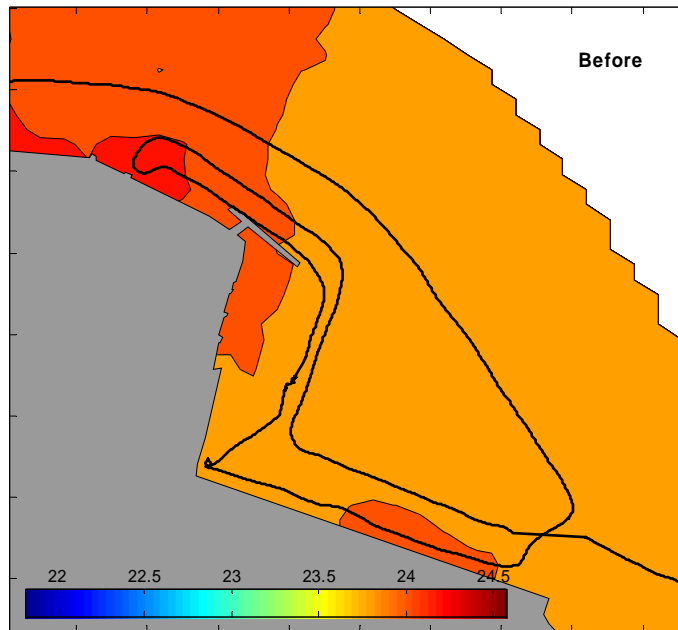
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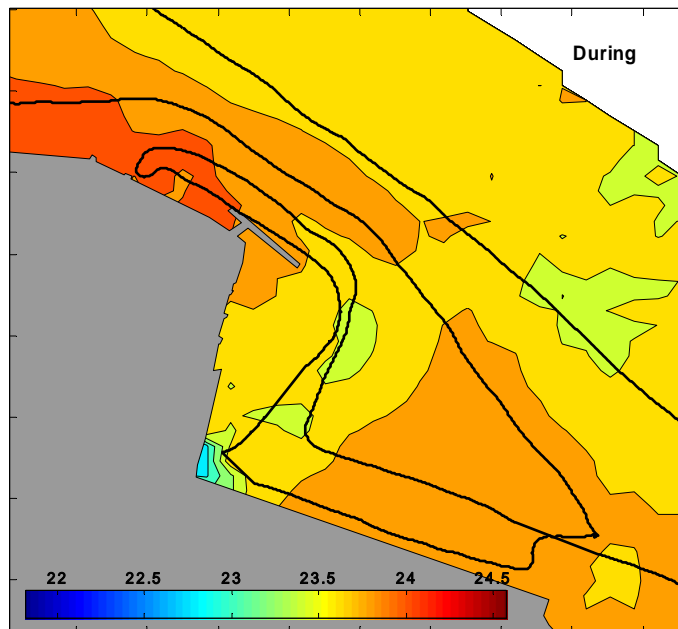
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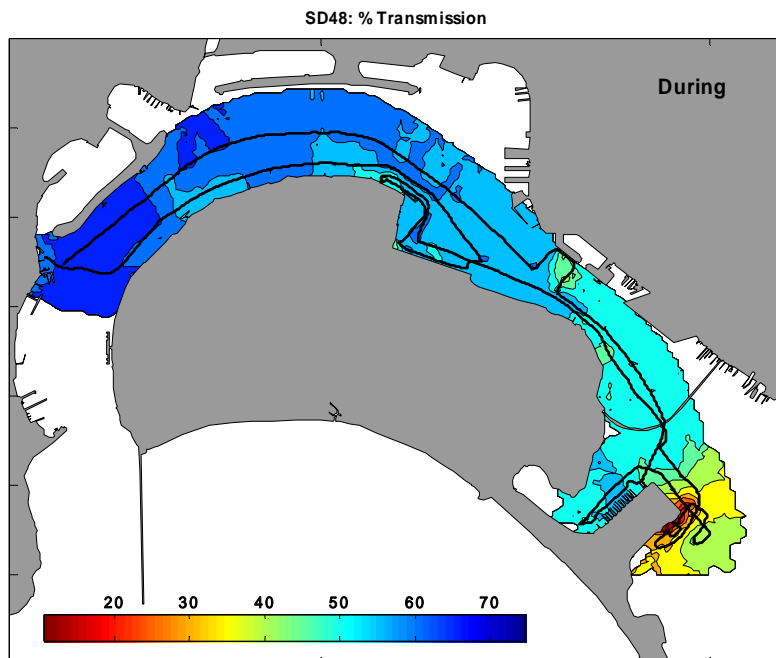
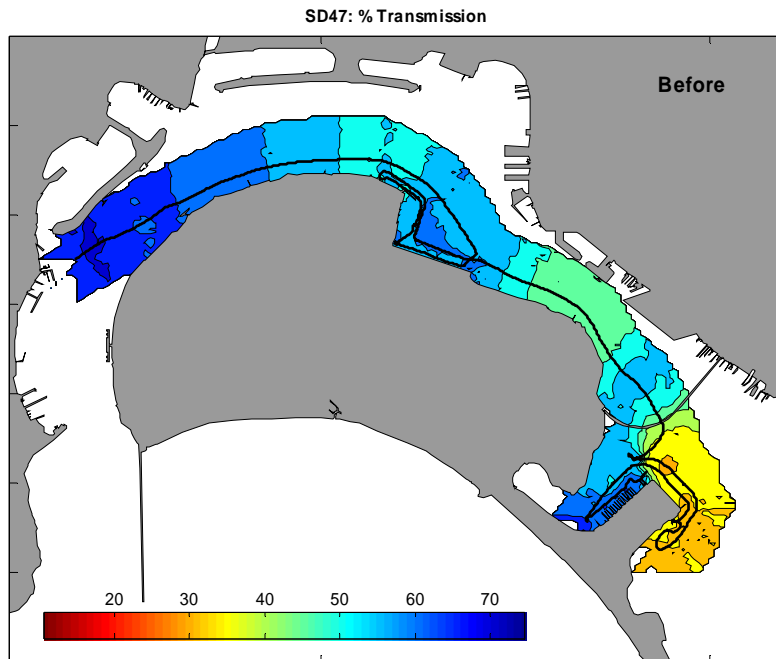


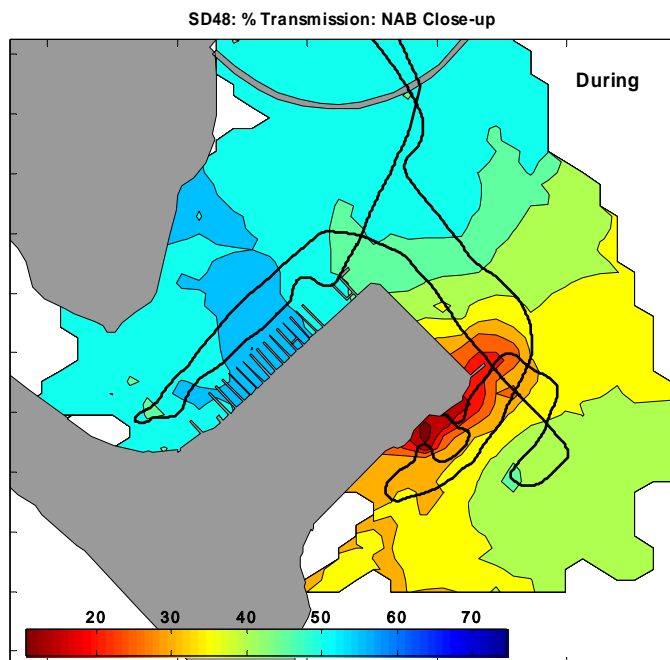
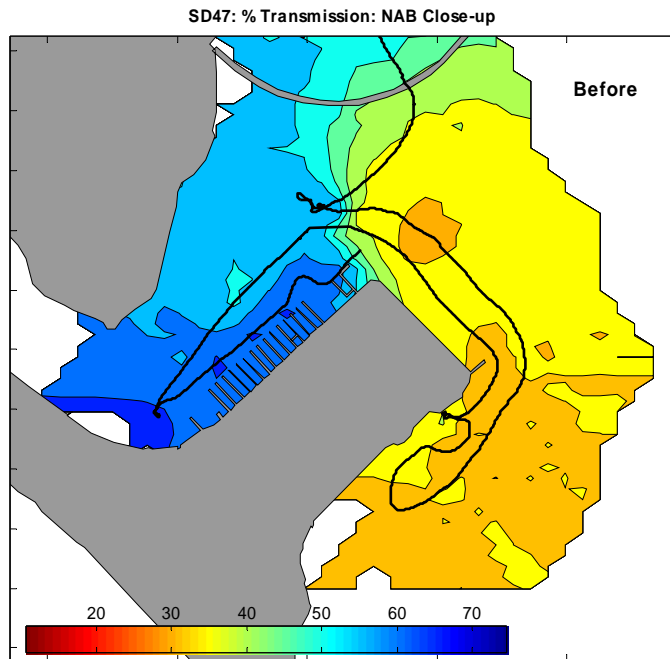
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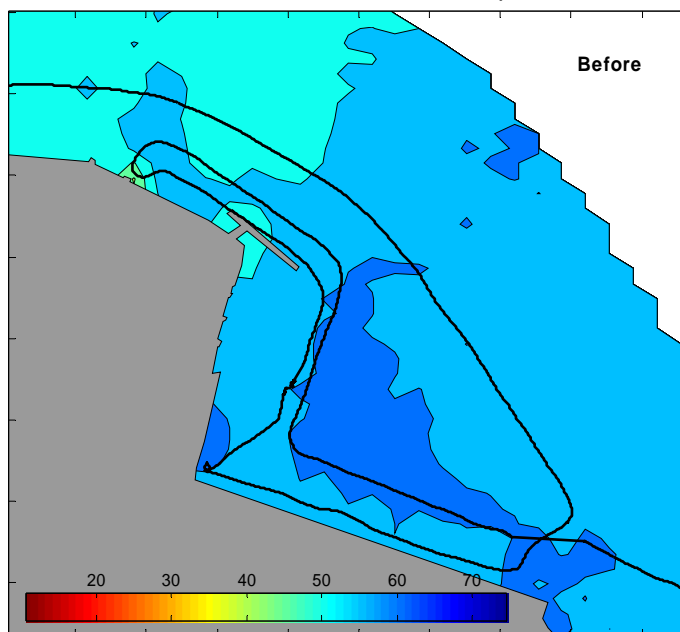
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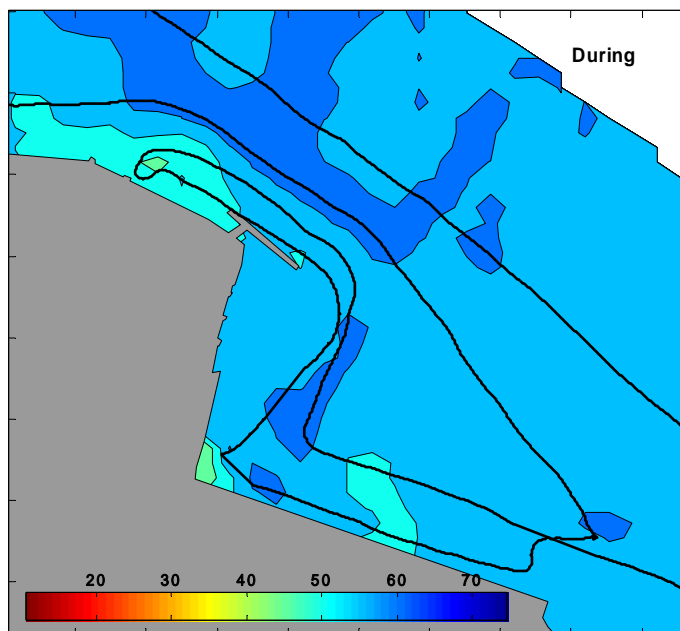




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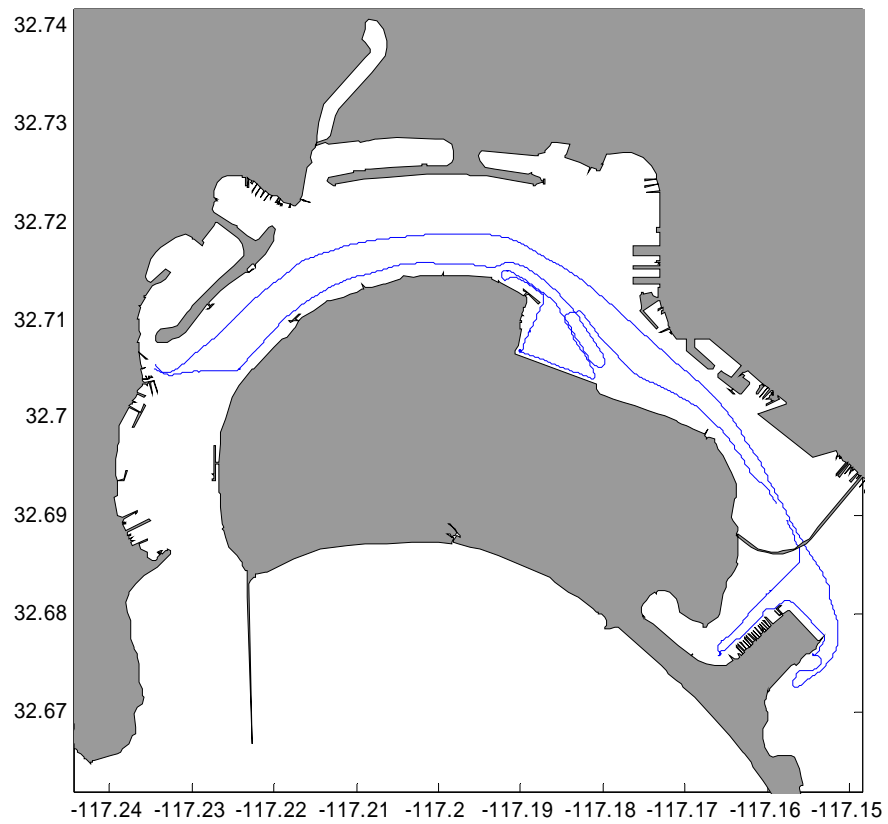


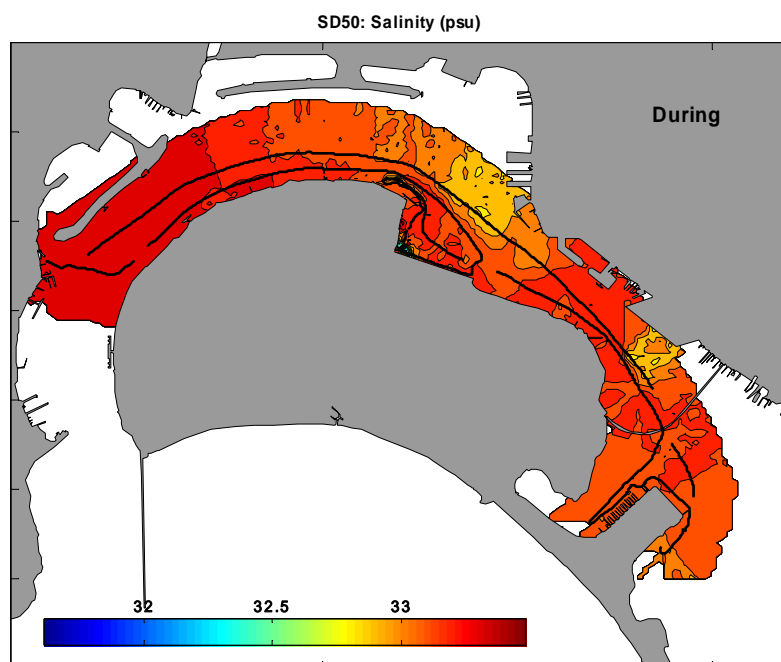
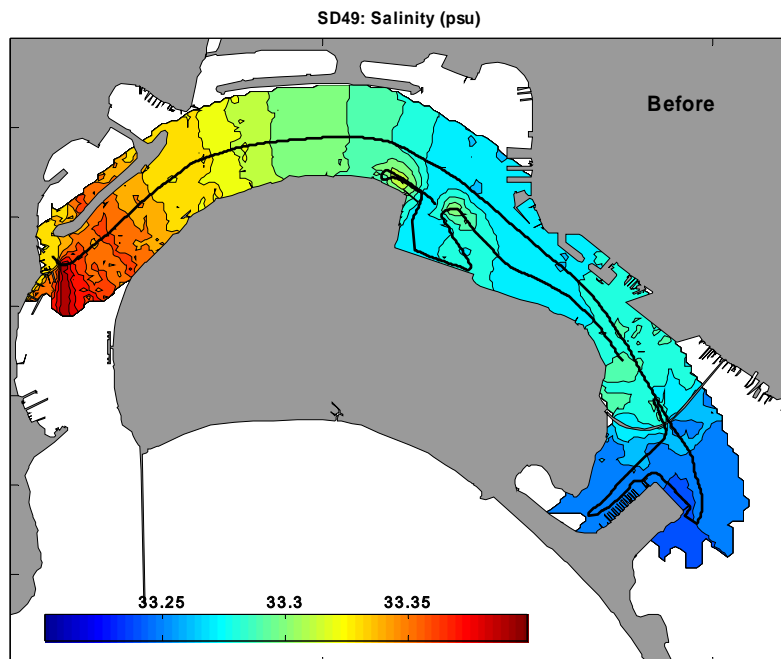
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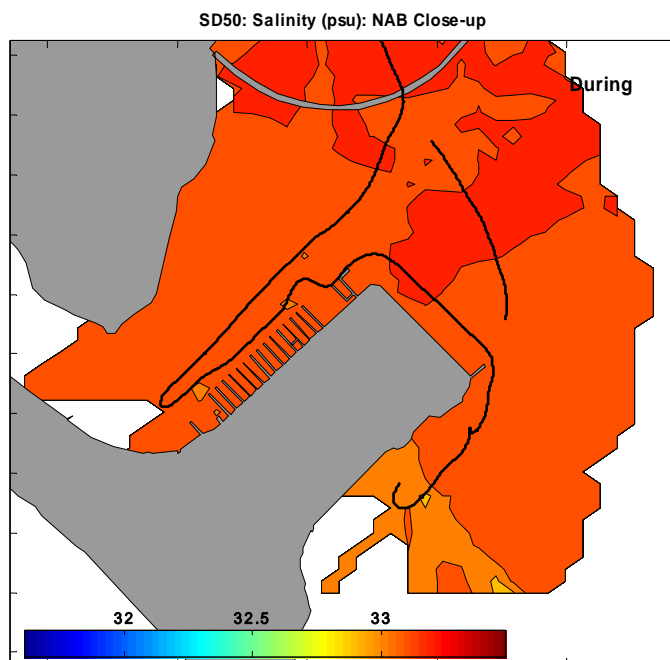
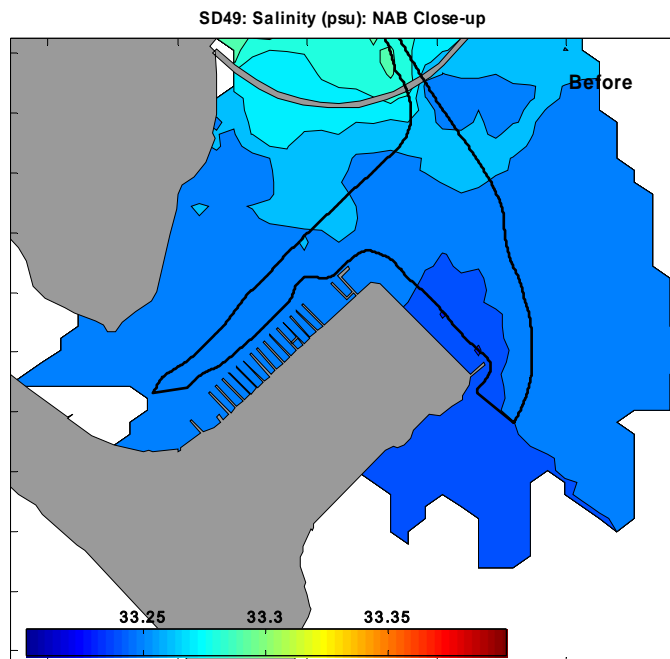




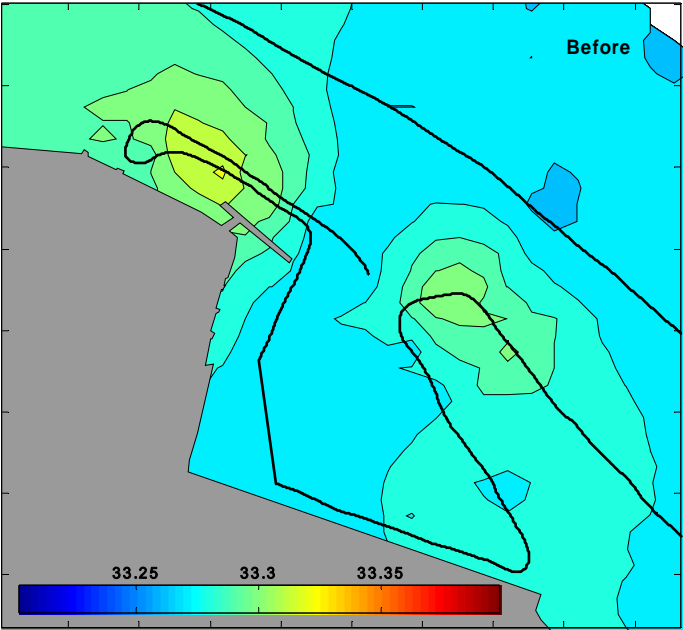
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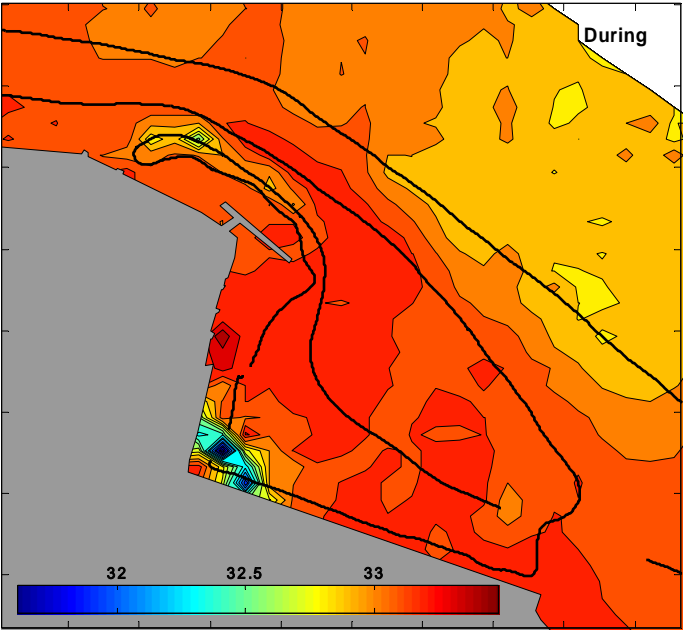


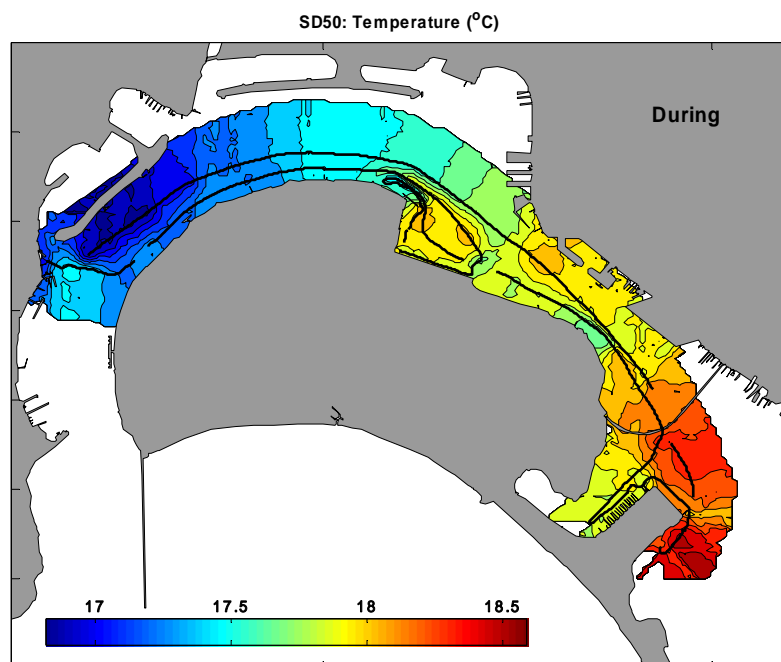
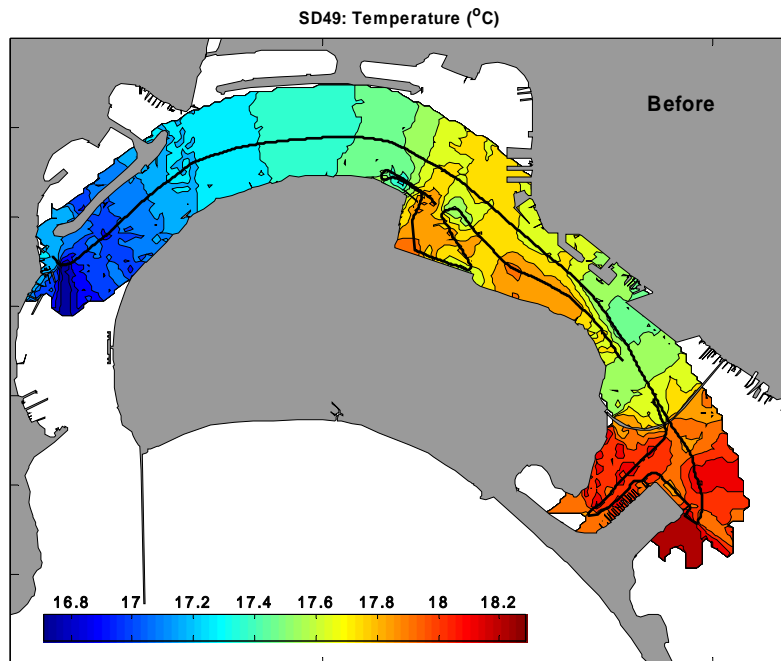


SD49: Salinity (psu): NASNI Close-up

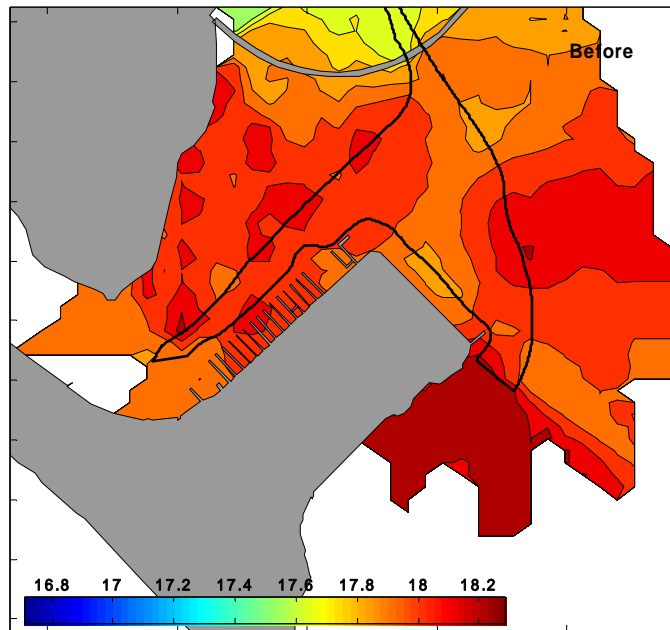


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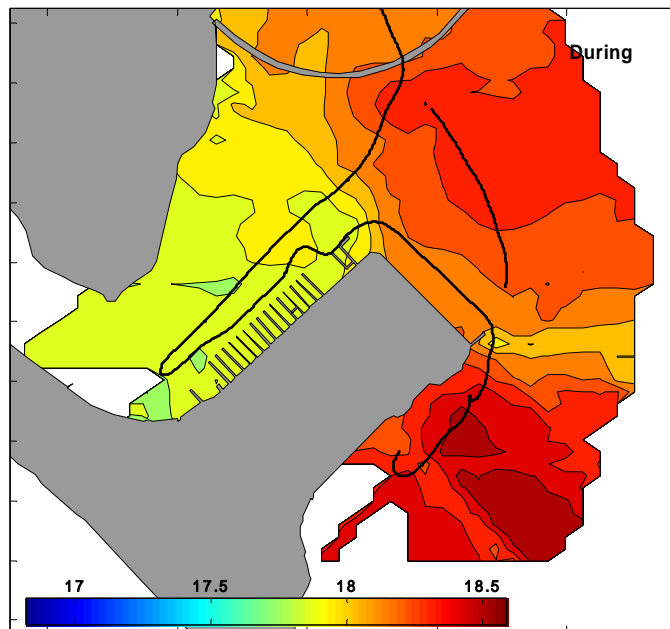




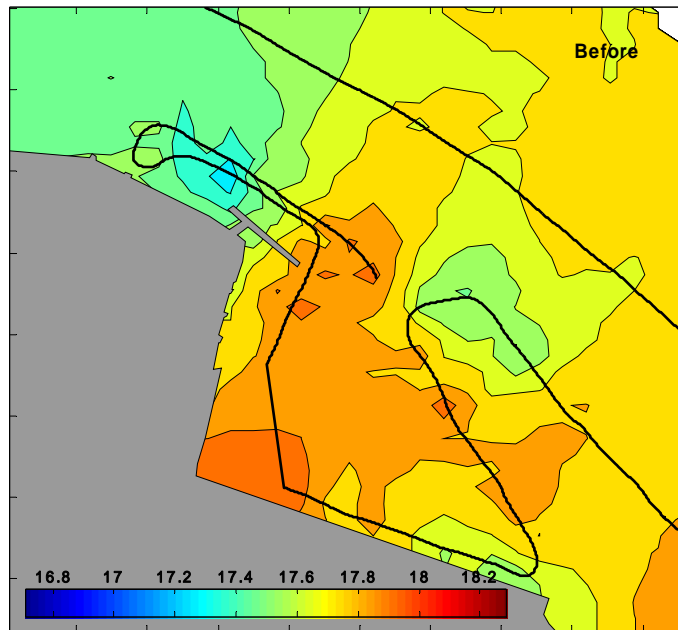
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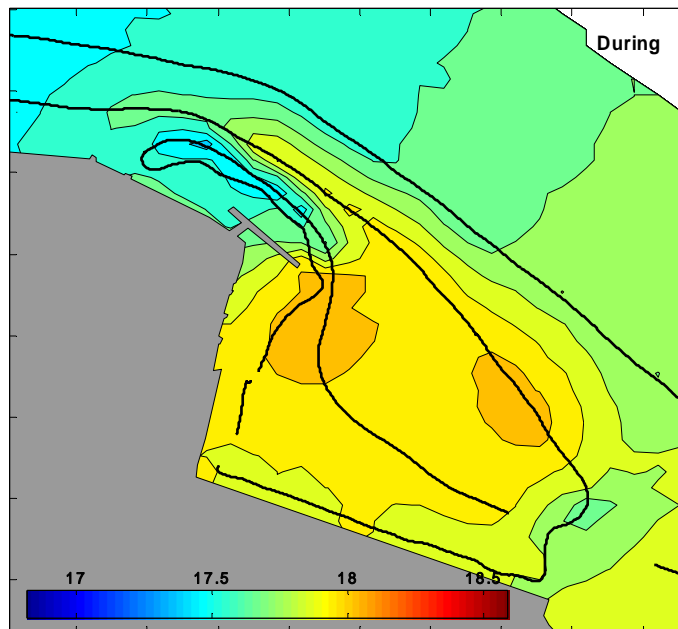
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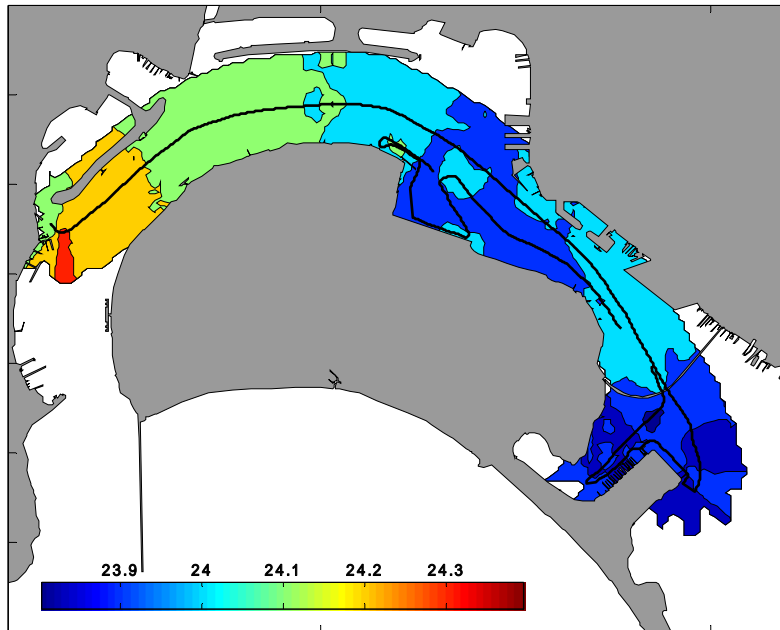
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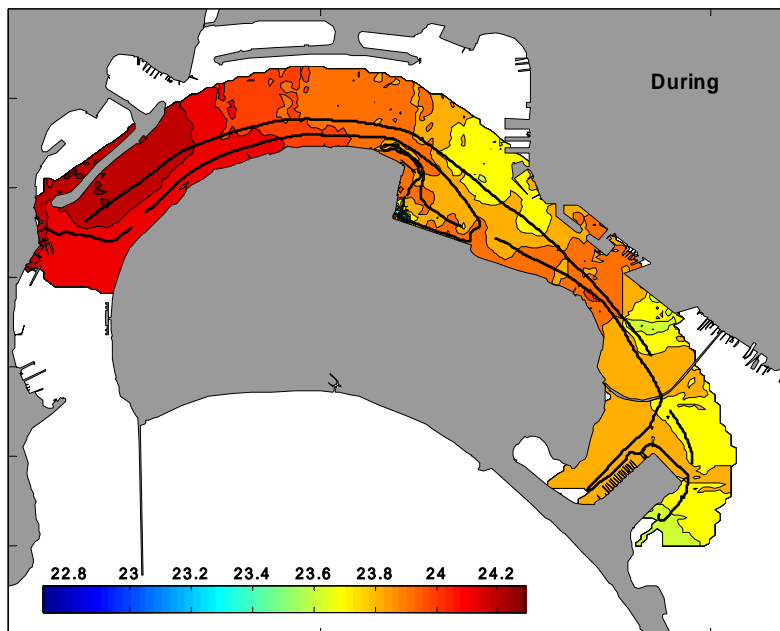
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SD49: Density ( $\sigma_t$ )

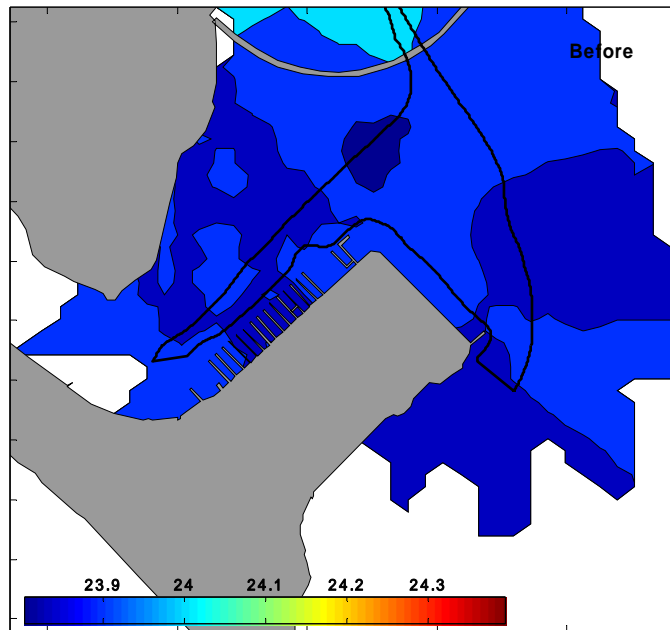


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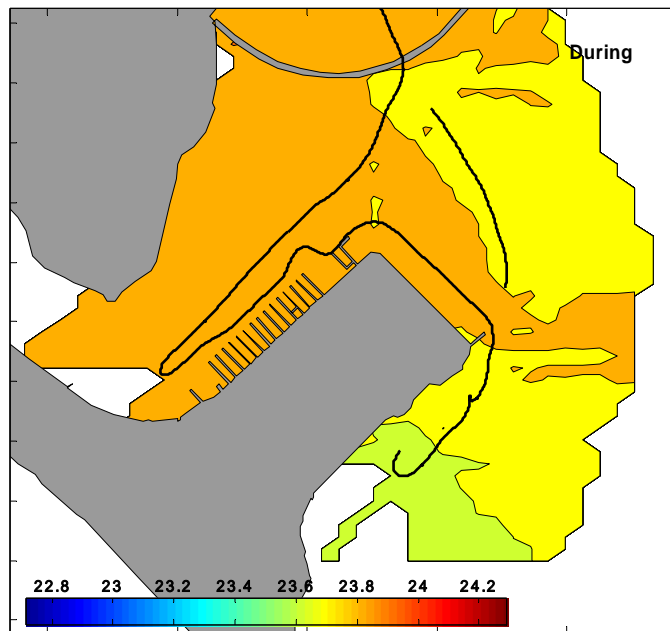




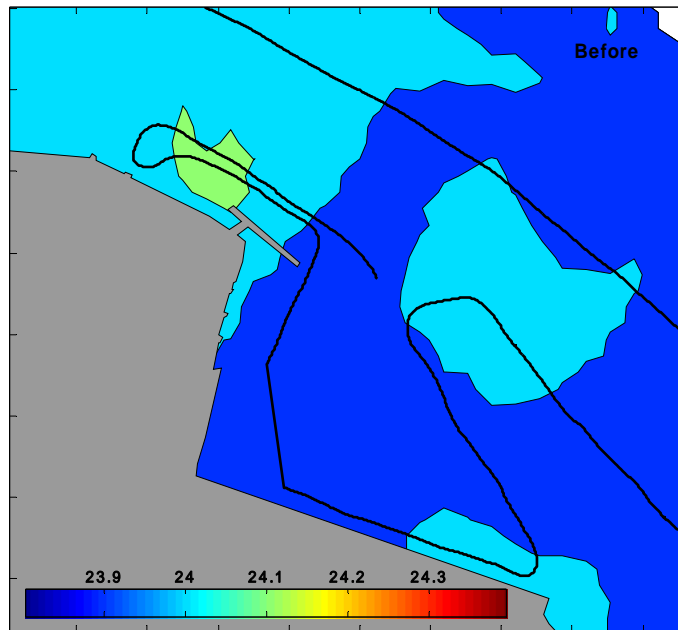
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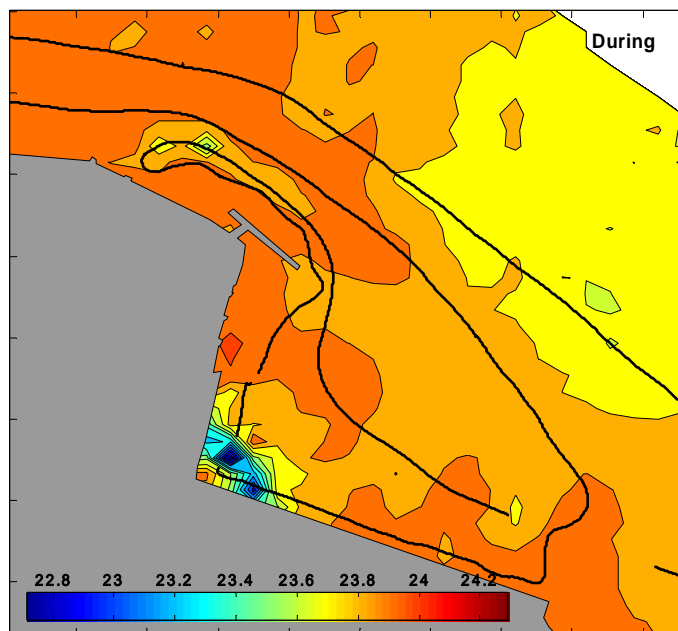
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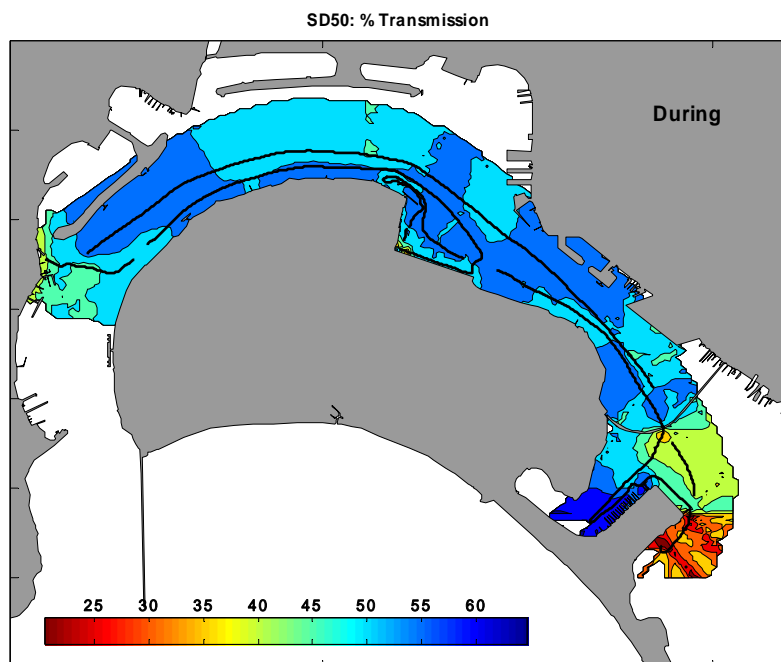
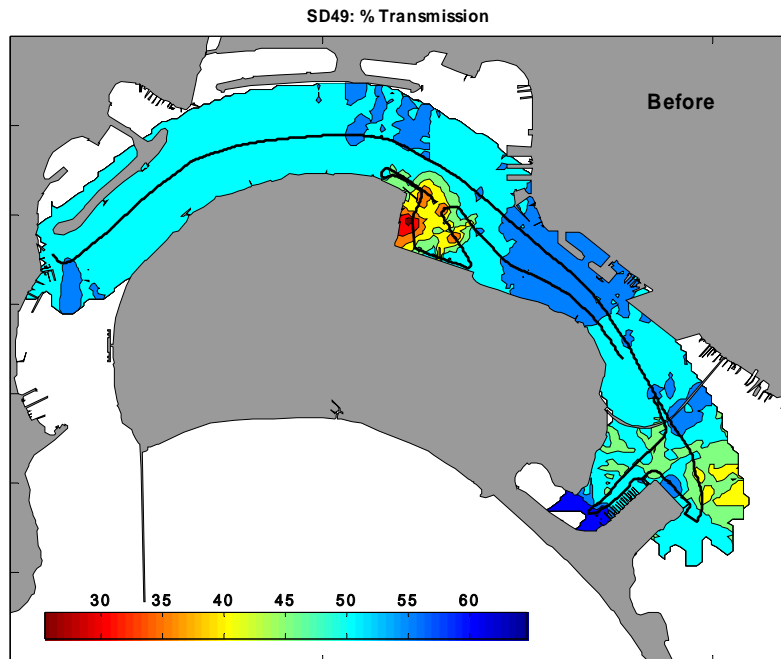


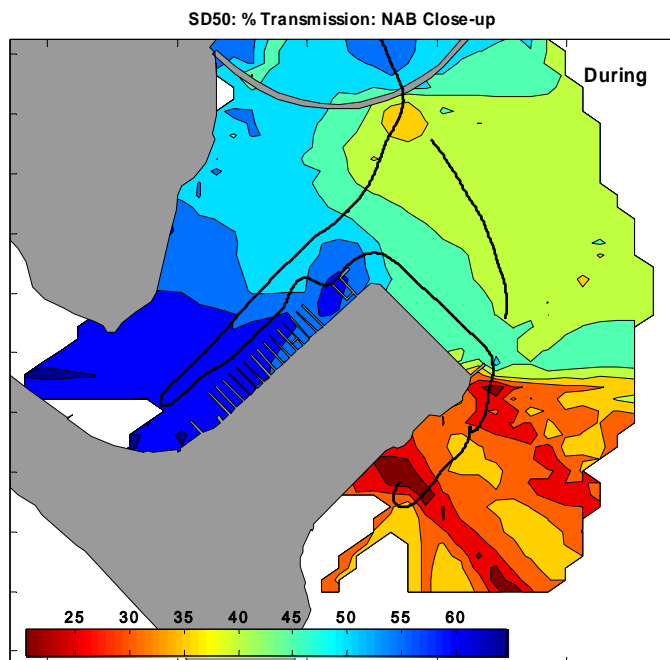
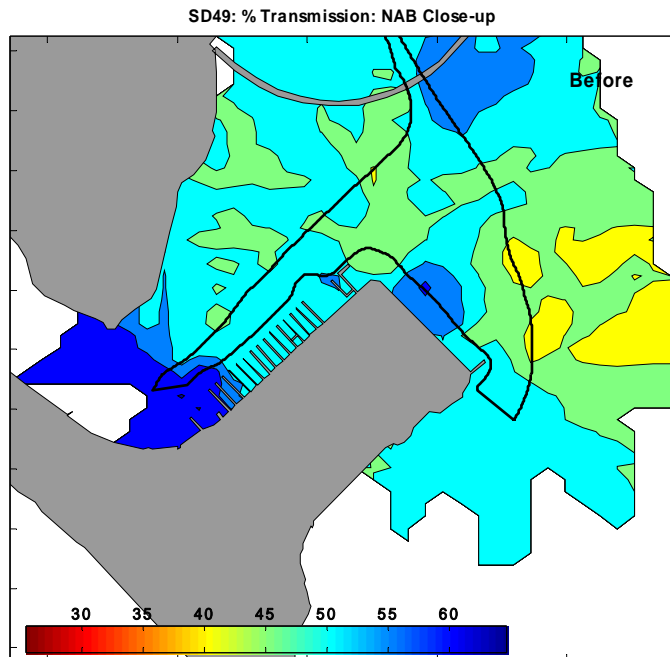
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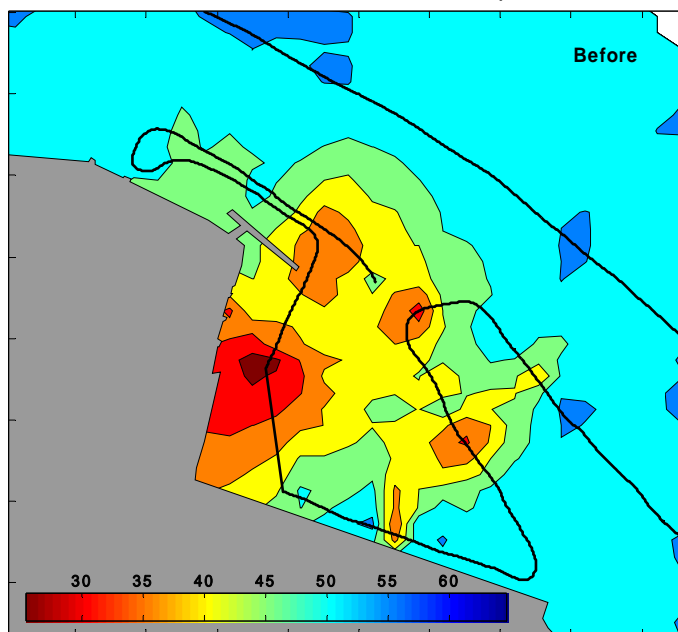
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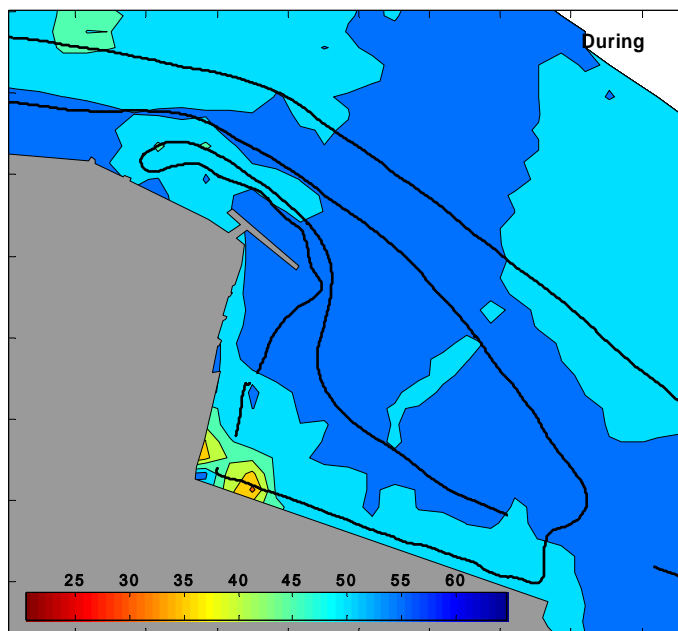




SD49: % Transmission: NASNI Close-up



SD50: % Transmission: NASNI Close-up



## **APPENDIX H**

### **Floating Bioassay Laboratory Study**

#### **Paper presented in Proceedings of Marine Technology Society, Oceans 2005 Conference**

Katz, C.N. and G. Rosen, 2005. *Evaluating storm water impacts- monitoring the receiving environment using a floating bioassay laboratory system*, In: Proceedings of the Marine Technology Society, Oceans 2005 Conference, September 18-23, 2005, Washington, D.C. 8 pp.

# Evaluating Storm Water Impacts- Monitoring the Receiving Environment Using a Floating Bioassay Laboratory System

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San Diego, CA 92152

**Abstract** - The U.S. Navy is conducting an evaluation of impacts from facility storm water discharges to San Diego Bay. The investigation was prompted by the implementation of local regulations that require a 90% survival rate of fish or mysid shrimp in acute toxicity tests using undiluted storm water. An underlying conceptual approach was to monitor toxicity directly in receiving waters as well as in the undiluted discharge to evaluate impacts. Data collected to date have shown a full range in toxic response in outfall discharge samples. No toxic effects, however, have been observed in bay waters collected immediately outside the outfalls. These results, along with plume mapping, have suggested that the relatively small magnitude and ephemeral nature of these discharges were sufficient to explain the removal of toxicity of the storm discharge once it reaches the bay.

One of the outstanding issues presented by standard toxicity testing is the relevance of 48- or 96-h exposure times to test organisms when actual storm exposures likely occur over much shorter times. To investigate this issue, we conducted toxicity tests with a boat-mounted flow-through bioassay system, which was positioned immediately outside an outfall before, during, and after a storm event. The bioassays included survival of the mysid (*Americamysis bahia*) and topsmelt (*Atherinops affinis*) as well as embryo-larval development of the mussel (*Mytilus galloprovincialis*). Surface bay water was continuously pumped to the test organism containers for the full 48- (mussel) or 96-h (mysid and topsmelt) exposure requirement. Bay water was analyzed continuously for salinity, temperature, dissolved oxygen, pH, light transmission, oil fluorescence, copper, and zinc. Additionally, dilution series toxicity and chemistry were conducted on first-flush and composite samples taken from the outfall prior to discharge. The floating-bioassay system results were consistent with previous monitoring that indicated toxicity of first-flush discharges but no toxicity in the receiving environment. Continuous monitoring showed that storm water was completely mixed out within minutes of discharging to the bay even though the observation point was only 15 feet away from the outfall. The reduction of toxicity in the receiving environment was a result of the very limited time exposure that occurs with this type of discharge.

## INTRODUCTION

Industrial storm water discharges from Navy Facilities were investigated in 2003 through 2005 for their impact to San Diego Bay. The investigation was prompted by implementation of a new National Pollutant Discharge Elimination System (NPDES) storm water permit that required storm water collected at the end-of-pipe meet a

toxicity requirement of 90% survival using a standard laboratory acute bioassay. The ostensible goal of this requirement is to ensure that bay waters are protected from these discharges. While the 90% threshold should be protective of the receiving environment, the Navy believed that the requirement was overly stringent. The Navy asked the local regulatory agency for permission to conduct an evaluation of storm water toxicity and propose a scientifically-based toxicity requirement.

The Environmental Sciences and Applied Systems Branch at the Space and Naval Warfare Systems Center San Diego (SSC-SD) executed a study to investigate the nature of industrial storm water toxicity and its impacts from four Navy facilities bordering San Diego Bay. The approach taken was to evaluate storm water collected at or near its point of discharge to the bay as well as in bay waters collected immediately outside these discharge points. Additionally, bay waters were monitored before, during, and after storm events using plume tracking techniques to evaluate both their spatial and temporal extent. This approach was designed to evaluate if the measurements made at onshore monitoring locations were predictive of actual receiving water impacts. A summary of the overall results of this investigation is provided here as background.

## BACKGROUND

The toxicity investigation was conducted during the October through April wet seasons from 2002 through 2005. During that time period, 11 storms were sampled with rainfall totals ranging from 0.1" up to a record 3.5". Antecedent dry periods ranged from five days up to a record dry period of six months. A total of 13 different industrial storm water drainage areas were sampled at four bases including four piers. The samples represented drainage from 0.5 to 75 acres that included industrial facilities. A total of 41 storm water samples were collected from the end-of-pipe, including 26 first-flush samples (as required in the permit) and 15 full-storm composite samples. A total of 63 bay samples were collected outside these outfalls before, during, and after the storm events. These samples were evaluated using three standard EPA-approved laboratory bioassays: the 96-h survival of *Atherinops affinis* (topsmelt) larvae and *Americamysis bahia* (mysid) juveniles, and 48-h normal embryo-larval development of *Mytilus galloprovincialis* (mussel). The two survival tests were called out in the NPDES permit, whereas the embryo development test was added to provide a highly sensitive test for bay samples. The samples were also analyzed for a

suite of chemicals that included total and dissolved metals, dissolved organic carbon (DOC), total suspended solids (TSS), polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and chlorinated pesticides.

Results of the storm water bioassays with topmelt and mysid varied the full range from 0% to 100% survival and averaged about 75%. The tests failed the 90% toxicity requirement about 60% of the time with no significant differences between species. In contrast, the toxicity measured in bay waters immediately outside the outfalls were not toxic and had a very narrow range of results (90 to 100%), averaging ~97% survival for the two species. The mussel embryo-larval development test showed comparable results with a high degree of variability in the storm water samples, ranging from 0 to 97% and averaged 15% normal development. Bay samples averaged 90% normal development, with the exception of two samples collected during a storm event collected after a record six month antecedent dry period. A Toxicity Identification Evaluation (TIE) established copper and zinc as the primary causative agents of the observed toxicity in the storm water samples.

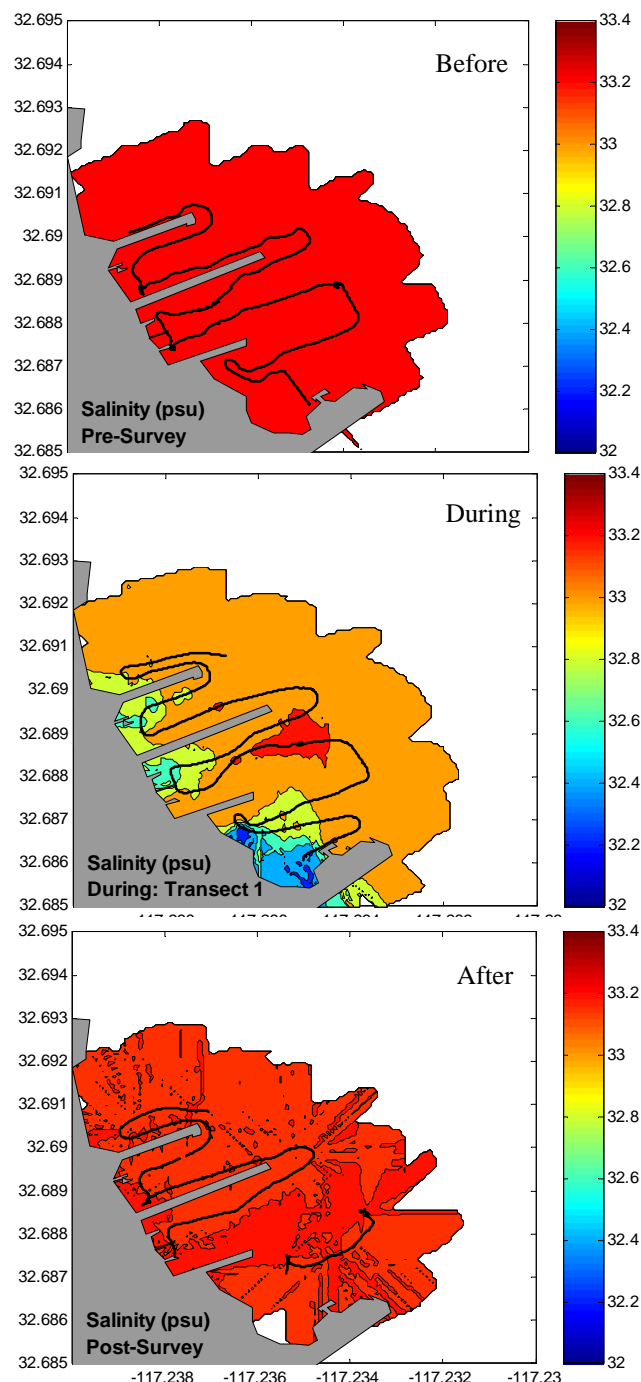
The observed reduction in toxicity was attributed to rapid dilution in the receiving environment, as measured by reduced chemical concentrations and observed from the plume mapping data. As shown in Fig. 1, the maximum amount of fresh water observed (minimum salinity/pre-storm salinity) during storm surveys was about 5%, representing a 20-fold dilution. The storm water signatures were also ephemeral, returning to pre-storm conditions within 12 to 24 hours. Thus, bay waters were able to assimilate the industrial storm water discharges from these facilities without resulting in a toxic impact, thus meeting the Clean Water Act narrative goals of “no toxics in toxic amounts” [1].

## STUDY GOALS

The rapid reduction of toxicity of storm water after introduction into San Diego Bay waters was investigated further, using a floating bioassay laboratory system. The goal was to monitor the receiving environment throughout a storm event to evaluate impacts under actual exposure conditions immediately outside the point of discharge. The study was designed to provide a detailed understanding of the interaction of storm water with bay waters to help explain the apparent absence of receiving water toxicity.

## METHODS

To perform this task, a flow-through bioassay system was placed aboard the research vessel (RV) ECOS, which also housed the Navy’s Marine Environmental Survey Capability (MESC). The MESC is a real-time data acquisition system that was used to continuously monitor surface seawater conditions and to supply water to the bioassay system [2-4]. These techniques provided actual exposure conditions for the test organisms and continuous monitoring of the receiving water conditions.



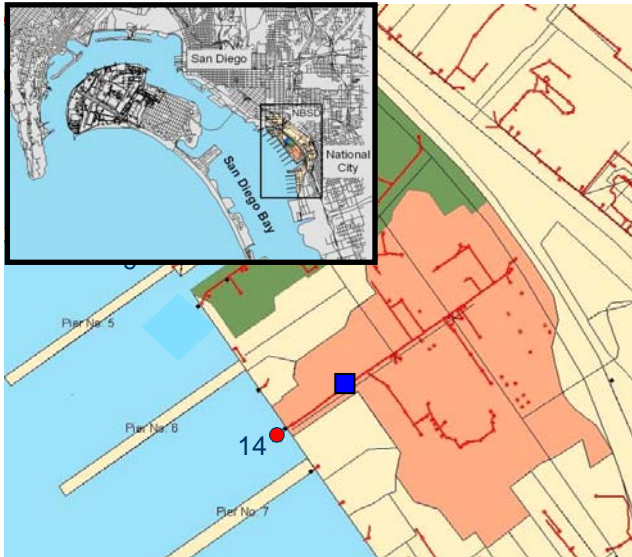
**Fig. 1.** Surface salinity distribution outside of Submarine Base San Diego before, during, and 28 h after a 25 Feb 2003 storm event.

## MONITORING SITE

The site chosen for monitoring was Outfall 14 (OF14) at Naval Base San Diego (NBSD), which enters the bay between Piers 6 and 7 (Fig 2.). The onshore monitoring location was located in a large parking lot about 200 m upstream from the discharge point through the quay wall. The outfall drains ~53 acres, virtually all of which is



impervious surface. The onshore location was estimated to effectively sample 92% of the drainage area. Industrial facilities in this drainage area include vehicle maintenance and divers storage facilities. The outfall is tidally influenced with bay water reaching the monitoring location at a tide height of ~1m. The pipe diameter at the monitoring location was 91 cm. This outfall had been monitored on previous occasions and had shown toxicity in storm water samples, particularly to mussel embryos.



**Fig. 2.** NBSD Outfall 14, its conveyance system in red and drainage area in pink. The onshore monitoring location is identified by the blue square. The offshore monitoring point was located is identified by the red circle.

## STORM EVENT

Monitoring was performed over a four-day period from 26 to 30 October 2004. The storm event, which began @ 0330 on the 27<sup>th</sup> and ended @ 1145 on the 28<sup>th</sup>, produced 3.4" of rainfall. The bulk of the rainfall came during two periods; 2.1" during the first six hours of the event, and 0.7" between 1045 and 1140 on the 28<sup>th</sup>. The remaining rainfall fell during three half-hour periods, each producing about 0.2". The rainfall total was a record for the month of October and came after a five day dry period.

## ONSHORE MONITORING

Onshore monitoring was conducted using an automated American Sigma 850 autosampler to collect both first-flush and composite storm water samples, and to measure rainfall and storm water flow. First-flush samples were collected during the first hour of flow, whereas composite samples were collected throughout the first 2.1" of rainfall. The samples collected onshore were analyzed for toxicity and the suite of chemicals identified earlier.

## BAY MONITORING

The RV ECOS with MESC system was tied up on the quay wall just outside OF14 (Fig 3.) so that its sensors and water intake system were directly in line with the outfall pipe discharge, about 5 m away from the quay wall. The MESC sensors and water intake were placed at about 1 m depth, though the full water column to about a depth of 7m was periodically evaluated. Surface salinity, temperature, sample depth, light transmission, pH, and oil fluorescence data were collected every four seconds. Two trace metal analyzers, using anodic stripping voltammetry techniques [5], were used to measure dissolved copper and zinc about every 15 minutes. The MESC's trace metal clean Teflon® seawater pumping system was used to supply surface seawater to the bioassay flow- through system at a rate of about 10 L/min, as well as to collect discrete samples for chemical analysis before, during (4 samples), and after (3 samples) the storm event.



**Fig. 3.** RV ECOS tied up along quay wall outside OF14. The sensors and pump intake were directly in line with the outfall. Note sheet runoff over quay wall.

## FLOATING BIOASSAY LABORATORY SETUP

**Water Bath System.** A fiberglass water bath measuring 106 cm long X 61 cm wide X 20 cm high was used to house the flow-through exposure chambers (Fig. 4). Water was pumped through a PVC grid fitted with adjustable valves to regulate water flow to individual chambers. Inside the water bath, an acrylic stand with a series of 7.5 cm diameter cutouts held the chambers in place throughout the exposure period. Seawater overflow from the exposure chambers filled the water bath to approximately 5 cm in height to help insulate against temperature shift.

**Exposure Chambers.** Test organisms were held in clean, seawater-leached 400 mL polyethylene containers (Fig. 4). Matching lids with cutouts were used to prevent organism ejection during boat movement, yet allow access for water flow and feeding. Both control (static) and flow-through

chambers contained 250 mL of seawater at all times. Overflow ports on flow-through chambers measured approximately 2 cm and were covered with 300  $\mu\text{m}$  PeCap mesh. The flow rate resulted in an average of 15 turnovers per hour. Control chambers were filled with clean, filtered, natural seawater from the research pier at Scripps Institution of Oceanography. One renewal of the control water was performed for 96-h exposures, while 48-h exposures were not renewed. Topsmelt and mysids swam freely in the chambers, while mussel embryos were contained in 5 cm diameter polycarbonate drums with 20  $\mu\text{m}$  Nitex® mesh on each side, as described in [6].

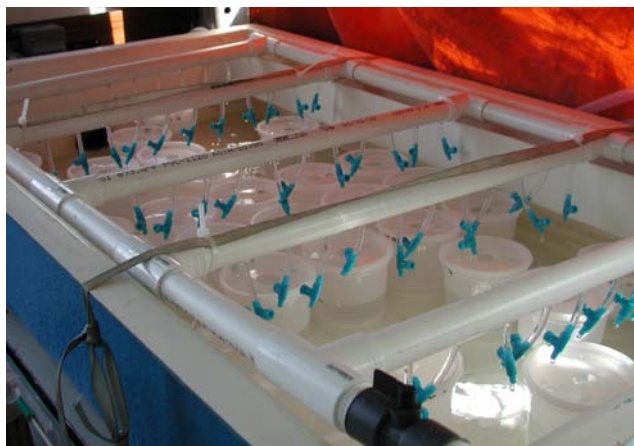
## TOXICITY TESTING

Toxicity testing generally followed standard methodology for assessing acute whole effluent toxicity with topsmelt larvae and mysid juveniles [7] and chronic toxicity with mussel embryos [8]. Mysid and topsmelt exposures were 96-h in duration with a survival endpoint. Mussel exposures were 48-h, with an endpoint based on the proportion of normally developed, D-shaped larvae as examined by microscope. Onshore testing included exposures with effluent representing the first-flush and composite storm water. Effluent salinity was increased to 34 ‰ with bioassay grade synthetic sea salt (Crystal Sea Marinemix) for topsmelt and mysid exposures. Salinity for the mussel exposures was adjusted with hypersaline brine made from clean natural seawater, resulting in a maximum effluent concentration of 61.4%. Onshore tests consisted of 3 replicates of 10 mysids, 4 replicates of 5 fish, or 5 replicates of 150 mussel embryos, for each treatment. At least four dilutions of effluent (0.5 dilution factor) were prepared for each species. An insufficient volume of the composite sample prevented dilutions below 100% for mysid exposures, and any exposure to topsmelt. Negative controls included clean natural seawater and synthetic salt or brine adjusted to 34 ‰ with deionized water. Copper added to natural seawater was used as a positive control, to assess the relative sensitivity of the test organisms.

Offshore testing included two treatments, one under flow-through conditions and the other a “floating” control to assess any impacts associated with being in the field. Six replicates of 10 mysids, 8 replicates of 5 topsmelt, and 6 replicates of 150 mussel embryos were used for each treatment.

All test organisms were purchased from outside vendors and acclimated for ~24 h in the laboratory prior to use. Organisms used in the floating bioassay were acclimated to expected testing temperatures in the exposure chambers over approximately 1 hr and carefully transported to the water bath system aboard the RV ECOS. All topsmelt and mysids were fed twice daily with freshly hatched *Artemia* nauplii. MESC sensors were used to monitor temperature, pH, and salinity for all flow through chambers, and a HOBO® data logger was used to monitor temperature in both static controls and the water bath. Dissolved oxygen was also

monitored hourly in all chambers using a YSI oxygen meter.



**Fig. 4.** Flow-through bioassay setup aboard RV ECOS. Water was continuously dripped into each of the treatment beakers containing topsmelt, mysids, and mussel embryos.

## CHEMISTRY

All discrete samples were analyzed for total and dissolved copper and zinc, TSS, and DOC. First-flush and composite storm water samples were also analyzed for total and dissolved aluminum, iron, chromium, manganese, nickel, arsenic, selenium, silver, cadmium, tin, lead, and mercury, 41 PAH analytes, 31 PCB congeners, and chlorinated pesticides including DDT, its metabolites and chlordane.

Chemical analyses were performed in-house and by Battelle’s Ocean Sciences and Marine Sciences laboratories, in Duxbury, MA and Sequim, WA, respectively. All analyses were performed using standard NS&T low-detection methods with appropriate QA/QC controls including method blanks, blank-spikes, matrix spikes, duplicates, and standard reference materials. Storm water samples were analyzed for metals using EPA methods 1631m and 1640. Bay water samples were analyzed for metals using trace metal analysis techniques described in [9]. DOC was analyzed using EPA method 415.1. TSS analysis was performed using standard protocols developed at the University of New Hampshire [10]. Water samples analyzed for organic chemicals were extracted using EPA SW846 3510C. Extracts were analyzed for PAH using EPA method EPA SW846 Method 8270C, for PCB congeners using EPA Method 1668A and for chlorinated pesticides using EPA SW846 Methods 8081A and 8082.

## RESULTS

### ONSHORE

Roughly 13,000 m<sup>3</sup> of water was discharged through OF14 during this storm event. An additional, but unmeasured amount also discharged as sheet runoff (Fig. 3). Maximum observed flow was roughly 0.5 m<sup>3</sup>/s.

Undiluted first-flush (FF) storm water was significantly toxic ( $p < 0.05$ ) to mysids and to mussel larvae, but did not negatively impact topmelt survival (Table 1). Composite (Comp) samples showed a reduced toxic effect with minimal toxicity to mysids and no toxicity to mussel larvae (topmelt were not tested). Laboratory control survival was ~100% for both mysids and topmelt, and normal development was 89% for mussel larvae. The positive control, a reference toxicant test with copper, indicated normal sensitivity of all species (within 2 standard deviations of the laboratory control chart mean), with LC50 values of 287, 98, and 7.6  $\mu\text{g/L}$ , for mysids, topmelt, and mussels, respectively. All water quality data were within acceptable limits.

**Table 1.** Summary of toxicity data. Data represent percent survival (mysid, topmelt) or percent normal larval development (mussel). Lowest observable effect concentration (LOEC) and the concentration causing 50% mortality (LC50) or effect (EC50) are included. Dashed lines indicate no data.

Exposure Type	Sample Type	Parameter	Mysid	Topmelt	Mussel
Onshore	FF	Neg. Control	98.3	100.0	92.6
		100% effluent	63.3	90.0	1.2
		LOEC	100.0	>100.0	50.0
		LC50 or EC50	>100.0	>100.0	49.1
	Comp	Neg. Control	98.3	-	92.6
		100% effluent	80.0	-	86.4
		LOEC	-	-	50.0
		LC50 or EC50	-	-	>61.4
Offshore	Receiving	Floating Control	93.3	70.0 <sup>a</sup> /100.0 <sup>b</sup>	92.2
		Flow-through	98.3	62.5 <sup>a</sup> /89.3 <sup>b</sup>	80.5

<sup>a</sup> Actual percent survival

<sup>b</sup> Percent survival relative to floating control

Chemistry results are shown in Table 2. All metals (except aluminum) were lower in the composite samples by about half the amounts measured in the first-flush sample. TSS, however, was higher in the composite sample as were some individual organic, though in the case of the organics the increase may have resulted from being at or near the detection limit. Aluminum, iron, silver, lead, mercury, and tin were nearly all in the particulate phase, with the remaining metals ranging between 30% and 70% dissolved phase. Copper, individual DDT isomers, total PCB (TPCB), and some of the higher molecular weight PAH concentrations were elevated above their respective water quality standards (WQS) in both first-flush and composite samples [11]. Zinc was above its WQS in the first-flush sample but below it in the composite sample. The typical elevation above a WQS was between a factor of 2 and 8 in the first-flush sample and about half that amount in the composite sample.

**Table 2.** Summary of chemistry data. Metals data are for dissolved fraction only. Organic summations Priority Pollutant PAH (PP PAH), Total PCB congeners (TPCB), Total DDT isomers (TDDT), and Total Chlordane isomers (TCHLOR) were calculated using 1/2 method detection limit for analytes measured at or below the detection limit. Dashed lines indicate no data.

Analyte	Units	ONSHORE		OFFSHORE		
		FF	COMP	BEFORE	DURING *	AFTER+
Ag	$\mu\text{g/L}$	0.00601	0.00378	-	-	-
Al	$\mu\text{g/L}$	14.7	17.7	-	-	-
As	$\mu\text{g/L}$	2.04	1.72	-	-	-
Cd	$\mu\text{g/L}$	0.492	0.244	-	-	-
Cr	$\mu\text{g/L}$	2.22	9.99	-	-	-
Cu	$\mu\text{g/L}$	18.9	9.89	3.9	4.7	3.7
Fe	$\mu\text{g/L}$	26.4	25.0	-	-	-
Hg	$\mu\text{g/L}$	0.00597	0.00330	-	-	-
Mn	$\mu\text{g/L}$	29.2	13.2	-	-	-
Ni	$\mu\text{g/L}$	3.67	1.66	-	-	-
Pb	$\mu\text{g/L}$	0.493	0.441	-	-	-
Se	$\mu\text{g/L}$	0.848	0.356	-	-	-
Sn	$\mu\text{g/L}$	0.25**	0.25**	-	-	-
Zn	$\mu\text{g/L}$	175	68.4	7.8	9	8.7
TSS	$\text{mg/L}$	61.2	78.7	1.4	3.8	2.2
DOC	$\text{mg/L}$	11.7	6.0	0.91	1.2	0.90
PP PAH	$\text{ng/L}$	596	387	-	-	-
TPCB	$\text{ng/L}$	71	30	-	-	-
TDDT	$\text{ng/L}$	7.5	3.6	-	-	-
TCHLOR	$\text{ng/L}$	2.4	1.8	-	-	-

\* Average of 4 samples

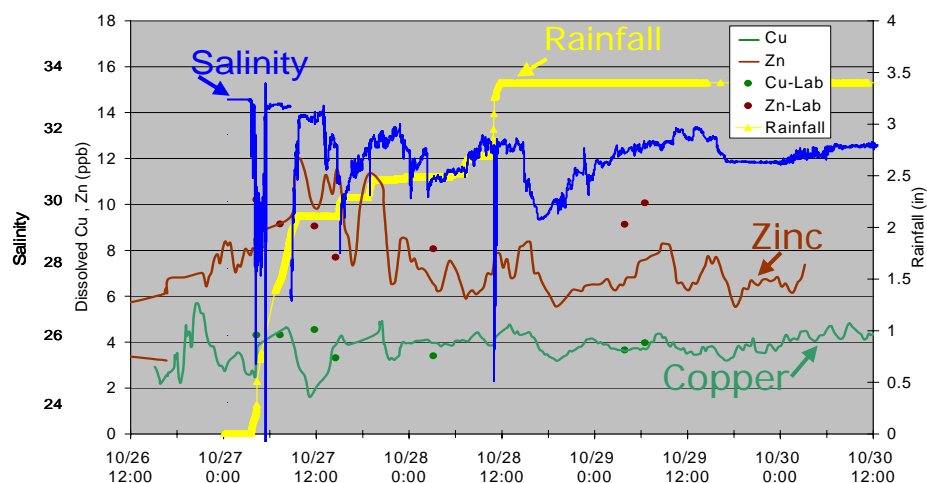
+ Average of 3 samples

\*\* Value=1/2 Method detection limit

## OFFSHORE

Mysid survival and mussel normal larval development were high in the floating controls, each exceeding 90% (Table 1). Mysids in the flow-through treatment experienced nearly no mortality. Mussel development in the flow-through treatment was slightly lower than the floating control, but the difference was not statistically significant. Topmelt survival was reduced in both floating controls and flow-through treatments (Table 1). However, 86% of the topmelt mortalities occurred in the first 24 hours. Though water quality of the offshore treatments was within a range tolerated by all species, a spike in water temperature (maximum of 26.3 °C) was measured at the beginning of the field exposure for both the floating control and flow-through treatments. This spike occurred when a sun block had not yet been put into place. Because of the low control values, the topmelt data are also reported as percent survival relative to the controls.

The chemistry of discrete bay water samples collected before, during, and after the storm event are shown in Table 2. For simplicity, data in the table for the four “during” and three “after” samples were averaged. “During” samples were collected during the first 2.1” of rainfall when it was actively raining and there was visual storm discharge to the bay. “After” samples were collected ~ 8, 16, and 40 h after rainfall and storm flow had ceased.



**Fig. 5** MESC full-storm monitoring data for salinity, dissolved copper and zinc. Dissolved copper and zinc in discrete samples and cumulative rainfall data are also

Concentrations of dissolved copper and zinc measured in the discrete bay samples during the storm were about 20% higher than those measured in either the pre-storm or post-storm samples, and overall varied about 11% relative standard deviation (rsd). These metals were consistently 60 and 90%, respectively in the dissolved phase. Copper was always above its WQS of 3.1  $\mu\text{g/L}$ , probably due to chronic hull paint leachate. Zinc was well below its WQS of 81  $\mu\text{g/L}$ . DOC and TSS levels measured in bay samples were more variable (42 and 59% rsd, respectively) and increased by a factor of  $\sim 3$  during the storm, but decreased to pre-storm levels in the “after” samples.

#### REAL-TIME MONITORING

Salinity, temperature, pH, light transmission, and oil fluorescence data measured by MESC were highly variable during storm flow conditions. In particular, salinity varied from a pre-storm value of 33.5 psu to near zero during the most intense rainfall periods. However, these low salinity conditions were maintained for very short periods of time; on the order of minutes or tens of minutes (Fig. 5). Over the exposure time period, salinity averaged 32.4 psu and thus this freshwater signal of 3.5% translated into an average dilution factor of  $\sim 30$ . Some of the observed variations could also be attributed to tidal fluctuations, which were particularly noticeable after the storm was over (Fig. 5). Continuous copper and zinc monitoring, representing between 165 and 265 analyses, showed a slightly lower variability with a maximum change of about a factor of two. The continuous monitoring with the MESC trace metal analyzers produced comparable (but not exact) results to the analysis made in the discrete samples.

#### DISCUSSION

The storm event monitored was an exceptionally high rainfall event, falling in the 98th percentile for rainfall totals in the region [12]. Therefore, this storm is representative of the upper range of volume discharge to the bay from this

drainage area. Though outfall chemistry data are historically quite variable, the measured levels during this storm were uniformly lower than those previously observed at this site, a result likely due to the short 5-d antecedent dry period. Even with lower event mean concentrations than observed on other occasions (by approximately a factor of five), this discharge event still represents an upper bound for contaminant mass load to the bay from this site.

Only copper and zinc were measured in the storm water samples at levels likely to cause the observed acute toxicity. Two separate TIE studies conducted at San Diego Navy facilities (as part of the Navy’s overall toxicity investigation) identified both copper and zinc as the primary contributors to observed toxicity. In this study, it also appeared that both copper and zinc concentrations were predictive of toxicity. A strong negative correlation was observed between mysid survival and copper and zinc concentrations ( $r^2 = 0.977$  and  $0.966$ , respectively). For mysids, zinc very likely contributed to the observed toxicity in the effluent, as measured concentrations were high enough to cause lethality to this species (96-h mysid zinc  $\text{LC}_{50} = 303 \mu\text{g/L}$ ; [13]) while copper concentrations were not high enough (96-h mysid copper  $\text{LC}_{50} = 153 \mu\text{g/L}$ ; [13]). Strong relationships between mussel larval development and copper and zinc concentrations were also observed ( $r^2 = 0.931$  and  $0.882$ , respectively). In this case, copper and zinc both likely played a role in the observed effects based on the sensitivity of this species (48-h copper  $\text{EC}_{50} = 6.43 \mu\text{g/L}$  [9]; 48-h zinc  $\text{EC}_{50} = 178 \mu\text{g/L}$  [14]). The absence of observed effects for any sample with topmelt is consistent with the relatively low sensitivity of this species to the measured metal concentrations (96-h copper  $\text{LC}_{50} = 238 \mu\text{g/L}$  [15]; 96-h zinc  $\text{LC}_{50} = 627 \mu\text{g/L}$  [16]).

Dilution series data for storm water effluent samples resulted in  $\text{EC}_{50}$  and  $\text{LOEC}$  values of  $\sim 50\%$  for mussel embryos. These values were higher than the 23% average value observed in samples collected from San Diego Navy facilities. These toxicity values should translate into a



dilution factor of between 2 and 5 needed to reduce toxicity to these organisms. Because pre-storm bay water was the diluent in these tests, the dilution factors need no adjustment for bay background conditions.

Even though the magnitude of the contaminant load to the bay during this event was relatively high, the copper and zinc levels measured in the bay were insufficient to cause acute toxicity. The minimum dilution factor determined by dividing the first-flush sample concentration by the difference between the maximum bay water value during the storm and the pre-storm concentration (MESC trace metal analyzer data) was 5 and 22 for copper and zinc, respectively. The average dilution factor, determined comparably by dividing the composite sample concentration by the difference in the average values measured during and before the storm, was 15 for copper and 24 for zinc. The similar calculation using the discrete sample data, yielded an average dilution factor of 12 for copper and 57 for zinc. These dilution factors bracket the average value of 30 calculated from the salinity measurements.

The range in observed dilution factors was more than sufficient to explain the observed reduction in toxicity of bay waters. The rapid mixing that occurred immediately outside the point of discharge led to a significant reduction in both chemical concentrations and limited the exposure duration to minutes rather than the 48- or 96-h exposures used in standard bioassays. The use of standard methods, therefore, overestimates the impact of episodic ephemeral discharges like storm water. These findings support results measured to date at all San Diego Navy facilities, which show that toxicity measured at the end-of-pipe does not reflect actual toxic impacts in the receiving environment.

The use of the floating bioassay laboratory system with the unique MESC continuous monitoring capability provided a useful means to directly evaluate receiving water impacts. Though reports of marine larval fish and invertebrates as field-based bio-monitoring tools are limited [17-20], these results suggest that mysids, topmelt larvae, and mussel embryos have good potential for use in exposures outside of the laboratory. These test organisms performed well under highly fluctuating seawater conditions. In particular, they did not appear to be impacted from the drop in salinity to near zero detected in the early stages of the storm. The relatively low (70%) floating control survival observed for topmelt suggests this species may have a heightened sensitivity to fluctuating temperature, which spiked high at the start of the exposure period. This temperature fluctuation, however, could be better controlled in future efforts.

## CONCLUSIONS

The data provided by the floating bioassay system confirms that bay exposures are very limited as a result of rapid mixing and dilution immediately outside the point of discharge. Observed exposure times were on the order of

minutes rather than the 48- or 96-h exposures used in standard bioassays. Thus, using standard laboratory bioassays of storm water discharges made at the end-of-pipe potentially overestimate the acute toxic impact of storm water discharges to receiving waters by overestimating exposure times. The unique data afforded by continuous monitoring with a floating bioassay laboratory provided a detailed understanding of the interaction of storm water with bay waters in explaining the lack of receiving water toxicity.

## Acknowledgments

The authors thank the Navy Pollution Abatement Ashore Prevention Technology and Demonstration/Validation Program, a part of the Naval Facilities Engineering Command (Andy Del Collo, program manager) and Commander Navy Region Southwest (Brian Gordon and Rob Chichester, environmental program managers) for their financial support. We also thank E. Arias, A. Blake, M. Brand, B. Davidson, P. Earley, R. Fransham, R. Gauthier, J. Guerrero, C. Kurtz, and C. Zacharias for their crucial help in the field, in the laboratory, and with data processing.

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## **Appendix I**

### **REVIEWER COMMENTS ON DRAFT STUDY REPORT and PROPOSED ALTERNATIVES**

#### **Technical Review Team Members:**

Dr. Debra Denton, United States Environmental Protection Agency Region IX (no comments on proposed alternatives)  
Mr. Shaun Halvax, Southwest Marine Shipyard (no comments provided)  
Ms. Ruth Kolb, City of San Diego (no comments provided)  
Ms. Eileen Maher, Port of San Diego (comments on report and proposed alternatives)  
Mr. Ken Schiff, Southern California Coastal Water Research Program (no comments on proposed alternatives)  
Mr. Scott Sobiech, US Fish and Wildlife Service (no comments provided)

#### **Additional Outside Reviewers:**

Dr. Allen Burton, Professor and Director of Institute of Environmental Quality, Wright State University  
Dr. Robert Spies, Applied Marine Sciences, Livermore, CA.

#### **Appendix Organization:**

Comments and response to comments on the draft study report and proposed alternatives are organized alphabetically by reviewer name:

Burton	p. I-2
Denton	p. I-10
Maher	p. I-27
Schiff	p. I-31
Spies	p. I-36

**NOTE:** The comments made here refer to a draft report that has been modified in producing the final report. References to specific page, table, or figure numbers may not match the final report.

**Dr. Allen Burton, Professor and Director of Institute of Environmental Quality, Wright State University**

<b>BURTON STUDY COMMENTS:</b>	<b>RESPONSE TO COMMENTS:</b>
<p><b>a. General Comments:</b> This four year study is the most extensive and advanced on-site stormwater runoff study that I am aware of. The study uses a state-of-the-art approach, combining multiple lines-of-evidence (LoE) (chemistry, lab and field toxicity, plume mapping, and effluent and off-shore monitoring). This study consisted of 136 discrete samples and 350 toxicity tests conducted during a wide range of meteorological conditions and seasonal extremes. The LoE were combined to form weight-of-evidence (WoE) based conclusions on the degree of toxicity of stormwater and its effects on the receiving waters, the causes of the toxicity, and its sources. It is well known that stormwater runoff varies widely in quality and potential impacts even on a site specific basis, due to the myriad of interacting and fluctuating factors that affect it (e.g., frequency, duration, magnitude of precipitation events, source variability, seasonal factors affecting physical, chemical and biological characteristics). Nevertheless, this study effectively characterized the bounds of that variability to such a degree that the statistical confidence of the key parameters and study factors is known. This degree of precision and confidence in the data allows for conclusions to be drawn from the study that have a low degree of uncertainty. The principal conclusions and the uncertainties that I find apparent are as follows:</p>	No response necessary.
<p><b>i.</b> Relatively undiluted stormwater samples from the study area vary in toxicity; and are more likely to be toxic when measured by standard laboratory exposures (48 to 96 hr constant exposure to first flush waters).</p>	No response necessary.
<p><b>ii.</b> Corresponding samples that are composites (collected throughout the event) are likely to be non-toxic in similar laboratory exposures.</p>	No response necessary.
<p><b>iii.</b> Bay waters are likely to be non-toxic during a storm event.</p>	No response necessary.
<p><b>iv.</b> The statistical power (ability to detect differences) of the laboratory toxicity assays was very good, indicating low replicate variability.</p>	No response necessary.
<p><b>v.</b> More realistic, <i>in situ</i> exposures during a storm event showed no toxicity.</p>	No response necessary.



BURTON STUDY COMMENTS:	RESPONSE TO COMMENTS:
<p><b>vi.</b> Plume mapping showed freshwater runoff stayed nearshore and on the surface of the bay prior to mixing. This suggests that benthic organisms are not affected by the runoff events, even near the outfalls. Note, the most sensitive toxicity test species is a benthic organism.</p>	<p>No response necessary.</p>
<p><b>vii.</b> Copper and zinc appear to be the toxicants of concern, based on the chemical data and toxicity identification evaluation (TIE) studies. However, the potential for toxicity from new-age pesticides (e.g., diazinon and pyrethroids), and from photo-induced toxicity from polycyclic aromatic hydrocarbons (PAHs) were not assessed. These compounds are common and known to be a source of toxicity in runoff. The low level discharge of PCBs is worrisome, given their propensity for biomagnifications and that there should not be on-going sources. The information from the TIE studies may contribute to source control, but given the complexity of the site and the prevalence of these chemicals (Cu, Zn, PAHs) on impervious surfaces of industrial and urban areas, it will be a challenge to reduce their occurrence.</p>	<p>The focus of this study was to evaluate the potential for toxicity of receiving waters from storm water discharges. The study used a list of CoCs that were thought to be the most likely causative agents generated at these types of sites. One purpose of performing toxicity tests is to evaluate the overall potential impact of all constituents whether or not they were measured in the sample. A lack of toxic response in bay waters would suggest that if these compounds were present in sufficient amounts to cause toxicity that this would have been observed.</p>
<p><b>viii.</b> The laboratory based exposures using first flush samples do not provide useful information to meet the goals of the Clean Water Act. Resident organisms in the Bay do not remain in the plume for 48 to 96 hrs and the first flush water does not remain in the plume for 48 to 96 hrs. Composite samples would provide a more realistic relationship to receiving water conditions. However, <i>in situ</i> exposures of toxicity test organisms provide the greatest degree of realism (thus least degree of uncertainty).</p>	<p>No response necessary.</p>

BURTON STUDY COMMENTS (cont.):	BURTON STUDY COMMENTS:
<p><b>ix.</b> The continued discharge of low levels of chemicals during runoff events may result in elevated sediment concentrations in the outfall area. These sediments should be assessed for their impact on benthic organisms.</p>	<p>The focus of this study was to evaluate the potential for toxicity of receiving waters from storm water discharges. The best way to evaluate long-term impacts to sediments is within current TMDL programs that are used to evaluate the magnitude and extent of impaired sediments using a weight of evidence approach and identify sources of the impairment. These programs are currently underway at several locations in San Diego Bay including at Navy facilities. Additional programs that can provide a better evaluation of long-term impacts to sediments include the Bay Protection and Toxic Cleanup Program, the Bight'98 program organized by the Southern California Coastal Water Research Program, and the Port of San Diego/Regional Water Quality Control Board Baywide Monitoring program.</p>
<p><b>x.</b> The USEPA is adopting the Biotic Ligand Model for improving the water quality criteria for Cu. Given the role of DOC at the site, the BLM approach may provide useful information.</p>	<p>We agree that the BLM may provide useful information once it is adopted.</p>
<p><b>xi.</b> Metal toxicity determinations are confounded by the influence of salinity and rapidly changing salinity during a runoff event. This has been the subject of previous studies and should be investigated.</p>	<p>We agree that metal toxicity may be confounded. Though salinity may vary in the receiving environment, toxicity test protocols require fixed salinity conditions.</p>

BURTON STUDY SPECIFIC COMMENTS:	RESPONSE TO COMMENTS:
<b>b. Specific Comments</b>	
<p><b>i.</b> The Executive Summary and Discussion/Conclusion sections should be modified, incorporating and better emphasizing some of the issues raised above. These issues include the reliable WoE approach, the lack of reality of the laboratory toxicity test exposures, and the findings of the field exposure test. At present, the field exposure test is virtually not mentioned in any section except Methods. The likely rapidly fluctuating concentration of Cu and Zn in the plume should be discussed in relation to WQS exceedances. Finally, the spatial and temporal limitation of resident organism exposures due to the shallow surface water, nearshore stormwater plume should be emphasized. The following references provide a wealth of information and cited peer reviewed studies that support the points I am making. You may want to include some of these citations and content for additional justification of permit conditions: Burton, G.A., Jr., and R. Pitt. 2001. <i>Stormwater Effects Handbook: A Tool Box for Watershed Managers, Scientists and Engineers</i>. CRC/Lewis Publishers, Boca Raton, FL, 924 pp., available online from USEPA at: (<a href="http://www.epa.gov/ednrmrl/publish/book/handbook/index.htm">http://www.epa.gov/ednrmrl/publish/book/handbook/index.htm</a>); Burton, G.A., Jr., R. Pitt, and S. Clark. 2000. <i>The role of traditional and novel toxicity test methods in assessing stormwater and sediment contamination</i>. CRC Critical Reviews in Environmental Science &amp; Technology 30: 413-447 (pdf attached); and, Burton GA Jr., Greenberg MS, Rowland CD, Irvine CA, Lavoie DR, Brooker JA, Eggert LM, Raymer DFN, McWilliam RA. 2005. <i>In situ exposures using caged organisms: a multi-compartment approach to detect aquatic toxicity and bioaccumulation</i>. Environ. Pollut.134:133-144 (pdf attached).</p>	<p>The comments provided above have led us to focus the report findings on the major goal of evaluating the efficacy of using WET testing and its use in “assessing and protecting against impacts upon water quality and designated uses caused by the aggregate toxic effects of the discharge of pollutants” (EPA, 1991). The comments above suggest that our conclusions were a bit broader than the data support and that the conclusions need to be focused on toxicity testing and what it shows. These comments will therefore serve to improve the report.</p> <p>We have reviewed the cited literature (some prior to the reviewed draft) and intend to re-evaluate where their citation can be used to support discussions and conclusions in the report.</p>
<p><b>ii.</b> Study Goals: While a goal was to “evaluate toxic impacts on the receiving environment”, this was done in a limited manner – using only 3 standard test species. A survey of resident benthic organisms along a gradient of exposures would be a useful LoE for future studies.</p>	<p>The study focused on the WET test requirement in the permit which is used in “assessing and protecting against impacts upon water quality and designated uses caused by the aggregate toxic effects of the discharge of pollutants” (EPA, 1991). The study fully evaluated the impacts that can be determined by WET testing. A survey of benthic organisms is best done within a full sediment investigation such as those being done at Navy facilities under the TMDL program to evaluate magnitude and extent of impairment using a weight-of-evidence approach.</p>

<b>BURTON STUDY SPECIFIC COMMENTS:</b>	<b>RESPONSE TO COMMENTS:</b>
<b>iii.</b> The field bioassay study by Katz and Rosen (2005) should be presented in greater detail in the Results and Discussion sections.	Additional text was added.
<b>iv.</b> Monitoring sites: Greater than 90% impervious surface area is amazingly high. Consider adding background information from Burton and Pitt (2001) concerning typical contaminants and loadings from similar sites.	Additional text was added where applicable.
<b>v.</b> Spell check needed throughout – occasional misspells.	A spell check was completed after all report modifications to text.
<b>vi.</b> Table 5. Was organism age not a QA/QC objective?	Organism age is a QA/QC objective. Table 5 was altered to include the
<b>vii.</b> Table 6. Units missing.	Units were added.
<b>viii.</b> Recheck all tables and figures to ensure they are stand alone. Some are missing explanations of acronyms/abbreviations.	Additional text added where applicable.
<b>ix.</b> Some levels of PAHs observed in first flush samples have been associated with photo-induced toxicity. This is not addressed in this study, nor could it be measured in typical laboratory exposures with fluorescent lighting.	The issue of photo-activated PAH was not addressed in this study. A comparison of toxic thresholds on an analyte by analyte basis showed that there were a six instances when either fluoranthene or pyrene concentrations exceeded an acute effect threshold (including photoactivation) found in the literature. None of the bay PAHs was above a chronic toxic effect level (also including photoactivation). Additional data found in Scannell et. al., 2005 was evaluated for the report and appropriate text added.
<b>x.</b> Diazinon has been identified as a problem chemical in southern California, but apparently was not evaluated. It is toxic at the ppt level and has been found in rainfall.	Diazinon was not identified as a likely contaminant of concern at the start of the study as the Navy has not allowed its use for several years. The lack of toxicity in the receiving waters suggests that even if diazinon was present in the storm water, it did not lead to toxic effects in the receiving water.
<b>xi.</b> The summation of the pesticides found may be a problem, and some produce synergistic effects in combination (see several papers by Mike Lydy). The pyrethroids are also a problem in California. Note recent studies by Don Weston.	The lack of toxicity in the receiving waters suggests that the amounts present in storm water were insufficient to cause a toxic effect in the receiving water. The value of toxicity testing it that it allows an evaluation of toxic components even if they are not measured independently.
<b>xii.</b> P. 103, paragraph 2 (remove future tense).	Text adjusted.

BURTON STUDY SPECIFIC COMMENTS:	RESPONSE TO COMMENTS:
<p><b>xiii.</b> The correlations of Cu and Zn with toxicity were weak. Despite their sporadic short term exceedance of WQS, the salinity, DOC and fluctuations in concentration make the causality issue uncertain. Nevertheless, they are often identified in stormwaters as compounds of concern.</p>	<p>No response necessary.</p>

BURTON ALTERNATIVES COMMENTS:	RESPONSE TO COMMENTS:
a. The “Alternative” document was not reviewed until the above “Storm Study” report review was completed. It is good to see the authors of the “Alternative” document have identified the key issues and problems associated with the existing permit language.	No comment necessary.
b. The existing permit toxicity limits are in no way based on scientific evidence that shows a relationship to protecting receiving waters. Such limits also ignore current USEPA draft guidance and a wealth of scientific evidence provided by a range of stakeholders that documents the limitations of WET testing.	No comment necessary.
c. Realistic MSD levels must be incorporated into any permit that utilizes toxicity testing. Given the huge law suit challenging previous WET guidance, the years of effort put into developing the draft guidance, and the extensive documentation which is publicly available, it is amazing that the proposed permit language was used.	No comment necessary.
d. The Ohio EPA has allowed stormwater permittees to focus on receiving water impacts, rather than end-of-pipe limits, given the complex exposure issues that preclude use of conventional WET approaches. This approach is very reasonable and should be considered here.	No comment necessary.
e. The goals of the Clean Water Act (CWA), and issues of anti-degradation and anti-backsliding, are not at risk, when receiving waters are protected. Receiving water protection cannot be extrapolated from laboratory toxicity testing under erroneous exposure scenarios or from chemical data that do not consider fluctuation concentration, complexation and bioavailability. The study site has very complicated exposure and complexation issues, due to tidal mixing, freshwater-saltwater density differences, and salinity-DOC complexation phenomena.	No comment necessary.

BURTON ALTERNATIVES COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>f. The suggested permit language used in Alternative 1 and 2 is a huge improvement over the current language, since a more realistic dilution is introduced and laboratory exposures times are reduced. The use of realistic MSD levels is appropriate and should dictate acceptability/exceedance criteria. However, the proposed testing procedures are still overly conservative, for the following reasons:</p> <ul style="list-style-type: none"> <li>i. The plume mapping data shows resident organisms are exposed for up to tens of minutes, IF they were to remain in the plume (a conservative assumption). An exposure of 48 hrs introduces a safety factor greatly exceeding two-fold. A top-to-bottom depth integrated sample would better characterize receiving waters adjacent to the outfall.</li> <li>ii. The resident organisms are marine, and, therefore, will not remain in the freshwater plume during a runoff event. Their exposure period will likely be on the order of a few minutes, maximum. Benthic organisms will have no exposure to unmixed effluent. This reality must be considered if the NPDES permit (and CWA goal) is trying to protect the receiving waters and their biota.</li> </ul>	<p>We agree with the comments regarding exposure magnitude and duration. Using conservative exposure conditions will provide an additional level of protection in the permit. We agree that benthic organisms will not be exposed to unmixed storm water.</p>
<p>g. The use of <i>in situ</i> exposures would provide realistic assessments of toxicity.</p>	<p>We agree, but <i>in situ</i> methods are still in a developmental stage.</p>
<p>h. The use of benthic colonization or transplant studies below the outfalls would provide a realistic assessment of resident organism effects.</p> <p>i. Sampling of benthic macroinvertebrates on a gradient from the outfalls would also provide an assessment of resident organism effects.</p>	<p>The scope of the effort was to evaluate potential toxic effects to receiving waters. Investigations into benthic impairments are best left a part of ongoing TMDL and Baywide monitoring programs where the data are evaluated using multiple lines of evidence including an evaluation of sources.</p>
<p>j. These approaches could be incorporated into permit language for assessment on a yearly basis. These types of tests would better assess whether or not the goals of the CWA are being met, than artificial exposures in the laboratory with single species.</p>	<p>No comment necessary.</p>

### Dr. Debra Denton, USEPA Region 9

<b>DENTON STUDY COMMENTS:</b>	<b>RESPONSE TO COMMENTS:</b>
<p>I complement the Navy on undertaking this study to determine the spatial and temporal potential for toxicity at the various Navy sites. For those of us, myself included who have implemented a storm water program, understand and appreciate the complexity of addressing sampling and testing logistics involved with storm water testing. Overall, the Navy has done an extensive job of collecting and analyzing storm water for toxicity assessment including TIEs over multiple storm events and years.</p>	<p>No response necessary.</p>
<p>I submitted comments on the study's design please refer to my letter dated December 8, 2003. The report does not address the following suggestions/recommendations as described in my letter. I will restate my specific recommendations from the December letter and highlight issues and comments.</p>	<p>Responses below:</p>
<p>1. "The Navy should prepare a Quality Assurance Project Plan (QAPP). All methods will utilize standard USEPA procedures and follow the project's approved Standard Operating Procedures (SOPs) and QAPP (see USEPA 2001). The QAPP will be consistent with the SWRCB's Surface Water Ambient Monitoring Program (SWAMP) program requirements. All data will be subjected to a 100% audit by the project QA Officer. Any deviations in SOPs for sample analysis or reporting will be recorded and corrective actions will be implemented according to the QAPP." The section on materials and methods should have clearly discussed and cited the QAPP and how it was followed. This must be added in the final report, an appendix would be appropriate.</p>	<p>This investigation started under a Navy research program to evaluate storm water methods and impacts at Navy facilities without a requirement to develop a QAPP. The project was expanded to evaluate toxicity after the SDRWQCB requested the study. Initial discussions with Regional board staff did not identify a QAPP as a requirement for the study. The recommendation that a QAPP be produced occurred well after initiation of the project, which is contrary to guidance that requires a QAPP be produced and accepted prior to that start of a study. However, the investigation followed the principals and elements that are included in formal QAPP documents. Where possible, we have added text within the appropriate report sections to improve the level of detail that support the elements that are included in a formal QAPP.</p>



DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>2. “The test methods and test species to be tested must be from the following methods:</p> <ul style="list-style-type: none"> <li>- 1st edition west coast marine short-term test methods (USEPA 1995)</li> <li>- 4th edition freshwater short-term test methods (USEPA 2002a)</li> <li>- 5th edition freshwater and marine acute test methods (USEPA 2002b).</li> <li>- For both acute (include invertebrate and vertebrates) and chronic test methods (include invertebrate, vertebrate, and plants) multiple test species must be evaluated for both study objectives.” <p>Most importantly, I specifically delineated that USEPA toxicity test procedures were to be followed. Therefore, why did the Navy choose to follow the ASTM 1994 bivalve development protocol instead of the USEPA 1995 bivalve development protocol? There are several discrepancies as to which WET test method was conducted for this species. For example, the report cites ASTM 1994, Appendix F cites ASTM 1999, and Appendix H cites USEPA 1995. It is unclear as to what method and whether the method was consistent for all these analyses? I suggest that in the final report that any differences between these methods be described. The report needs to specifically identify the mysid tested in this section (reader should not have to go to Appendix B or Executive Summary). Why were only three reps employed instead of the required four reps (a required minimum as specified in the manual)?</p> </li></ul>	<p>The permit requires testing survival of either a vertebrate or an invertebrate. The mussel development endpoint was added because it is among the most sensitive short-term tests available. The level of effort required to perform the toxicity tests for each storm event with multiple species, locations, and sample types was immense. Adding another test species would have surpassed the capabilities of most toxicity labs.</p> <p>EPA methods were used for the topsmelt and mysid testing specified in the permit. ASTM 1999 was used for the mussel tests and should have been uniformly cited in the documentation. ASTM methods are nearly identical to USEPA 1995 though they differ in their test acceptability criteria. ASTM protocols were referenced because results were based on normal shell development and not survival. This was considered appropriate because of the sensitivity of the sublethal endpoint, and the speed with which results could be evaluated, particularly because of large testing requirements. References to other than ASTM 1999 were corrected in the report and appendices.</p> <p>Text describing the specific test species used was added to the text.</p> <p>The test methods require two replicates for effluent testing and four replicates for receiving water testing. Three replicates were used for all tests to streamline laboratory work and to provide consistency between effluent and bay water testing. Though this was a departure for the number of replicates required for receiving water testing, test method variability was good. All receiving water test results were above 90% survival and a fourth replicate would not have changed this outcome.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>3. “The proposed technical approach must provide the basis for how the data will be evaluated for data analysis and evaluation steps. For example, how will the data be evaluated for whether the quality assurance/quality control (QA/QC), and test acceptability criteria (TAC) requirements were achieved? The QAPP should include data analysis and evaluation procedures. For each test endpoint and method, the results for various endpoints must be calculated according to EPA flowcharts in the WET manuals. The results must be examined on a test-by-test basis. Test results should be reviewed to ensure that (1) data were properly reported and (2) proper estimates were generated according to EPA flowcharts (see Report Preparation and Test Review section of the manuals). Note, all these steps should be specified in a document in advance of the data analysis to ensure that all data meets the appropriate and required QA/QC, TAC and statistical assumptions before the data is included in the overall data evaluation.”</p> <p>The discussion on toxicity data quality assurance/quality control starting on page 28, needs to be refined and more detail provided (e.g., the report has a better description of methods and materials provided in the TIE test method discussion). For example, the sentence “Exceedances in several data quality objective did not automatically invalidate a test” so how was this documented in the QAPP? Also, according to the manuals, the test acceptability criterion (TAC) (90% or greater survival and the controls for acute test methods) is mandatory. Please specify whether all tests achieved the TAC? Where is the discussion of the QAPP data analysis and evaluation procedures (include as an appendix)?</p>	<p>As mentioned previously, a formal QAPP was not generated. Table 5 did show the QA objectives and the test acceptability requirements. As described above, text was added to the methods and results sections that better describes and quantifies the evaluation of performance relative to QA/QC objectives and TAC.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>4. For the evaluating the acute toxicity objective, the study must determine the following statistical analysis for each test method, (1) standard t-test, (2) no-observed adverse effect concentration (NOAEC), and (3) the Lethal Concentration (LC50) accordingly to USEPA 2002. Each of these endpoints should be considered for this study objective.</p> <p>In Appendix B it appears that the analysis of the standard t-test was not conducted. Apparently, Appendix C does provide the statistical t-test analysis. However, a major oversight of Appendix C is that the control response data is not included. I suggest that these statistical endpoints be in one table for ease of comparison for the reader.</p>	<p>The endpoints cited in the comment were all conducted/ determined and reported in the appendices. Pre-storm bay water results act as the controls for the outfall samples. Because of the large amount of data and to minimize redundancy, a choice was made to show the pre-storm water bay results (which acted as controls) with the other bay water data. Appendix B was designed to be a summary only. It does have a column showing the endpoint value calculated relative to control, providing the reader with the ability to determine the control result. Text was added to the report and the appendices to aid the reader in the organization of the tables and to identify applicable control result.</p>
<p>5. The stormwater sample should be collected with a concurrent flow measurement and ability to relate the sample collection timing to the relationship on the storm hydrograph or a hyetograph as may be appropriate. The report does not include the concurrent flow measurement volume and relationship of the storm hydrograph. As the report states on page 2, “the composite samples were collected to provide sample data that was representative of the entire storm discharge as that could be used in mass loadings calculations in future TMDLs.” In order to do mass loading calculations flow measurements must be conducted at sample time.</p>	<p>The permit requires that first-flush samples be collected during the first hour of flow, with no measure of flow. Flow measurements were made as part of this study to allow the generation of flow-weighted composite samples (See Section: Onshore Sampling-Composite). Mass loading calculations are not pertinent to evaluating the toxicity threshold and were not included in the report. These data can be used in evaluating TMDLs associated with the watershed at a later date.</p>
<p>I have reviewed the December 2005 draft final report to evaluate Navy facility storm water toxicity and have the following comments. I will not be providing comments on the modeling and chemistry analysis as this is not my direct expertise. I do have extensive comments on the interpretation of PMSD, toxicity tests, and TIE analysis. Considering the amount of information in the report and appendices and my workload, I am sure that I would find additional thoughts and comments on this report.</p>	<p>No response necessary.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>Analytical analysis discussion:</p> <ul style="list-style-type: none"> <li>I question why a very limited list of contaminants of concern such as metals, PAH, PCB, and chlorinated pesticides including DDT were only initially targeted. Considering the wide range of land uses within these four stations, such as fuel storage, painting, sandblasting, vehicle repair and maintenance, why were not additional compounds tested (e.g., oil and grease, surfactants, pesticides such as organophosphates and/or pyrethroids etc?). What pesticides are used at these Navy stations? I suggest inserting the water quality criteria for both diazinon and chloryprifos to Table 40. Diazinon CCC = 0.8185 ug/L and CMC = 0.81850 ug/L (USEPA 2005). Chloryprifos CCC = 0.0056 ug/L and CMC = 0.011 ug/L (USEPA 1986).</li> </ul>	<p>The list of CoCs cited in the comment was originally identified for Naval Station based on their historical presence in sediments within the central pier area of Naval Station (Fairey et al., 1996; Chadwick et al., 1998) as well as from historical NPDES storm water data collected from 1994 through 1999. The sediments in this area are listed by the SDRWQCB for a TMDL investigation. The list of CoCs was vetted with the Technical Review Team (TRT) and matched up with the activities cited in the comment. Though samples were not specifically analyzed for the pesticides noted in the comment, they would have been identified during the TIE analyses if they were present at levels sufficient to cause toxicity. The lack of toxicity in receiving waters suggests that even if these pesticides were present in the storm water samples and not analyzed for TIEs, they did not lead to toxic effects in the receiving water.</p>
<ul style="list-style-type: none"> <li>Table 22 needs to include the NPDES performance goals for all the metals in addition to copper and zinc for comparison purposes.</li> </ul>	<p>The permit only has performance goals for copper and zinc.</p>
<ul style="list-style-type: none"> <li>In the Executive Summary it highlights that the “toxicity of undiluted first flush stormwater was highly variable, spanning the full range of impact, 0 to 100%, and average 72% for both topsmelt and mysid test species”. Coincidentally on page 48, the report states that “the data show considerable variability of the individual metals spanning a range of approximately 25% to 180% for both dissolved and total metal. Variability was typically about the same or lower in the composite samples than in first-flush samples.” The Executive Summary text needs to be clear that the variability of toxicity response is related to the fluctuating chemicals and concentrations (in particular metals) as to be expected. This point illustrates that is paramount to collect that first-flush stormwater sample to capture the magnitude of toxicity.</li> </ul>	<p>Text was added to clarify that variable toxicity was related to variable concentrations of contaminants. First flush storm water discharge samples only capture the magnitude of toxicity of storm water for the moment in time when the sample is taken. First-flush samples do not capture the toxicity of the discharge, nor do they capture the magnitude of toxicity that occurs in the receiving environment as a result of the discharge.</p>
<p>PMSD discussion:</p> <ul style="list-style-type: none"> <li>The tables showing PMSD (Table 12, 20, 27, 34) should show the number of tests included in the data set. For a direct comparison to USEPA 2000, I strongly suggest that the PMSD values for the 10th and 90th percentiles be provided.</li> </ul>	<p>Text was added to show the number of tests and 10<sup>th</sup> and 90<sup>th</sup> percentiles of the data.</p>

<b>DENTON STUDY COMMENTS (cont):</b>	<b>RESPONSE TO COMMENTS:</b>
<ul style="list-style-type: none"> <li>The sentence “the lower and upper PMSD bounds are recommended as test acceptability criteria” is inaccurate. The PMSD bounds are not applied as test acceptability criteria (TAC), however, are to be reviewed according to Section 12 (Report Preparation and Test Review) of USEPA 2002a,b.</li> </ul>	<p>The text was modified.</p>
<ul style="list-style-type: none"> <li>The definition of PMSD should be stated as “the minimum significant difference (MSD) is the smallest difference between the control and another test treatment that can be determined as statistically significant in a given test, and the PMSD is the MSD represented as a percentage of the control response.”</li> </ul>	<p>The text was modified.</p>
<ul style="list-style-type: none"> <li>In looking at the figures 55 - 57, I question how the EPA values were plotted? I would assume to plot the EPA values this report’s author would need the individual data points (not available to my knowledge), from the EPA 2000 document.</li> </ul>	<p>Tables (B-8a through B-8c) in the EPA document (EPA, 2000) identify the 5, 10, 15, 20, 25, 50, 75, 80, 85, 90, and 95<sup>th</sup> percentile PMSDs. These are the data plotted in the figures. Individual test data were not available.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>The sentence “The 90% requirement in the permit language exceeds the EPA's lower boundary for PMSD and has no statistical power to identify actual toxic effects”. This sentence is wholly inaccurate and confounding two separate and independent issues into one sentence. “Power can be characterized only by repeated testing. Power is an attribute not of a single test, but of the sequence of many tests conducted under similar conditions and with the same test design (USEPA 2000). Power is the probability of correctly detecting a true toxic effect (i.e., declaring an effluent toxic when in fact it is toxic). The sensitivity of the toxicity test will depend in part on the number of replicates per experimental units per treatment, the alpha and beta (provided beta is used to determine the effect size desired), and the variability (e.g., MSE). The power to detect differences increases (e.g., MSD decreases) as the variability decreases and the effect size increases. The MSD provides an indication of within test their ability, and smaller values of MSD are associated with increased power to detect a toxic effect. EPA recommends upper and lower PMSD bounds for each test method in order to minimize within test variability and increase statistical power (Denton et al., 2003). The expression of the permit language of toxicity shall not produce less than 90 percent survival 50% of the time has nothing to do with either test power or PMSD bounds, as this is a regulatory decision as to the interpretation of the Clean Water Act's interpretation of “no toxics in toxic amounts.”</li> </ul>	<p>The text was attempting to describe that the 90% requirement in the permit has no statistical basis for identifying a toxicity test result as toxic. Depending on control response the arbitrary 90% cutoff falls at or below the lower bound 10<sup>th</sup> percentile PMSD indicating that only 10% of labs could declare a result toxic. Additional text and tables were added to the report to clarify these points.</p> <p>The basis of the Board’s decision to include a study of storm water toxicity was to develop a science-based toxicity threshold for industrial storm water discharges. The choice of toxicity metric must therefore be scientifically defensible and not based on an arbitrary decision or interpretation. Because the Navy’s proposed standards are based on scientific measurements, data, and statistical compilation, PMSD was included in developing the Navy’s proposed standards. It should be noted that the Water Quality Control Plan for the San Diego Basin states: “The survival of aquatic life in surface water subjected to a waste discharge or other controllable water quality factors, shall not be less than that for the same water body in areas unaffected by the waste discharge...”. It is the Navy’s position that the lack of toxicity measured in receiving waters meets the narrative requirement of "no toxics in toxic amounts".</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>The sentence “even using the PMSD upper bound, the EPA found only 50% of the labs were able to detect a 25% difference from control” should be restated. See USEPA 2000 page 5-7, “EPA found that about half of the labs in the days that were able routinely to detect a 25% difference between control and treatment.” I suggest that inserting this sentence solely from the EPA document without context is inappropriate. Labs not achieving routinely the PMSD (i.e. sufficient within-test sensitivity) must reduce the PMSD by decreasing within-test variability, increase control mean and/or increase number of replicates within a test. The point is that labs should be achieving PMSD lower than the 90th percentile in order to not exceed this upper bound.</li> </ul>	<p>The text was altered to match the statement “EPA found that about half of the labs in the data set were able routinely to detect a 25% difference between control and treatment.”</p>
<ul style="list-style-type: none"> <li>I do agree that the PMSD values from this study are reasonable and it was good to examine with the additional test results using the Natilus data set for comparison purposes.</li> </ul>	<p>No response necessary.</p>
<p>TIE discussion:</p> <ul style="list-style-type: none"> <li>TIE Appendix E cites the use of the ASTM 1993 mussel development test and appendix F cites the use of ASTM 1999 of which neither is the method cited and used in the routine toxicity tests cited in the main report, ASTM 1994. So what test method was conducted, and if different versions (what are the differences)?</li> </ul>	<p>As described above, the correct citation for the larval bivalve tests should have been ASTM (1999) and was changed in the text.</p>
<ul style="list-style-type: none"> <li>The acronyms mean to be consistent with the body of the main text (e.g., NAVSTA, SUBASE, NASNI).</li> </ul>	<p>The acronyms used by the TIE laboratory did not match those used in the final report. These reports were delivered as *.pdf files and we are not able to modify them to match. Instead, an introductory paragraph was added to the Appendices E and F describing the relationships between acronym usage. NAV=NAVSTA, SUBASE=SUB and NI=NASNI.</p>
<ul style="list-style-type: none"> <li>On page 3, did the researchers follow the Marine Phase I TIE procedures? If so reference is not included (USEPA 1996). This document details the procedures for the marine test species.</li> </ul>	<p>Marine Phase I TIE procedures following methods outlined in EPA/600/R-96/054 were employed throughout both study years. This citation was inadvertently left out of the reports and was inserted as appropriate.</p>
<ul style="list-style-type: none"> <li>As stated on page 48, why were only 11 of the 16 outfall samples analyzed for copper and zinc? According to EPA Phase II of the TIE procedures, EDTA also chelates the divalent metals cadmium, magnesium, lead, and nickel. Therefore, complete metal scans should have been conducted for each of these outfall samples.</li> </ul>	<p>A metals screen was conducted for all TIE samples. The statement on p. 48 refers to the fact that some outfall samples (not the TIEs) were analyzed only for copper and zinc.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>A major limitation of the TIE analysis (Appendix E) is that only two manipulations were conducted with the samples, the addition of EDTA and C18 column extraction. It appears that the researchers went in thinking only metals were the toxicants and not wishing to ascertain the total toxicity of the samples? For example, the pH adjustment tests would have provided more information on the nature of pH dependent toxicants. In addition conducting the thiosulfate addition would elicit further which metals are complexed with only one or both additives (EDTA and thiosulfate).</li> </ul>	<p>The TIE laboratory was requested to identify the causative agents in storm water samples to three test endpoints. There was no direction given to look for a particular category of toxicants.</p> <p>The approach taken was consistent with the USEPA Marine Phase I TIE manual that states that the number of treatments is only a recommendation and may require modification depending on each application. The Phase I treatments selected were sufficient for a Phase 1 Characterization since they eliminated all toxicity associated with the samples. The choice of Phase 1 treatments reflected prior knowledge of toxicants likely to be present as well as limitations on sample volume. Application of pH-adjustments would have been of limited benefit because of difficulties in controlling pH in highly buffered seawater, as well as intrinsic toxic effects of pH on bivalve larval development. Sodium thiosulfate may have been of some benefit in terms of distinguishing between different metals, but analytical data were available for the metals, and it was more cost-effective to proceed directly to spiking studies to identify specific metals responsible for toxicity.</p>



DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>The study did not conduct any Phase III analyses. Unless the researchers consider figures 5 - 6 and the metals additivity study to demonstrate the relationship of TUs to copper and zinc? However, the reported r2 values are weak. In addition, the figure for both copper and zinc, the figures intercept is ~ 1.8 TUs meaning that there is still toxicity unaccounted for in the sample. On page 31, it states for Subbase of 23 c+e that EDTA clearly removed toxicity, however sufficient copper was not present to account for all the toxicity present and there was barely enough to zinc account for all of the toxicity.</li> </ul>	<p>Phase III TIE analyses were conducted and included: 1) copper and zinc toxicity studies; 2) studies with mixtures of copper and zinc; 3) comparison of sample metal concentrations with available literature values; 4) statistical comparisons of predicted and actual TUs present in the samples; and 5) comparisons of species sensitivity.</p> <p>The TIE reported that r2 values for copper and zinc alone were weak, indicating that neither metal by itself could account for toxicity observed across all of the samples. However, the relationship for a combination of copper and zinc was strong with an r2 of 0.8 and a p-value of 0.02. The text in the report stated that "...both metals contributed to toxicity...". The accompanying Figure 11 also shows this conclusion.</p> <p>Though Figure 5c shows a relationship with an intercept of 1.8 TUs, all of the data points show that there is more than enough copper and zinc present to account for toxicity in the sample. It is inappropriate to extrapolate results to the intercept because all of the samples exhibited toxicity (above 3 TU) and had sufficient residual copper and zinc to explain toxicity. This is further complicated by the fact that some portion of the metals is not bioavailable.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>In addition, there is mysid toxicity which was not addressed. I suggest a copper and zinc spiking study to ascertain whether these two toxicants are the cause of toxicity to the mysids? This is important because mysid toxicity was demonstrated with several the samples (see page 28) however only one TIE was conducted?</li> </ul>	<p>Mysid toxicity was clearly addressed in this study. However, sample SUBASE OF23c+e was the only sample collected in February 2004 that exhibited a sufficiently strong reduction in survival (approximately 43%) to justify performing a TIE. Toxicity was completely removed by the EDTA treatment, indicating divalent cationic metals were the cause of toxicity in this sample. Other samples collected in February exhibited marginal reductions in survival, the greatest of which was only 18% less than the control, which would be problematic in terms of detecting differences among treatments. Conversely, three samples collected in March 2005 were subjected to TIEs with mysids. While metal spiking studies were not performed with mysids in conjunction with the February samples, toxicity tests on copper and zinc were conducted in support of TIEs performed with mysids on the March 2005 samples, and the results and conclusions presented in the associated report.</p>
<ul style="list-style-type: none"> <li>I question why the initial toxicity tests were conducted on February 19, 2004 and the TIE manipulations were not conducted until February 27? As stated in the report, toxicity dissipated during this time, therefore some level was lost in the samples. Given that the mussel development was 0% development for the February 18 sample (see page B-5) therefore, it is reasonable and doable to have initiated a TIE as soon as February 21-22.</li> </ul>	<p>The reason was explained on Page 3 of the TIE report. The TIEs were not initiated until February 27 because the lab was awaiting results of the 7-day exposures with mysids and silversides. This test design was intended to ensure that a toxic outcome could be evaluated even if acute toxicity was not identified. When toxicity was identified to the mussel, a decision was made to focus TIEs on the clearly toxic result. The design was modified in the second round of TIEs to evaluate acute exposures only.</p>
<ul style="list-style-type: none"> <li>On page 28, was the fraction 95% methanol fraction analyzed with GC/MS?</li> </ul>	<p>Yes. GC/MS was performed on the 90, 95, and 100% methanol fractions. The results of this analysis are included in the addendum report prepared on January 12, 2005.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>Appendix F, Table 4 should note that cadmium and lead are above or near the EPA criterion continuous concentration (CCC) (EPA 2002c). As indicated on page 45 the relationship between topsmelt and mysid survival is reasonably strong with a <math>r^2</math> value 0.76 and both copper and zinc for topsmelt <math>r^2 = 0.23</math> and 0.44 respectively were relatively weak. The researchers speculate that surfactants may be the primary cause to topsmelt. However, additional Phase II and III TIE procedures are necessary to confirm this hypothesis. Therefore, the Navy must conduct these additional Phase II and III TIEs with additional toxic samples to topsmelt and mysid test species (see Table 10).</li> </ul>	<p>Lead and cadmium were present in some of the samples, but were not related to the observed responses. No relationships were calculated between mysid and topsmelt survival; the <math>r^2</math> value (0.76) in the second sentence above refers to the relationship between zinc and mysid survival and, compared with the substantially lower <math>r^2</math> values obtained between metals and topsmelt survival, suggests that metals were not responsible for adverse effects observed with topsmelt. Surfactant toxicity was implicated for both mysids and topsmelt in one of the samples for which EDTA did not remove toxicity, but C18 extraction and aeration did. Toxicity of the foam fraction collected after aeration was also demonstrated with mysids, and toxicity was strongly correlated with MBAS (<math>r^2 = 0.9</math>), a measure of anionic surfactants. While this evidence supporting surfactant toxicity is relatively strong, toxicity in the sample dissipated before the investigation could be fully completed. Though the TIE laboratory recommended that additional steps be taken to confirm the findings, there was insufficient sample and toxicity to perform further work.</p>
<ul style="list-style-type: none"> <li>Check math errors in Tables 8 and 9.</li> </ul>	<p>The numbers were checked and corrected.</p>
<p>Discussion section of report:</p> <ul style="list-style-type: none"> <li>The discussion on page 105 text does not match the referenced figure 52. According to the figure, first flush failed 70% of the time for the 90% survival and composites failed ~ 42% of the time. Also, first flush failed ~28% of the time for the 70% survival and composites failed ~ 4% of the time.</li> </ul>	<p>Both the figure and the text are correct. A failure of a threshold is the point that falls to the left of the “threshold” line on the graph because the thresholds are for greater than or equal to criteria. For first-flush, the cumulative percentage is 58%. Tables were inserted to clarify these data.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<ul style="list-style-type: none"> <li>Throughout this discussion, it incorrectly refers to the amount of dilution necessary to remove toxicity. The mechanism to remove toxicity is to control and/or treat the toxicant(s) not by dilution.</li> </ul>	<p>WET testing of effluents specifically requires that dilution series be run to evaluate the dilution level at which there is no longer a toxic effect. WET guidance states “impact from toxics would only be suspected where effluent concentrations after dilution are at or above toxicity effect concentrations” (EPA1991). The report was trying to describe the observation that toxicity was rarely observed in the receiving environment regardless of the magnitude of toxicity measured in first-flush storm water samples.</p>
<ul style="list-style-type: none"> <li>I don’t recall reviewing the bay sample study plan? Where is a map showing the relationship of the samples to the various outfalls and timing of the samples to the storm events. Some of these they samples were collected up to 10 to 20 days after a storm event? How is this representative of toxicity after a storm event? I suggest that figure 54 be separated into three different figures showing before, during and after storm events.</li> </ul>	<p>Receiving water sampling was one of the critical measurement components of the study. The sampling plan provided to the TRT in September 2003 included this component as part of the plan, described receiving water results from sampling events, and provided a map detailing sample locations during the next phase of the investigation. A brief given to the TRT in September 2004 described the efforts in receiving water sampling and described their results to date.</p> <p>The report has maps showing all receiving water sampling locations (Figures 2, 6, 7, and 11) and text to go along with them.</p> <p>Pre-storm water samples were collected before rainfall began, “During” samples were collected while it was raining or storm water was still flowing out drains, and “after” rainfall samples were collected between 12 and 30 hours after rainfall or storm flow stopped. No samples were collected 10 to 20 days after a storm event.</p> <p>Additional figures were added showing before, during, and after storm events.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>Overarching recommendations:</p> <p>It is apparent that the Navy did an extensive job of assessing the temporal and spatial toxicity for their outfalls (n = 136 of the total 350 toxicity tests only 40% on outfalls vs 60% on bay waters). However, clearly toxicity is demonstrated that the various outfalls as taken from Appendix B of the report (see Table 1). I would consider the test results with less than 10% survival or development to be highly toxic samples. Taken from the conclusion of the report, “The 90% survival requirement in the NPDES permit failed in 58% of first flush samples.” Please verify the number 58% (see comment above regarding page 105). Clearly this statement demonstrates that the Navy must be addressing toxicity in first flush samples discharges to the Bay. Partial TIEs were conducted and identified copper and zinc as outfall toxicants. The Navy needs to further verify that these are the sole toxicants in these outfalls as this was not clearly demonstrated. The Navy needs to conduct a Toxicity Reduction Evaluation (TRE) to identify the sources and remove those metal sources from these outfalls. In addition, the Navy must conduct additional Phase II and III TIEs (and possible TRE) with additional toxic samples to determine if surfactants and additional toxicant(s) are causing toxicity to topsmelt and mysid test species.</p>	<p>We appreciate the reviewer’s acknowledgment of the effort put forward.</p> <p>The Navy agrees that organisms exposed to 100% storm water for 48 or 96 hours may show a toxic response. However, the study clearly shows that receiving water organisms are not exposed to 100% storm water for even a fraction of that time. This fact was demonstrated by the 200+ observations that there was (except in two cases) no toxicity found in receiving waters. This issue is also partially affected by the use of a 90% survival cutoff that declares a sample as toxic when it is not, using normal toxicity reporting methods.</p> <p>The principal CoCs identified by the TIEs were copper and zinc. The Navy uses a continuous and iterative process of BMP implementation, storm water analysis, CoCs source identification, and BMP enhancements to improve storm water discharge quality.</p>
<p>The report needs to be revised based on the peer review comments. A response to comment document which addresses the peer review comments needs to be prepared along with the revised final report. In addition, I suggest a technical editor review the document for consistency purposes. For example, many tables do not include the number of tests there were used to conduct the analyses (Table 12, 20, 27, 34, 41). All tables need clear headings and proper notation of the information within the table (e.g., what is the meaning of it - within Tables in Appendix B?). The paper titled “Evaluating Stormwater Impacts - Monitoring the Receiving Environment Using a Floating Bioassay Laboratory System” has this been submitted to a peer-reviewed journal? If so how will the peer review comments on this report be reconciled prior to submitting for journal publication?</p>	<p>This peer review, along with others, was added as an appendix. The report was edited for technical and editorial content.</p> <p>The paper cited was published in conference proceedings as indicated in the text. It is currently being modified for submission to a peer review journal. Because of deadlines for generating the report and delivering it to the SDRWQCB, peer reviews for this paper will not be available.</p>

DENTON STUDY COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>The data as prepared and documented in this report does not provide a rationale for an alternative approach to determine a valid survival rate for acute exposure to discharges of stormwater from industrial areas at Naval Base Point Loma Complex.</p>	<p>The data produced in this study provide a basis for an alternative toxicity requirement that is both scientifically defensible and protective of San Diego bay waters. The comment suggests that if the report were prepared and documented differently that it may support an alternative approach. The draft report was modified with additional text, tables, and graphics to respond to comments generated by this and other reviewers to better document and support a rationale for an alternative requirement. The final report, not the draft report should be evaluated when making a determination.</p>

DENTON ALTERNATIVES COMMENTS:	RESPONSE TO COMMENTS:
<p>Lastly, I will not be providing comments on “Navy's proposed alternative toxicity requirements for industrial storm water discharges report” as it is inappropriate based on nature of the document and my regulatory position. I would assume that the other peer reviewers should be excusing themselves because of the regulatory implications. This particular document needs to be reviewed and discussed with the San Diego Regional Water Quality Control Board. As you are aware, the draft final report did not include appendices A – H for our review. However, after a phone call, I did receive electronic versions of these appendices. Therefore, I question whether the other reviewers received and reviewed these appendices?</p>	<p>The document along with appendices will be provided to the San Diego Regional Water Quality Control Board. We regret the oversight that some reviewers did not receive appendices. Reviewers that did not receive them were contacted and offered electronic copies.</p>

# **DENTON TABLE 1 IDENTIFIED IN COMMENTS**

Table 1: Summary table of toxicity test results at the Navy outfalls.

Outfall	Test species	Tests with 0 - <10 % survival or developm ent <sup>a</sup>	Tests with < 70% survival or developm ent <sup>b</sup>	Tests with < 90% survival or developm ent <sup>c</sup>
<b>NAV</b>	<b>Topsmelt</b>	<b>2/13; 16%</b>	<b>4/13; 31%</b>	<b>6/13; 46%</b>
	<b>Mysid</b>	<b>2/13; 16%</b>	<b>5/13; 38%</b>	<b>6/13; 46%</b>
	<b>mussel</b>	<b>4/13; 31%</b>	<b>9/12; 70%</b>	<b>9/13; 70%</b>
<b>SUB</b>	<b>Topsmelt</b>	<b>0/10; 0%</b>	<b>0/13; 0%</b>	<b>4/10; 40%</b>
	<b>Mysid</b>	<b>0/10; 0%</b>	<b>1/10; 10%</b>	<b>7/10; 70%</b>
	<b>Mussel</b>	<b>9/9; 100%</b>	<b>9/9; 100%</b>	<b>9/9; 100%</b>
<b>NAB</b>	<b>Topsmelt</b>	<b>1/8; 13%</b>	<b>2/8; 25%</b>	<b>3/8; 38%</b>
	<b>Mysid</b>	<b>1/4; 25%</b>	<b>1/4; 25%</b>	<b>2/4; 50%</b>
	<b>Mussel</b>	<b>4/4; 25%</b>	<b>4/4; 100%</b>	<b>4/4; 100%</b>
<b>NI</b>	<b>Topsmelt</b>	<b>0/7; 0%</b>	<b>0/7; 0%</b>	<b>2/7; 29%</b>
	<b>Mysid</b>	<b>0/4; 0%</b>	<b>2/4; 50%</b>	<b>2/4; 50%</b>
	<b>mussel</b>	<b>3/4; 75%</b>	<b>3/4; 75%</b>	<b>3/4; 75%</b>

a = number of tests that had < 10% survival or larval development/total number of samples (i.e., considered highly toxic samples)

b = number of tests that had <70% survival or larval development in the 100%/total number of samples.

c = number of tests that had <90% survival or larval development in the 100%/total number of samples.

Note: no TIE test results were included in these numbers.

## **DENTON REFERENCES IDENTIFIED IN COMMENTS**

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U.S. Environmental Protection Agency. 1995. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine Organisms. Eds: Chapman GA, Denton DL, Lazorchak JM. EPA/600/R-95-136. Office of Research and Development. Cincinnati, OH.

U.S. Environmental Protection Agency. 1996. Marine Toxicity Identification Evaluation (TIE): Phase I Guidance Document. Eds: Burgess R, Ho K, Morrison G, Chapman GA and Denton DL. EPA/600/R-95/054. Environmental Effects Research Laboratory, Narragansett, RI.

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U.S. Environmental Protection Agency. 2002a. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. 4<sup>th</sup> Edition. EPA/821-R-02-013. Office of Water.

U.S. Environmental Protection Agency. 2002b. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. 5<sup>th</sup> Edition. EPA/821-R-02-012. Office of Water.

U.S. Environmental Protection Agency. 2002c. National Recommended Water Quality Criteria: 2002. US EPA Office of Water and Science and Technology. EPA-822-R-02-047.

U.S. Environmental Protection Agency. 2005. Aquatic Life Ambient Water Quality Criteria for Diazinon. EPA-822-R-05-006.



## Ms. Eileen Maher, Port of San Diego

MAHER STUDY COMMENTS:	RESPONSE TO COMMENTS:
<p>1. Early in the report, the abbreviations for each respective naval base were identified (NAV, SUB, NAB, NI) and used. The latter sections of the report (Results, Discussion and Conclusions) do not follow this naming structure. It is recommended that the entire report be consistent when naming the respective areas.</p>	<p>We have checked that acronym use for each base to ensure that is consistent throughout the document.</p>
<p>2. It does not appear that surfactants were measured in the general chemistry constituents, yet they have been identified through the TIEs (P61, 76, 90) as potentially being a cause, or partial cause of toxicity. Is there any way to find out the levels of surfactants at these sites? Furthermore, if the chemistry data for surfactants does not exist, how can the TIE results be validated?</p>	<p>Early data collection did not suggest surfactants as CoCs and they came to light as contributory toxic agents the last year of the project (January 2005). The lack of toxic response in bay waters after storm events reflects that these compounds are below levels that cause a toxic response in the bay. The benefit of performing toxicity tests is not all contaminants need to be measured to identify a potential problem.</p> <p>Nonylphenol was identified as a partial cause of toxicity in one sample in the last year of the project. It was identified as a probable cause of toxicity in the TIE based on previous observations of toxic levels by the toxicity laboratory. However, saltwater aquatic life criteria just became available (EPA, February 2006). The acute criterion is 7.0 ug/L. The estimated concentration of nonylphenol in the TIE first-flush sample was 0.18 ug/L. These latest EPA criteria will be included in the report text.</p>
<p>3. The conclusions section needs to be greatly expanded. It is recommended that the conclusions restate the goals and provide brief findings on how each goal was met or addressed and, more importantly, what final outcome was.</p>	<p>We will take these comments under advisement.</p>
<p>4. The recommendations for the proposed two alternative toxicity requirements seem fair and reasonable.</p>	<p>No comment necessary.</p>

<b>MAHER STUDY COMMENTS (cont.):</b>	<b>RESPONSE TO COMMENTS:</b>
<p>5. Exec Summ, p2, 2<sup>nd</sup> to last paragraph: The plume discussion does not identify that there are any differences in mixing or dispersion as the sites progress further back into the bay. The general understanding is that residence time of water (and possibly pollutants) in the bay and respective dilution/flushing takes longer as you get further into the bay, however this study does not indicate this. It seems likely that some slight differences in mixing times should be observed in the plume measurements because of the longer residence time. Should there be some mention of why this is/is not found during this study? If so, the text in the Exec Summary, as well as the Discussion, and Conclusion sections should address this.</p>	<p>Localized mixing of storm water plumes with the receiving water is driven by local conditions and not residence time of bay waters.</p>
<p>6. Methods, p9, 2<sup>nd</sup> paragraph: It is mentioned that several drains discharge into Chollas and Paleta Creeks before going into the bay. However, it does not appear that any of those drains were sampled. It is recommended that if drains leading to these creeks are not sampled as part of this project, that it be clearly stated. Otherwise it leads the reader to infer that they may be a part of the study area, especially given the TMDL concerns at those creeks.</p>	<p>The text was adjusted to remove this confusion.</p>
<p>7. Storm Design Criteria, p22: How does this study's design storm criteria differ from what triggers an acceptable storm for the Permit? If it differs, some wording should be added to identify the differences. Also, it may be appropriate to justify why using a storm design criteria that is different than the Permit, still provides data that can be used to develop adequate alternative standards.</p>	<p>The permits only specify that samples be collected during scheduled facility operating hours during the first hour of discharge when preceded by at least three working days without storm water discharge. As such, our design storm only differed in that we planned for sample collection 24hrs/7days per week. The minimum rainfall we imposed was used to ensure we could obtain sufficient sample. Permit language on the requirement was added to the text.</p>

MAHER STUDY COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>8. In the metals chemistry tables (Results section), the qualifier states that the “grayed out cells are values at the MDL”. Earlier in the section (p38), it states that non-detect results are reported as half the MDL value. Additionally, in Methods (p35, tbl 6) metals MDL values are identified. However, the gray shaded values in Tables 14, 15, 22, 29, 36 do not appear to follow the MDL reporting criteria identified on pg 35 or 38. Please clarify and modify if needed.</p>	<p>Table data reported as non-detect are shown as MDL values. The text was corrected to reflect this. A sentence was added to each appropriate section on organics that summations were made using ½ the MDL when there was a non-detect values.</p>
<p>9. Metals results (p 48, 66, 80, 94): The results for each of the sites show metals, namely copper and zinc, being compared to Permit performance goals (63.6 and 117ug/L). Are there other constituents identified in the Permit as having performance goals? It is recommended that a table be added to the methods sections identifying the benchmarks, chronic wq standards, water quality objectives, etc that each constituents will be compared to later in the report.</p>	<p>No other constituents have a performance goal in the permit. A section and table were added to the methods describing these chemical data benchmarks and comparisons.</p>
<p>10. TIE, p60: The text in this section mentions the 3 outfalls at Naval Station. I believe the site should be the Sub Base. Please review the section to see if 1) the text should be moved to appropriate part of the Naval Station’s results, or 2) the site was misnamed. This comment provides additional support for using a consistent naming scheme (see Gen Comment 1 above).</p>	<p>The site was misnamed and corrected in the text as Submarine Base.</p>
<p>11. Discussion, Toxicity Eval, p105: It is not clear if mussel larval development tests are required and/or used for the NPDES Permit.</p>	<p>Mussel larval development tests are not required under the permit. The text was altered to reduce confusion.</p>
<p>12. Conclusions, final paragraph, p122: While, I agree with the general assumption that the stormwater runoff is not causing receiving water toxicity, the text as written is very strong and appears too controversial. It is recommended that the language either be expanded or toned down to get the point across without offending those parties of whom you are hoping to gain buy-in for alternative standards.</p>	<p>We understand the nature of this comment and will take this under advisement in finalizing the text in the final report.</p>

MAHER ALTERNATIVES COMMENTS:	RESPONSE TO COMMENTS:
4. The recommendations for the proposed two alternative toxicity requirements seem fair and reasonable.	No comment necessary.

SCHIFF COMMENTS:	RESPONSE TO COMMENTS:
<p><b>1. Quality of Work</b></p> <p>First off, this document contains a lot of work; 11 storms, 136 samples, 350 tox tests. The authors are to be commended for just the sheer volume of effort applied to this study. I can only judge the quality of the work based on the summaries provided in the body of the text. The raw data were contained in the appendices that were not included with the document and, therefore, I cannot judge the quality at the raw data level. However, based on the textual summaries the data appear sound and of good quality. Negative and positive controls generally performed well. MSD calculations indicated that replicate variability, on average, was not extreme. In my reading of the document, no glaring discrepancies were discussed that should cause me to dismiss the work based on poor quality. However, greater quantification of deviations (i.e. pg 38, 1<sup>st</sup> Para) may be appropriate. Similarly, portions of the testing were conducted at another facility (Nautilus Environmental) and an intercalibration, or at least a comparison of reference toxicant responses, would seem appropriate. Similarly, chemical analysis deviations are described and qualified, but not well quantified. For example, an indication of holding times exceedence was described and flagged in the database, but no mention of the holding time exceedence magnitude (i.e. 1 day or 100 days?). Chemistry problems such as those described in the report are common in studies of this magnitude and are to be expected, but descriptions of their magnitude are important to ensure that they are not at a level of concern.</p>	<p>Text was added to better quantify the QA/QC items identified. There was no formal intercalibration between laboratories. A comparison of reference toxicant data was made and included in the text. The MSD data plots and discussion described in the discussion section do provide one type of comparison of the data generated from the two labs.</p>

SCHIFF COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>Ability to Answer Study Questions</p> <ol style="list-style-type: none"> <li>1. Evaluate the magnitude of industrial storm water toxicity from Navy facilities</li> </ol> <p>The study appeared capable of answering this question at the sampled sites. There is a constant struggle between a wet weather sampling design that favors more sites for fewer storms or fewer sites for more storms. While no specific facts are given to support their claim, the authors state that the sites selected are representative of all Navy facilities. With this caveat, the range of storm sizes and intensities fits well within the scale of meteorological extremes for this region. My suggestion to follow up on this thought, since the range of conditions is assumed to have been characteristically sampled, would be to conduct some power analysis to determine an optimum sample size for determining the mean, median or extremes in water quality or toxicity. This will also provide context for estimating the confidence bounds derived from this study when describing Navy water quality.</p>	<p>The reviewer clarified the comment on “power analysis” by phone. The suggestion was that Navy consider the numbers and type of data needed when moving forward rather than a calculation necessarily needed in the report.</p>

SCHIFF COMMENTS (cont):	RESPONSE TO COMMENTS:
<p>2. Evaluate causes of toxicity</p> <p>This question was only partially answered. The causes of toxicity were evaluated in three fashions: 1) toxicity identification evaluation manipulations (TIEs), 2) correlations between toxic responses and chemical concentrations; and 3) comparison of estimated toxicity and measured toxicity for presumed contaminants. This method of evaluation is well founded in the literature and entirely appropriate. The specific details of the implementation are difficult to evaluate however. For example, all of the TIE data are in an appendix, which I did not have, while only summaries are provided in the report.</p> <p>Based on the summaries, certain treatments consistently removed toxicity. The EDTA treatment was particularly effective. Therefore, the assumption regarding trace metals is appropriate and, based upon the chemistry data at these sites, trace metals are likely toxicants. Some discrepancies do occur. For example, NAV suffered from a consistent loss of toxicity between initial tests and TIE baseline testing, indicating that some other potential toxicants may have existed. The confounding issue of copper and zinc removal by the C18 column has been experienced in our lab. In later experiments, the laboratory uses C18 column elutions to confirm the presence/lack of toxicity, which is an appropriate step. In general, my recommendation to the authors is to expand the TIE results text a bit to provide more quantitative evaluations so the reader does not have to take the conclusions on faith (i.e. pg 43).</p> <p>One factor that prohibits me from completely buying into the fact that metals are the only or primary toxicants is the poor predictive relationships between toxic effect in both the mussel and mysid and the predicted toxic units based on copper + zinc. To overcome this obstacle, the authors may want to try predicting toxicity from chemistry using non-linear models. Alternatively, the use of other predictive tools such as the Biotic Ligand Model may work well. At a minimum, the authors should investigate and report on the quantitative relationships between dissolved trace metal concentrations and potential binding agents (i.e. hardness, DOC, etc.).</p>	<p>The appendices with the full report from the contractor will also be included in the final report (we regret the omission of these reports during the review process).</p> <p>We agree the dose-response curves were quite variable and are not definitive for a causal relationship of toxicity to metals. Non-linear models were attempted with similar outcome. Toxicity and chemistry correlations with DOC and other parameters were evaluated with no better outcome. Text was added that describes some of the evaluations performed.</p>

SCHIFF COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p><b>Additional data analysis</b></p> <p>The strong suit of this study is the sheer volume of data generated and it is in my opinion that the authors have not analyzed the data set completely. Either within this document, or as part of another document, the authors should start exploring a number of analyses well suited to this data set. Here are just a few examples: 1) effect of storm characteristics (i.e. storm size, intensity, timing within season, cumulative rainfall, etc.) on water quality or toxicity; 2) relationship of water quality to catchment activities (clearly some sites are worse than other (i.e. NAB); 3) comparison to other industrial activities (RWQCB 4 has a compilation of tox and WQ from all industrial SIC codes in their region) to see if Navy bases are better than or worse than other industrial types.</p>	<p>We appreciate the reviewer's acknowledgment of the effort put forward. The study design does not support a statistical evaluation of individual storm characteristics. However, the study clearly shows that receiving water quality and toxicity were affected after an exceptionally long dry period. The Navy is investigating ways to mitigate this worst-case potential for effects.</p> <p>The Navy has an active program that is continuously implementing and improving BMPs for industrial drainage areas within their SWPPP (iterative approach). Results of the study along with results of standard storm water monitoring have identified locations that are prioritized for additional efforts.</p> <p>While a comparison of the magnitude of toxicity and chemistry measured in other industrial discharges is interesting, mass loading and the potential for impacts to bay waters is dependent on relative discharge volumes. These evaluations are part of ongoing Bay TMDL investigations and should be made on a watershed approach.</p>





**Dr. Robert Spies, Applied Marine Sciences, Livermore, CA**

<b>SPIES MAJOR COMMENTS:</b>	<b>RESPONSE TO COMMENTS:</b>
<p>1. Applicability of the approach</p> <p>a. The sampling scheme appears to capture and be representative of the range of water quality in runoff samples. The sampling was extensive enough that it is not likely to have missed many important sources of runoff from naval facilities to San Diego Bay. The inclusion of first-flush samples was important as these are well established now as the most toxic component of runoff, especially in a climate with long periods without precipitation. There are some questions raised under minor comments (below) as to why some of the larger discharges at some sites were bypassed in the selection process for drains that did not recruit from very large areas.</p>	<p>No comment necessary.</p>
<p>b. The chemical analyses appeared to be carried out according to best practices of environmental chemistry. However, there are several aspects that deserve comment.</p>	<p>No comment necessary.</p>
<p>First, there were no field blanks taken and analyzed, which are an important quality assurance precaution, especially when collecting water samples for determining concentrations of dissolved trace substances in an industrial settings.</p>	<p>Field blanks were taken for metals but text identifying that fact was left out of Table 10. Text was added to Table 10 to indicate that field blanks were included as part of the QA/QC.</p>
<p>Second, since trace organic substances are a concern for the NAVY (e.g., PCBs and PAH) why were larger water samples not taken to avoid the large proportion of non-detects?</p>	<p>The laboratory and methods used provide the best detection limits for aqueous organic compounds available anywhere in the country. The volume of storm water sample needed for all analyses was a difficult logistical requirement. Increasing the sample volume by more than a factor of two would have been very difficult to meet logistically and would have been cost prohibitive.</p>

<b>SPIES MAJOR COMMENTS (cont.):</b>	<b>RESPONSE TO COMMENTS:</b>
<p>Third, only total tin (Sn) was measured, which was rather surprising considering the very high toxicity of the alkylated tins and the fact that the US Navy is the largest user of these anti-fouling compounds. Alkylated tin toxicity has a chronic component, as these compounds are known endocrine disrupters. For example they cause the development of male sex organs in female gastropod mollusks.</p>	<p>The Navy does not use alkylated tins for anti-fouling coatings.</p>
<p>Fourth, while it is impractical to measure every possible chemical, the attribution of toxicity in some TIE analyses to nonylphenol suggests that this surfactant may be an important contaminant originating from some of the Navy bases. Nonylphenol is both lethal in some conditions and an endocrine disrupting compound in some organisms (e.g., fish).</p>	<p>Nonylphenol was identified as a partial cause of toxicity in one sample in the last year of the project. It was identified as a probable cause of toxicity in the TIE based on previous observations of toxic levels by the toxicity laboratory. However, saltwater aquatic life criteria just became available (EPA, February 2006). The acute criterion is 7.0 ug/L. The estimated concentration of nonylphenol in the TIE first-flush sample was 0.18 ug/L. These latest EPA criteria will be included in the report text.</p>

SPIES MAJOR COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>c. The toxicity tests carried out for this study on effluent and on bay waters were 96 hours long and were only capable of measuring short-term, and, for two of the three tests, acute toxicity. Longer-term effects that are expressed after 96 hours are not captured by these tests. The mussel embryo deformity test is not on the RWQCB list of assays, but was carried out on many samples. This test measures acute effects (occurring in 96 hours) but could be considered to measure sublethal effects since some of the deformed larvae are alive at the end of the test. It is probably predictive of longer-term toxicity for at least mussels. The requirements that the test organisms survive the whole undiluted effluent at high rates for storm water discharges provide some assurance against longer-term effects (expressed after 96 hours) and against sublethal effects. The largest criticism that I have of this report is that it appears to undermine this strategy by suggesting that dilution of the whole effluent after it enters San Diego Bay so that it is no longer acutely toxic is sufficient by implication to protect marine life in San Diego Bay. There is not sufficient data in this report about the fate and effects of discharged contaminants originating from Navy facilities to show that there is no harm to Bay life. Having Bay waters pass acute toxicity tests is not a sufficient basis for establishing a lack of harm. For example, contaminants that are not acutely toxic in storm runoff can accumulate in sediments to levels that affect benthic organisms.</p>	<p>For clarification purposes to the comment, the mussel test uses a 48-h, not 96-h exposure. We agree that the mussel embryo development test can be considered a sublethal effect that is predictive of longer-term toxicity. The test was chosen because mussels are endemic to San Diego Bay and it is one of the most sensitive toxicity tests to metals, the reason it was used to set EPA's aquatic life copper criterion for marine waters. As such, the test is one of the most sensitive toxicity endpoints available to evaluate either acute or chronic toxicity in marine waters.</p> <p>We understand the criticism and realize we may have not focused the report findings sufficiently on the major goal of evaluating the efficacy of using WET testing in "assessing and protecting against impacts upon water quality and designated uses caused by the aggregate toxic effects of the discharge of pollutants" (EPA, 1991). The study showed that the toxicity threshold used at the end-of-pipe was not predictive of a toxicological impact in receiving waters. This is because WET testing usually takes into account the exposure concentration after an effluent mixes with the receiving environment. It is also because toxicity testing is subject to method variability and the current 90% threshold has no power to detect a true toxic result. By using one of the most sensitive toxicity tests available, acute or chronic, for measuring receiving water toxicity; by evaluating contaminants against chronic aquatic life criteria; and by quantifying the duration and extent of storm plumes, the report can conclude that receiving water quality was protected against impacts in 99% of all cases, regardless of what the end-of-pipe WET test indicated. The study cannot conclude that there is no potential for impacts to sediments, though meeting the current permit requirement also does not guarantee this. These types of impacts are best evaluated under current TMDL and Baywide monitoring programs.</p>

SPIES MAJOR COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>d. Toxicity identification evaluations (TIEs) are useful in helping to identify causative agents for toxicity in standard bioassays. However, these tests are only guides and they do carry their own set of problems that must be kept in mind. For example, stage 2 testing is usually carried out 5 days after collection of the original bioassay water sample. The samples obviously cannot be acidified to preserve their chemical properties at the time of collection as one would for chemical analysis. So, the water samples can be altered chemically in this 5-day period. Heavy metals can bind to the sides of the container, eliminating this source of toxicity. Other processes such as volatilization, biodegradation of organic compounds, or possibly photo-oxidation can occur depending on sample storage conditions. In addition, TIEs are a reductionist approach and cannot account for the interactive effects of contaminants.</p>	<p>We agree with and understand the limitations of TIEs. However, there are no other standardized methods available for identifying potential causative agents. The Tier III copper and zinc tests performed on some samples were able to evaluate their interactions though this portion of the TIE was a special effort.</p>
<p>2. General considerations for protecting marine life in San Diego Bay. Chronic effects on bay organisms. It appears that some engineering solutions will be required to meet the current standards of the RWQCB. I do not think that the current discharges can be established as safe without much more detailed study of long-term effects. If the Navy wishes to go beyond the legal requirements for obtaining a permit and acquire a deeper understanding of the possible contributions its operations make to San Diego Bay then longer term testing would be in order and more studies of the relationships between the impairment of marine life and the particular suite of contaminants that are discharged from its San Diego facilities. Such studies might include the possible combined effects of copper, zinc, alkylated tins, polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs) at ambient Bay concentrations on growth, reproduction and fitness over the life cycle of key native organisms. Particularly useful would be participation in a Bay-wide study of contaminant effects and mass balance budgets of key contaminants. This of course should involve as well other sponsors that contribute to contamination of San Diego Bay.</p>	<p>The Navy agrees that if the current toxicity standard stands that the only alternative is an engineering solution that is estimated to cost over \$300M.</p> <p>The focus of this study was to evaluate the potential for toxicity occurring in receiving waters as a result of storm water discharges. The best way to evaluate long-term impacts to sediments is within current TMDL programs that are used to evaluate the magnitude and extent of impaired sediments using a weight-of-evidence approach and identify sources of the impairment. These programs are currently underway at several locations in San Diego Bay including at Navy facilities. Additional programs that can provide a better evaluation of long-term impacts to sediments include the Bay Protection and Toxic Cleanup Program, the Bight'98 program organized by the Southern California Coastal Water Research Program, and the Port of San Diego/Regional Water Quality Control Board Baywide Monitoring program.</p>

SPIES MAJOR COMMENTS (cont.):	RESPONSE TO COMMENTS:
<p>a. The role of the surface microlayer in ambient toxicity. In urban bays the very top layer of the water often has a microlayer that is about 75-100 micrometers thick. This layer is very important as it contains concentrations of most contaminants that may be several orders of magnitude higher than in the underlying water. In addition, it is subject to intense sunlight which photo-oxidizes some compounds (e.g., PAH) to much more toxic forms. Marine animals that spend anytime in this layer as adults, or in the larval or egg stages (some fish), will be subject to much greater toxicity than they otherwise might experience in water from beneath the surface. The microlayers persist under surprisingly energetic conditions and only break up in rather rough seas. I have little doubt that the microlayer plays a role in toxicity of contaminants in San Diego Bay in ways that were not anticipated in the design of the present study. It is quite likely that contaminants entering the Bay as storm water expose surface-dwelling organisms at higher concentrations than they experienced in toxicity tests carried out in this study with ambient sub-surface water. I would recommend that any future studies take the potential sequestration of storm water contaminants in the microlayer and their toxicity into account.</p>	<p>The study of the microlayer is a highly specialized area of research that has shown the potential for elevated concentrations of certain contaminants at levels above those found in the underlying water. The Navy study also did not specifically evaluate the potential for PAH photoactivation.</p> <p>Though the study did not evaluate this unique portion of the receiving water habitat, it did capture the exposure and toxic responses of the bulk surface water. An end-of-pipe measurement of toxicity is not likely to better predict toxicity that might occur in the microlayer.</p> <p>Techniques and studies to evaluate toxicity to microlayer organisms are in still in their infancy and would be highly impractical to implement at this time.</p>
<p>b. Was SDB4 an unusual circumstance? San Diego has a climate in which there are long dry periods in many years, so a 180-d period without rain before this particular event is probably not that unusual.</p>	<p>As stated in the report, the 182 day dry period was the longest dry period ever recorded (156 yr). Though dry periods can be relatively long in San Diego, 85% of dry periods were less than 127 days (National Weather Service, personal communication).</p>

SPIES MINOR COMMENTS:	RESPONSE TO COMMENTS:
1. p. 17. Why weren't some of the largest drains of NAB (15, 17. 41) sampled? The drains that were measured appear to be rather minor ones.	As stated in the text, the choice of drains was based on several criteria including the presence or absence of industrial activities, logistical constraints and safe access during all hours. The reference to "minor" would only relate to size and not potential for impact. The data show that some of the smaller sites had similar contaminant levels and impacts as larger drainages.
2. p. 23. Where are results of the contaminant mass loading calculations mentioned here?	Mass loading data were not included in the report as they were not required to evaluate the efficacy of the toxicity requirement.
3. pp. 26-27. The RV ECOS-MESC system for real time chemical analyses and flow-through bioassays is innovative. Was there a comparison made between the outcome of split samples run in this system and those run under the usual conditions?	No comparisons were made during this effort. However, previous bay surveys have validated these techniques (Katz, 1998; Blake et al., 2004).
4. p. 33. Water samples could have been adjusted in volume or filtered part way through the study to provide greater detection limits for some analytes.	MDLs from our contract lab were as low or lower than any available from any lab in the country. Filtering samples for organics analysis is not recommended because of potential losses onto the filter during filtration
5. p. 39. Were mass flows reported in the Appendix?	No.
6. p. 43. The TIE exercise here and elsewhere was done for a small storm event and is probably not representative of a larger storm event.	The key component for performing TIEs is that the samples show a toxic response, not the size of the event.
7. p. 48. Hull coatings are apparently leaching copper into the Bay. What about alkylated tins?	The Navy does not use alkylated tins for hull coatings.
8. p. 51. Recheck latest literature on PAH chronic toxicity levels. In some cases concentrations of PAH in the low parts per billion have been chronically toxic to developing fish (e.g., Heintz et al., 2000; Carls et al., 1999).	We have rechecked the literature that was reviewed as a part of the study and found an additional comprehensive review article by Scannell et al., 2005 that expands our database and cites the two papers identified in the comment. None of the receiving water samples contained PAHs above a chronic toxic effect level, including effects with photoactivation under UV light. The text in the report was modified to account for the additional database information.

SPIES MINOR COMMENTS (cont.):	RESPONSE TO COMMENTS:
9. p. 32. Because of naphthalene contamination in Battelle's laboratory blanks, the elevated naphthalenes in Fig. 21 may be artifacts.	Procedural blanks were run with each batch of samples. Methylated naphthalene values in these blanks were typically between the MDL and the reporting limit though one blank analysis showed an elevated MDL of 16 ng/L. The methylated naphthalene data shown in Figure 21 were well above values found in the associated blanks and not a result of high blanks.
10. p. 55. Chronic WQOs are exceeded for DDT in these samples. Why were chronic WQOs not dealt with in more detail when considering the effects of the effluents in San Diego Bay?	The appropriate way to evaluate short-lived episodic discharge such as storm water is to compare levels against acute WQS. Results in receiving water samples, when available were compared to chronic WQS.
11. p. 78. Nonylphenol is implicated in the toxicity of NAB runoff but is not analyzed chemically in other samples on a routine basis.	MBAS, not nonylphenol was identified as a partial cause of toxicity in these samples.
12. p. 79-81. Copper and zinc exceeded chronic WQOs in Bay water after SDB4 and apparently were in the dissolved phase. This is at odds with your overall conclusion that these compounds are quickly diluted or chemically complexed to harmless levels in the Bay.	The overall conclusions of the study are based on the observation that 99% of bay water samples showed no toxicity and with some exceptions for copper and two for zinc, no elevation above chronic water quality standards of any contaminant. The study showed two instances of toxic effects. Discharges at these levels are not acceptable and should be targeted for additional BMPs. The proposed toxicity alternatives would identify these samples as a permit exceedance.
13. pp. 88-89. Another case of the apparent toxic effects of surfactants.	No comment necessary.
14. p. 97. 6484 ng/L is enough PAH to be of concern for chronic toxicity to some fish.	The value identified in the comment was for storm water discharges which should be compared to acute rather than chronic WQS. No receiving water sample exceeded a chronic toxic threshold identified in the literature.
15. p. 105. Combining top smelt and larval fish bioassay results is not well justified and I would question this.	We believe the comment should read: "combining topsmelt and mysid data is not well justified". The tests were combined mainly for the purposes of evaluating the percentage of tests failing or passing the toxicity thresholds. Because both tests can be used to meet the requirement, their results are in essence, interchangeable and can reasonably be combined for this purpose.



SPIES CONCLUSIONS:	RESPONSE TO COMMENTS:
<p>This is a very extensive study and was competently carried out by the Navy and its contractors. It sets a new standard for storm water runoff studies. As in all studies there are some aspects that should be done differently if the study is to be repeated. Some important contaminants were not analyzed (tin chemical species, i.e., alkylated tins, and surfactants). Fifty-eight percent of the first flush samples failed the 90% survival criteria for whole effluent and copper and zinc are strongly implicated as serious problems in the runoff with other compounds possibly also contributing. While acute toxicity generally quickly dissipates with the mixing of the effluent in the Bay, this is not always the case. Chronic effects of the effluent in the Bay are not considered or addressed in any meaningful way. This reviewer does therefore not accept the conclusion that “The Bay is able to rapidly assimilate storm water discharges and effectively attenuate potential impacts, thus meeting the Clean Water Act narrative of ‘no toxics in toxic amounts’ (33 U.S.C. 125).” Attenuation of acute toxicity does not assure lack of chronic toxicity.</p>	<p>We appreciate that the reviewer acknowledged the magnitude of the effort conducted. We agree that every study could be improved or modified, particularly after the fact, when all the results become available. However, we believe that the main criticism that “chronic effects...are not considered...in any meaningful way” disregards the bulk of the findings that show there is no chronic exposure present in bay waters.</p> <p>The study showed in every instance that the magnitude of storm water plumes were very short lived, lasting typically less than 24 hours. The plume measurements also showed that their magnitude was negligible away from the immediate shoreline source. The special bioassay study showed that peak exposures are on the order of minutes before falling off to background levels. The chemical data suggest that there were only limited instances when concentrations of contaminants exceeded an aquatic life chronic toxicity threshold. These measures that show a lack of potential for chronic toxicity are supported by the fact that 99% of all receiving water toxicity tests, using one of the most sensitive endpoints available, acute or chronic, showed no toxicity. The goal was not show that there could never be chronic toxicity, but rather, to identify the appropriate test that can be used to determine when that occurs.</p>

## COMMENTS ON ALTERNATIVE TOXICITY REQUIREMENT

SPIES ALTERNATIVES COMMENTS:	RESPONSE TO COMMENTS:
<p>This draft set of more lenient criteria than those in force under Permits CA 0109163, CA 0109169 and CA0109185 are proposed based on the assumption that dilution of storm water in San Diego Bay with a corresponding reduction of acute toxicity in 96-h assays is protective of marine life in San Diego Bay. The changes in the criteria would allow testing to be carried out on diluted Bay water close to the effluent discharges and the testing to be of 48 h duration rather than 96 h.</p> <p>I am unable to support this change in the criteria as protection of marine life in San Diego Bay means protection from chronic effects of discharged contaminants as well. In the report which I reviewed there were no studies of long-term effects of discharged contaminants. However, this report did include data on discharge of nonylphenols and tin, and since nonylphenol and some chemical forms of tin are known endocrine disruptors in marine organisms, these specific sources and others with the potential for long-term toxicity to marine life in San Diego have not been investigated.</p> <p>In the storm water toxicity studies carried out by the Navy under these permits 58% of the first flush samples failed the 90% survival criteria for whole effluent. This reviewer does therefore not accept the conclusion that “The Bay is able to rapidly assimilate storm water discharges and effectively attenuate potential impacts, thus meeting the Clean Water Act narrative of ‘no toxics in toxic amounts’ (33 U.S.C. 125).” Attenuation of acute toxicity does not assure lack of chronic toxicity. The high threshold of effects imposed for storm water discharge in California are to compensate for less vigorous mixing in the inshore marine environment that allow point dischargers in offshore environments to use mixing zones and effluent dilution in their toxicity testing criteria. These high criteria for inshore discharges in water bodies with restricted circulation such as San Diego Bay also compensate to some degree for the lack of data on long-term chronic effects that can occur from low concentrations of water-borne contaminants. Many of these contaminants accumulate in sediments and organisms to much higher concentrations than in water through partitioning and bioaccumulation. I therefore cannot support the more lenient criteria as there are not sufficient data to demonstrate lack of harm to marine life from their implementation.</p>	<p>The main thesis of Dr. Spies’ disagreement with the proposed alternatives is that the study failed to measure or account for chronic toxicity caused by low levels of chemicals that may or may not have been measured in the study. A secondary thesis is that chemicals derived from storm discharges may accumulate in sediments and/or organisms and eventually lead to impairment.</p> <p>The study results show that the current end-of-pipe toxicity requirement is not predictive of acute or chronic toxic effects in receiving waters. Of all the storm water samples identified as “toxic”, only two receiving water samples showed a toxic result. The study dataset covers the full range of conditions likely to occur, including a condition that clearly represents a chronic exposure condition to bay organisms (SDB5 collected outside 4 outfalls after 6” of rainfall over a two-week period). We know of no other EPA approved toxicity endpoint, chronic or acute, that would provide a more sensitive measure of effects, particularly to the main CoCs of copper and zinc. The magnitude and extent of storm water plumes indicates and the special floating bioassay study show that chronic exposures are not likely.</p> <p>The current permit requirement for end-of-pipe toxicity has little ability to predict acute or chronic toxicity or other impacts to sediments. We believe that an evaluation of impairment to benthic organisms is best done within sediment TMDLs that are already underway at two Navy bases. These studies evaluate the magnitude and extent of impairment using multiple lines of evidence and can be used to identify likely sources of the contaminants causing the impairment.</p>

References cited that were not included in the draft report:

Chadwick, D.b., A. Zirino, I. Rivera-Duarte, C. N. Katz, and A. C. Blake (2004). *Modeling the mass balance and fate of copper in San Diego Bay*. Limnol. Oceanogr., 49(2), 2004, 355–366.

Scannell, P.W, D.D. Duffy, R. Perkins, and T. O'Hara (2005). *Acute and chronic toxicity of hydrocarbons in marine and fresh water with an emphasis on Alaska species, A review of the literature*. Review performed for the Alaska Dept. Environmental Conservation, 610 University Avenue, Fairbanks, AK 99709/

EPA (2006). *FACT SHEET Aquatic Life Ambient Water Quality Criteria - Nonylphenol – Final*, United States Environmental Protection Agency Office of Water 4304T EPA-822-F-05-003, February 2006.





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