Sampling and Analysis Plan

Sediment Quality Verification Study and Baseline for Process Improvement for Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, WA

Draft April 19, 2011

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Water Body Numbers
WA-15-0040 Sinclair Inlet
WA-15-0050 Dyes Inlet

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ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
Ag	Silver
As	Arsenic
AVS-SEM	Acid Volatile Sulfide Simultaneously Extracted Metals
AWA	Area-weighted average
BNC	Bremerton Naval Complex
CAB	cellulose acetate butyrate
CAD	Confined Aquatic Disposal Pit
CAS	Columbia Analytical Services
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CH3D	Numerical Modeling System
COC	Chain of Custody
Cr	Chromium
CSO	Combined Sewer Overflow
Cu	Copper
CVAF	Cold Vapor Atomic Fluorescense
DGT	Diffusive Gradients in Thin films passive sampler
DMA	Direct Mercury Analyzer
DQA	Data Quality Assessments
ECD	Electron Capture Detector
Ecology	Washington Department of Ecology
EDD	Electronic Data Deliverable
ELISA	Enzyme-linked immunosorbent assay
ENVVEST	Environmental Reinvestment
EPA	Environmental Protection Agency
FAS	Focus Area Study
FC	Fecal Coliform
Fe	Iron
GC-MS	Gas Chromatography Mass Spectrometry
GPS	Global Positioning System
H_2S	Hydrogen Sulfide
Hg	Mercury
HPAH	High Molecular Weight PAHs
HSPF	Hydrological Simulation Program Fortran
HTL	Holding Time Limits
iaPAH	Screening analysis of PAHs using immunoassay
iaPBC	Screening analysis of PCBs using immunoassay
ICP-MS	Inductively-coupled Plasma-Mass Spectrometry
ICP-OS	Inductively-coupled Plasma-Optical Spectroscopy
ID	Identification
IR	Installation Restoration
LCS	Laboratory Control Sample
LPAH	Low Molecular Weight PAHs
MB	Method Blank

MCUL	Minimum Cleanup Level
MDL	Method Detection Limit
MDR	Mixed Diamine Reagent
Mn	Manganese
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSL	(Battelle) Marine Sciences Laboratory
NAD	North American Datum
NaOH	Sodium Hydroxide
NBK	Naval Base Kitsap
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollution Discharge Elimination System
NSB	Naval Station Bremerton
OUBM	Operable Unit B Marine (Bremerton Naval Complex IR Site)
PAH	Polycyclic aromatic hydrocarbons (total PAH is tPAH)
Pb	Lead
PCB	Polychlorinated biphenyls
PNNL	Pacific Northwest National Laboratory
PSEP	Puget Sound Estuary Project
PSNS & IMF	Puget Sound Naval Shipyard & Intermediate Maintenance Facility
QA/QC	Quality Assurance and Quality Control
RI/FS	Remedial Investigation/Feasibility Study
RIS	Recovery Internal Standard
RL	Reporting Limit
ROD	Record of Decision
RPD	Relative Percent Difference
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
SIS	Surrogate Internal Standard
SIZ	Sediment Impact Zone
SL1	Sediment Level 1
SMS	Sediment Management Standards
SOP	Standard Operating Procedure
SQS	Sediment Quality Standard
SRM	Standard Reference Material
SSC	Space and Naval Warfare Systems Center
SVS	OUBM Sediment Monitoring Study
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
UTM	Universal Transverse Mercator
WAC	Washington Administrative Code
WRIA	Water Resource Inventory Area
WWTP	Waste Water Treatment Plant
XRF	X-Ray Fluorescence
Zn	Zinc

Sediment Quality Verification Study and Baseline for Process Improvement for Puget Sound Naval Shipyard & Intermediate Maintenance Facility

1.0 Introduction

The Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF) and Naval Base Kitsap-Bremerton (NBK-Bremerton, herein after referred to as Shipyard for brevity) located in Bremerton, WA are committed to a culture of continuous process improvement for all aspects of Shipyard operations, including reducing the releases of hazardous materials and waste in discharges from the Shipyard. The Shipyard is located within the Sinclair and Dyes Inlet watershed of Puget Sound (Figure 1). The historic contamination in the marine sediments of Sinclair Inlet has been documented since the 1970s (Malins et al 1980, 1982, 1984). Contaminants included heavy metals, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) (URS 2002a). Sediment reconstructions spanning back to pre-industrialization suggest the maximum contaminant loading occurred around the middle of the 20th Century (noted as the subsurface peak in sediment cores) followed by marked declines as Navy processes changed, environmental regulations were enacted, and pollution abatement, control, and cleanup programs were implemented (Brandenberger et al. 2008a, Figure 2). For Sinclair Inlet in 2002, that subsurface peak was located at a depth of ~12-13 cm for heavy metals and 20-25 cm for PCBs (Figure 2). Legacy PCB and mercury (Hg) contaminated sediments are being addressed by the Navy's Installation Restoration (IR) program (URS 2002b, Paulson et al. 2010) pursuant to Section 121(c) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Oil and Hazardous Substances Pollution Contingency Plan (NCP). Operable Units within the Shipyard were defined to focus IR activities on achieving remediation goals. For Operable Unit B Marine (OUBM), which encompassed the contaminated sediments within the Shipyard and surrounding Sinclair Inlet, a remedial investigation and feasibility study was completed (URS 2002a), the Record of Decision (ROD) to remediate contaminated sediments was signed in 2000 (U.S. Navy 2000), and a long term monitoring program to track the attainment of clean up goals for OUBM was implemented in 2003 (URS 2002b).

The sediments of Sinclair and Dyes Inlets accumulate contaminants from a variety of point and non-point sources within the watershed including Shipyard operations, marina and vessel traffic, non-point source runoff, combined sewer overflows (CSOs), discharges from waste water treatment plants (WWTP), industrial effluents, atmospheric deposition, and surface streams (Brandenberger et al. 2008a). The location of industrial outfalls, stormwater drains, dry docks, and remediation dredging, navigational dredging, and the confined aquatic disposal pit created in 2001 are shown Figure 3. The industrial discharges from the Shipyard are regulated by the National Pollutant Discharge Elimination System (NPDES) permit program as authorized by the Clean Water Act. Many metal and organic contaminants released within the Inlets, as well as, those transported into the Inlets from the Puget Sound will tend to partition to the particulate phase and subsequently accumulate in depositional areas located within the Inlets including the Shipyard (Figure 4, McLaren 1997, 2008).

The improvement and recovery of sediment quality in Sinclair Inlet is actively being addressed by the Navy under the CERCLA and NPDES programs, Washington Department of Ecology

(Ecology) under the Urban Waters Initiative (Dutch et al. 2009), and the Shipyard ENVvironmental reinENVment (ENVVEST) Project. Under ENVVEST, a cooperative agreement among PSNS&IMF, U.S. Environmental Protection Agency (EPA), Ecology, and local stakeholders has been helping to improve the environmental quality of the Sinclair and Dyes Inlet Watershed and develop Total Maximum Daily Loads (TMDLs) for priority pollutants (Johnston et al. 2009, Lawrence et al. 2011).

The objective of this sediment sampling and analysis plan (SAP) is to leverage the cooperation between the various programs addressing sediment and water quality in Sinclair Inlet to characterize the current sediment quality at priority areas within the Shipyard for a suite of heavy metals, PCBs, and PAHs both at the sediment surface and at depths representative of sediment that could be redistributed to the surface. This potential redistribution of historically contaminated sediment may act as a source in addition to those listed above.

The study design is laid out to identify data gaps, characterize surface (0-10 cm depth) and deep (0-20 cm) sediments, evaluate bioavailability, assess enhanced natural recovery rates, and support research and development (R&D) studies of treatability (SSC-Pacific 2010) and bioavailability (ERDC-ERL 2010) of sediments from selected sites within the Shipyard. The various tasks to be performed are designed to partially address the following questions:

1. Are discharges from Shipyard industrial outfalls and storm drains protective of beneficial uses of Sinclair Inlet?
2. Are discharges from all sources of contamination into Sinclair and Dyes Inlets impacting the quality of water, sediment, and biota in the Inlets?
3. What is the status and trend of water, stormwater, sediment, and biota residue quality in Sinclair and Dyes Inlets?

Specific objectives of this study are to:

- Establish baseline for continuous process improvement
- Characterize silt and sediment in the vicinity of outfalls and dry docks (e.g. operational areas not included in OUBM sediment monitoring)
- Provide data to assess sediment impact zones for NPDES discharges
- Provide data to assess anti-degradation requirements for water quality certifications needed for pier and dry dock infrastructure improvements
- Support R&D studies of sediment treatability and bioavailability

1.1 Previous Studies

Previous studies have developed a wealth of environmental quality information from both a watershed-scale perspective (e.g. regional water and sediment quality within Kitsap County) and the localized Shipyard area. The two scales are necessary to provide information for the development of TMDLs and provide resource managers with a relative scale of what is achievable in this region. Enhancing cooperation between the IR and ENVVEST programs is not straight forward as each program has different objectives requiring different study designs (e.g. compositing grab samples versus individual grabs, sediment collection of 0-10 cm versus core profiles with 2.5 cm resolution, etc.). The following is a short description of each of these programs and synopsis of data available to date that was used to inform this study design.

1.1.1 ENVVEST Studies

A cooperative watershed-based approach to meet clean water objectives has been implemented through Project ENVVEST. In 2003, a review of the available sediment and water quality information for Sinclair and Dyes Inlets found the two inlets should be treated as a single water body with respect to TMDL study plans as hydrodynamic modeling confirms significant exchange of water and transport of sediment between the Inlets (Diefenderfer et al. 2003). It also found that much of the data used in the 1998 303(d) list were collected prior to significant source control (pollution prevention, hazardous waste minimization, CSO reduction, remediation, etc), sediment cleanup, dredging, and capping activities.

Project ENVVEST began addressing these data gaps with the following studies either completed or in draft final reporting phases:

1. Fecal coliform (FC) source study and model development to support a TMDL for the Sinclair/Dyes Inlet surface water system adjacent to PSNS&IMF (May et al. 2005, Johnston et al. 2009, Lawrence et al. 2011);
2. Characterization of surface and storm event runoff water quality for the Sinclair/Dyes Inlet watershed (Brandenberger et al. 2007a,b; Cullinan et al. 2007),
3. Characterized Cu, Pb, Zn and PAH concentrations in sediment through sediment verification studies in collaboration with the OUBM sediment monitoring (Kohn et al. 2004, 2006, 2008);
4. Developed a mass-balance of pollutants entering the Sinclair and Dyes Inlet system (Brandenberger et al. 2008a);
5. Assessed tissue residue concentrations in demersal fish, invertebrates, indigenous and caged mussels from Sinclair Inlet and selected areas of the Puget Sound (Johnston et al. 2007, Brandenberger et al. 2008b, Applied Biomonitoring 2009);
6. Assessed the toxicity of copper (Cu) in marine waters of the Inlets (Rosen 2009);
7. Collected five sediment cores in Sinclair Inlet and four in Dyes Inlet in 2002 to provide historical trends in sediment recovery (Brandenberger et al. 2008a);

ENVVEST monitoring studies currently being conducted for the Shipyard include:

1. Ambient monitoring and toxicity testing of effluents, marine and nearshore waters (Figure 5 and Figure 6) and mussel watch for Sinclair and Dyes Inlets (Figure 7 and Figure 8 Johnston et al. 2010a);
2. Monthly ambient monitoring for fecal coliform in marine and nearshore waters and selected stormwater outfalls at PSNS&IMF and NBK-Bremerton (Figure 9, Johnston et al. 2010b)
3. Non-Drydock Stormwater Monitoring for PSNS&IMF and NBK-Bremerton (Figure 10, Taylor Associates, Inc. and Pacific Northwest National Laboratory 2011).

Coupled watershed and receiving water models have been calibrated and verified to simulate the total loading of FC (Johnston et al. 2009) and Cu (Wang et al. in prep.) from all sources within the Sinclair and Dyes Inlet watershed. Understanding and addressing all sources of pollution coming into the Inlets will help regulatory agencies and stakeholders prioritize pollution control and water cleanup plans and focus resources on obtaining measurable improvements in the quality of the environment.

Data from this study will provide information for modeling contaminant loading into the Inlets (Wang et al. 2005, Johnston et al. 2009, Wang et al. 2011 in prep) and assessing the long-term impact of storm water discharge on sediment and water quality of the Inlets. In addition, data from the sediment sampling will compliment the ambient and stormwater monitoring projects to assess the status and trend of ecological resources, assess the effectiveness of cleanup and pollution control measures, and determine if discharges from all sources are protective of beneficial uses including protection of aquatic life (Johnston et al. 2010a,b).

1.1.2 Installation Restoration OUBM Program

In an Early Action ROD the CERCLA Puget Sound Naval Shipyard Operable Unit-B marine project area (OUBM) was signed on June 13, 2000. The selected remedy included dredging of contaminated sediments with on-site disposal in a Confined Aquatic Disposal (CAD) pit, thick and thin-layer capping, enhanced natural recovery, monitoring natural recovery, and institutional controls (U.S. Navy, 2000). Sinclair Inlet is naturally depositional in nature, and modeling in support of remedy selection predicted that the ultimate cleanup goal would be met within 10 years from the completion of active remedial measures through the processes of natural sediment recovery (U.S. Navy, 2000). Clean up and navigational dredging was conducted for OUBM in 2000-2001 under the Navy's Installation Restoration (IR) Program (URS Group Inc. 2002a) and a long term monitoring plan was approved (URS Group Inc. 2002b). The OUBM sediment monitoring consists of collecting composite samples from 3 grabs (0-10 cm depth) for analysis of PCBs, Hg, TOC, and grain size from 71- 500 ft grids within the Shipyard (Figure 11) and 30-1500 ft grids in Sinclair Inlet (Figure 12).

The primary objective of the marine sediment cleanup was to address the potential risk from PCBs in the tissues of bottom-dwelling fish consumed by humans engaged in a subsistence lifestyle (U.S. Navy, 2000). The PCBs found in fish tissues are believed to have resulted from consumption of prey species impacted by contamination in marine sediments. A secondary consideration in the cleanup was the presence of elevated levels of Hg measured in species collected in Sinclair Inlet and marine sediments above the state cleanup screening level throughout much of the inlet.

A summary of the sediment investigations occurring under the CERCLA program includes:

1. 2003, 2005, and 2007 Marine Monitoring Report OU B (summarized in URS Group, Inc. 2009);
2. Final 2010 Marine Monitoring Report OU B (report in progress May 2010).
3. Pier D repair in 2004;
4. Pier 7 Pre-construction sampling for fender pile replacement permit (URS Group, Inc. 2008a) and Pier 7 Post-construction sampling in 2009 (report in progress May 2010);
5. Pier B and Pier 8 Pre-construction sampling for Pier B upgrade permit and Pier 8 removal (URS Group, Inc. 2008b); and Pier B Under Pier sampling in 2009 (report in progress May 2010).
6. A detailed study of mercury in sediment, water, and biota of Sinclair Inlet, was compiled by the United States Geological Survey (USGS; Paulson et al. 2010).

The OUBM sediment monitoring for PCB and total Hg was conducted in 2003, 2005, 2007, and 2010. The U.S. Navy conducted this monitoring to assess and document conditions in Sinclair Inlet subsequent to remedial actions carried out between 2000 and 2004 to address sediments contaminated with PCBs. The goals of the ROD are to (1) reduce the area-weighted concentration of PCBs to the minimum clean up goal of 3 mg of PCB per 1 Kilogram of organic carbon (3 mg PCB/Kg OC) within 10 years, (2) selectively remove high concentrations of Hg collocated with PCBs, and (3) control shoreline erosion of contaminated fill. The status of sediment recovery, as monitored by the IR program, was detailed in the 2007 OU B Marine Monitoring report (URS Group, Inc. 2009). Sediment sampling consists of composites of three samples per grid (discussed further in 2.1.2) to characterize sediment quality on an area-weighted average (AWA) basis. The 2007 conclusions specific to the Shipyard area (500 ft. grids) status of sediment and biota recovery included:

- The median area weighted geometric mean (geomean) concentration of total PCBs was 6.7, 6.1, and 4.5 mg/kgOC in 2003, 2005, and 2007, respectively. All exceed the minimum cleanup level of 3 mg/kgOC. The median geomean PCB concentration within OUBM decreased between 2005 and 2007. Trend analysis predicts that the cleanup goal for OUBM could be achieved by approximately 2012.
- The median arithmetic mean Hg concentration in OUBM was 1.0, 1.1, and 0.85 mg/kg in 2003, 2005, and 2007, respectively. For all of Sinclair Inlet, the concentrations were 0.61, 0.61, and 0.56 mg/Kg. These values exceed Ecology's Sediment Quality Standard (SQS) of 0.51 mg/Kg. The decrease through time was statistically significant.
- The average total PCB concentration in the English sole tissue samples was 0.085 and 0.033 mg/kg wet weight in 2003 and 2007, respectively. They exceeded the remedial goal of 0.023 mg/kg. The median arithmetic average English sole Hg concentration was 0.044 and 0.025 mg/kg, in 2003 and 2007, respectively. English sole PCB and Hg concentrations were lower in 2007 than in 2003.

In addition to OUBM sediment monitoring, Repair Projects conducted pre- and post-construction investigations inside the Shipyard to meet the requirements of the state water quality certification permit. Recent sediment investigations included Pier 7 fender pile replacement, Pier 8 removal, and Pier B expansion (see Figure 13 and citations above). The Pier 7 pre-construction sediment samples were analyzed for PCBs, Hg, total organic carbon (TOC), grain size, arsenic (As), cadmium (Cd), chromium (Cr), Cu, lead (Pb), silver (Ag), and zinc (Zn). Significant pre-construction results for sediment samples can be summarized as follows (URS Group, Inc. 2008):

1. Carbon-normalized PCB results ranged from 2.0 to 1,100 mg/Kg OC (highest values at P7-04 and P7-05,
2. The Hg concentrations ranged 0.24 to 5.9 mg/Kg with the highest values at P7-04 and P7-06 and 10 out of 12 samples exceeded the SQS of 0.41 mg/Kg,
3. Other metals exceeding the SQS included Cu where concentrations ranged from 48 to 1,200 mg/Kg and 2 out of 12 sediment exceeded the SQS of 390 mg/Kg and Zn ranged from 120 to 2,400 mg/Kg and 4 out of 12 sediment exceeded the SQS of 410 mg/Kg.

The post-construction sediment sampling report for Pier 7 has not been finalized, but the draft report summarizes the conclusions as (report in progress May 2010):

- TOC-normalized PCB concentrations ranged from 1.0 to 140 mg/kg OC. Eight of the eleven locations where both pre-construction and post-construction samples were collected had post-construction PCB concentrations lower than the pre-construction concentrations.

- Hg concentrations ranged from 0.14 to 2.4 mg/Kg. Six of the eleven locations where both pre-construction and post-construction samples were collected had lower mercury concentrations in the post-construction sampling.
- The other metals where post-construction samples exceeded SQS include Cu which ranged from 18 to 16,000 mg/Kg and Zn from 56 to 1,400 mg/Kg.

Post-construction reports have not been finalized for Pier 8 and Pier B, the pre-construction data and under Pier B data identify PCB, Hg, Zn, and Ag as chemicals exceeding the cleanup goal or SQS. The estimated concentrations for PCB ranged from 2.0 to 30 mg/Kg OC, Hg ranged from 0.32 to 1.5 mg/Kg, Zn ranged from 120 to 1000 mg/Kg, and Ag ranged from 0.15 to 13 mg/Kg (SQS is 6.1 mg/Kg) (URS Group, Inc. 2008b and report in progress May 2010).

1.2 Data Quality Objectives

This study plan was developed to support enhanced collaboration between the IR program and ENVVEST monitoring activities for the Shipyard. The study area will focus on the sediment quality within the Shipyard boundaries which are defined as the area where the 500 ft grid cells in the OUBM monitoring program are sampled (Table 1). This sampling plan describes specific sampling activities to assess the impact of sedimentary bound contaminants to support the characterization of the status and trend of ecological resources, assess the effectiveness of cleanup and pollution control measures, and determine if discharges from local sources are protective of beneficial uses including aquatic life in the receiving waters of Sinclair Inlet. This document identifies the objectives, procedures, and quality assurance/quality control (QA/QC) requirements for sampling to be completed during 2010-2011.

This study is divided into three primary tasks to achieve the overall objectives:

1. **OUBM Monitoring:** evaluate the 2010 surface sediment conditions throughout Sinclair Inlet for a suite of metals and PAHs by collaborating with the OUBM as described in Kohn et al. (2004, 2006, and 2008).
2. **Sediment Quality Verification (SQV) Study:** characterize sediment quality adjacent to dry dock outfall and stormwater discharge locations within the Shipyard.
3. **Focus Area Study:** conduct additional pore water measurements and toxicity evaluations at selected high priority sites and support R&D studies at Pier 7.

These sediment studies will be guided by state sediment management sampling and analysis requirements to assure collection of appropriate samples and data with which to meet the state Water Quality Program Policy. The OUBM maintains a sediment management plan with oversight by Ecology's Sediment Management Unit. This SAP addresses the ENVVEST sediment analyses occurring through cooperation with OUBM Sediment Monitoring Studies and the sediment collection and analyses tasks for the SQV Study. The data quality objectives for this sediment sampling plan are provided in Table 1.

Table 1. ENVVEST sediment sampling data quality objectives.

Sediment Sampling Data Quality Objectives
STEP 1: State the Problem The Shipyard, Bremerton, WA historically received pollution from industrial activities, which is being addressed under the CERCLA program. Historical practices have changed significantly and led to an overall decrease in contaminants entering Sinclair Inlet from Shipyard activities. However, sediment quality may still be impacted by pollution from a variety of active sources including current shipyard operations, marina and vessel traffic, storm event runoff, discharges from waste water treatment plants, industrial outfalls, and surface streams and legacy sources, such as historically contaminated sediments, that are being addressed by cleanup and restoration activities. Sediment quality verification studies are needed to establish the baseline of current sediment quality conditions in selected areas, assess the effectiveness of cleanup and pollution control measures, identify areas of potential re-contamination, provide data to assess sediment impact zones from industrial outfalls and stormwater drains, and determine if discharges from all sources are protective of beneficial uses including aquatic life.
STEP 2: Identify the Decision 1. Are discharges from shipyard industrial outfalls and storm drains protective of beneficial uses of Sinclair Inlet? 2. Could remediation, construction, and/or navigational dredging activities expose and mobilize or release historically deposited sediment-associated contaminants within the Shipyard? 3. What is the status and trend of sediment quality in the Shipyard?
STEP 3: Identify Inputs to the Decision 1. Verify surface sediment quality in Sinclair Inlet to inform Ecology's Water Quality Assessment for Water Resource Inventory Area 15 (WRIA). 2. Using a weight of evidence approach, select sediment sampling areas that are co-located near suspected sources within the Shipyard (e.g. dry dock outfalls and stormwater drains). 3. Identify focus areas where historically contaminated sediment are either potentially redistributed into surface sediment (e.g. construction areas) or historically deposited sediment-bound contaminated are released into overlying waters (e.g. porewater gradient). 4. Coordinate with IR, Ecology, and NPDES sampling programs to optimize resources. 5. Provide logistical and data support for R&D studies on sediment treatability and bioavailability
STEP 4: Define the Study Boundaries Spatial boundaries are Sinclair Inlet marine sediment with a focus area on the nearshore sediments in Shipyard located within 200 ft of industrial outfalls, storm drains, and other potential sources

STEP 5: Develop a Decision Rule

The data collected will be used to assess the impact of pollution sources on the quality of water, sediment, and biota in Sinclair Inlet, determine the effectiveness of cleanup and pollution control measures, and determine if discharges from all sources are protective of beneficial uses including aquatic life. The results of this study will be used to inform adaptive management by identifying the need for pollution control measures, best management practices, and other corrective actions.

STEP 6: Evaluate Decision Errors

Data will be evaluated to assure accuracy, precision, completeness, comparability, and representativeness.

STEP 7: Optimize the Design for Obtaining Data

Optimize sampling locations with the follow considerations:

- Obtain split samples from 2010 OUBM sediment monitoring;
- Proximity to current contaminant sources (e.g. industrial outfalls and storm drains);
- Sediment locations not included in the OUBM sampling grids; and
- Sediment locations where historically-deposited contaminated sediment may be remobilized or contaminants released into overlying waters (e.g. dredge walls, construction, etc.).

Optimize sample types:

- Sediment cores in focus study areas to provide information on contaminants at depth that could be remobilized and porewater profiles to evaluate bioavailability.
- Sediment grabs to evaluate surface sediment quality near current sources.
- Composites of sediment grabs split from OUBM to optimize spatial coverage to all of Sinclair Inlet.

Optimize analytes and analytical methods:

- Couple rapid screening analysis for metals (Cu, Pb, and Zn), PCBs and PAHs with laboratory confirmatory analyses to supplement OUBM analytes list and obtain better coverage and estimates of variance from non composited samples.
- Detection limits that support comparison to sediment quality standards and other ecologically relevant benchmarks (i.e., salmonid effects thresholds) and regional monitoring data.
- Collect data on ancillary parameters important in controlling contaminant mobility, reactivity, and bioavailability (total organic carbon, grain size, oxidation-reduction potential, porewater salinity and other oxidants) for the pore water profiles.

2.0 Sampling Design

The sampling design was optimized for each of the subtasks and described in detail in the following sections. The overall sampling design for the OUBM Sediment Monitoring Study has been detailed by Kohn et al. (2004, 2006, 2008) and is a directed sampling utilizing splits from the surface sediment composite samples collected by the 2010 OUBM sediment monitoring. The SQV sites were selected based on a weight of evidence approach to rank sediment areas of concern located within the Shipyard. A targeted sampling design in the priority areas includes surface grabs and sediment cores for heavy metals, PCBs, and PAHs analyses to evaluate sediment quality and assess bioavailability and toxicity.

2.1 OUBM Sediment Monitoring

The primary objectives of the OUBM Sediment Monitoring are 1) to provide present-day sediment concentrations for metals and organics in Sinclair Inlet segments that are considered impaired for sediment quality, and 2) to provide sediment data at a spatial distribution throughout Sinclair Inlet that supports the determination of sediment recovery trends, modeling of contaminant loading and transport, and a baseline to measure continuous process improvement. The results of this study will help prioritize management actions if sediment remains a source of impairment.

To the degree possible, the OUBM Sediment Monitoring study incorporates the requirements of Sediment Management Standards (SMS) regulation (WAC 173-204, Washington State 1995) and the 303(d) listing policy (Ecology 2002a, b). The following information and guidance was considered:

- The OUBM Marine Monitoring Program, Bremerton Naval Complex (BNC);
- Design for adequate spatial coverage for short-term (CH3D) and long-term (Box Model) contaminant transport modeling efforts;
- Segments that were already sampled since 2002. This includes the sediment mass balance study (Brandenberger et al. 2008a), where sediment data are available from cores and depositional areas associated with the major streams and storm water outfalls;
- Ecology's Water Quality categories (i.e., no impairment, waters of concern, or TMDL required) (Ecology 2002a); and
- Ecology's updated Sampling and Analysis Plan guidance (April 2003).

2.1.1 ENVVEST OUBM Sediment Monitoring Sampling Design

The ENVVEST OUBM Sediment Monitoring Study will increase the yield of the 2010 IR OUBM sediment monitoring by including data on metals and PAHs. As previously described by Kohn et al. (2004, 2006, 2008), the design maximizes sample distribution (high density) and data utility while reducing field sampling costs. This will directly support the development of existing sediment conditions for more parameters than monitored by the IR program, provide temporal trends utilizing the bi-annual monitoring, and provide the ability to evaluate sediment quality improvement, or lack thereof, in the watershed. This plan details the sampling objectives, weight of evidence approach used to rank the OUBM samples for confirmatory analyses, the screening analyses for all the OUBM samples, and the ~ 30 samples selected for confirmatory analyses.

The list below identifies the sampling and analysis approach elements and the weight of evidence used to rank the OUBM grid samples for confirmatory sample selection.

1. Sampling density will be appropriate to the need for data to determine necessity of further management.
2. The following tiered approach will be employed:
    - Tier 1 - Rapid screening analysis on all samples to be conducted by the Space and Naval Warfare Systems Center Pacific (SSC-Pacific), San Diego, CA. Sediment will be screened for metals by X-ray fluorescence (XRF metals) and PAHs by using enzyme-linked immunosorbent assay (ELISA) methods (iaPAH) previously described in Kohn et al. (2004, 2006, 2008).
    - Tier 2 - Confirmatory analysis of at least 20-25% of samples to be conducted by Pacific Northwest National Laboratory (PNNL), Battelle Marine Sciences Laboratory (MSL), Sequim, WA. Confirmation for metals will include analyses by inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emissions spectroscopy (ICP-OES). Confirmation for PAHs will include gas chromatograph mass spectrometry (GC-MS).
    - Tier 3 – For the chemicals of concern with a good correlation between screening and quantitative confirmatory results, a regression equation between the screening result and the laboratory result will be used to estimate contaminant concentrations for all other OUBM samples that were not confirmed by the quantitative analyses. This method is described in detail by Kohn et al. (2004, 2006, 2008).
3. Considerations for selection of metals confirmatory samples include:
    - samples in which XRF result exceeds 90% of the SQS for one or more target metals (Cu, Pb, and Zn),
    - predicted concentrations based on Kohn et al. (2008) relational equations are ≥90% SQS,
    - variability between 2003, 2007, and 2010 screening concentrations ≥ 50%,
    - corresponding 303(d) Segment listed as Category 4B for metals, and
    - samples are representative of screening concentration range.
4. Considerations for selection of PAH confirmatory samples were altered because screening results only provide estimates of the total concentration rather than compound specific. The considerations include:
    - immunoassay result ≥ 90% SQS,
    - immunoassay result < 90% SQS but >10 mg/kg dry weight,
    - select samples to represent areas where there appears to be potential for PAH to exceed SQS,

  - select at least one sample in segments on the 2008 Category 2 listed segments,
  - screening results with high variability,
  - locations with anomalous confirmatory results from previous verification studies, and
  - samples are representative of the concentration range.
5. It is anticipated that the majority of confirmatory samples will be located in the 500-foot grid for OUBM.
6. The material remaining from each sample (volume permitting) will be archived frozen for possible future contaminant analyses.

The screening methods and their relationships with the confirmatory analyses were discussed in detail in Kohn et al. (2004, 2006, 2008). Table 2 summarizes the 2010 verification study design.

Table 2. ENVVEST OUBM Sediment Monitoring Study Design Summary for Sinclair Inlet

Location	Objective(s)	Approach	Number of Stations
Sinclair Inlet, Shipyard 500-foot grid for OUB Marine	1. Present-day sediment quality in segments listed as Category 5 or 4B and focus areas within the Shipyard. 2. Spatially representative data to support contaminant transport modeling in Sinclair Inlet	Directed sampling: screen all 2010 OUBM sediment samples for Cu, Pb, Zn and total PAHs, select 25% for quantitative confirmatory analyses, and conduct quantitative analyses on ~30 samples.	71
Sinclair Inlet, 1500-foot OUB Marine	1. Present-day sediment quality throughout Sinclair Inlet and two grid previously exceeding SQS. 2. Spatially representative data to support contaminant transport modeling in Sinclair Inlet		32
		Sinclair Inlet Total	103

Sediments throughout the entire Sinclair Inlet are sampled as part of post-remedial monitoring of OUBM. However, under the monitoring plan, samples will be analyzed only for the contaminants that were identified as ecological or human health risk drivers under the IR program: i.e., PCBs and Hg, including total organic carbon and grain size. Therefore, the ENVVEST Study will analyze samples collected by the 2010 OU BM for the additional metals and a suite of PAHs (see Table 10 and Table 12). The OUBM sediment monitoring and ENVVEST Study coordination is briefly summarized below. See the *Long Term Monitoring Plan, OU B Marine Bremerton Naval Complex* (URS 2002b) and previous verification studies (Kohn et al. 2004, 2006, 2008) for more detail.

Summary of OUBM Sediment Monitoring Program:

- Intensive sampling within the Shipyard 500-foot grid where dredging and/or capping was conducted (Figures 4):
  - 71 grids at 500-ft grid spacing, 3 randomly located stations per grid;
  - Sediment collected to 10 cm depth from three stations composited into one sample representing the grid; and

  - Sediment composites are to be analyzed for PCBs, total Hg, grain size, and total organic carbon (TOC) using Puget Sound Estuary Program methods (PSEP 1997).
- Sampling throughout Sinclair Inlet in the 1500-foot grids for OUB (Figure 5):
  - 32 grids at1500-ft grid spacing, 3 randomly located stations per grid; and
  - Sediment collection and analyses as described above.

OUBM Sediment Monitoring ENVVEST Coordination:

There is a strong rationale for coordinating the ENVVEST activities with those of the OUBM sediment monitoring. Nearly all of the sediment stations historically exceeding SQS were located within the intensive 500-ft OUBM grid, which is the focus of ENVVEST sampling. Selected OUBM grids represent the locations where present activities (dry dock pumping, stormwater discharge) are most likely to exhibit impacts to sediment. The 1500-foot grid cells provide additional coverage in the 303(d)-listed segments and a wider spatial coverage to evaluate overall sediment trends in Sinclair Inlet. Additionally, coordinating with the monitoring program is a very cost-effective means of obtaining a larger number of samples in the areas of interest.

The primary outcome of the study is a nonstatistical comparison of target metal concentrations with Washington State SQS and MCUL, but the sampling and analytical design is intended to reduce uncertainty associated with the target measurements. The chance of false negatives (samples in which true metal concentration exceeds MCUL but measured concentration is less than MCUL) is limited by 1) increased sampling density where concentrations are likely to exceed SQS, 2) selecting methods and setting quality control limits to minimize analytical error, and 3) comparing screening values to 90% SQS. The chance of false positives (samples in which true metal concentration is below MCUL but measured exceeds MCUL) is also limited by these measures.

2.1.2 ENVVEST OUBM Selection Criteria

2.1.2.1 ENVVEST OUBM Metals Criteria

Sediment samples collected by the 2010 OUBM sediment monitoring program were screened for Cu, Pb, and Zn concentrations using XRF conducted by SSC-Pacific (Appendix A1. XRF Screening Results) as described in Kohn et al. 2004, 2006, 2008. All 103 sediment samples collected during the 2010 sampling were screened and a subset of 30 samples was selected for confirmatory analysis by ICP-MS or ICP-OES (see Table 10 in Section 5.0 for list of analytes and detection limits). The selection process was based on a weight of evidence approach detailed by Kohn et al. (2004, 2006, 2008) and modified to add additional lines of evidence. The six lines of evidence are summarized below. Samples exceeding the first three criteria receive a score of 1 per metal for a maximum score of 3 per each line of evidence. Those exceeding the last three lines of evidence received a maximum score of 1 per line. The total score an individual segment could receive is 12. Thirty samples were selected for confirmation based on a weight of evidence score ≥ 2. Table 3 summarized the samples selected for confirmation, if that OUBM grid was previously selected for confirmation in the 2003 and 2007, and the scoring for each of the lines of evidence used to select the 2010 list. Eleven samples were selected for confirmatory analysis from the 1500-ft grid and 19 from the 500-ft grid.

1. **XRF Screening result ≥ 90% SQS for Cu, Pb, or Zn (Max score 3)**

The screening data from the 2010 OUBM sampling were compared to the SQS. The screening concentrations for four samples were ≥ 90% of the SQS for Zn.

2. **Predicted concentration based on Kohn et al. (2008) ≥ 90% SQS (Max score 3)**

Predicted concentrations were estimated using the regression relationship between XRF and ICP/MS results for Cu, Pb, and Zn obtained during the 2007 Metals Verification Study (Kohn et al. 2008). Of the predicted concentrations , one sample exceeded 90% of the Cu SQS and eight samples exceeded 90% of the SQS for Zn (A1. XRF Screening Results).

3. **Variability between 2003, 2007, and 2010 screening ≥50% (Max score 3)**

The screening data from the 2003, 2007, and 2010 sediment verification studies (Kohn et al. 2004; 2008, respectively) were evaluated for trends. The coefficient of variation (CV) between the three sampling events was calculated for Cu, Pb, and Zn. Samples with a CV ≥ 50% received a score of 1 for each metal. This provided a measure of change through time as typical laboratory variability was less than 30% relative percent difference (RPD); therefore greater than 50% variability was ascribed to field variability through time and not analytical. There were eight samples scored for Cu, nine for Pb, and seven for Zn.

4. **Corresponding 303(d) Segment listed for metals. (Max score 1)**

Sinclair Inlet contains no sediment segments listed as Category 5 for Cu, Pb, or Zn. The 2008 Water Quality Assessment listed segments F6E4, F6F2, F6F3, F6F4, F6F5, F6G2, F6G3 as Category 4b for Ag, Cr, Cu, Zn, As, Cd, and Pb based on 2003 data. Samples located within these grids received a score of 1. Sixty-three samples met this criterion.

5. **Representative of Screening Concentration Range. (Max score 1)**

The 2007 relationship between XRF and ICP-MS analyses was used to predict the 2010 concentrations for Cu, Pb, and Zn (Kohn et al. 2008). The predicted concentrations increased or decreased relative to the screening by 25% to 159% for Cu, -15% to 103% for Pb, and -4% to 20% for Zn. The smallest increases were noted in the highest screening concentrations suggesting as the concentrations decreased the XRF screening required the greatest correction factor. Screening concentrations in the middle and lower range were scored to further support regressions with additional data in these ranges. Predicted concentrations that increased by 50-60% and >200% for Cu were given additional weight in the selection process.

6. **Other. (Max score 1)**

This criterion was used to apply a variety of criteria in combination with those listed above. The additional criteria ensured two or three OUBM grids were selected for each Category 4b 303(d) grid, 2010 screening results that appeared anomalous would be confirmed, and OUBM grid samples where the RPD between 2007 and 2010 screening was >75% for at least two metals.

Table 3. 2010 Samples Selected for Confirmatory Analysis of Metals

OUB Grid ID	**Grid Size**	**47122**	**Selected for Confirmation**			**Wt. Evidence Score**	**2010 XRF > 90% SQS**			**2010 Predicted >90%SQS**			**2003, 2007, 2010 CV Screening >50%**			**2008 Cat. 4b**	**Rep of Conc. Range**	**Other**
		303d Grid	**2003**	**2007**	**2010**	**Max = 12**	**Cu**	**Pb**	**Zn**	**Cu**	**Pb**	**Zn**	**Cu**	**Pb**	**Zn**			
1	1500	F6C9	Y	Y	Y	**4**							1	1	1		1	
3	1500	F6C8, F6D8			Y	**2**							1				1	
12	1500				Y	**2**							1				1	
19	1500	F6E4			Y	**2**											1	1
22	1500	F6E4			Y	**2**										1	1	
23	1500	F6E3			Y	**2**							1					1
24	1500	F6F3	Y	Y	Y	**2**										1	1	
25	1500	F6E3		Y	Y	**2**									1			1
27	1500	F6F3	Y	Y	Y	**2**										1	1	
29	1500	F6F2			Y	**3**							1			1	1	
32	1500	F6F2			Y	**2**										1	1	
12	500	F6E5, F6E6		Y	Y	**2**								1			1	
14	500	F6F6, F6F5			Y	**3**							1			1	1	
19	500	F6F5		Y	Y	**2**										1	1	
30	500	F6F4, F6F5		Y	Y	**3**								1	1	1		
38	500	F6F4			Y	**4**			1			1			1	1		
39	500	F6F5	Y	Y	Y	**3**			1			1				1		
43	500	F6F4	Y	Y	Y	**4**			1			1			1	1		
44	500	F6F3, F6F4			Y	**2**										1	1	

OUB Grid ID	Grid Size	47122	Selected for Confirmation			Wt. Evidence Score	2010 XRF > 90% SQS			2010 Predicted >90%SQS			2003, 2007, 2010 CV Screening >50%			2008 Cat. 4b	Rep of Conc. Range	Other
		303d Grid	**2003**	**2007**	**2010**	**Max = 12**	**Cu**	**Pb**	**Zn**	**Cu**	**Pb**	**Zn**	**Cu**	**Pb**	**Zn**			
46	500	F6F4, F6F3	Y		Y	**2**							1			1		
51	500	F6F3			Y	**2**										1	1	
52	500	F6F3	Y	Y	Y	**2**						1				1		
53	500	F6F3		Y	Y	**2**										1	1	
54	500	F6F3			Y	**2**										1	1	
60	500	F6F3	Y	Y	Y	**4**						1		1	1	1		
61	500	F6F3, F6F2		Y	Y	**2**						1				1		
65	500	F6F2, F6F3		Y	Y	**2**						1				1		
67	500	F6G3	Y	Y	Y	**7**			1	1		1	1	1	1	1		
68	500	F6G2	Y	Y	Y	**2**										1		1
71	500	F6G2		Y	Y	**2**								1		1		

2.1.2.2 ENVVEST OUBM Organic Criteria

Immunoassay screening analysis for PAHs (iaPAH) was conducted by SSC-Pacific on 103 sediment samples collected by the 2010 OUBM sediment monitoring program (Appendix A2). The screening data were examined against the following criteria to select 26 samples for confirmatory analysis. Samples for confirmatory analysis of PAHs by GC/MS, as described in Kohn et al. (2004, 2008), were selected based on six lines of evidence listed below. The 2010 OUBM samples selected for confirmation of PAHs are listed in Table 4. Eight confirmatory samples are from the 1500-ft grid and 22 from the 500-ft grid.

1. **Immunoassay result ≥90% SQS (Max score 2)**

There is no SQS value for total PAHs (tPAH), but there are SQS values normalized to organic carbon (OC) for low molecular weight (LPAH) and high molecular weight (HPAH) PAHs (370 mg/kg OC and 960 mg/kg OC, respectively). Immunoassays screening results reported as tPAH were normalized to OC using the TOC values provided by the 2010 OUBM. These values were compared to 90% of the sum of LPAH and HPAH SQS values. In addition, the Northwest Sediment Evaluation Framework provides sediment quality guidelines for PAHs on a dry weight basis. The equivalent value to the SQS is called screening level 1 (SL1) of sediment quality guideline (SQG), and is 5.2 mg/kg dry weight for LPAH and 12 mg/kg dry weight for HPAH. No OUBM grids exceeded these criteria.

2. **Immunoassay result < 90% SQS but >10 mg/kg dry weight**

This criterion selects for moderate to high PAH concentrations to span the regression range and provide additional support for these areas of the calibration range. Only one grid exceeded this criterion.

3. **Confirmatory sample in 303(d) segment listed for PAHs or phthalates**

There are no segments listed for PAHs on the 2008 303(d) list, but one sediment segment in Sinclair Inlet is listed as Category 2 for LPAH and HPAH (F6E3). Individual PAHs, phthalates, and chlorobenzenes listed on the 2008 Water Quality Assessment are all on the Category 1 list thus they were not considered in this OUBM Sediment Monitoring .

4. **Screening results with high variability.**

The CV of the immunoassay results from 2003, 2007, and 2010 were calculated for all samples. Segments with a CV >50% received additional weight. Nineteen grids exceeded this criterion.

5. **Locations with anomalous confirmatory results from previous analyses.**

Two criteria were used to determine the anomaly in the previous confirmatory analysis: 1) tPAH confirmatory concentration in 2007 was higher than the 2007 screening value and 2) tPAH confirmatory concentration in 2007 was higher than 20 mg/kg dw.

6. **Representative of concentration range.**

In addition to the criteria above, selected OUBM grids should cover the concentration range in 2010 immunoassay results (e.g. lowest, median, and highest concentrations).

Table 4. 2010 Samples for Confirmatory Analysis of PAHs

OUB Grid	303d Grid	Selected for Confirmation			Wt. Evidence Score	>90% SQS	>90% SQG-SL1	<90% SQS, >10 mg/kg dw	Cat 2	CV screening >50%	RPD Screening >75%	Screening < Conf.	Conf. >20 mg/kg	Rep. of Conc. Range
		2003	2007	2010	Max = 9				2008		2007-10	2007	2007	2010
23	F6E3			Y	1				1					
25	F6E3			Y	1				1					
26	F6E2			Y	1									1
32	F6F2			Y	1					1				
1	F6E6		Y	Y	2					1	1			
16	F6E5			Y	1									1
18	F6F6, F6F5		Y	Y	2					1	1			
19	F6F5			Y	1					1				
26	F6F5			Y	1									1
39	F6F5	Y	Y	Y	3					1		1	1	
40	F6F4			Y	2					1	1			
42	F6F4			Y	2					1	1			
43	F6F4		Y	Y	1					1				
45	F6F4	Y	Y	Y	2					1	1			
48	F6F3		Y	Y	1					1				
49	F6F4, F6F3			Y	1						1			
55	F6F3	Y	Y	Y	1					1				
56	F6F3	Y	Y	Y	5					1	1	1	1	1
57	F6F3			Y	1					1				
59	F6F3		Y	Y	2					1	1			
60	F6F3	Y	Y	Y	2					1	1			
61	F6F3, F6F2	Y	Y	Y	4			1				1	1	1
63	F6F3	Y	Y	Y	1					1				
67	F6G3		Y	Y	3					1	1		1	
69	F6F2, F6G2		Y	Y	2					1	1			
71	F6G2	Y		Y	2					1	1			

2.2 Sediment Quality Verification Study

The primary objectives of the SQV are:

1) to provide present-day sediment concentrations for metals and organics in the Shipyard areas of concern for Ag, Cu, Pb, Zn, Hg, and PCBs not currently addressed by OUBM monitoring;
2) characterize silt and sediment in the vicinity of outfalls, storm drains, and dry docks;
3) provide data to assess sediment impact zones for NPDES discharges;
4) provide data to assess anti-degradation requirements for water quality certifications needed for pier and dry dock infrastructure improvements;
5) support R&D studies of sediment treatability and bioavailability.

The data from this study can also be used to assess sediment recovery trends, support contaminant loading and transport modeling, and establish a baseline to measure continuous process improvement. The existing stormwater monitoring data and the spatial resolution of the sediment data is not sufficient to determine or rule out sediment degradation from active processes (e.g. stormwater runoff, ship maintenance, repair, and decommissioning) or re-distribution of historically contaminated sediment. The results of this study will inform adaptive management by identifying the need for pollution control measures, best management practices, and other corrective actions and help prioritize management actions if sediment remains a source of impairment.

2.2.1 Identify Data Gaps

The 1998 303(d) list included As, Cd, Cu, Pb, Zn, and Hg in sediments of Sinclair Inlet and Cd, Hg, and Ag in the sediments of Dyes Inlet due to exceedences of the SQS or minimum cleanup level (MCUL). Sediment verification studies conducted on splits of the 2003 and 2007 OUBM were included in the data set used for the 2008 303(d) list (Kohn et al. 2004, 2006, and 2008). Previously, two Category 5 sediment segments were listed in Sinclair Inlet for metals (47122F6F3 and 47122F6F4), but in 2008, these segments were designated as Category 4B for As, Cd, Cr, Cu, Pb, Ag, and Zn. The Ecology 2008 water quality assessment for Sinclair Inlet listed three sediment grids as Category 5: one for PCBs based on a 2003 sample (47122F6E3_SE), and two for sediment bioassays based on 1998 samples (47122F6E7_NE and 47122F6E6_NW). The Category 4b listings included 7 sediment grids for As, Cd, Cr, Cu, Pb, Ag, and Zn (F6E4, F6F2, F6F3, F6F4, F6F5, F6G2, and F6G3) based on 2003 data and 2 grids for PCBs (F6E5, F6E4) based on 1999 data. Several sediment grids also exceed SQS for Hg, but they are not included in the 2008 listing due to the CERCLA monitoring.

In addition to the 303(d) sediment listings, Ecology and EPA identified nine priority areas of concern for sediment quality under the NPDES permit review and mixing zone request (Figure 13, Table 5; Ecology 2010). These areas were selected based on existing sediment data in Ecology's database and the locations within the Shipyard of the 156 stormwater outfalls, 4 dry dock outfalls, remediation dredging, and navigational dredging (Figure 13). These included areas around specific piers, moorings, and locations near outfalls of concern (outfall are identified using EPA outfall number). Ecology (2010) concluded there is not enough information to determine if outfall discharges are in compliance with the SQS and sediment data from the past 10 years for Hg, Zn, Cu and PCB show there are areas with elevated concentrations and exceedances of the SQS. Ecology provided the following recommendations:

- Sediment monitoring at dry docks and 14 major outfalls listed in Table 5;
- “Diagnostic” monitoring for Cu, Zn, Hg, and PCB in areas of concern;
- Sediment sampling near outfalls to support a mixing zone for Cu and Zn; and
- Discrete sediment monitoring (not composites) for source control evaluations.

Table 5. Areas of sediment quality concern for PCBs, Hg, Cu, and Zn around specific piers, moorings, and outfalls (numbers are EPA outfall numbers) in the Shipyard.

	PCB	Hg	Cu	Zn
Pier D	X	X		
Mooring E	X	X		
Pier 7/8	X			
Pier 4, 5, 6		X	X	X
Outfalls 15, 95	X			
Outfalls 3, 4, 5, 6, 7, 26, 27, 28, 35, 37, 42, 43, 44, 46, 48, 49, 50, 51, 52, 53, 97		X		
Outfalls 13, 14, 25, 38, 39, 40, 41, 82, 83, 84, 85	X	X		
Outfall 1 - East of Pier 8		X		
Dry Dock Outfall 096 (Pier 3/4)		X	X	

In addition to these recommendations and identified areas of concern, data from previous IR monitoring and ENVVEST studies discussed in Sections 1.1.1 and 1.1.2 were compiled and prioritized to further support the identification of the SQV and focus areas for this study. Previous verification studies were conducted by ENVVEST on the OUBM sediment samples collected in 2003 and 2007 PCBs (URS Group, Inc. 2009). Figure 11 and Figure 12 illustrate the OUBM 500-foot and 1500-foot grids, Ecology’s 303(d) grids, and the OUBM grids where 2003 and/or 2007 sediment concentrations exceeded the SQS for Cu, Pb, and/or Zn in either the screening or confirmatory analyses. Table 6 displays the Cu, Pb, and Zn data for the OUBM grids where the composite sediment sample concentrations were greater than the SQS, MCUL, or 90% of the SQS. This identifies 303d grids F6C9, F6E3, F6F4, F6F5, F6F3, F6F2, F6G3, and F6G2 as areas that should be targeted for further sediment quality evaluations and serves as a line of evidence in the selection of the 2010 OUBM composite samples for confirmatory analyses.

Table 6. The OUBM sediment composite samples collected in 2003 and 2007 where screening and/or confirmatory analysis exceeded the Sediment Quality Standard (SQS), Minimum Contaminant Level (MCUL), or 90% of the SQS for Cu, Pb, and/or Zn.

OUB Grid ID	Grid Size	47122	Screening Cu (mg/Kg)		Cu Confirmation (mg/Kg)		Screening Pb (mg/Kg)		Pb Confirmation (mg/Kg)		Screening Zn (mg/Kg)		Zn Confirmation (mg/Kg)	
		303d Grid	**2003**	**2007**	**2003**	**2007**	**2003**	**2007**	**2003**	**2007**	**2003**	**2007**	**2003**	**2007**
1	1500	F6C9	63	47	102	31.8	102	23	198	19.1	260	48	**547**	71.2
25	1500	F6E3	60	24		55.9	32	63		42.1	87	**436**		101
30	500	F6F4, F6F5	108	186		159	49	167		74.6	120	**522**		250
34	500	F6F5, F6F4	138	191	171		104	92	132		250	252	**391**	
39	500	F6F5	181	195	173	205	94	169	128	142	**425**	316	288	304
46	500	F6F4, F6F3	133	117	142		92	67	155		286	149	**428**	
52	500	F6F3	247	219	**398**	261	171	159	279	265	**417**	339	**785**	**483**
59	500	F6F3	152	252	272	237	117	183	**439**	197	280	366	**736**	**505**
60	500	F6F3	126	**351**	200	**413**	75	**488**	180	320	291	**931**	**1480**	**863**
61	500	F6F3, F6F2	75	233		170	167	153		266	191	**375**		**463**
63	500	F6F3	192	**368**		296	107	174		140	253	**386**		**383**
64	500	F6F3	149	248	230		113	126	209		279	292	**425**	
65	500	F6F2, F6F3	118	175		124	70	73		131	197	315		**381**
66	500	F6F2	87	115	227		66	106	159		249	166	**428**	
67	500	F6G3	211	**1618**	**710**	**683**	140	378	204	281	283	**863**	**547**	**954**
68	500	F6G2	129	280	217	230	67	146	144	**605**	**558**	347	**526**	**2632**
	WA SQS		**390**	**390**	**390**	**390**	**450**	**450**	**450**	**450**	**410**	**410**	**410**	**410**
	WA MCUL		**390**	**390**	**390**	**390**	**530**	**530**	**530**	**530**	**960**	**960**	**960**	**960**
	90% SQS		**351**	**351**	**351**	**351**	**405**	**405**	**405**	**405**	**369**	**369**	**369**	**369**

The coarseness of the 303(d) grids does not allow for the detail necessary to target the areas of concern within the Shipyard. Therefore, Table 7 lists the ENVVEST ambient monitoring station code and a description of the target areas along with the available data for Ecology (2010) areas of concern, CERCLA repair projects, and ENVVEST sediment and stormwater investigations. Data that exceeds the SQS, the discharges within those areas identified using the PSNS outfall number that corresponds to the EPA outfall numbers, and the potential source or process of concern within that area are also listed (see Appendix B. Stormwater Basin Description Table for cross reference list of outfall ids, size and location). This identified 11 areas of concern, which most overlap with the Ecology areas of concern (Figure 13). The potential sources identified include stormwater or drydock outfalls where dissolved and/or particulate contaminants may partition to the sediment and accumulate in sediment near the outfalls, maintenance or remedial dredging that may have exposed historically contaminated sediment (e.g. dredge walls) and allows either physical redistribution of those sediment or chemical release of the contaminants from the sediment as the areal extent of sediment/water boundary post dredging increased and the exposed walls provide an oxidation pathway to release metals from reduced sediment complexes (e.g. metal sulfides), sediment areas not included in the OUBM sediment monitoring grids and therefore not monitored, and/or specific processes within that area that will either change or have changed.

The ENVVEST ambient marine monitoring program provides seasonal surface water samplings for metals (see Figure 5 and 6) from 2009 to present and bi-annual indigenous mussel sampling (see Figure 7 and 8) for metals, PAHs, and PCBs (Johnston et al. 2010b). The five seasonal surface water sampling events identified potential water quality concerns for Cu around PS07, PS08, PS09, and PS10 ambient monitoring stations. Dissolved concentrations of Cu were evaluated against the Washington Toxic Substance chronic (3.1 µg/L) and acute (4.8 µg/L) criteria for the protection of aquatic life (WAC-173-201A-240). The Cu chronic criterion was exceeded in September and November at PS07 (average 3.4 µg/L) and PS08 (average 3.8 µg/L) and in November at PS09 (3.9 µg/L).

Indigenous mussels were sampled by ENVVEST in 2010. The data were evaluated against tissue residue benchmarks, which were developed to assess the potential for ecological and human health effects (see Table 1 in Johnston et al. 2007). Ecological benchmarks consisted of water quality criteria based tissue screening values (TSV) and threshold concentrations above which adverse effects could occur in an organism expressed as the critical body residue (CBR). The benchmark values for Cu are expressed as parts per million (ppm) dry weight and TSV =21.3 and CBR = 20. Only PS08 exceeded these benchmarks. The benchmarks for Zn are TSV=142 and CBR= 200. The CBR for Zn was exceeded at PS01, PS03, PS08, PS09, and PS11. At PS11 the Pb concentration exceeded the TSV=2.8 for Pb, but not the CBR=3.5. For the PAHs the CBR of 317 parts per billion (ppb) was exceeded PS08 and PS11 and the PCB TSV = 437 ppb was not exceeded, but the CBC=28.2 ppb was exceeded at all shipyard stations. Each of these lines of evidence was used in the site prioritization process.

Table 7. The ENVVEST ambient monitoring station name and description, available data, outfalls and sources of concern for areas considered for Sediment Quality Verification Sampling. See Figure 5 for station locations.

ENVVEST Station ID Target Area	Available Data	Exceed SQS[5] or Marine Water Quality Criteria[7]	Outfalls of Concern (PSNS #)	Source(s) of Concern
PS03 Mooring E to Pier D	1. Stormwater outfall monitoring PSNS015[1] 2. Sediment OUBM[2] 3. Ambient Monitoring[6] 4. ENVVEST Mussel Watch Station[8]	• OUBM Grid 30,39 increasing for PCB • OUBM Hg • Mussel watch tissue screening values for Zn, PCB[9]	012, 011.2, 011.3, 014, 015, 017.1, 017; OF82 removed	Dredging, stormwater outfalls, 303(d) segments F6F5 and F6F4 for PCB and Zn
PS08 Mooring A to Pier 3	1. Stormwater outfall monitoring PSNS082.5[1] 2. Sediment OUBM[2] 3. Ambient Monitoring[6] 4. ENVVEST Mussel Watch Station[8]	• OUBM Hg • 2007 OUBM Zn; 2010 screen passes • PS08 AMB marine Cu • Mussel watch tissue screening values for Cu, Zn, PAHs, PCB[9]		Stormwater outfall, dredging, shoreline stabilization, outside CERCLA grid, 303(d) segments for Cu, Pb, Zn F6F3
PS06, PS07 DD6 Entrance to Pier 9	1. Outfall NPDES019 2. Stormwater outfall monitoring PSNS081.1[1] 3. Sediment OUBM[2] 4. ENVVEST silt grabs DD6 5. Ambient Monitoring[6] 6. ENVVEST Mussel Watch Station (PS06)[8]	• OUBM Hg and Zn • Caisson silt Hg • 2010 grabs • PS07 AMB marine Cu • Mussel watch tissue screening values for PCB[9]	019	Drydock outfall, Pier B construction
PS09 Pier 3 to Pier 4	1. Stormwater outfall monitoring PSNS096[1] 5. Outfall NPDES018 2. Sediment OUBM[2] 3. Ambient Monitoring[6] 4. ENVVEST Mussel Watch Station[8]	• OUBM Hg, Pb, Zn • PS09 AMB marine Cu • Mussel watch tissue screening values for Zn, PCB[9]	018 , 099, 101 to 104, 106	Drydock outfall, dredging, stormwater outfalls, outside CERCLA grids, 303(d) segment F6F3, F6G3
PS10 Pier 4 to 5	1. Ambient Monitoring[6] 2. Sediment OUBM[2]	• OUBM Hg, Cu, Pb, Zn	107, 108	Stormwater outfall, drydock activities, dredging, 303(d) segment F6F3
PS 10.1 Pier 5 to Pier 6	1. Ambient Monitoring[6] 2. Sediment OUBM[2]	• OUBM Hg, Cu, Zn, Pb	122, 123, 117, 115.1, 113, 118.2, 116, 110, 121	Stormwater outfalls, Drydock 1, dredging, outside CERCLA grids, 303(d) segments F6F3 and F6G3

ENVVEST Station ID Target Area	Available Data	Exceed SQS[5] or Marine Water Quality Criteria[7]	Outfalls of Concern (PSNS #)	Source(s) of Concern
PS11 Pier 6 to Pier 7	1. Stormwater outfall monitoring PSNS126[1] 2. Sediment OUBM[2] 3. ENVVEST Pier 7 Focus Study 4. Pre/Post Const. Pier 7[3] 5. Ambient Monitoring[6] 6. ENVVEST Mussel Watch Station[8]	• OUBM Hg, Zn, Pb • Post Pier 7 Zn, Hg • Mussel watch tissue screening values for Zn, Pb, PAHs, PCB[9]	124, 124.1, 126	Process change for outfall PSNS126, Pier 8 removal
PS04 Pier D to Pier C	1. Stormwater outfall monitoring PSNS008[1] 2. Sediment OUBM[2] 3. Ambient Monitoring[6]	• OUBM grid 35 increasing for PCB • OUBM Hg	020.1, 031, 024	Dredging, stormwater outfalls
PS05 Pier C to Pier B	1. Stormwater outfall monitoring PSNS032[1] 2. Sediment OUBM[2] 3. Pier B Pre-Construction[4] 4. Ambient Monitoring[6]	• Pre-Const. Hg	NA – construction will alter outfalls	Outfalls, construction on Pier B
PS 12 Pier 8	1. Stormwater outfall monitoring PSNS126[1] 2. Sediment OUBM[2] 3. Pier 8 Pre-Construction[4] 4. Ambient Monitoring[6]	• OUBM Hg • Pre-Pier Ag, Zn, Hg	126, 126.4	Process change for outfall PSNS126, Pier 8 removal
PS01 Mooring E to Mooring F	1. Sediment OUBM[2] 2. Ambient Monitoring[6] 3. ENVVEST Mussel Watch Station[8]	Mussel watch tissue screening values for Zn, PCB[9]	011, 011.1	Outfall

[1] Non Dry-Dock Stormwater Sampling Plan (Taylor Associates, et al. 2011)

[2] Sediment composites from OUBM monitoring 2003, 2005, 2007, 2010

[3] Pier 7 Pre-construction sampling for fender pile replacement permit (URS Group, Inc. 2008) and Pier 7 Post-construction sampling in 2009 (report in progress May 2010)

[4] Pier B and Pier 8 Pre-construction sampling for Pier B upgrade permit and Pier 8 removal (URS Group, Inc. 2008b) and Pier B Under Pier sampling in 2009 (report in progress May 2010).

[5] SQS evaluations were done on post construction data unless unavailable, then pre-construction data was used. The number of sediment samples exceeding SQS for the metal of interest is noted in parentheses.

[6] Five Ambient marine water quality surveys conducted from 2009 to 2010 (Figure 5 and 6 and Johnston et al. 2010b).

[7] Washington Toxic Substance dissolved copper concentration chronic (3.1 µg/L) and acute (4.8 µg/L) criteria for the protection of aquatic life (WAC-173-201A-240).

[8] ENVVEST Mussel Watch program (Figure 7 and 8 and Johnston et al. 2010b).

[9] Mussel data evaluated against ecological benchmarks of tissue screening values (TSV) and critical body residue (CBR; Johnston et al. 2007).

2.2.2 Ranking Areas for Site Selection

Eleven areas of concern were identified based on existing sediment data or information on potential sources. Since sampling at all areas of concern was not feasible, the locations were prioritized and ranked based on all the lines of evidence discussed above. Nine sediment sampling sites were selected for sampling (Figure 14 and Figure 15). Ranking factors included evaluating the available data for SQS exceedances, determining if there was a specific process change occurring within that area (e.g. construction), and prioritizing those areas in discussion with ENVVEST, NPDES, and CERCLA program managers. Table 8 lists each of the eleven sites, the relative ranking score, and the justification. The nine areas of concern identified by EPA and Ecology (see Table 5) were included in the selected areas except Pier 8, which has active stormwater monitoring occurring at outfall PSNS126 and is awaiting post-construction data reports, Pier B which is still under construction, and Mooring E to Pier D where increasing PCBs in OUBM grid 30 and 39 are being addressed by OUBM (see Figure 13).

Table 8. Sediment area rankings, suggested sediment study, and justification.

Sediment Area	Rank	Justification
PS09 OF18 DD4	Highest	OF 18, No Data for outside OUBM grids Dredge Wall/shoreline stabilization Elevated Monitoring Data – Water (Cu), Mussels (Zn, PCBs), Sediment (Hg, Pb, Zn)
PS08 DD5 RMTS	Highest	No Data for outside OUBM grids Dredge Wall/shoreline stabilization Elevated Monitoring Data – Water (Cu), Mussels (Cu, Zn, PAH, PCB), Sediment (Hg, Zn)
PS03 Mooring E –Pier D	High	Ecology/EPA concern area No Data for outside OUBM grids Elevated Monitoring Data – Water (Hg), Mussels (Hg, Pb, Zn, PCB), Sediment (Hg, PCB)
PS11 DD3	High	Ecology/EPA concern area Elevated Monitoring Data – Mussels (Pb, Zn, PCB, PAH), Sediment (Hg, Pb, Zn)
PS06 OF19 DD6	High	OF19, Ecology/EPA concern area No Data for outside OUBM Dredging, Pier Improvement Elevated Monitoring Data – Mussels (PCB), Sediment (Hg, Zn)
PS07 Finger Pier	High	No Data for outside OUBM grids Elevated Monitoring Data – Water (Cu), Sediment (Hg, Zn)
PS10 DD2	High	Ecology/EPA concern area Elevated Monitoring Data – Sediment (Hg, Cu, Pb, Zn)
PS10.1	High	Ecology/EPA concern area, No Data for outside OUBM grids

Sediment Area	Rank	Justification
DD1		Elevated Monitoring Data – Sediment (Hg, Cu, Pb, Zn)
PS12 Pier 8	Medium	Ecology/EPA concern area Waiting for Post Demolition Data Elevated Monitoring Data – Sediment (Hg, Ag, Zn)
PS04 Pier D to C	Low	On target to meet PCB cleanup goal Waiting for Pier B construction to finish Elevated Monitoring Data – Sediment (PCB, Hg)
PS05 Pier C to B	Low	Waiting for Pier B construction to finish
PS01, PS02 Mooring E to F	Lowest	Stormwater, mussel, and ambient monitoring continues

2.2.3 Conceptual Model of Sedimentary Environment

The sedimentary environment offshore of the Shipyard is very heterogeneous consisting of different bathymetries and varying sediment facieses and substrates as a result of shoreline modifications and developments, industrial activities, shipyard operations, and historical dredging operations (Figure 16). This creates a very complex geochemical environment that affects the accumulation, distribution, bioavailability, and impact of contaminants that may be present. Based on sediment core profiles (Figure 2, Brandenberger et al. 2008a) and OUBM sediment monitoring results (URS 2004, 2008, 2010; Kohn et al. 2005, 2008) the sediments deposited over the last l50 years represent the top 20-30 cm of undisturbed sediment. Dredging, pier construction, and channel deepening projects have removed or displaced these deposits and exposed materials deposited during past glaciations including recessional outwash and till deposits (Whitney and Wright 2003). The most recent deposits, comprising the surface (0-2 cm) of the bottom, consists of a mixture of geological material from the bottom, biogenic organic matter, resuspended silts and clays, particulates from runoff, anthropogenic debris, and other sedimentary materials present in the system. The biologically active layer usually consists of the top 5-10 cm and the amount of biological activity is highly dependent on the geochemical conditions of the sediment, the substrate characteristics, the level of contamination, and other ecological conditions present at the site.

2.2.4 Sediment Quality Verification Sampling

The Sediment Quality Verification sites (Figure 14 and Figure 15) were selected to enhance the spatial coverage of sediment sampling within the Shipyard, identify if degraded sediment quality is present, and assess possible sources of impact for degraded conditions. Discreet sediment grab samples (0-10cm) and sediment cores (0-25cm) will be collected from all sites and at two selected sites, an additional core (0-25 cm “squeeze core”) will be collected to evaluate pore water and biogeochemical availability and surface sediments (0-5 cm) will be collected for toxicity testing. Samples will also be collected from the Pier 7 site to support R&D studies of sediment treatability and bioavailablity. A summary of the samples to be collected and the parameters to be evaluated is provided in Table 9.

The list below identifies the sampling and analysis elements.

1. Sampling density and type (grab versus sediment core profile) is appropriate to the need for data to determine necessity of further management. The eight SQV sites will be sampled with grabs to obtain a measure of site variability and a (0-25 cm) core profile will be obtained at each site to evaluate contaminant levels and geochemical processes with depth. At two sites (PS03 and PS09) additional sampling will consist of a 0-25 cm squeeze core and samples of sediment surface (0-5 cm) will be collected for toxicity evaluations.
2. All samples will be analyzed for Hg.
3. For Ag, As, Cd, Cu, Cr, Pb, Zn, PAHs, and PCBs the same tiered approach discussed above for OUB will be employed for all samples except the squeeze core where each core segment will be confirmed.
    - Tier 1 - Rapid screening analysis on all samples as described above in Section 2.1.1 with the addition of PCB screening as described in Kohn et al. (2006, 2008).
    - Tier 2 - Confirmatory analysis of at least 20-25% of samples for metals and PAHs as described above. The PCB confirmatory analyses will be conducted by GC-Electron Capture Detection (ECD).
    - Tier 3 – For the chemicals of concern with a good correlation between screening and quantitative confirmatory results, the relational model equation will be used to estimate contaminant concentrations for all other samples that were not confirmed by the quantitative analyses.
    - Considerations for selection of confirmatory samples will follow the criteria stated above in the OUBM Sediment Monitoring study design.

The screening methods and their relationships with the confirmatory analyses were discussed in detail in Kohn et al. (2004, 2006, 2008). Table 9 summarizes sampling to be conducted for the SQV sites. The sites to be sampled are shown in Figure 174 to Figure 23. All samples will be screened for Metals (XRF); PAHs, PCBs (ImmunoAssay – iaPAH, iaPCB), confirmed for total Hg (HgDMA), and then a subset of about 20% of the samples will be confirmed for metals, PAHs, and PCBs. Bioavailability will be evaluated by analyzing pore water concentrations of metals, dissolved sulfide, and dissolved organic carbon (DOC) and other binding species, and conducting toxicity assessments of sediment and overlying water. The numbers of samples and analyses to be conducted are provided in Appendix C1. The number of samples and analyses to be conducted.

Silt samples were also collected inside Dry Dock 6 (DD6). During the repair of Pier B, DD6 was open to the Inlet for almost 5 months from March to July 2010. During that time about 2 cm of silt accumulated on the dry dock floor. Prior to dewatering, divers collected 6 silt samples along the sides at the front, middle, and rear of the dry dock. Immediately following dewatering, two silt samples of material accumulated on the dry dock floor were also sampled. The silt samples will also be analyzed for metals, PCBs, PAHs, Hg, TOC, and grain size.

Table 9. Summary of Sediment Quality Verification sampling.

	Number of Samples							
Stations	**PS03**	**PS06**	**PS07**	**PS08**	**PS09**	**PS10**	**PS10.1**	**PS11**
0-10cm grab	6	6	6	6	6	6	6	6
0-25cm core	1	1	1	1	1	1	1	1
0-25cm squeeze core	1				1			
0-5cm Tox Eval	1			1	1			

	Analysis							
	XRF*	iaPAH*	iaPCB*	HgDMA	Pore Water	GrainSize	TOC	AVS/SEM
0-10cm grab	x	x	x	x		x	x	
0-25cm core	x	x	x	x			x	x
0-25cm squeeze core	x	x	x	x	x		x	x
0-5cm Tox Eval	x	x	x	x	x	x	x	x
	* Includes confirmation analysis of 20% of the samples by ICPMS and GC/MS							
0-25cm core	Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20							
0-25cm squeeze core	PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-20							
0-5cm Tox Eval	Media		Endpoint					
A.	Sediment		polychaete (*Neanthes arenaceodentata*) survival and growth,					
B.	Sediment		amphipod (*Leptocheirus plumulosus*) survival					
C.	Sediment		amphipod (*Ampelisca abdita)* survival					
D.	Overlying Water		bivalve (*Mytilus galloprovincialis*) embryo-larval development					

2.2.5 Evaluate Bioavailability

Acid volatile sulfide (AVS) has been used to predict the sediment toxicity of Cu, Cd, nickel (Ni), Pb and Zn (Ankley et al. 1996; Berry et al. 1996, Johnston 1993). This relationship results from the volatilization of AVS present in sediment and simultaneous release of previously sulfide bound metals (simultaneously extracted metal - SEM). Research indicates that metals bound to sulfides are not available for uptake by benthic organisms. Under this assumption, the amount of AVS present in sediment limits the metal bioavailability and subsequent toxicity in sediments. Sulfide is an important binding component in modeling metal sorption in sediments (Morse et al. 1987). In the presence of excess sulfide, most of the reactive metal will form insoluble metal sulfides. The AVS becomes an indicator of the ratio of available sulfide to the SEM metals and allows the partitioning of free aqueous phase metal and solid phase metal in sediments. The divalent metals form metal sulfide complexes at the expense of iron and manganese sulfide ($FeS \cong MnS << NiS < ZnS < CdS < PbS < CuS < HgS$). If the sum of the molar ratios of the SEMs is greater than that of the AVS, the excess fraction of the metals may have a high potential for bioavailability. For divalent metals, one mole of SEM will react with one mole of AVS. The AVS/SEM analysis will be conducted on the 0-25 cm sediment cores to identify the bioavailability of these metals within the core profile.

Previous studies of Sinclair Inlet sediments showed that AVS production was high and that most of the divalent metals were bound as nonreactive and nonmobile sulfides (Johnston 1993). In situ benthic flux rates of metals measured at the same time (Chadwick et al 1992) reported higher flux rates of Ni and Zn when AVS was lower, probably due to the low sulfide solubility of Ni and Zn which would be the first metals to be released as AVS decreases (Johnston 1993, Chadwick et al. 1992). The AVS/SEM measurement will provide information on the geochemical binding capacity of sediments.

2.2.6 Pore Water Evaluation

Mechanisms for the transport of dissolved and particulate constituents from the sediment into the water column include diffusion and advection of porewater, sediment resuspension, and bioturbation (biologically mediated mixing). Paired porewater and sediment sampling provides a means to understand the impact of these processes, flux of the contaminants out of the sediment into overlying water, and their bioavailability. For example, methylmercury (MeHg) concentrations in aquatic systems are controlled by the balance of methylation and demethylation rates, the bioavailability of Hg and MeHg for transformation, and exchanges between sediment and water compartments (Munthe et al. 2007). Measuring sediment porewater concentrations in the upper few cm of the sediment cores supports an estimation of flux from the sediment into overlying water and supports the mass balance approach used by ENVVEST for Sinclair Inlet (Brandenberger et al. 2008a).

The limited volume of porewater requires microscale analyses and prioritization of the parameters of interest and utilization of modeled partitioning for organics. The porewater samples will be analyzed in priority order for dissolved Hg, Ag, As, Cd, Cu, Cr, Ni, Pb, Zn, DOC, and sulfide. The DOC and dissolved sulfide measures provide ancillary information to support the calculation of partitioning between the sediment and porewater using established coefficients (K_d and C_w) [e.g. IAEA 2004; Persson et al. 2005; USEPA 2005]. The bulk sediment from each core segment where porewater will be extracted will be analyzed for the same list of metals, TOC, PAHs, and PCBs. This will allow the calculation of porewater concentrations for the organic parameters.

2.2.7 Toxicity Evaluation

Samples at selected sites will be evaluated for toxicity using the protocols developed in support of the Navy's research program to assess bioavailability and toxicity of sediments contaminated with Cu, Zn, and other contaminants. As part of toxicity evaluations being conducted at selected Navy sites, the surface sediments will be collected from the top 0-5 cm and tested for toxicity with a maximum holding time of two weeks (USEPA, 1994). Toxicity testing will include testing exposure to bedded sediments obtained from the top 5 cm and overlying water from an intact core. The sampling will also employ the use of passive samplers using diffusive gradients in thin films (DGT) to make *in situ* measurements of chemical exposure. The toxicity tests to be conducted include:

- *Ampelisca abdita*: whole sediment 10-day amphipod survival (USEPA, 1994)
- *Leptocheirus plumulosus*: whole sediment 10-day amphipod survival (USEPA, 1994)
- *Neanthes arenaceodentata*: whole sediment 28-day polychaete survival & growth (Farrar and Bridges, 2011)
- *Mytilus galloprovincialis*: sediment-water interface 48-hour survival and embryo-larval development (Anderson et al., 1996; USEPA, 1995b).

See Appendix E. Preliminary Evaluation of Tools Towards Improved Assessment of Copper and Zinc Bioavailability and Toxicity at Contaminated Navy Sediment Sites, Space and Naval Warfare Systems Center (SSC) Pacific for the details of these tests.

2.2.8 Assess Sediment Deposition

The sediment sampling will provide a means to evaluate continual process improvement and provide a baseline for existing conditions. The sediment core profiles and repeated sampling of the OUBM grids provide a measure of concentration change through time to assess the state of the sediment quality. Sediment grain size analysis will also provide information about the texture and potential source of materials deposited around the dry docks, piers, and pilings. Sediments collected during this study will be analyzed for their complete grain-size distribution using a laser particle sizer, which employs lenses of different focal lengths to quantify the portions of the total range of grain sizes that may be present. The distributions, combined with sieve data for sizes >1500 microns, will be "merged" to obtain the complete grain size distribution (McLaren 2004, 2008). Previous grain size analysis has shown that:

> “(1) During the interval between 1998 and 2003 the sediments in Sinclair Inlet changed significantly in texture by becoming, on average, nearly a full phi size coarser (from medium to coarse silt). These changes and possible causes are fully discussed in McLaren (2004); however, the simplest and probably best explanation for such a change to occur is by the addition of coarse material to the preexisting grain-size distributions. Of all the possible causes, the dredging operations associated with the waterfront in the intervening years are most plausible explanation for the changes.
> (2) Another sampling episode took place in 2007, four years after the 2003 sampling date. In a similar analysis as described in the McLaren (2004) report, the sediments in Sinclair Inlet appear to be returning to distributions more similar to those found in 1998.
> (3) Given that dredging activities ceased altogether between 2003 and 2007, this provides a reasonable inference that the sedimentological environment of Sinclair Inlet is presently recovering from the earlier effects of channel deepening and sediment remediation projects.” (McLaren 2008)

In addition, systematic sediment samples taken in the vicinity of Pier 7 and possibly DD6 will be evaluated for sediment trend analysis (STA). The STA is a technique used by SedTrend to identify patterns of net sediment transport and their dynamic behavior in all environments (SedTrend 2011).

2.2.9 Support R&D studies of sediment treatability and bioavailability (SPAWAR/ERDC)

Sediment will be collected to support treatability (SSC-Pacific 2010) and bioavailability (ERDC-ERL 2010) R&D studies. Based on high PCB concentrations measured in samples collected as part of repair projects conducted at Pier 7, additional sampling was conducted to determine the nature and extent of contamination around Pier 7. Divers were used to collect 0-6 cm surface cores along a grid of 10 transects perpendicular to the pier, for a total of 51 samples Figure 23. Each sample was screened for PCBs using the immunoassay, and an area with elevated contamination was identified near the pier (Figure 23, Appendix D1. Pier 7 Immunoassay Results for PCBs). The samples were also screened for metals using the XRF (Appendix D2. Pier 7 XRF Results for Metals). Bulk samples were subsequently obtained from the area of elevated contamination for laboratory testing (SC-Pacific 2010, ERDC-ERL 2010). Following laboratory evaluations, 55 gal drum samples were obtained from the location of elevated contamination, by using divers to fill 5 gal buckets with sediment from the top 6 inches of bottom, hauling the buckets to the surface, and placing the material into 55 gal drums. Enough material was obtained to half-fill six 55 gallon drums which were shipped to ERDC-ERL to be used in laboratory studies. Following the drum sample, five grab samples of the top 2 inches was collected for chemical analysis of PCBs, PAHs, and metals.

3.0 Field Sampling Methods

If sampling requirements cannot be met due to sampling or measurement system failure, field conditions or other factors that cannot be controlled, corrective action will be discussed with the Navy Program Manager, Project Quality Assurance (QA) Manager, and PNNL Project Manager. A corrective action will be agreed upon based on the critical/non-critical nature of the parameter, it will be documented in the field log, and the action will be communicated to the sampling team. In general, if critical measurements or samples cannot be collected, then sampling will be re-scheduled. If a non-critical measurement or sample cannot be collected, then the deviation will be documented.

3.1 OUBM Sediment Monitoring

Samples will be collected by the 2010 OUBM in accordance with procedures that are detailed in the OUB Marine Monitoring Plan (URS 2002b; see Figure 11 and Figure 12). ENVVEST will provide the contractor with 16 oz. pre-cleaned glass jars with Teflon liners. The contractor will provide one aliquot of homogenized composite sediment sample from each grid cell to ENVVEST clearly labeled. ENVVEST will split this aliquot into a pre-cleaned plastic container for metals and pre-cleaned glass jar for organics as part of the OUBM sediment sampling.

3.2 Sediment Quality Verification

Surface grab samples and two types of short sediment cores will be collected for SQV studies by the Navy divers. The depth of the water and debris near the piers and shoreline may result in potential difficulties collecting sediment with traditional grab sampler. Therefore, we anticipate using a Navy dive team for sample collection. The divers will be given 16 oz. pre-cleaned amber glass jars for the 0-10 cm grabs, 40 cm cellulose acetate butyrate (CAB) plastic core tubes with caps for the short cores, and a specialized 60 cm squeeze core for the collection of porewater at two locations. Due to the many obstacles generally encountered in the Shipyard, there are several contingency plans. Sample collection near outfalls and piers is the priority. In the event that the sample is primarily sand, divers will be instructed to move from the position and resample. If the sample is primarily shell hash, divers will be instructed to try to “sweep” shell hash from surface and resample. Sediment from each station will be analyzed individually (e.g., samples will not be composited).

The sites to be sampled are shown in figures Figure 17 to Figure 23. Station coordinates will be recorded using a handheld global positioning system (GPS). All samples will be analyzed for Hg, TOC, and screened for Cu, Pb, Zn, PAH, and PCB as discussed above. A list of 20-25% will be selected for confirmatory analysis as discussed for the OUBM samples. The only exception is the squeeze core sediment sections will be confirmed for all the metal and organic parameters.

Sampling at each site will consist of six surface grabs and one 0-25 cm CAB core profile. In addition, 3 sites will be sampled for toxicity evaluation (see below), and two sites will be sampled with the squeeze core to obtain pore water for analysis. The squeeze cores (9 cm I.D.) will be collected by divers using specialized polycarbonate core liner fitted with sampling ports at 1-cm intervals. Porewater will be extracted from intact sediment cores using a modification of the whole core squeezing technique originally described by Jahnke (1988) with modified described by Warken et al. (2000; Figure 25). In summary, the core barrels are constructed of polycarbonate into which threaded ports were drilled at 1 cm intervals. The nylon end caps used contain a valve to allow pressurization from the top of the core. Nitrogen gas is used to pressurize the cores to 10 to 12 psi to limit sampling artifacts (i.e., drawdown of overlying water, channeling within the core, vertical replenishment, and cell lysis). The porewater will be extracted at intervals of 2.5 cm down to 10cm then 5 cm down to 20cm to allow sufficient volume without vertical displacement of the interface and dilution of the top-most sample. A syringe fitted with a Porex rod, Teflon tubing, and a leur fitting is threaded into each port. The Porex rod is cut so that upon insertion it extended half way into the core, approximately 5 cm, and was attached to the leur by a small piece of Teflon tubing, preventing the sampling of pore water close to the core wall. Pore water is extruded through the Porex rod and collected in a 10-ml all-plastic syringe. The porewater will be filtered through a 0.45 µm PVDF filter for metals and dissolved sulfide and an ashed glass fiber filter (GFF) for DOC. The metals will be filtered into a Teflon bottle and preserved to 0.2% double distilled nitric acid, dissolved sulfide will be placed in a separate 60mL Teflon bottle and immediately preserved with zinc acetate, and the DOC will be stored frozen in an ashed amber glass vial. Volumes will be limited and sampling priority order is metals (4 mL), DOC (3 mL), and dissolved sulfide (3 mL).

Sediment cores will then be sliced at the following intervals: 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-20 cm and stored in precleaned glass jars for organics and tared polypropylene vials for metals. It is anticipated each core will yield approximately 12 sections. The depth of core segmenting will depend on the depth of core penetration and the consolidated nature of the sediment core.

3.3 Toxicity Evaluation Samples

Divers will be used to collect intact cores from the sampling locations. In this case divers will insert core tubes into the top 5-10 cm of sediment, cap the top of the core with at least 2 cm of overlying water, remove core tube from the sediment and cap the bottom of the core tube and bring to the surface without disturbing the sediment. Replicate cores will be taken within 20x20 cm location on the bottom, which is about the same size as the box core. Following core removal, the top 5cm remaining of the 20x20cm location will be also sampled to obtain about 4L (1 gallon) of sediment for homogenization. Only the top 5 cm of the core tubes will be used in the bioassays. The replicates cores tubes will be processed in the same manner as the cores tubes from the box core

3.4 Sample Containers and Labels

The sediment from each station will be split into various labeled jars for 1) SSC screening analysis, 2) grain size, 3) TOC, 4) Metals, etc. Each container will be labeled with waterproof, adhesive-back tape or labels and waterproof ink. Sample labels will provide sufficient detail to uniquely identify each sediment sample and allow tracking to field activities. Sample identification numbers will be in the format: **SQV001-xxx** to indicate the sediments were sampled during a particular SQV event (e.g. event SQV001 will be Special Studies, 002 Dry Dock Silt, etc.) and xxx is a unique 3-digit sequential number. The grab and sediment core sampling planned for April 2011 will be SQV-005. Sample labels will include this unique sample identification number, date and time of collection, sample collector's initials, and container number. An example is provided below.

Survey ID: SQV005
Area : SQVPS03
Unique Sample ID: SQV005-_ _ _
Aliquot Code:_______________ **Sample Type: grab or core**
Date: __________ Time: ___________
Sample Collector:__________________

3.5 Field Documentation

A daily record of all field activities will be recorded on a Field Daily Log Form. A grab sample collection form will be completed for each station that is visited. Sample documentation will include, at a minimum, the following information: station ID, GPS determined location, date and time of sample collection, recorder's initials, water depth, sediment characteristics, collection method (diver grab or core, etc.) and any other relevant observations. All field sampling forms will be completed using indelible ink, and data recording and documentation errors will be corrected as follows: 1) draw a single line through the error, 2) make the correction, and 3) initial, date, and provide justification for the error correction.

3.6 Decontamination Procedures

Field personnel will wear Nitrile® gloves during sample collection activities, and will change gloves between stations. Surface sediment sample cross-contamination will be avoided by using new equipment for each sample or cleaning equipment thoroughly between sampling stations, and collecting only sample material that is not in direct contact with sample collection equipment. If a grab sampler is used it will be scrubbed with a stiff brush and thoroughly rinsed with site water at the beginning of each day and between each sampling station. Utensils such as stainless steel spoons or spatulas used to collect sediment from the samplers will be precleaned (soap/water washed, rinsed 3x using deionized water, air dried, and methylene-chloride-rinsed) and packaged in Ziploc bags prior to use in the field. Utensils will not be reused once the sediment sample has been collected. Equipment blanks will not be collected as part of this study, because sediment used for chemical analysis will contact only pre-cleaned surfaces.

3.7 Disposal of Contaminated Sediments

Field sampling and sample preparation activities will be conducted so as to minimize generation of waste materials. All solid waste will be bagged or otherwise contained prior to disposal in standard refuse containers (dumpsters). In the field, sediment and rinse water from sampling equipment will be washed overboard. Flammable solvent waste will not be generated in the field; any solvent waste generated in the laboratory will be contained in appropriately labeled containers and disposed of in compliance with state and federal waste handling regulations. Wastewater generated during sample preparation of sediment samples at the MSL will be managed in compliance with a project-specific wastewater treatment plan as required by that facility. No excess sediment is expected to be generated, as only sufficient sample for the proposed analyses and archiving will be retained in the field.

4.0 Sample Handling Procedures

4.1 Sample Storage Requirements

Sample holding conditions and recommended holding time limits (HTLs) are defined in Table 10. HTLs will be calculated from the time of sample collection unless archive at -18°C and then it will be calculated from first thaw. The HTLs specified in this table are routine, generally accepted HTLs and laboratories will endeavor to meet these HTLs. However, all project participants recognize that the ability of the participating laboratories to meet these HTLs will also be affected by the workload caused by submitting a large number of samples to a laboratory all at once, which can not be controlled because all samples need to be held until the screening analyses are completed. Documentation must be sufficient to track sample holding, processing, and analysis times to ensure that HTLs are met. Sample must be held in a controlled area with limited access and deviations from the defined storage requirements must be documented and reported with the data even if alternative HTLs are required due to archiving samples**.**

Table 10. Sample Containers, Sample Size, Preservative Requirements, and Holding Time for Analytical Samples.

Parameter	Container Type [a]	Minimum Sample Size	Notes	Sample Preservative	Holding Time
Sediment					
Metals – XRF Screening Organics Screening	G	8-oz	¾ full	4°±2°C or frozen	1 year
PAH, PCB - GCMS	G	8-oz	¾ full	Freeze, -18ºC	1 year
TOC	G	4-oz	¾ full	Freeze, -18ºC	1 year
Grain Size	P	2-oz	¾ full	4°±2°C	1 year
AVS/SEM	G	8-oz	no headspace	4°±2°C	14 days[b]
Metals – Quantitative	P	4-oz	¾ full	Freeze, -18ºC	1 year
Porewater					
Hg + ICP-MS	T	4 mL	#1 priority	0.2% nitric acid	90 days
DOC	G	3 mL	#2 priority	Freeze, -18ºC	1 year
Dissolved Sulfide	T	3 mL	#3 priority	Zinc Acetate	14 days[b]

a. Container Type: G = pre-cleaned glass with Teflon-lined lid, P= acid-cleaned, tared polypropylene, T = Teflon

b. The holding time may be extended if the samples are frozen and the oxidized layer is removed prior to analyses.

4.2 Chain-of-Custody Procedures

Sample custody records are the administrative records associated with the physical possession and/or storage history of each individual sample from the receipt of each sample, final analytical result, and sample disposal. Sample custody will be documented throughout the life of the sample. Samples should not be left unattended unless properly secured. Sample custody procedures in the field and laboratory will be in accordance with the PNNL SOP MSL-A-002, *Sample Chain-of-Custody (COC)*. The sample custody form provides a record of the samples collected and analyses requested. The custody of the samples as they are transferred from field to laboratory must be documented.

Each analytical laboratory must have a formal, documented system designed to provide sufficient information to reconstruct the history of each sample, including preparation of sampling containers, sample collection and shipment, receipt, distribution, analysis, storage or disposal, and data reporting within the laboratory.

The custody form summarizes the samples collected and analyses requested. Each COC will be signed by the person relinquishing samples. The receiving laboratory will verify that all samples present in the shipping containers are listed on the COC and that sample descriptions, requested analytical methods, and sampling dates are legible. The original COC will accompany the samples and the shipper will keep a copy. Any discrepancies will be noted on the form (in addition to any internal laboratory documentation policy) and the sample receiver will immediately contact the project manager to report missing, broken, or compromised samples (e.g. cooler temperature outside recommended range).

4.3 Sample Delivery to Analytical Laboratories

The sediment samples along with the appropriate COC will be delivered by the field sampling team to Battelle Pacific Northwest National Laboratory (PNNL), Marine Science Laboratory (MSL). Samples will remain in coolers with ice until delivered to the laboratory. Sediment samples for MSL will be delivered to:

Carolynn Suslick, Sample Custodian
1529 West Sequim Bay Road
Sequim Washington 98382
(360) 681-3624

Sediment samples for screening analysis will be sent to the SSC laboratory in San Diego, California. Samples will be delivered to:

Mr Joel Guerrero, Code 71751
SPAWARSYSCEN
53605 Hull St.
San Diego, CA 92152-5410
619 553-1395

The samples for ancillary parameters (e.g. TOC) analysis will be sent to Columbia Analytical Services (CAS), Kelso, Washington. Samples will be delivered to:

Mr. Howard Holmes
Columbia Analytical Services, Inc.
1317 South 13th Avenue
Kelso, WA 98626
(360) 501-3364

Samples will be packaged and shipped in accordance with the procedures in the MSL SOP MSL-A-001, *Sample Log-In Procedure*, and MSL-A-002, *Sample Chain of Custody*. Samples must be preserved (chilled) as soon as possible after collection.

Receipt of samples at MSL will also follow MSL-A-001 and MSL-A-002. Immediately upon receipt by a laboratory, the condition of samples must be assessed and documented. The contents of the shipping container must be checked against the information on the custody form for anomalies. If any discrepancies are noted, or if laboratory acceptance criteria or project-specific criteria are not met, the laboratory must contact the Field Manager for resolution of the problem. The discrepancy, its resolution, and the identity of the person contacted must be documented in the project file. The following conditions may cause sample data to be unusable and must be communicated to the laboratory team leader:

- The integrity of the samples is compromised (*e.g.,* leaks, cracks, grossly contaminated container exteriors or shipping cooler interiors, obvious odors, etc.);
- The identity of the container cannot be verified;
- The proper preservation of the container cannot be established;
- Incomplete sample custody forms (*e.g.,* the sample collector is not documented or the custody forms are not signed and dated by the person who relinquished the samples);
- The sample collector did not relinquish the samples; or,
- Required sample temperatures were not maintained during transport.

The custodian must verify that sample conditions, amounts, and containers meet the requirements for the sample and matrix (Table 10). A unique sample identifier must be assigned to each sample container received at the laboratory, including multiple containers of the same sample.

5.0 Laboratory Analytical Methods

5.1 Sediment Screening and Confirmatory Methods

The screening and laboratory confirmation analytes and methods were discussed in detail in previous verification studies (Kohn et al. 2004, 2006, 2008). Two types of analyses will be conducted on the sediment from this study: 1) screening analysis using XRF and immunoassays and 2) quantitative analysis. For the OUBM Sediment Monitoring Study all sediment samples collected by the 2010 OUBM will be screened by the SSC laboratory for Cu, Pb, Zn, and tPAHs followed by a subset of samples submitted for confirmatory analyses. Confirmatory analyses will include metals listed in Table 11and PAHs listed in Table 12. For the Sediment Impact Zone and Focus Area Studies, the sediment will be screened and then submitted for confirmatory analyses for all metals plus Hg, PAHs, and PCBs identified in those tables. The methods, reliable detection limits, SQS, and MCUL are summarized in Table 11.

Sample aliquots for XRF screening will be homogenized and analyzed directly using modified EPA Method 6200 (EPA, 1998) described in SSC SOP SSC-SD. The screening analyses method for PAHs will be an ELISA methods. Sample aliquots for tPAH screening will be extracted with methanol and measured by immunoassay techniques using a modification of EPA Method 4035 (EPA, 1996). Sample aliquots for PCB screening will be extracted with methanol and measured by immunoassay techniques using a modification of EPA Method 4020 (EPA, 1996). The screening method reports only total PCBs and PAHs rather than individual constituents.

Table 11. Reliable detection limits of XRF screening method compared with state sediment management standards for ENVVEST metals of concern.

Analyte	Units	Reliable Detection Limit for XRF	Method	Method Detection Limits [a]	Washington State Sediment Management Standards	
					SQS	MCUL
OUBM Sediment Monitoring Study Metals						
Al	mg/kg dry wt	N/A	ICP-OES	2	none	none
Ag	mg/kg dry wt	10.0	ICP-MS	0.01	6.1	6.1
As	mg/kg dry wt	20.0	ICP-MS	0.2	57	93
Cd	mg/kg dry wt	5.0	ICP-MS	0.003	5.1	6.7
Cr	mg/kg dry wt	100	ICP-OES	0.2	260	270
Cu	mg/kg dry wt	18.0	ICP-MS	0.1	390	390
Ni	mg/kg dry wt	50.0	ICP-OES	0.3	none	none
Pb	mg/kg dry wt	8.0	ICP-MS	0.005	450	530
Zn	mg/kg dry wt	16.0	ICP-OES	0.2	410	960
SQV Studies (above plus)						
Hg	mg/kg dry wt	N/A	DMA	0.0016	0.41	0.59

a. The MDL study was conducted in compliance with 40 CFR Part 136 Appendix B Revision 1.11, which entails the analyses of at least seven replicates of the matrix (quartz sand) to calculate the MDL value.

Table 12. Detection and Reporting Limits for Organic Analytes, ENVVEST Organics Verification Study

Analytes	Laboratory Values for Sediment Analysis	
	Method Detection Limit (µg/kg dry wt)	Reporting Limit (µg/kg dry wt)
PAHs		
Naphthalene	0.28	4
2-Methyl naphthalene	0.54	4
Acenaphthylene	0.45	4
Acenaphthene	0.43	4
Fluorene	0.54	4
Phenanthrene	0.70	4
Anthracene	0.76	4
Fluoranthene	0.62	4

Pyrene	0.60	4
Benzo(a)anthracene	0.55	4
Chrysene	0.66	4
Benzo(a)pyrene	0.81	4
Total Benzofluoranthenes	NA[a]	NA
Indeno(1,2,3-c,d)pyrene	1.05	4
Dibenz(a,h)anthracene	0.80	4
Benzo(g,h,i)perylene	0.89	4
PCBs		
PCB Congeners (NOAA NS&T 20 congeners)	0.075	0.4

a. Not available for sum, typically analyzed via GC/MS (MSL-O-015).

Samples selected for confirmatory metals analyses will be freeze-dried and homogenized using a ball-mill prior to digestion according to Battelle SOP MSL-C-003, Percent Dry Weight and Homogenizing Dry Sediment, Soil and Tissue. The homogenized sediment will be analyzed for total Hg according to SOP MSL-I-034, Direct Determination of Total Mercury in Tissues and Sediments by Thermal Decomposition, Gold Amalgamation and Cold Vapor Atomic Absorption Spectrometry (DMA), EPA Method 7473m (modified). An approximately 20-mg aliquot of each dried, homogeneous sample will be heated in a controlled decomposition furnace flushed with oxygen to liberate Hg from solid and aqueous samples. The decomposition and catalyst furnaces maintain a temperature of at least 750˚C. The decomposition products are then carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to a gold amalgamator that selectively traps Hg. The amalgamator is rapidly heated, releasing elemental Hg vapor, which is then detected by atomic absorption spectrophotometer (AAS).

For all other metals sediment samples will be digested in accordance with Battelle SOP MSL-I-006, Mixed Acid Sediment Digestion. An approximately 300-mg (dry weight) aliquot of each sample will be combined with nitric, hydrochloric, and hydrofluoric acids in a Teflon digestion vessel and heated in an oven at 130ºC (±10ºC) for a minimum of eight hours. After cooling, boric acid will be added to the digestate to neutralize the hydrofluoric acid and deionized water added to achieve analysis volume.

Digested samples will be analyzed for Al, Cr, Ni, and Zn using inductively coupled plasma optical emissions spectroscopy (ICP-OES) according to Battelle SOP MSL-I-033, Determination of Elements in Aqueous and Digestate Samples by ICP-OES. This procedure is based on two methods modified and adapted for analysis of low level samples: EPA Method 6010B and 200.7.

Digested samples will be analyzed for Ag, As, Cd, Cu, and Pb using inductively coupled plasma-mass spectrometry (ICP-MS) according to Battelle SOP MSL-I-022, Determination of Elements in Aqueous and Digestate Samples by ICP/MS. All results will be reported in units of µg/g on a dry-weight basis.

The MSL will perform clean-up procedures according to the low-level methods developed for the National Oceanic and Atmospheric Administration (NOAA) Status and Trends Program (Lauenstein and Castillo 1993). Analysis of organic analytes will be according to the MSL SOPs

MSL-O-015 (Identification and Quantification of Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry Following EPA Method 8270B Quality Control Criteria) and MSL-O-016 (Analysis of PCBs and Chlorinated Pesticides by Gas Chromatography with Electron Capture Detection Following EPA METHOD 8080A Quality Control Criteria). Both MSL methods are modifications of SW-846 EPA Methods 8270B and 8080A. Specific analytes and their respective detection and reporting limits are provided in Table 12. Results will be reported in units of µg/kg for each sample and normalized to the TOC.

For the verification study the TOC and grain size data will be provided by the 2010 OUBM. For the other sediment studies TOC will be analyzed by CAS following Method ASTM D4129-82 M. The analyses will observe the following QC procedures:

1. Method Blank: analyze a method blank at a rate of 1:20 samples, do not blank correct data; level <20x lowest sample.
2. Precision: Duplicate sample analyzed at a rate of 1:20 samples; RPD ≤ 20%;
3. Reference Material: Reference sample analyzed at a rate of 1:20 samples; Recovery Range 85-115%
4. Matrix spike/matix spike duplicate: MS/MSD analyzed at rate of 1:20 samples; Recovery range 75-125% and RPD ≤ 20%.

5.2 AVS/SEM

Sediment samples will be extracted and analyzed for AVS in accordance with MSL SOP MSL-C-001. This procedure is based on a peer-reviewed, published procedure for the analysis of AVS in sediment and dissolved sulfide in aqueous samples, which was adopted from a draft USEPA Method (Allen et al. 1991.). In this method, sulfide in the sample is converted to hydrogen sulfide by the addition of hydrochloric acid at room temperature. The hydrogen sulfide (H_2S) is purged from the sample by an inert gas and trapped in a sodium hydroxide (NaOH) solution. With the addition of a mixed-diamine reagent (MDR), the sulfide is converted to methylene blue and measured on a spectrometer. The AVS results will be reported in units of µmole/g on a dry-weight basis.

The SEM extracts will then be analyzed for Cd, Cu, Ni, Pb, and Zn by ICP-MS in accordance with SOP MSL-I-022.The analysis guidelines for this procedure are adapted from USEPA Method 1638 Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry. The SEM extract will also be analyzed for total Hg by Cold Vapor Atomic Fluorescence (CVAF) following EPA Method 1631 revision E. The SEM metal solution concentrations will be determined in units of µg/L and then converted to µg SEM/g of sediment extracted for AVS. These data are further converted to µmole/g for each SEM metal.

5.3 Porewater

Porewater will be analyzed for the SEM metals plus iron (Fe), manganese (Mn), and dissolved sulfide. The porewater will be analyzed at a dilution to provide sufficient volume for the analyses of metals by ICP-MS, Hg, dissolved sulfide, and DOC. Analytical methods for the metals are described above. The dissolved sulfide will be analyzed following MSL SOP MSL-C-001 and the DOC will be analyzed by high temperature combustion methods modified from Spyres et al. (2000).

6.0 Quality Assurance and Quality Control Requirements

This section defines the quality assurance (QA) program that will be applied to all the sediment studies. Appropriate field and laboratory quality control (QC) procedures are designated in order to assess data quality through the measures of accuracy and precision. If data fall outside the specified accuracy or precision criteria defined for a procedure or measurement, or if problems affecting comparability are identified, the field or laboratory team leader must contact the PNNL QA Manager to discuss options available for rectifying the out-of-control situation. The Navy Program Manager, PNNL QA Manager, PNNL Project Manager will have final authority on decisions made to address problems.

6.1 Measurement and Data Definitions

Accuracy is defined as the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations.
Precision is defined as the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative terms.

Completeness is the amount of data collected as compared to the amount needed to ensure that the uncertainty or error is within acceptable limits. The goal for data completeness is 100%. However, the project will not be compromised if 90% of the samples collected are analyzed with acceptable quality.

Comparability is a measure of the confidence with which one data set can be compared to another. This is a qualitative assessment and is addressed primarily in sampling design through use of comparable sampling procedures or, for monitoring programs, through accurate re-sampling of stations over time. In the laboratory, comparability is assured through the use of comparable analytical procedures and ensuring that project staff is trained in the proper application of the procedures. Study comparability will be assessed through analytical performance (results from the analysis of QC samples), especially those that assess accuracy (standard reference materials, matrix spikes).

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population. This is a qualitative assessment and is addressed primarily in the sample design, through the selection of sampling sites, and procedures that reflect the project goals and environment being sampled. It is ensured in the laboratory through (1) the proper handling, homogenizing, and storage of samples and (2) analysis within the specified holding times so that the material analyzed reflects the material collected as accurately as possible.

Sensitivity is the capability of a test method or instrument to discriminate between measurement responses representing different levels (*e.g*., concentrations) of a variable of interest. Sensitivity is addressed primarily through the selection of appropriate analytical methods, equipment, and instrumentation. The methods selected for the Metals Verification Study were chosen to allow analysis of a large number of samples yet provide the sensitivity required for the end-use of the data. This is a quantitative assessment and is monitored through the instrument calibrations and calibration verification samples and the analysis of procedural blanks with every analytical batch.

Method Detection Limits (MDLs) must be determined annually through an MDL Verification Study or full MDL study according to MDL SOP Q-007.

Reporting Limits (RLs) for trace metals are calculated by multiplying the target analyte MDL by 3.18. The value 3.18 is based on the Student's *t*-value for 7 to 10 replicates, the number of replicates usually analyzed to generate the MDL. The standard practice for PAHs is to use the lowest standard as the RL. The data qualifier "J" will be added to any reported values that are less than the RL.

6.2 QA/QC for Field Sampling

Field sampling as outlined in this plan is designed to assess sampling reproducibility. If sampling requirements cannot be met due to sampling or measurement system failure, field conditions or other factors that cannot be controlled, corrective action will be discussed with the PNNL Project Manager, PNNL QA Manager, and ENVVEST Program Manager. A corrective action plan will be agreed upon based on the critical/non-critical nature of the parameter, it will be documented in the field log, and the action will be communicated to the sampling team. In general, if critical measurements or samples cannot be collected, then sampling will be re-scheduled. If a non-critical measurement or sample cannot be collected, then the deviation will be documented. The PNNL QA Manager will review corrective actions to assess their effectiveness. Any deviations from the SAP will be documented.

6.3 QA/QC for Chemical Analyses

The study design and QC samples are intended to assess the major components of total study error, which facilitates the final evaluation of whether environmental data are of sufficient quality to support the related decisions. The QC sample requirements are designed to provide measurement error information that can be used to initiate corrective actions with the goal of limiting the total measurement error. The QC samples and frequency applicable to analytical chemistry laboratories are detailed in Table 13. Measurement quality objectives for the analyses can be expressed in terms of accuracy, precision, completeness, and sensitivity goals. Accuracy and precision are monitored through the analysis of QC samples. Table 14 defines the required accuracy and precision for QC samples, along with corrective actions that must be implemented when QC criteria are not met. Table 15 provides formulas for the calculation of QC sample assessment statistics. All QC sample failures and associated corrective actions will be documented. If data must be reported with failing QC results, then data qualifiers will be assigned to the QC sample data. Table 15 defines project data qualifiers.

Table 13. Definitions, Requirements, and Frequency for Laboratory Quality Control Samples

QC Sample	Definition	Frequency
Method or Procedural Blank (MB)	A combination of solvents, surrogates, and all reagents used during sample processing, processed concurrently with the field samples. Monitors purity of reagents and laboratory contamination.	1/sample batch[a] All analytes
Standard Reference Material (SRM)	An external reference sample which contain a certified level of target analytes; serves as a monitor of accuracy. Extracted and analyzed with samples of a like matrix.	1/ sample batch[a] Analyzed for metals
Matrix Spike (MS) [b]	A field sample spiked with the analytes of interest is processed concurrently with the field samples; monitors effectiveness of method on sample matrix; performed in duplicate for sediments. An MS must be processed for each distinct matrix.	1/sample batch[a] Analyzed for metals
Duplicate Sample	Second aliquot of a field sample processed and analyzed to monitor precision; each sample set should contain a duplicate.	1/sample batch[a] All analytes
Recovery Internal Standards (RIS)	All field and QC samples are spiked with recovery internal standards just prior to analysis; used to quantify surrogates to monitor extraction efficiency on a per sample basis.	Each sample analyzed for organic compounds
Surrogate Internal Standards (SIS)	All field and QC samples are spiked with a known amount of surrogates just prior to extraction; recoveries are calculated to quantify extraction efficiency.	Each sample analyzed for organic compounds

a. A batch is defined as 20 field samples or less processed simultaneously and sharing the same QC samples.
b. Non-Navy samples may not be substituted to meet this requirement.

Table 14. Measurement Quality Criteria

QC Parameter	Acceptance Criteria	Corrective Action
Accuracy		
• *Method Blank (MB)*	B or B<MDL If B>MDL and <RL[1], then perform corrective action	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action.
(For this table, MB or EB = B)	B or B<MDL If B>MDL and >RL; sample values > 10X B, then perform corrective action	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
	B<MDL If B>MDL and >RL; sample values ≤10X B, then perform corrective action	Perform corrective action as above and re-process (extract, digest) sample batch. If batch cannot be re-processed, notify client and flag data.
	XRF Instrument Blank (quartz): Sample values >10X MB	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
	Immunoassay MEOH Instrument Blank: Sample values >10X MB	Review data and analysis for possible sources of contamination. Reanalyze and/or document corrective action. Data must be flagged.
• *Standard Refernce Material (SRM)*	Organic compounds: Average PD ≤30%; ≤35% for each analyte. Metals: ≤20% PD. XRF (PACS-1 and/or PACS-2): ≤20% PD Determined vs. certified range. Analyte concentration must be 10xMDL to be used for DQO.	Review data to assess impact of matrix. Reanalyze sample and/or document corrective action. If other QC data are acceptable then flag associated data if sample is not reanalyzed.

QC Parameter	Acceptance Criteria	Corrective Action
• *Matrix Spike (MS)/MS Duplicat (MSD)*	Organic compounds: 40 - 120% recovery Metals: 70 - 130% recovery	Review data to assess impact of matrix. If other QC data are acceptable and no spiking error occurred, then flag associated data. If QC data are not affected by matrix failure or spiking errors occurred, then re-process MS. If not possible, then notify client and flag associated data.
• *Surrogate Spike (SIS)*	Organic compounds: 40 - 120% recovery	Review data. Discuss with Project Manager. Reanalyze, re-extract, and/or document corrective action and deviations.
• *Laboratory Control Sample (LCS)*	Organic compounds: 40 - 120% recovery Metals: 70 - 130% recovery Immunoassay (Aroclor 1254 and Phenanthrene): ±20% Recovery	Perform corrective action. Re-analyze and/or re-process sample batch. Batch data associated with failed LCS (LCS data outside control limits) cannot be reported. If batch cannot be re-processed: notify client, flag data, discuss impact in report narrative.
• *Instrument Check*	Organic compounds: 85 - 115% recovery	Perform corrective action. Re-analyze and/or re-process sample batch. Data outside control limits cannot be reported. If batch cannot be re-processed, notify client, flag data, discuss impact in report narrative.
Precision: *Laboratory Duplicates*	Organic compounds (MSD): <30% RPD Metals: <30% RPD XRF: <20% RPD Immunoassay Extraction duplicate <30% RPD Immunoassay Assay duplicate <30% RPD	Review data to assess impact of matrix. If other QC data are acceptable, then flag associated data. If QC data are not affected by matrix failure, then re-process duplicate. If not possible, then notify client and flag associated data.

a. See abbreviation definitions

Table 15. Calculation of Quality Control Assessment Statistics

Percent Recovery

The percent recovery is a measurement of accuracy, where one value is compared with a known/certified value. The formula for calculating this value is:

$$Percent\ Recovery = \frac{amount\ detected}{amount\ expected}\ x\ 100$$

Percent Difference

The percent difference (PD) is a measurement of precision as an indication of how a measured value is difference from a "real" value. It is used when one value is known or certified, and the other is measured. The formula for calculating PD is:

$$Percent\ Difference = \frac{X_2 - X_1}{X_1}\ x\ 100$$

where: X_1 = known value (*e.g.*, SRM certified value)
X_2 = determined value (*e.g.*, SRM concentration determined by analyst)

Relative Percent Difference

The relative percent difference (RPD) is a measurement of ***precision***; it is a comparison of two similar samples (matrix spike/matrix spike duplicate pair, field sample duplicates). The formula for calculating RPD is:

$$RPD = \left| \frac{2\ x\ (X_1 - X_2)}{(X_1 + X_2)} \right|\ x\ 100$$

where: X_1 is concentration or percent recovery in sample 1
X_2 is concentration or percent recovery in sample 2

Note: Report the absolute value of the result -- the RPD is always positive.

Relative Standard Deviation

The relative standard deviation (RSD) is a measurement of ***precision***; it is a comparison of three or more similar samples (*e.g.*, field sample triplicates, initial calibration, MDLs). The formula for calculating RSD is:

$$\%RSD = \frac{Standard\ Deviation\ of\ All\ Samples}{Average\ of\ All\ Samples}\ x\ 100$$

Table 16. ENVVEST Data Qualifiers.

#	Outside Project DQO guidelines for SIS recovery (40-120%)
*****	Associated Surrogate recovery exceeded guidelines (40-120%)
&	Outside Project DQOs for Spike Recovery (40-120% recovery) or Replicate Analysis (≤30% RPD) or SRM (<30% difference)
E	Estimate; see narrative
ME	Estimate due to matrix effect; see narrative
D	Results determined from dilution
T	Hold time exceeded; see narrative
NC	Not able to calculate
NR	No result reported; see narrative
NS	Sample not spiked
NA	Not applicable/available
A	Result is most likely an outlier; see narrative
B	Analyte detected in the method blank above the RL, sample concentration < 10 times detected blank value.
U	Analyte not detected at or above the laboratory achieved detection limit, MDL reported
J	Analyte concentration is less than the RL, but greater than the MDL
c	Exceeds Project DQO but meets contingency criteria
R	Data exceeds calibration range; see narrative for data use limits
N	Spiked sample recovery outside QC criteria of 70-130% recovery
&	Accuracy result outside QC criteria of ≤ 20% PD
*****	Precision result outside QC criteria of < 30% RPD

6.4 Data Quality Review Procedures

Data quality review includes data verification, validation, and oversight, as well as reconciliation of the data quality with user requirements. The data verification process includes the initial review of the data packages to ensure that the analyses requested have been provided. Data validation is the process of reviewing data and accepting, qualifying, or rejecting data on the basis of sound criteria. Data will be reviewed by the Chemistry Task Leader to assure that it is complete. The data report for quantitative metals analysis will be submitted by the Chemistry Task Leader to the PNNL QA Manager for QA review. All QA review comments and corrective actions will be resolved before the final data report and narrative is provided to the client. The PNNL QA Manager will conduct project reviews frequently enough to ensure that the work is being conducted according to the SAP and SOPs, and that corrective action plans are implemented to address any deficiencies identified. They will conduct laboratory inspections as appropriate, and data audits to ensure that data quality meets project requirements.

6.4.1 Electronic Data Deliverables (EDDs)

Electronic data deliverables (EDDs) are generally reviewed based on client-provided specifications. The EDD architecture is defined by ENVVEST. Client specifications for EDDs should be provided to the reviewer prior to or at the time the review is requested. Levels of EDD review depend on the complexity of the array of information, the number of samples and analytes, and client-specified requirements. At PNNL, the EDD is generated from an Excel version that has previously been submitted for QA review and all issues resolved. The EDD will be subject to a 10% verification to ensure all fields are populated, there was no skewing of the data when converted to EDD format, and overall review of valid values. The general approach is to review all rows and columns, especially at breakpoints, for accuracy, completeness, and range and reasonableness of the data. Discrepancies will be resolved following the processes previously described above. EDDs will not be provided to clients without prior review. Staff who prepare EDDs are not allowed to review their own work.

6.4.2 EIM Reporting

All final data from this project will also be formatted for submittal to Ecology's EIM database.

6.5 Instrumentation/Equipment Testing, Inspection, and Maintenance

Field Equipment. The Navy will provide field equipment, instruments, the boat(s), GPS, and other supplies for the field-sampling program. The GPS used to determine actual sampling station coordinates will be inspected and tested prior to use in the field. The GPS manual or SOP must be available in the field. Any problems with the operation of these units must be documented, along with corrective action and the results of performance verification. Sampling station coordinates will be reported in Universal Transverse Mercator (UTM) grid coordinates (decimal degree) to the USGS 1983 North American Datum (NAD 83). Note that all GPS positions will be recorded onboard the vessel or surface location of where the sediments are collected.

Laboratory Equipment. All analytical instruments and equipment are to be maintained according to SOPs and the manufacturers' instructions. Equipment and instrument maintenance and frequency are defined in SOPs and are summarized in Table 17 and Table 18. All routine maintenance and non-routine repairs are to be documented in a bound logbook. The information recorded should include analyst initials, date maintenance was performed, a description of the maintenance activity, and (if the maintenance was performed in response to a specific instrument performance problem) the result of re-testing to demonstrate that the instrument performance had been returned to acceptable standards prior to re-use. The return to analytical control is demonstrated by successful calibration.

Table 17. Maintenance Procedures for General Laboratory Equipment

Equipment	Activity	Frequency
Deionized water system	Replace seals Replace cartridges	As needed for leaks and to maintain resistivity > 18 mOhms
MilliQ deionized water system	Replace seals Replace cartridges	Every 6 months or as needed for leaks and to maintain resistivity > 18 mOhms
Electronic balances	Clean	As needed
Freezers/refrigerators	Clean Defrost	As needed

Ovens	Clean	As needed
Glass thermometers	Store in protective case	Always except when in use
Digital thermometer	Avoid bending thermocouples	Always

Table 18. Maintenance Procedures for Analytical Instruments

Equipment	Activity	Frequency
ICP-MS Maintenance		
Argon supply	Check and record; replace as needed	Daily
Vacuum	Check and record	Daily
Cooling chiller	Check and record temperature	Daily
Nebulizer flow	Check and adjust	Daily or as needed
Sensitivity and stability	Check and record	Daily
Auto sampler tubing	Change	As needed
Cones	Clean or change	As needed
ICP-OES Maintenance		
Pump tubing	Check and replace	Daily
Diluent bottle	Check and refill	Daily
Torch	Check and clean or replace	Weekly
GC/MS Maintenance		
Rough pumps Turbomolecular pump Diffusion pumps	Routine service (service contract) Check fluid levels	Six months Weekly
Foreline traps Helium gas traps	Inspect trap pellets for color change Replace adsorbent pellets	Routinely 6-12 months, as needed
Injection port septum	Replace	As needed to maintain EPC pressure
Injection port liners	Replace	Approximately every 30-40 samples
Precolumn	Replace	As needed to improve peak shape, resolution, or sensitivity
Calibration vial (PFTBA)	Refill	4 months or as needed
Back grills of the MS	Vacuum dust	6 months or as needed
Ion source	Clean	As indicated when usage-dependent surface deposits degrade ion source function
GC Maintenance		
Injection port	Replace	Weekly (~50 injections) or as needed
Injection port liner	Replace	Weekly or as needed

Equipment	Activity	Frequency
Injection port	Clean	Monthly or as needed
Column	Clip	As needed to maintain performance
Precolumn	Replace	As needed when chromatographic degradation is observed
Gas cylinders	Replace	When PSI is < 300
Autosampler rinse vial	Fill	Prior to analysis
Autosampler syringe	Replace/align	As needed
Ferrule	Replace	As needed for leaks
Gas drying/purification traps	Replace	Annually or as needed
Column, detector	Bakeout	As needed
SSC Instruments for Immunoassay Screen		
Lamp	Check linearity	Daily with standard series
SSC Instruments for XRF Screen		
Energy	Check calibration	Daily
Cu-stability	Check stability	Bi-monthly

7.0 Data Analysis, Record Keeping, and Reporting Requirements

7.1 Analysis of Sediment Chemistry Data

Laboratory documentation requirements are defined in PNNL MSL SOPs. The documentation of all environmental data collection activities must meet the following minimum requirements.

- Data must be entered directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.
- Handwritten data must be recorded in ink. All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample identification (ID) and station or location ID (if applicable), name (signature or initials) of the person collecting the data, and date of data collection.
- Any changes to the original (raw data) entry must not obscure the original entry. The reason for the change must be documented, and the change must be initialed and dated by the person making the change.
- The use of pencil, correction fluid, and erasable pen is prohibited.

Any changes to the SAP (*e.g.*, QA procedures, analytical procedures, sampling locations and frequencies, etc.) must be documented in writing and approved by the PNNL QA Officer and PNNL Program Manager prior to implementation of the changes. Minor deviations from the SAP (*e.g.,* those that would not impact the study objectives, design, or data quality) will be reported to and approved by the appropriate team leader and the PNNL Project Manager, and documented for QA review. Major deviations (*e.g.,* those that could impact the study objectives, design, or data quality) will additionally be reported to the PNNL Program Manager, the PNNL QA Manager, the Navy Project Manager, and the Navy Technical Coordinator. A discussion of major deviations and potential impact on the project objectives will be included in the final report.

7.2 Recordkeeping Procedures

Data generated in support of these studies will be tracked and reviewed by the PNNL Program Manager. Data management (*e.g.,* paper flow; data tracking, data entry, etc.) and data assessment (*e.g.,* verification, validation, and Data Quality Assessment (DQA)) activities require adequate QC procedures to ensure that the SOPs are followed and result in records and reports that are accurate and appropriate. The QA procedures include peer review of each step and management review of a certain percentage of the data. Data management at the laboratory begins with the receipt of samples. Samples are logged in and assigned unique identification numbers that are used to identify samples throughout storage, processing, analysis, and reporting. A combination of hand-recorded and electronically captured data is generated, and includes information on sample container labels such as the unique sample identification number and the date. Hand-recorded data include sample processing and spiking procedures. Hand-recorded data are transcribed to spreadsheets using established formats. The raw data are maintained in the project files and the transcribed data are 100% verified. Laboratory data and data from the field logs will be entered into an EDD using a format supplied by the ENVVEST Technical Coordinator.

7.3 Reporting Procedures

A data report, consisting of a case narrative, summary data tables, COCs, laboratory receipt documentation and EDD will be generated once the internal data review process is satisfactorily completed. The Chemistry Task Leader is responsible for preparing these reports.

Data reports must include the following:

- Complete field sample identification;
- Sample identification numbers assigned by the laboratory;
- Date of sample collection;
- Date sample is received by the laboratory;
- Date of sample analysis;
- Sample matrix;
- Analytical SOP number and base EPA method (when applicable);
- Results (with clearly defined concentration units) for each targeted analyte;
- Electronic file identification codes (when applicable, identify instrument data files);
- Data qualifying flags;
- Dilution factor(s);
- Method detection and reporting limits (MDLs and RLs)
- Date of report; and,
- Review date and signature of the laboratory manager.

– Review date and signature of the QA Manager

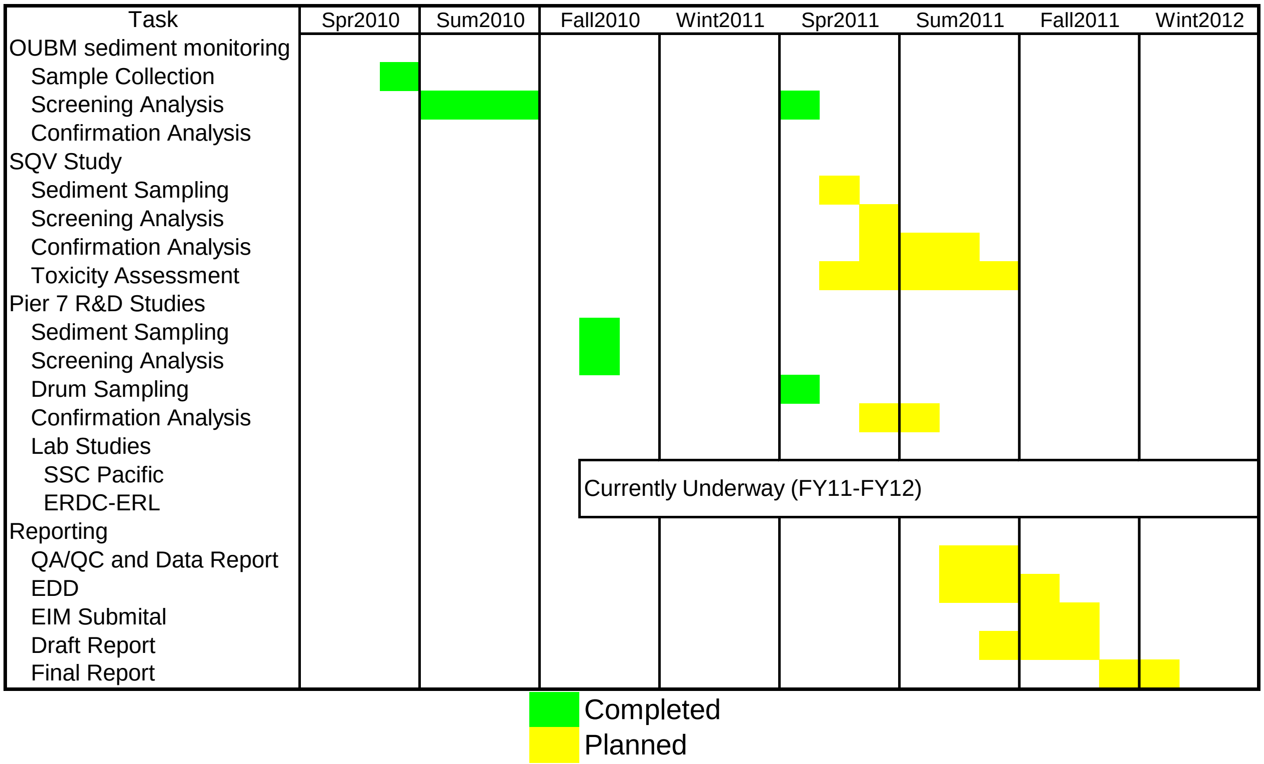
Documentation of field sampling will include:

- a chronology of events;
- a table of field statistics (date/time, depth, and coordinates of each station);
- a table of samples collected, together with location coordinates, date/times, sample IDs, amount of sample and intended analyses; and,
- a summary of problems encountered, deviations, and corrective actions.

EDDs containing the results of the quantitative metals chemistry analyses conducted at MSL will be prepared in two formats: the ENVVEST database format and in Ecology's SEDQUAL database format.

8.0 Schedule

This study consists of three major tasks: 1) OUBM sediment monitoring, 2) Sediment Quality Verification (SQV) Study, 3) Pier 7 R&D studies, and 3) Data reporting and analysis. The overall schedule of milestones is shown below:



Task	Spr2010	Sum2010	Fall2010	Wint2011	Spr2011	Sum2011	Fall2011	Wint2012
OUBM sediment monitoring								
Sample Collection	🟩							
Screening Analysis		🟩🟩🟩			🟩			
Confirmation Analysis								
SQV Study								
Sediment Sampling					🟨			
Screening Analysis					🟨			
Confirmation Analysis					🟨	🟨🟨		
Toxicity Assessment					🟨🟨	🟨🟨🟨		
Pier 7 R&D Studies								
Sediment Sampling			🟩					
Screening Analysis			🟩					
Drum Sampling					🟩			
Confirmation Analysis					🟨	🟨		
Lab Studies								
SSC Pacific			Currently Underway (FY11-FY12)					
ERDC-ERL								
Reporting								
QA/QC and Data Report						🟨🟨		
EDD						🟨🟨	🟨	
EIM Submital							🟨🟨	
Draft Report						🟨	🟨🟨	
Final Report							🟨	🟨

🟩 Completed
🟨 Planned

All milestones are subject to funding, and due dates are subject to the date of notice to proceed.

9.0 Project Personnel and Responsibilities

The general responsibilities of the key individuals for this study are:

Mr. Bruce Beckwith is the Project ENVVEST Program Manager. He is responsible for the final approval for the conduct of all activities associated with this project particularly design to meet NPDES requirements for the Navy.

Dr. Robert K. Johnston is the Project ENVVEST Technical Coordinator. He is responsible for technical guidance for this project for the Navy.

Mr. Dwight Leisle is the IR program manager for BNC OUBM. He is responsible for assisting with the coordination between the CERCLA program activities and the NPDES activities for the Navy.

Ms. Jill Brandenberger, M.S. is the Battelle, Pacific Northwest National Laboratory (PNNL) Program Manager. She is responsible for overall coordination of the project activities. She will communicate directly with the Navy Program Managers and Technical Coordinator. She reports program status to, and implements the directives of the PSNS Program Manager. She prepares program schedules, ensures analyses are assigned to the analysts, prepared data deliverable schedules, and that the final data report is prepared and meets project requirements. She is responsible for preparing and implementing requirements of the SAP, scheduling the sampling trip, arranging for equipment, and Navy base access. She coordinates the field and laboratory components of the study, and is responsible for ensuring that all technical logistics are identified and addressed. In addition, she works as the Health and Safety Officer and coordinates with the Program QA Manager to ensure that field activities are conducted safely and in accordance with QA requirements. She is authorized to stop work if staff safety is threatened and will report the situation immediately to the Project Manager.

Ms. Julie Snelling-Young is the Battelle PNNL Program QA Manager. She is responsible for ensuring that the QA systems required for this project are adequately addressed in QA documents that describe project activities: this SAP and SOPs. She reviews and approves the SAP. She ensures that project reviews are conducted frequently enough to ensure that the work is being conducted according to the SAP and SOPs, and that corrective action plans are implemented to address any deficiencies identified. She is authorized to stop work for cause if data quality or staff safety is threatened. She ensures that all SOPs cited in the SAP are approved and available to study participants and that appropriate training is documented for team members. She verifies that adequate forms and labels are designed for the sampling and analysis effort. She reviews custody forms to verify that custody is maintained. She conducts data audits to ensure that data quality meets project requirements.

10.0 References

Anderson BS, Hunt JW, Hester M, Phillips BM. 1996. Assessment of sediment toxicity at the sediment water interface. In: G.K. Ostrander (ed.) Techniques in Aquatic Toxicology. Lewis Publishers, Ann Arbor, MI.

Applied Biomonitoring 2009. Using Caged Mussels to Characterize Exposure & Effects over Small Spatial Scales in Sinclair Inlet: A Risk Assessment Based Approach. A Caged Mussel Study for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST. Final Report. Prepared for: Robert K. Johnston, Space and Naval Warfare Systems Center, Pacific, San Diego, California. Prepared by: Applied Biomonitoring, Kirkland, WA. October 16, 2009. 360pp

Allen, H.E., F. Gongmin, W. Boothman, D. DiToro, and J. Mahoney. 1991. Determination of Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals in Sediment. Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment. USEPA Office of Science and Technology, Washington, DC. April, 1991.

Ankley, G. T., Di Toro, D. M., Hansen, D. J., and Berry W. J. 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environmental Toxicology and Chemistry. 15:2056-2066.

Berry, W. J., Hansen, D. J., Mahony, J. D., Robson, D. L., Di Toro, D. M., Shipley, B. P., Corbin, J. M. and Boothman, W. S. 1996. Predicting the toxicity of metals-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalization. Environmental Toxicology and Chemistry. 15:2067-2079.

Blake, A.C., D.B. Chadwick, P.J. White, and C.A. Jones. 2007. User's Guide for Assessing Sediment Transport at Navy Facilities. Technical Report 1960. SSC San Diego, CA. [4.44 MB PDF file] See APPENDIX C BREMERTON NAVAL COMPLEX OPERABLE UNIT B MARINE. http://www.spawar.navy.mil/sti/publications/pubs/tr/1960/tr1960cond.pdf

Brandenberger, J. M., C.W. May, V.I Cullinan, R. K. Johnston, 2007a. Draft Surface and Stormwater Quality Assessment for Sinclair and Dyes Inlet, Washington. Draft June 2007, Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility Project ENVVEST Bremerton, Washington, under Contract DE-AC06-76RLO 1830 Pacific Northwest National Laboratory Richland, Washington,

Brandenberger, Jill M., Chris May, and Valerie Cullinan Robert K. Johnston, Dwight E. Leisle, Bruce Beckwith, and Gerald Sherrell, David Metallo, and Ryan Pingree, 2007b. 2003-2005 Contaminant Concentrations in Storm Water from Sinclair/Dyes Inlet Watershed a Subasin of Puget Sound, WA, USA. Proceedings of the 2007 Georgia Basin Puget Sound Research Conference, Puget Sound Action Team and Environment Canada. http://www.engr.washington.edu/epp/psgb/2007psgb/2007proceedings/papers/9f_brand.pdf

Brandenberger J. M., E.A. Crecelius, and R. K. Johnston 2008a. Contaminant Mass Balance for Sinclair and Dyes Inlets, Puget Sound, Washington. Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility Project ENVVEST Bremerton, Washington under Contract DE-AC06-76RLO 1830, Pacific Northwest National Laboratory, Richland, Washington.

Brandenberger J. M., C.R. Suslick, R. K. Johnston, 2008b. Biological Sampling and Analysis in Sinclair and Dyes Inlets, Washington: Chemical Analyses for 2007 Puget Sound Biota Study. Report PNNL-15834 May 2006. Prepared for the Puget Sound Naval Shipyard and Intermediate Maintenance Facility Project ENVVEST Bremerton, Washington under Contract DE-AC06-76RLO 1830, Sept. 2008, 207pp. http://www.pnl.gov/main/publications/external/technical_reports/PNNL-17948.pdf

Chadwick, D.B., S.H. Lieberman, C.E. Reimers, and D. Young, 1992. An evaluation of contaminant flux rates from sediments of Sinclair Inlet, WA, using a benthic flux sampling device, Naval Command, Control and Ocean Surveillance Center, RDT&E Division, Technical Document 2434, San Diego, CA. 186 pp.

Cullinan,Valerie I., Christopher W. May, Jill M. Brandenberger, and Chaeli Judd, and Robert K. Johnston, 2007. Development Of An Empirical Water Quality Model For Stormwater Based on Watershed Land-Use in Puget Sound. Proceedings of the 2007 Georgia Basin Puget Sound Research Conference, Puget Sound Action Team and Environment Canada. http://www.engr.washington.edu/epp/psgb/2007psgb/2007proceedings/papers/5e_culli.pdf

Diefenderfer, H. L., N. P. Kohn, E. A. Crecelius, R. K. Johnston, and G. M. Sherrell. 2003. Technical Approach to Address Section 303(d) Lisgints for Metals in Sinclair and Dyes Inlets. May 2003. Prepared for Project ENVVEST, Bremerton, WA.

Dutch, M. et al. 2009. 2009 Puget Sound Assessment and Monitoring Program (PSAMP) and Urban Waters Initiative (UWI) Sampling and Analysis Plan. State of Washington, Department of Ecology. http://www.ecy.wa.gov/urbanwaters/index.html

Ecology (Washington State Department of Ecology). 2002a. Assessment of Water Quality for the 303(d) List. Washington State Department of Ecology, Water Quality Program Policy 1-11, Revised September 2002. http://www.ecy.wa.gov/programs/wq/303d/2002-revised/303d_policy_final.pdf

Ecology (Washington State Department of Ecology). 2002b. Response to Public Comments on Draft Water Quality Program Policy 1-11: Assessment of Water Quality for the Section303(d)List. http://www.ecy.wa.gov/programs/wq/303d/2002-revised/303d_resp-to-comments.pdf

Ecology (Washington State Department of Ecology). 2010. Puget Sound Naval Shipyard (NPDES Permit WA-000206-2) NPDES Permit Review and Mixing Zone Request, June 2010. Letter to EPA dated August 24, 2010.

EPA (U. S. Environmental Protection Agency). 2005. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver, and zinc). EPA-600-R-02- 011. Washington, DC.

EPA (U. S. Environmental Protection Agency). 2001. Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual. EPA-823-B-01-002. U. S. Environmental Protection Agency, Office of Water, Washington, DC. http://www.epa.gov/waterscience/cs/collectionmanual.pdf

EPA (U.S. Environmental Protection Agency). 1998. Method 6200: Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC. http://www.epa.gov/SW-846/pdfs/6200.pdf

EPA (U. S. Environmental Protection Agency). 1995a. Ambient water quality criteria—Saltwater copper addendum (Draft). Washington DC: USEPA. (U.S. Environmental Protection Agency. 2003. "Update of Ambient Water Quality Criteria for Copper." EPA 822-R-03-06. Washington, DC.)

EPA (U. S. Environmental Protection Agency). 1995b. Short-term methods for measuring the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. EPA/600/R-95/136. Office of Research and Development, Narragansett, RI.

EPA (U. S. Environmental Protection Agency). 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA 600/R-94/025. Office of Research and Development, Washington, D.C.

ERDC-ERL (Engineering Research and Development Center-Environmental Research Laboratory) 2010. Assessing the bioavailability of contaminated sediments, proposal for the Strategic Environmental Research and Development Program (SERDP). Army Corps of Engineers, Vicksburg, MS. http://www.serdp.org/

Farrar D, Bridges TS. 2011. 28-Day Chronic Sublethal Test Method for Evaluating Whole Sediments Using an Early Life Stage of the Marine Polychaete Neanthes arenaceodentata. ERDC TN-DOER-R14, February 2011.

International Atomic Energy Agency (IAEA) (2004). Sediment distribution coefficients and concentration factors for biota in the marine environment. Technical Report Series number 422, International Atomic Energy Agency, Vienna, 95 p. Document available on-line at: http://www-pub.iaea.org/MTCD/publications/PDF/TRS422_web.pdf.

Jahnke, R. A. 1988. A simple, reliable, and inexpensive pore water sampler. Limnology and Oceanography 33:483–487.

Johnston, R.K. 1993. Acid Volatile Sulfides and Simultaneously Extracted Copper, Lead, and Zinc in Sediments of Sinclair Inlet, Washington. Technical Report 1552. NCCOSC RDTE DIV, San Diego, CA. http://environ.spawar.navy.mil/Publications/pubs2.html

Johnston RK, DE Leisle, JM Brandenberger, SA Steinert, M Salazar, and SM Salazar. 2007. Contaminate Residues in Demersal Fish, Invetebrates, and Deployed Mussels in Selected Areas of The Puget Sound, WA. In Proceedings, 2007 Georgia Basin Puget Sound Conference, Vancouver, British Columbia, March 26-29, 2007, p. 9 pages. PNNL-SA-55152.

Johnston, R.K., Wang, P.F., Loy, E.C., Blake, A.C., Richter, K.E., Brand, M.C, Kyburg, C.E., Skahill, B.E., May, C.W., Cullinan, V., Choi, W., Whitney, V.S., Leisle, D.E., and Beckwith, B. 2009. "An Integrated Watershed and Receiving Water Model for Fecal Coliform Fate and Transport in Sinclair and Dyes Inlets, Puget Sound, WA." Space and Naval Warfare Systems Center, Technical Report 1977, San Diego, CA. Dec. 2, 2009, 182pp. http://environ.spawar.navy.mil/Projects/ENVVEST/FC_Model_Report/index.html

Johnston, RK, GH Rosen, JM Bandenberger, J.M. Wright, E. Mollerstuen, J. Young, and T. Tompkins 2010a. Sampling and Analysis Plan for Ambient Monitoring and Toxicity Testing for Sinclair and Dyes Inlets, Puget Sound, Washington. Prepared for Project ENVVEST, Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, WA. Revised Sept. 18, 2010. http://www.mesodat.org/ENVVEST/AMB_Monitoring/

Johnston, R.K., Jacquelyn Young, Eric Mollerstuen, Joseph Wright, Bruce Beckwith, and Eric Beckley 2010b. Fecal Coliform (FC) Monitoring, Assessment, and Control: Water Year 2011 Quality Assurance Project Plan. October 2010. Prepared for PSNS&IMF and NBK, Bremerton, WA. http://www.mesodat.org/ENVVEST/AMB_Monitoring/

Kohn, NP, MC Miller, JM Brandenberger, and RK Johnston. 2004. Metals Verification Study for Sinclair and Dyes Inlet, Washington. Prepared for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST, Bremerton, Washington. September, 2004. PNNL-14872. Pacific Northwest National Laboratory, Richland, Washington.

Kohn NP, LA Niewolny, JM Brandenberger, and RK Johnston. 2006. Organics Verification Study for Sinclair and Dyes Inlets, Washington. PNNL-16070, Pacific Northwest National Laboratory, Richland, WA.

Kohn, NP, JM Brandenberger, and RK Johnston. 2008. Metals and PAH Verification Study—2008. Prepared for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST, Bremerton, Washington. September, 2008. PNNL-. Pacific Northwest National Laboratory, Richland, Washington.

Lawrence, S., M. Roberts, C. Erikson, and R.K. Johnston, 2011. Sinclair and Dyes Inlets Fecal Coliform Bacteria Total Maximum Daily Load Water Quality Improvement Plan. Stakeholder REVIEW DRAFT Feb 2011 Prepared for Washington State Department of Ecology, Northwest Regional Office, Bellevue, WA.

Lauenstein, G. G. and A. Y. Cantillo, editors. 1993. Sampling and analytical methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch projects, 1984-1992. NOAA Tech. Memo. NOS ORCA 71. National Oceanic and Atmopheric Administration, Silver Spring, MD.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins, 1980. Chemical contaminants and biological abnormalities in central and southern Puget Sound. NOAA Technical Memorandum OMPA 2. National Oceanic and Atmospheric Administration. Boulder, Co.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, H.O. Hodgins and S-L Chan, 1982. Chemical contaminants and biological abnormalities in fish and invertebrates from Puget Sound. NOAA Technical Memorandum OMPA 19. National Oceanic and Atmospheric Administration. Boulder, Co.

Malins, D.C., B.B. McCain, D.W. Brown, S-L. Chan, M.S. Myers, J.T. Landdahl, P.G. Prohaska, A.J. Friedman, L.D. Rhodes, D.G. Burrows, W.D. Gronlund, H.O. Hodgins, 1984. Chemical pollutants in sediments and diseases of bottom-dwelling fish in Puget Sound, Washington. Environmental Science & Technology 18: 705-713.

May, C.W. Dana Woodruff, Valerie Cullinan, Nathan Evans, Lohna O'Rourke, Lee Miller, Robert K. Johnston, P.F. Wang, Heather Halkola, K.E. Richter, B. Davidson, Victoria Whitney, and Joseph Wright, 2005. An analysis of microbial pollution in the Sinclair-Dyes Inlet Watershed. Washington Department of Ecology, Report No. 05-03-042, 428pp + Appendices. http://www.ecy.wa.gov/biblio/0503042.html

McLaren, P. 1997. The Sediment Transport Regime of Dyes Inlet/Ostrich Bay: Implications for Contaminant Mitigation. Prepared for Engineering Field Activity, Northwest Naval Facilities Engineering Command, Poulsbo, Washington, August 1997 under a subcontract with EA Engineering, Science, and Technology, Bellevue, Washington.

McLaren, Patrick 2004. The Sediments of Sinclair Inlet: An Assessment of Progressive Change From 1998 To 2004. GeoSea, LLC. Prepared for Project ENVVEST.

McLaren, Patrick 2008. The Sediments of Sinclair Inlet: An Assessment of Progressive Change From 1998 To 2008. GeoSea, LLC. Prepared for Project ENVVEST. https://www.mesodat.org/ENVVEST/Reports/McLaren_2008_SedimentTexture.pdf

Morse, J. W., Millero, F. J., Cornwell, J. C. and Rickard, D. 1987. The chemistry of the hydrogen sulfide and iron sulfide systems in natural waters. Earth Science Review. 24:1-42.

Munthe, J. and others. 2007. Recovery of mercury-contaminated fisheries. Ambio 36: 33–44, doi:10.1579/0044-7447(2007) 36[33:ROMF]2.0.CO;2

Paulson, A.J., Keys, M.E., and Scholting, K.L., 2010, Mercury in sediment, water, and biota of Sinclair Inlet, Puget Sound, Washington, 1989–2007: U.S. Geological Survey Open-File Report 2009-1285, 220 p. http://pubs.usgs.gov/of/2009/1285/

Persson, N.J., T. D. Bucheli, Ö. Gustafsson, D. Broman, K. Næs, R. Ishaq, Y. Zebühr (2005). Testing common sediment–porewater distribution models for their ability to predict dissolved concentrations of POPs in The Grenlandsfjords, Norway. *Chemosphere* 59:1475-1485.

PSEP (Puget Sound Estuary Program). 1997. Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound. U.S. Environmental Protection Agency Region X, Office of Puget Sound, and Puget Sound Water Quality Authority, Seattle, Washington. April 1997.

Rosen, G., I. Rivera-Duarte, J. Thompson, and R.K. Johnston 2009. An Assessment of Copper Bioavailability and Toxicity in Surface Waters Adjacent to the Puget Sound Naval Shipyard & Intermediate Maintenance Facility. FINAL REPORT. Prepared by: Environmental Sciences & Applied Systems Branch, Code 71750 Space and Naval Warfare Systems Center Pacific, San Diego, CA

SedTrend 2011. Understand how your environment works with Sediment Trend Analysis (STA®) http://www.sedtrend.com/

Spyres, G., M. Nimmo, P. J. Worsfold, E. P. Achterberg, A. E.J. Miller (2000). Determination of dissolved organic carbon in seawater using high temperature catalytic oxidation techniques. Trends in Analytical Chemistry 19: 498-506

SSC-Pacific (Space and Naval Warfare Systems Center, Pacific) 2010. Laboratory Reactive Amendment Treatability Studies. Environmental Security Technology Certification

Program (ESTCP) Proposal. SSC-Pacific, San Diego, CA. http://www.serdp.org/About-SERDP-and-ESTCP/About-ESTCP

Taylor Associates, Inc. and Pacific Northwest National Laboratory 2011. Non-Dry Dock Stormwater Monitoring Conducted at Puget Sound Naval Shipyard Bremerton, WA Project ENVVEST Study Area. Prepared for U.S. Navy, January 2011.

URS Group, Inc. 2002a. Final Remedial Investigation Report, Operable Unit B Marine, Bremerton Naval Complex, Washington. Prepared by URS Greiner, Inc. for U.S. Navy, Engineering Field Activity, Northwest, Poulsbo, Washington.

URS Group, Inc. 2002b. Draft Long Term Monitoring Plan, Operable Unit B Marine, Bremerton Naval Complex, Washington. Appendix B, 12/06/02. Prepared by URS Greiner, Inc. for U.S. Navy, Engineering Field Activity, Northwest, Pouslbo, Washington.

URS Group, Inc. 2009. Final 2007 Marine Monitoring Report OU B Marine, Bremerton Naval Complex, Bremerton, Washington. Prepared for Naval Facilities Engineering Command Northwest Silverdale, Washington U.S. Navy Contract No. N44255-05-D-5100, Delivery Order 0012, July 2, 2009.

URS Group, Inc. 2008a. Pre-construction Marine Sediment Sampling Report Pier 7, Bremerton Naval Complex, Bremerton, Washington. Prepared for Naval Facilities Engineering Command Northwest Silverdale, Washington U.S. Navy Contract No. N44255-05-D-5100, Delivery Order 0050, September 10, 2008.

URS Group, Inc. 2008b. Pre-construction Marine Sediment Sampling Report Pier B and Pier 8, Bremerton Naval Complex, Bremerton, Washington. Prepared for Naval Facilities Engineering Command Northwest Silverdale, Washington U.S. Navy Contract No. N44255-05-D-5100, Delivery Order 0046, September 10, 2008.

U.S. Navy. 2000. Final Record of Decision for Bremerton Naval Complex, Operable Unit B Marine. U.S. Navy, Engineering Field Activity, Northwest Date: 06/06/00 Contract No. N62474-89-D-9295, CTO 0131, Bremerton, Washington. http://yosemite.epa.gov/r10/cleanup.nsf/webpage/Superfund+(CERCLA)#sites

U.S. Navy. 2003. Final Five-Year Review of Record of Decision Bremerton Naval Complex, Revision Number 0. U.S. Navy, Engineering Field Activity, Northwest Date: 10/17/02 Contract No. N44255-00-D-2476 Delivery Order 0017. http://yosemite.epa.gov/r10/cleanup.nsf/webpage/Superfund+(CERCLA)#sites

Wang, P.F., W. Choi, and R.K. Johnston 2011 (in prep). A Modeling Study of Copper Loading in Sinclair and Dyes Inlets, Washington. Prepared for Puget Sound Naval Shipyard & Intermediate Maintenance Facility Project ENVVEST. Space and Naval Warfare Systems Center Pacific, San Diego, CA.

Warnken, K. W., G. A. Gill, P. H. Santschi, L. L. Griffin. 2000. Benthic Exchange of Nutrients in Galveston Bay, Texas. Estuaries 23: 647-661.

Washington State. 1995. Chapter 173-204 WAC Sediment Management Standards. http://www.ecy.wa.gov/pubs/wac173204/index.html. See also http://search.leg.wa.gov/wslwac/WAC%20173%20%20TITLE/WAC%20173%20-204%20%20CHAPTER/WAC%20173%20-204%20%20Chapter.htm

Whitney, V.S and Wright J.M., 2003. Integrated and Predictive Valuation Modeling of Gorst Creek Basin, Kitsap County, Washington. Master Environmental Studies, The Evergreen State College, Olympica, WA, 44pp + appendices

40 CFR Appendix C to Part 136. Code of Federal Regulations, Title 40 *Protection of Environment*, Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", Appendix C: Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11.

11.0 Figures

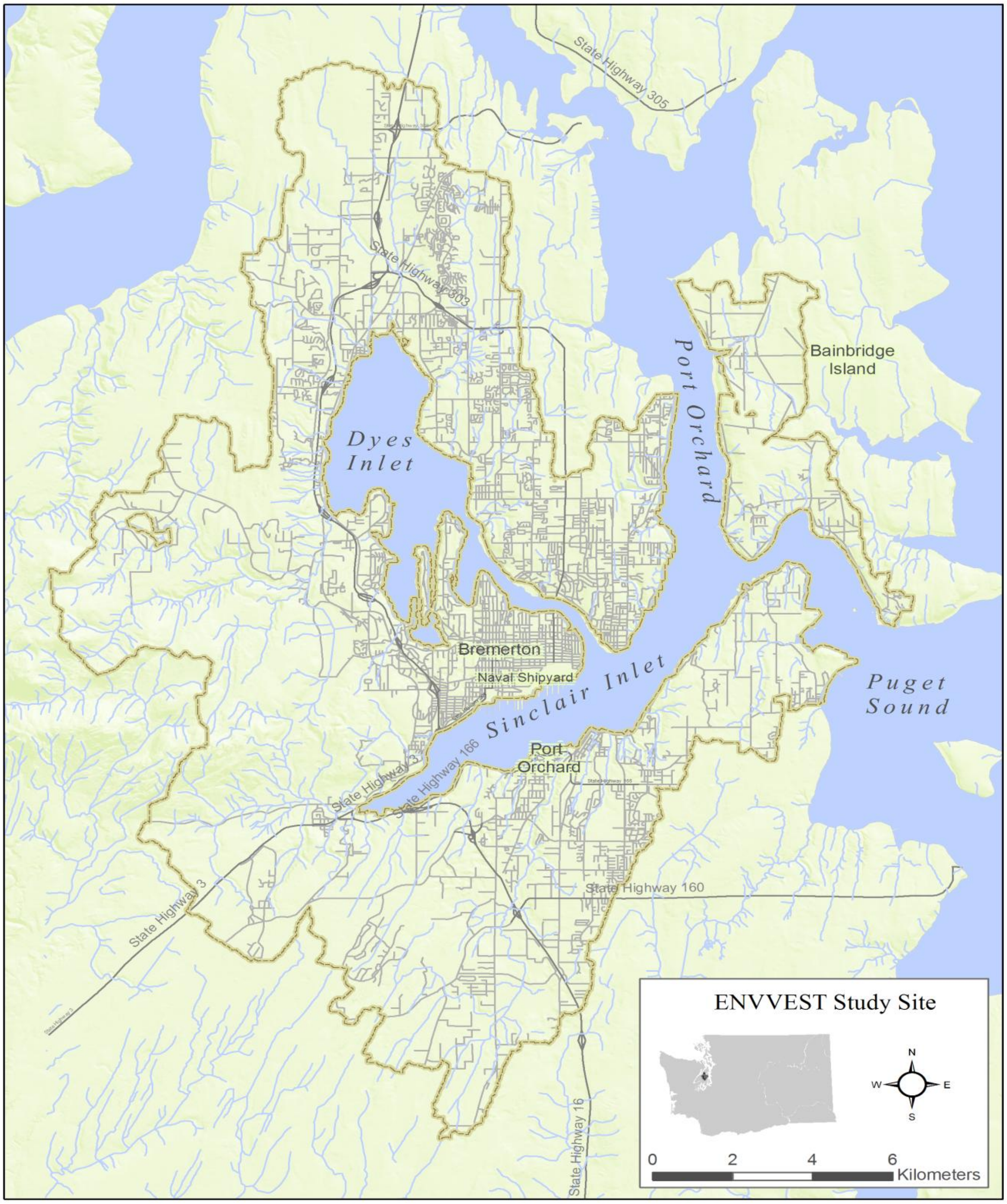


Figure 1. The Puget Sound Naval Shipyard & Intermediate Maintenance Facility and Naval Base Kitsap-Bremerton (Shipyard) is located in Bremerton, WA within the Sinclair and Dyes Inlet watershed. These Inlets are a subbasin of Puget Sound, WA.

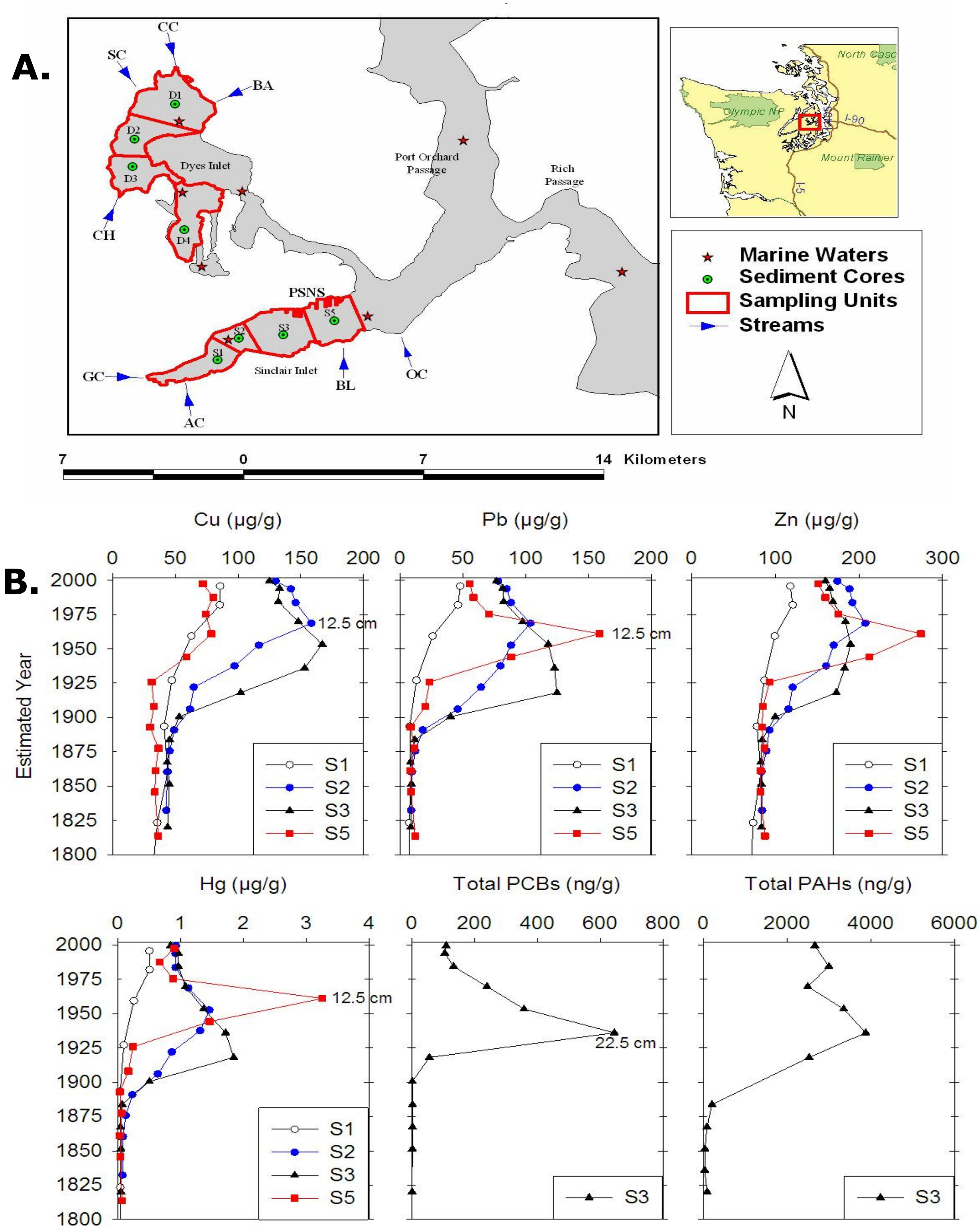


Figure 2. (A) The location of depositional areas in Sinclair and Dyes Inlets where sediment cores were collected and aged dated using radionuclide tracers and (B) the resulting sediment core profiles for Cu, Pb, Zn, Hg, PCBs, and PAHs in sediment cores collected from Sinclair Inlet (Brandenberger et al. 2008).

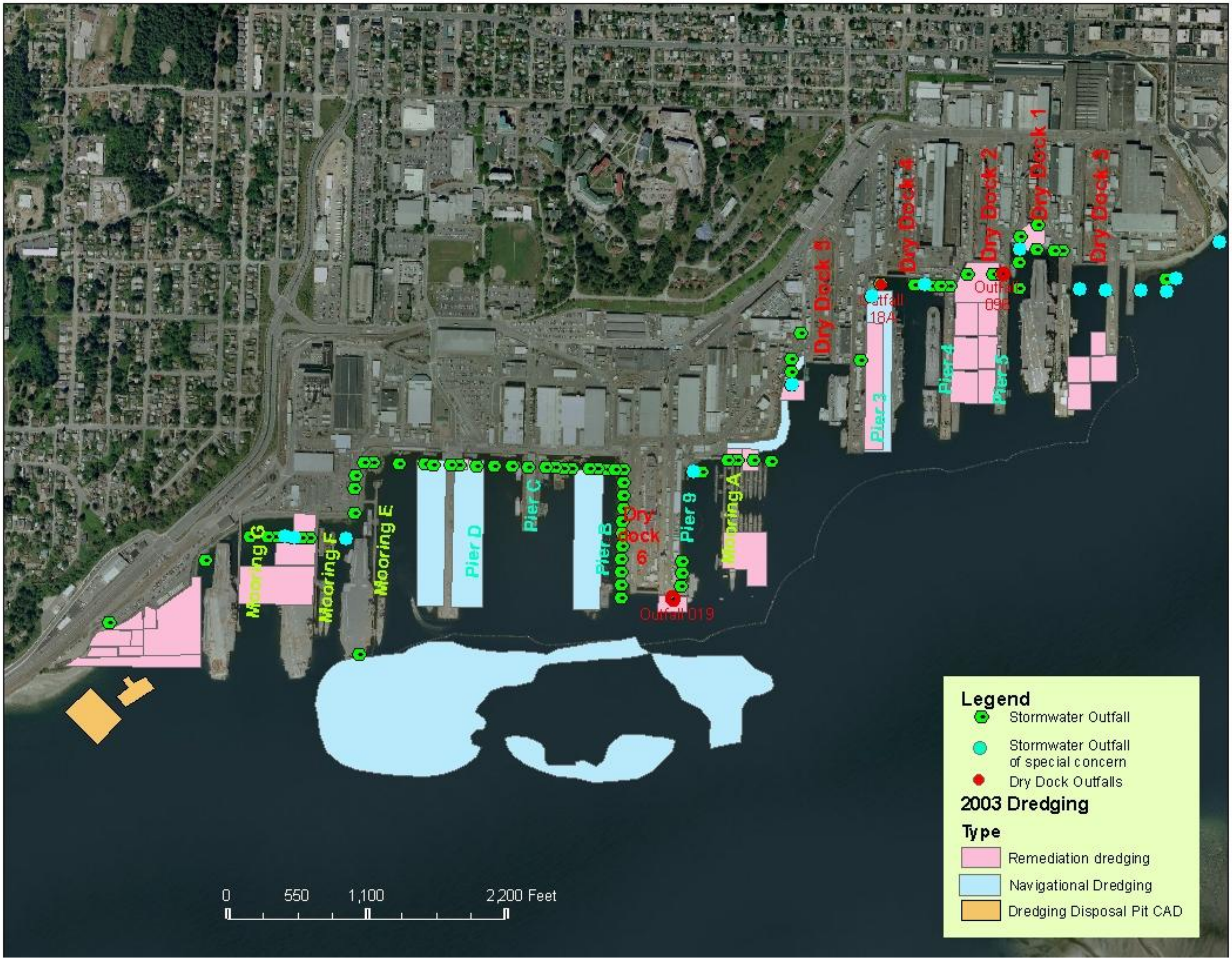


Figure 3. Locations within the Puget Sound Naval Shipyard of the stormwater outfalls, dry dock outfalls, remediation dredging, navigational dredging, and the confined aquatic disposal pit created in 2001.

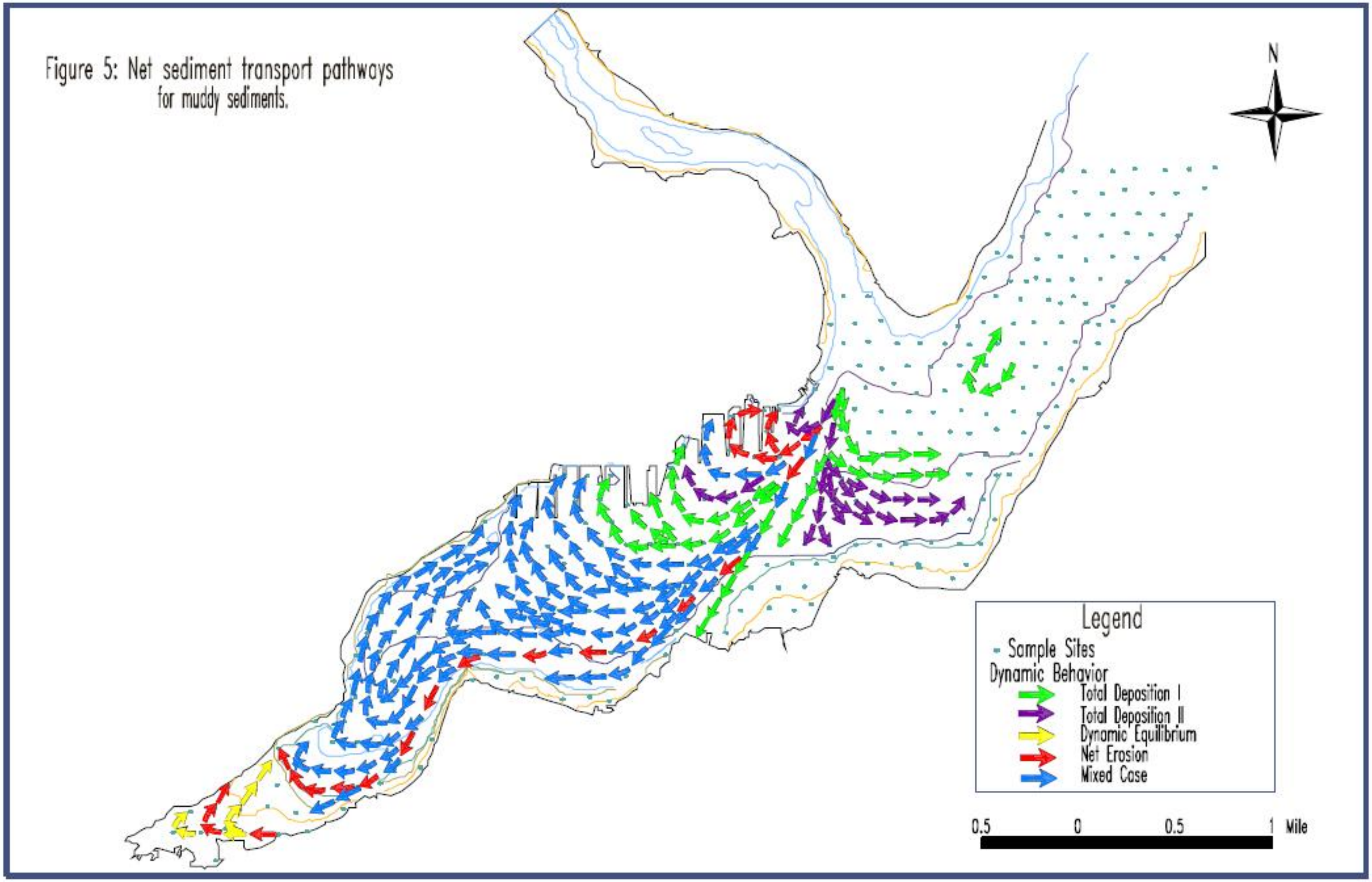


Figure 4. Net transport for muddy sediment obtained from Sediment Trend Analysis performed on samples collected from Sinclair Inlet between May 20, 1998 and July 21, 1998 (McLaren 1998).

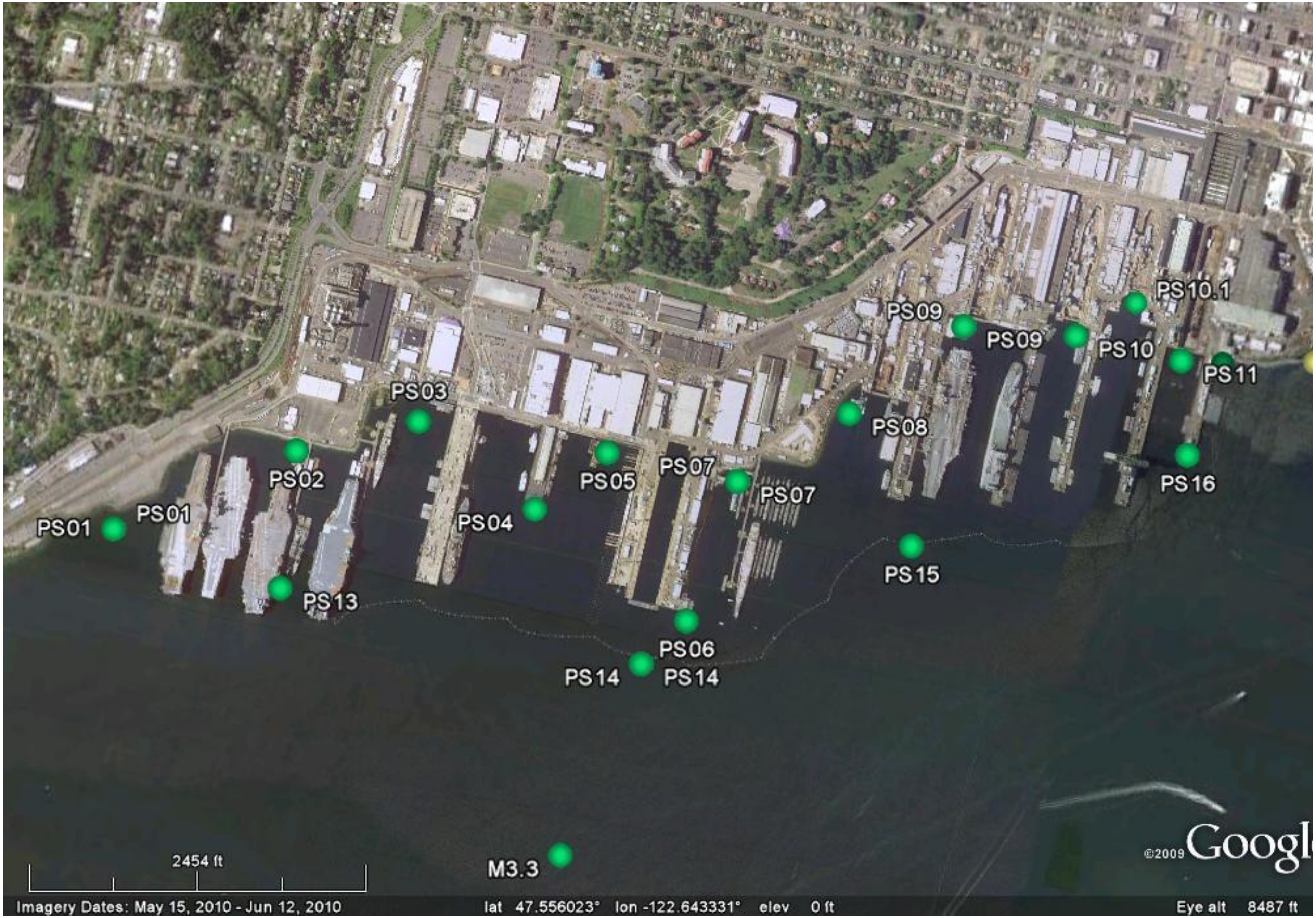


Figure 5. Location of ambient monitoring stations (green dots) and effluent discharges (red boxes) being monitored for metals and toxicity seasonally since Sept. 2009 within the Shipyard (Johnston et al. 2010a).

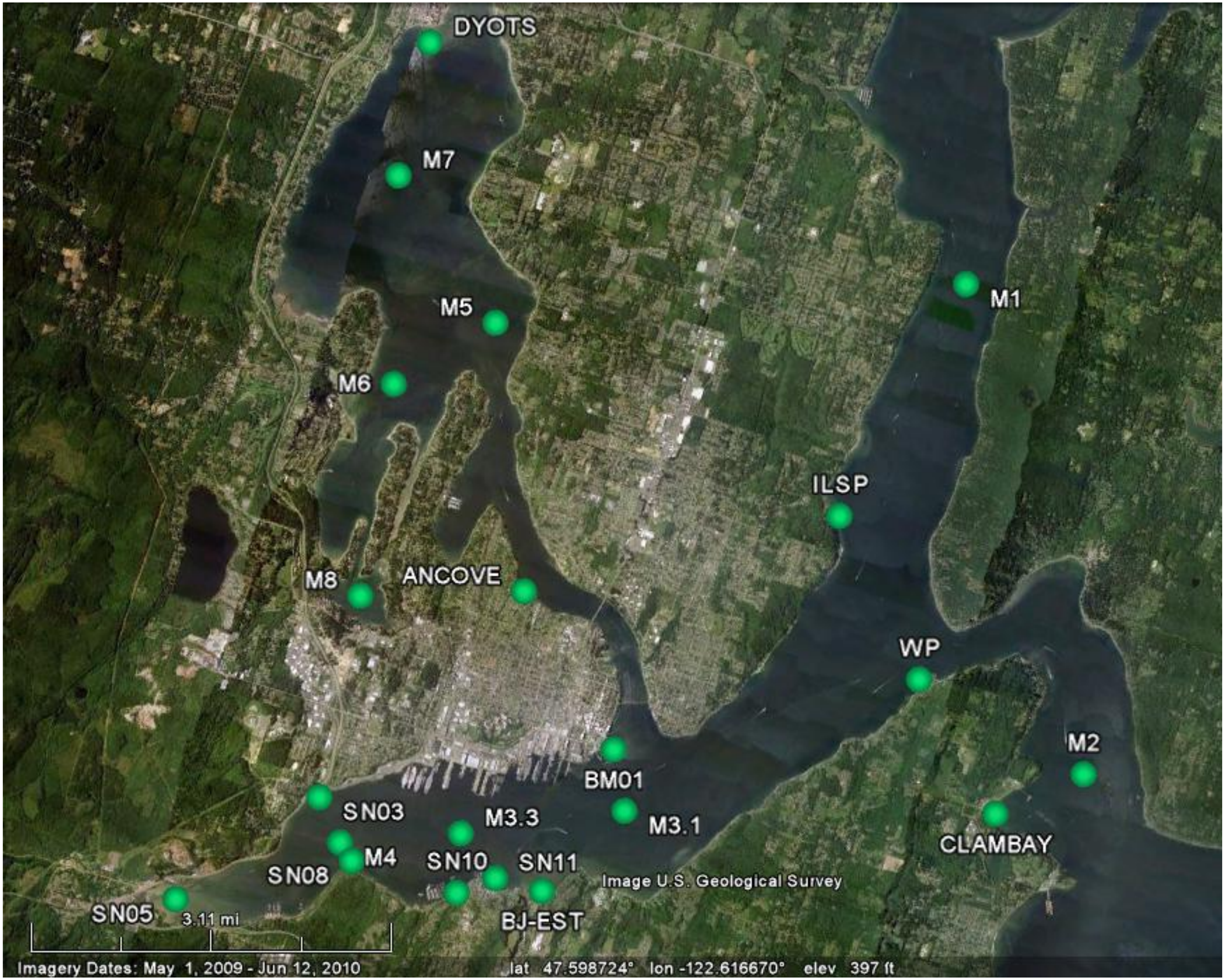


Figure 6. Seasonal ambient monitoring stations in Sinclair and Dyes Inlets (Johnston et al. 2010a)

Figure 7. Mussel watch stations within the Shipyard established in Jan-Feb 2010 (Johnston et al. 2010a).

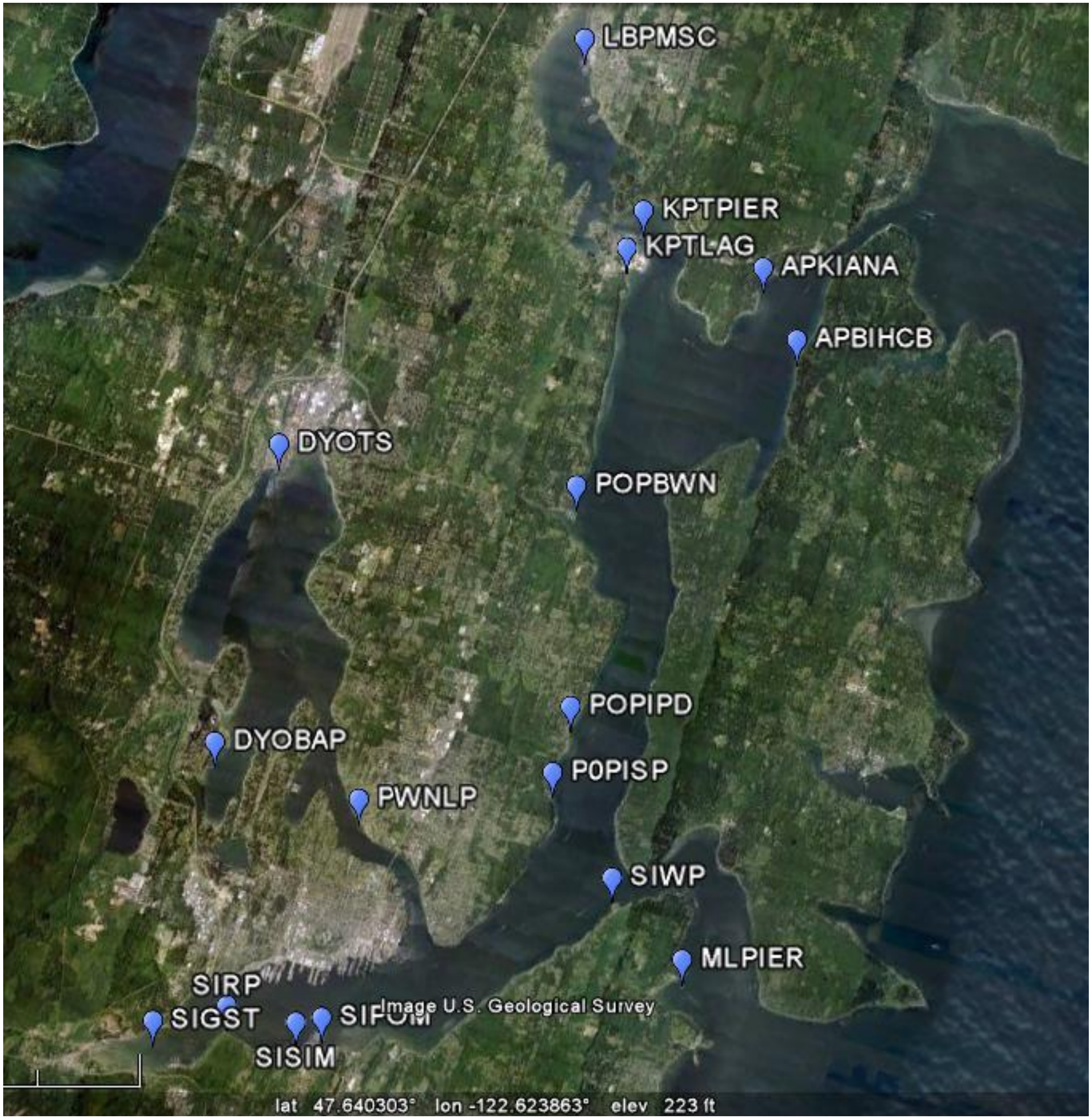


Figure 8. Mussel watch stations within Sinclair and Dyes Inlets established in Dec 2009-Feb 2010 (Johnston et al. 2010a).

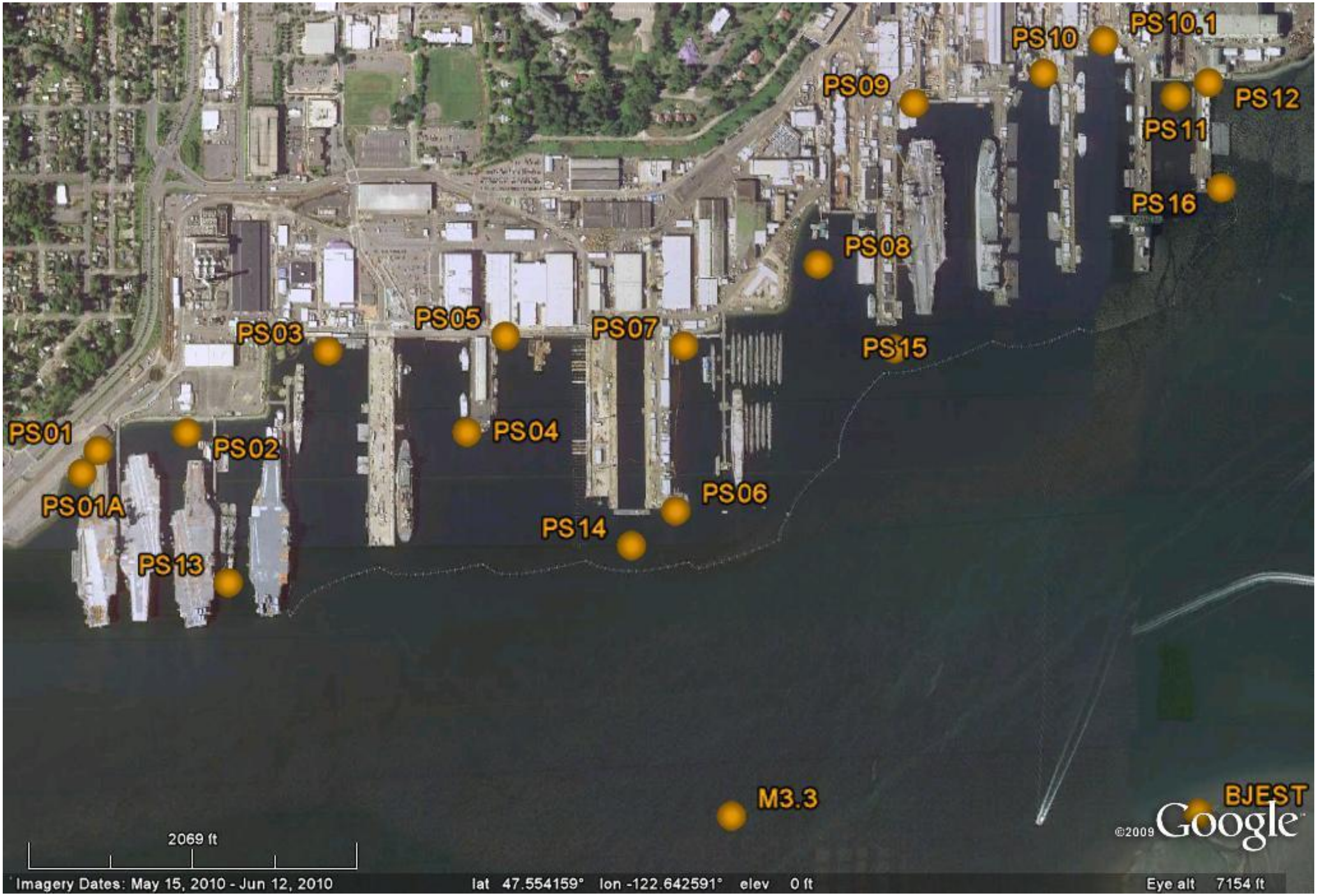


Figure 9. Fecal coliform ambient monitoring stations within the Shipyard that have been sampled monthly since Sep. 2010 (Johnston et al. 2010b).

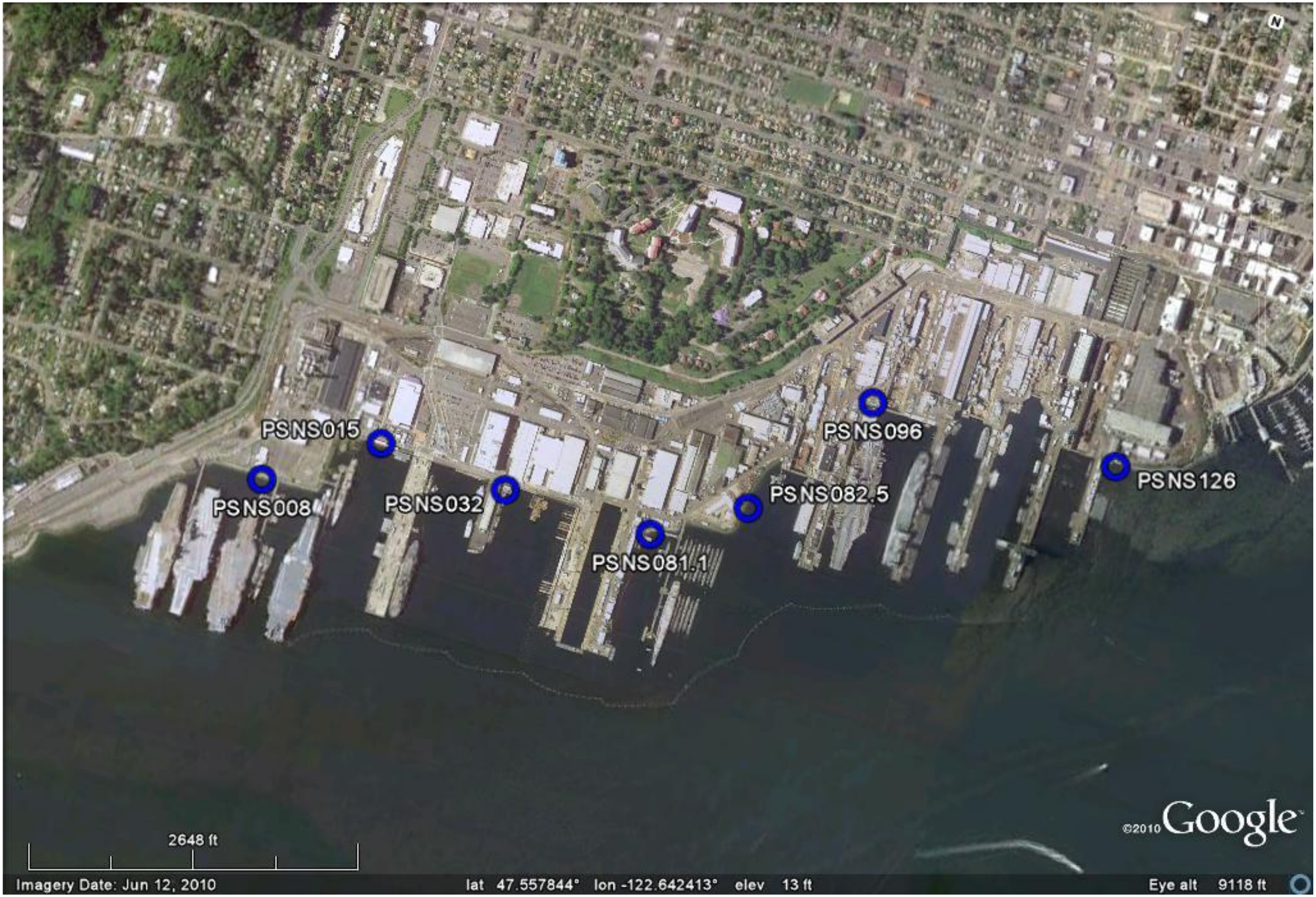


Figure 10. Non Dry Dock Stormwater drains monitored during storm events from Nov. 2010 – April 2011 (Metallo et al. 2011).

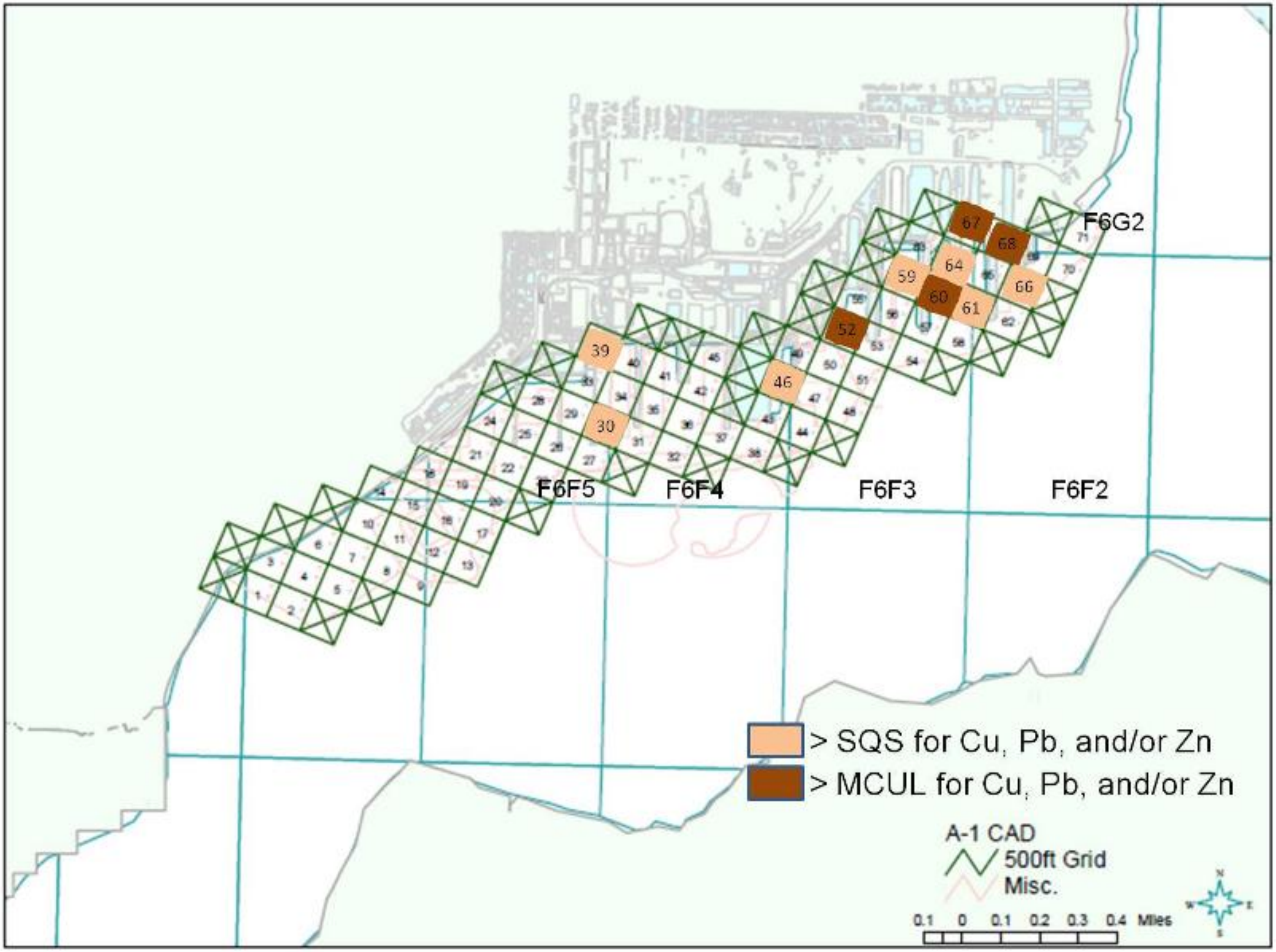


Figure 11. The 500-ft sediment monitoring grids (OUBM Marine boundary), the grids where sediment concentrations exceeded the Washington Sediment Quality Standard (SQS) or Minimum Clean Up Level (MCUL) for Cu, Pb, and/or Zn. The 303(d) segments are overlaid in blue.

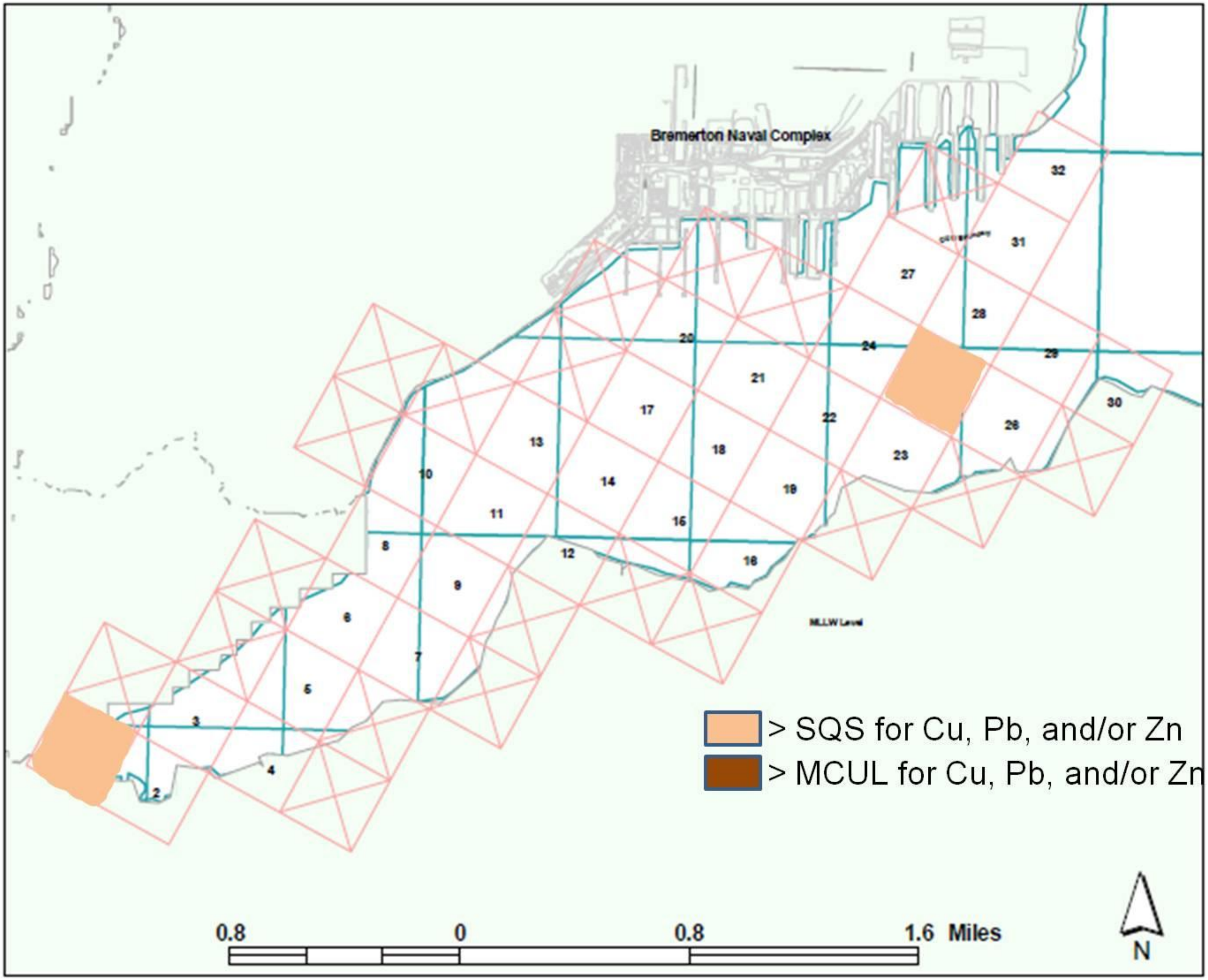


Figure 12. The 1500-ft sediment monitoring grids (OUB Marine boundary and the grids where sediment concentrations exceeded the Washington Sediment Quality Standard (SQS) or Minimum Clean Up Level (MCUL) for Cu, Pb, and/or Zn. The 303(d) segments are overlaid in blue.

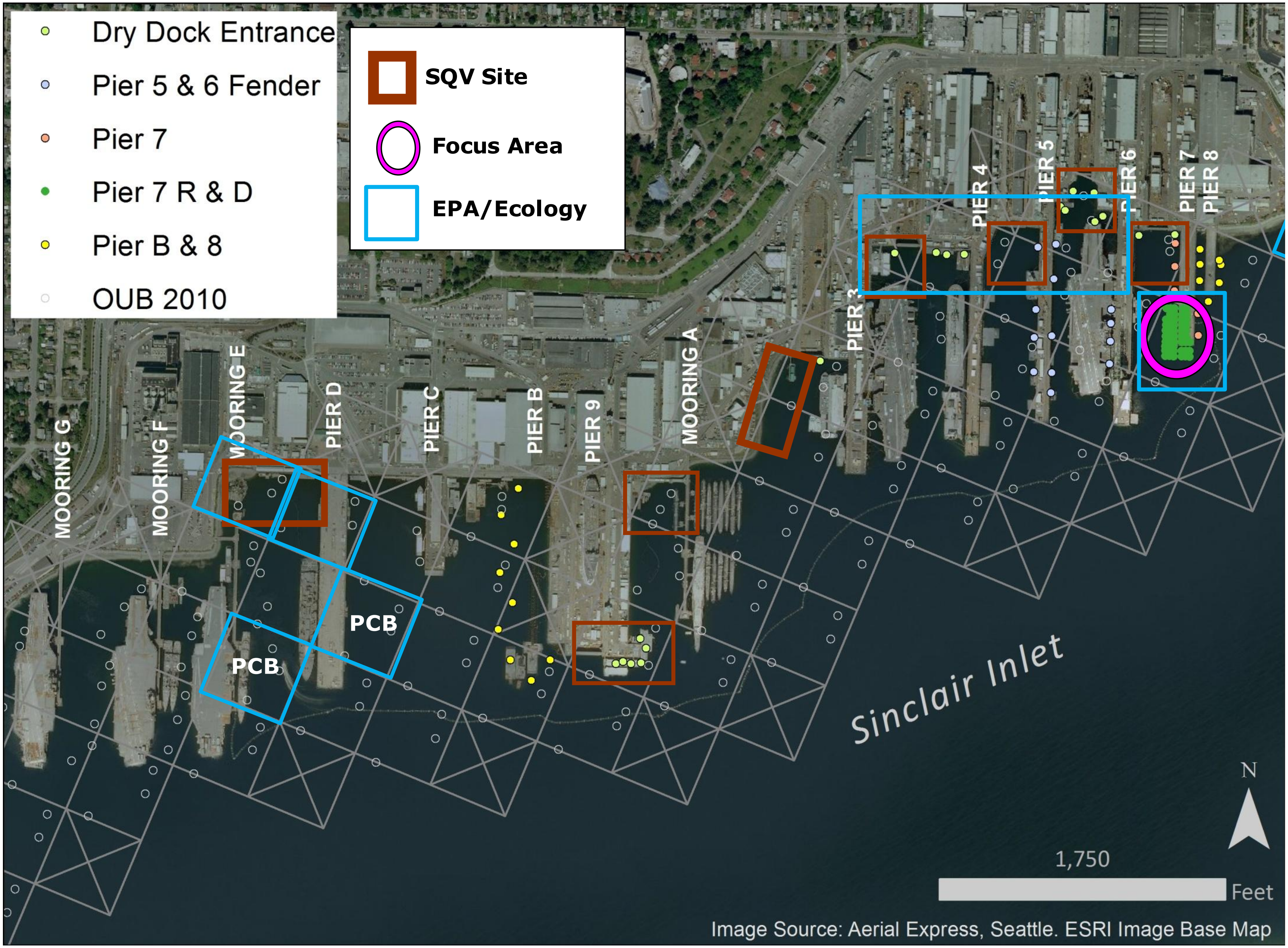


Figure 13. Locations of the Sediment Quality Verification (SQV) sites and areas of concern identified by Ecology (2010). Other sediment sampling includes: Dry Dock entrance, Pier 5 and 6 repair, Pier 7 pre-post construction and Pier 7 R&D, Pier B and 8 Pre-Construction sediment sampling, and 2010 OUBM sediment monitoring 500 ft grid and sample locations.

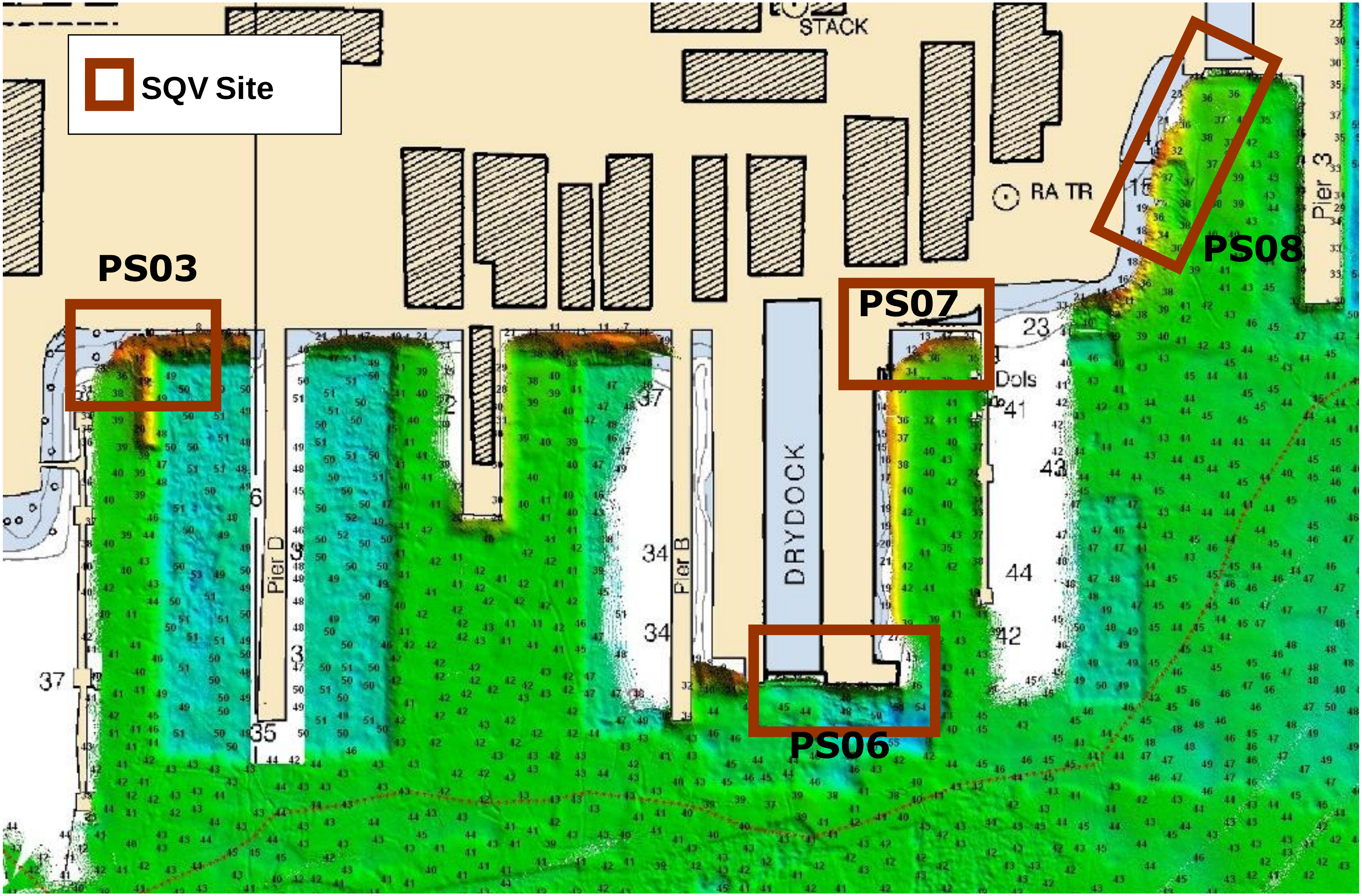


Figure 14. Sediment Quality Verification sites located within NBK-Bremerton and PSNS&IMF CIA.

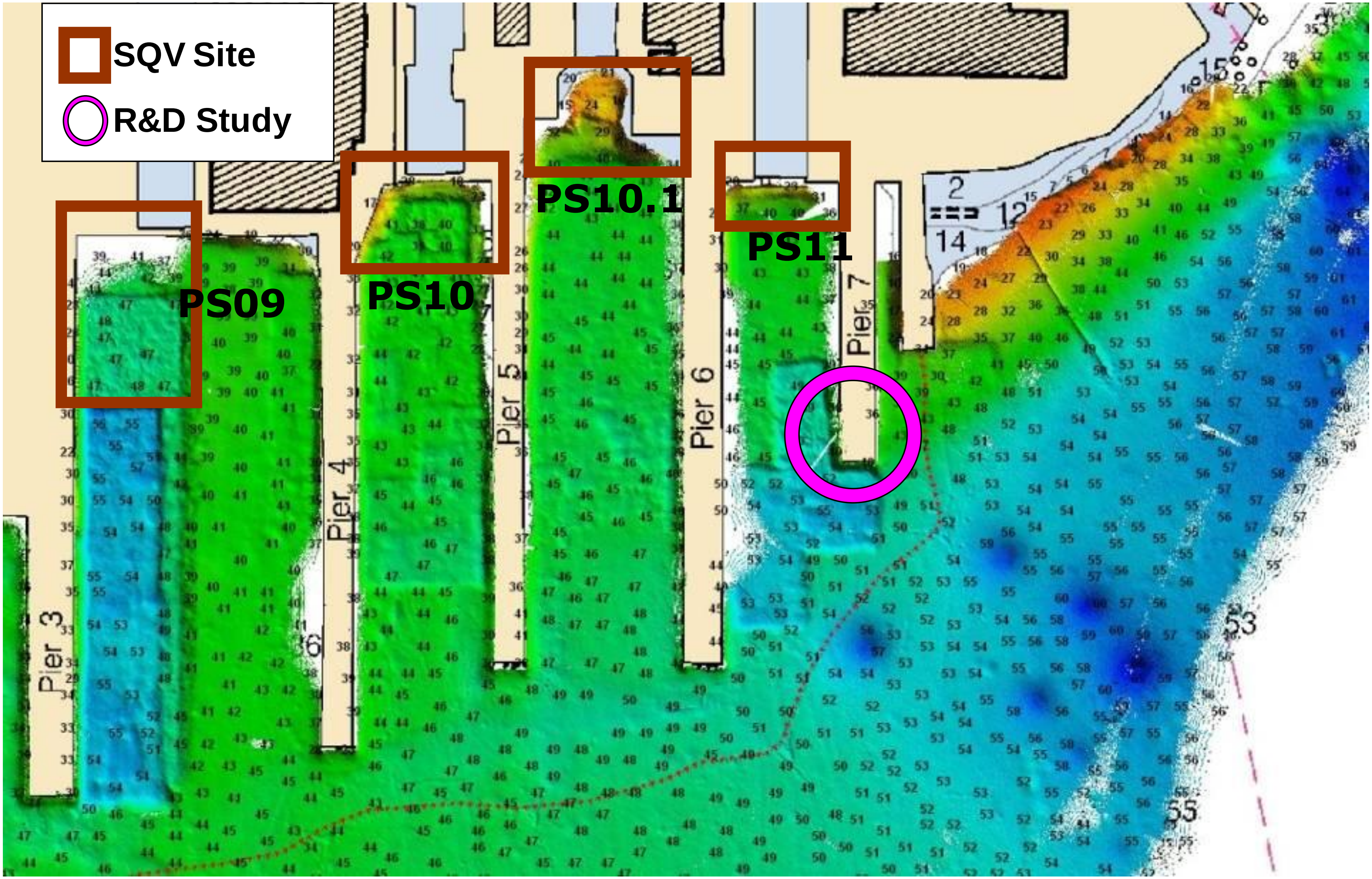


Figure 15. Sediment Quality Verification sites located within PSNS&IMF CIA.

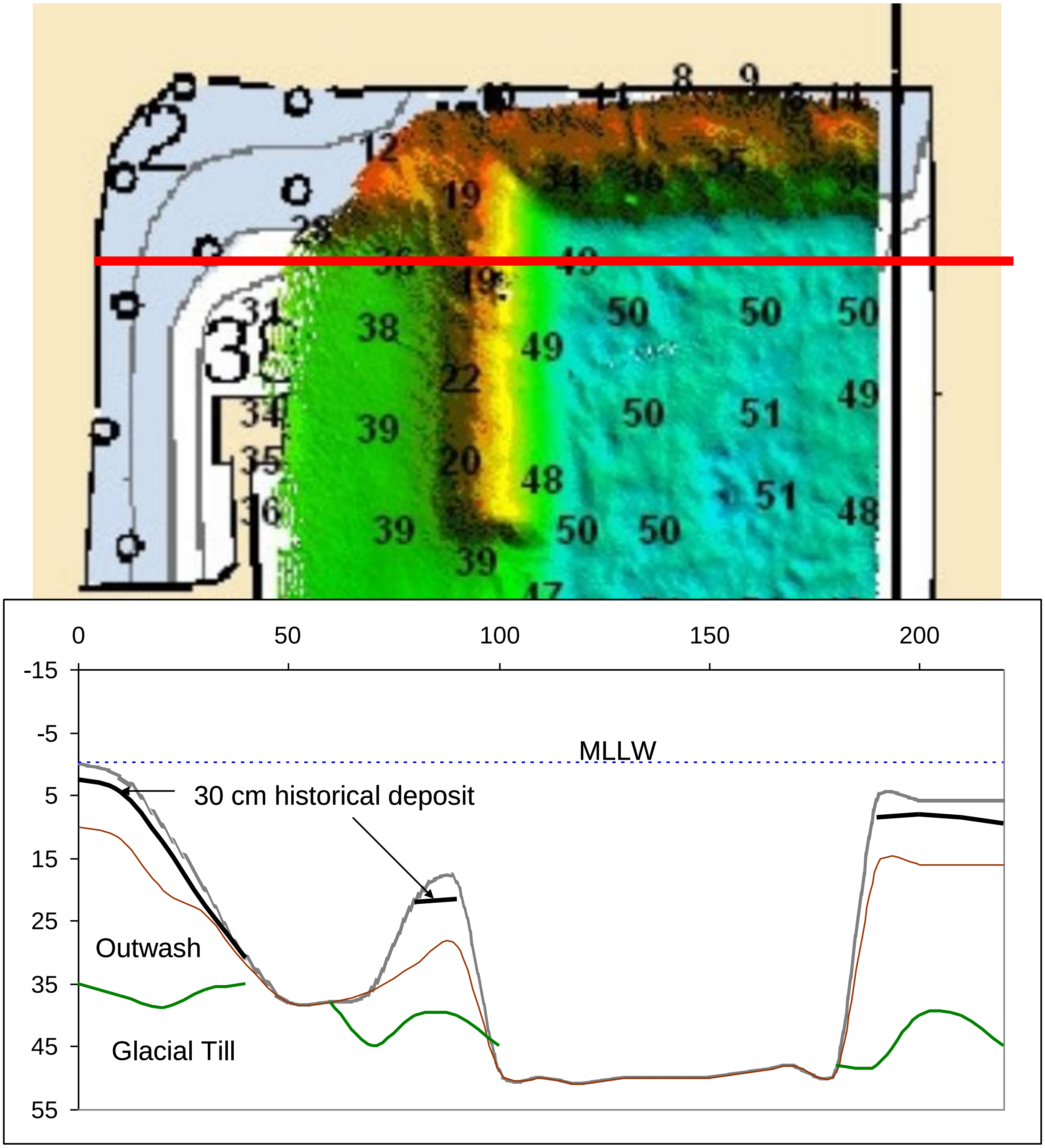


Figure 16. Conceptual model of sediment environment showing a hypothesized bottom profile along a transect (red line) at SQVPS03.

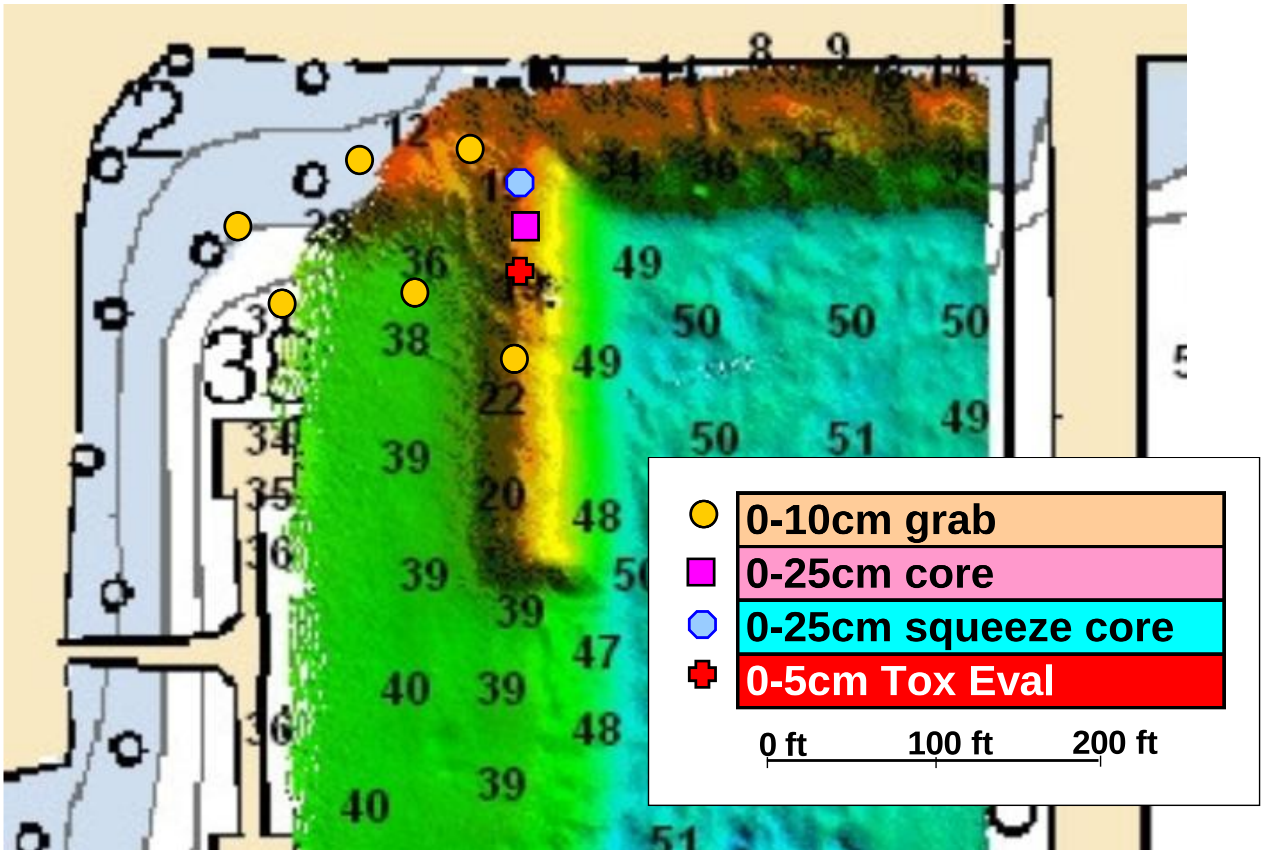


Figure 17. SQVPS03 target sampling locations.

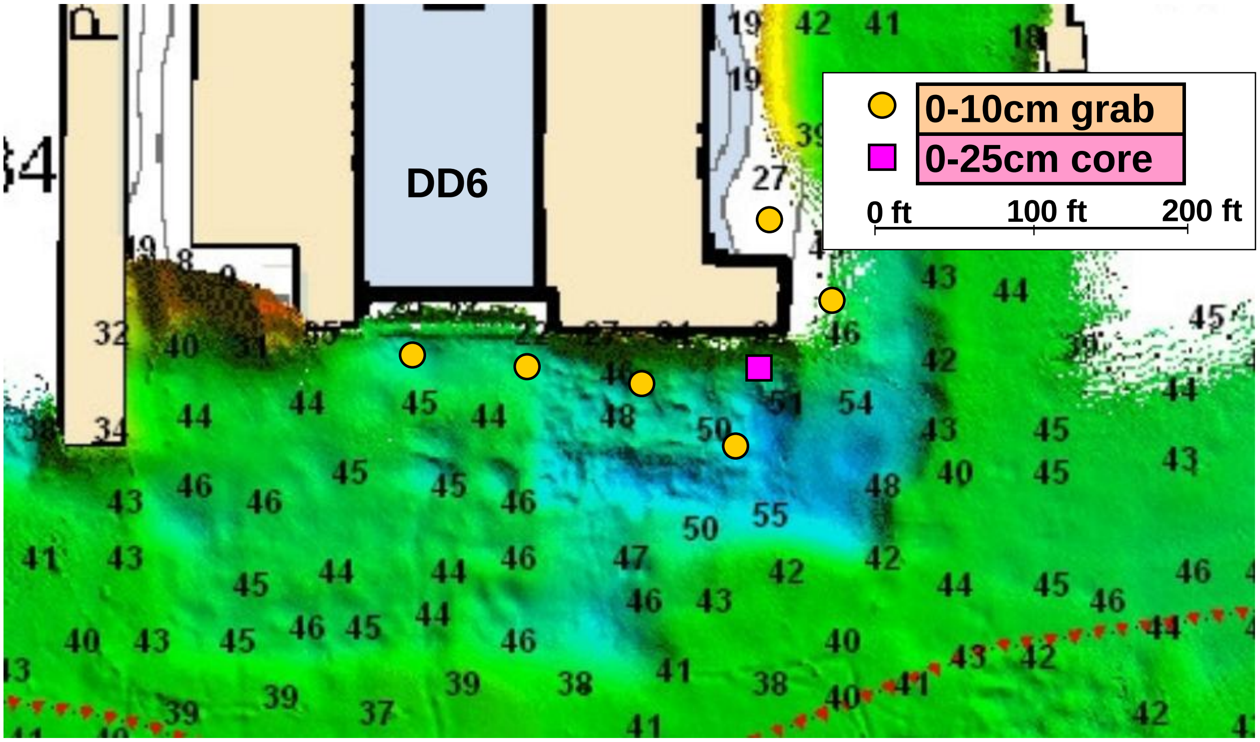


Figure 18. SQVPS06 target sampling locations.

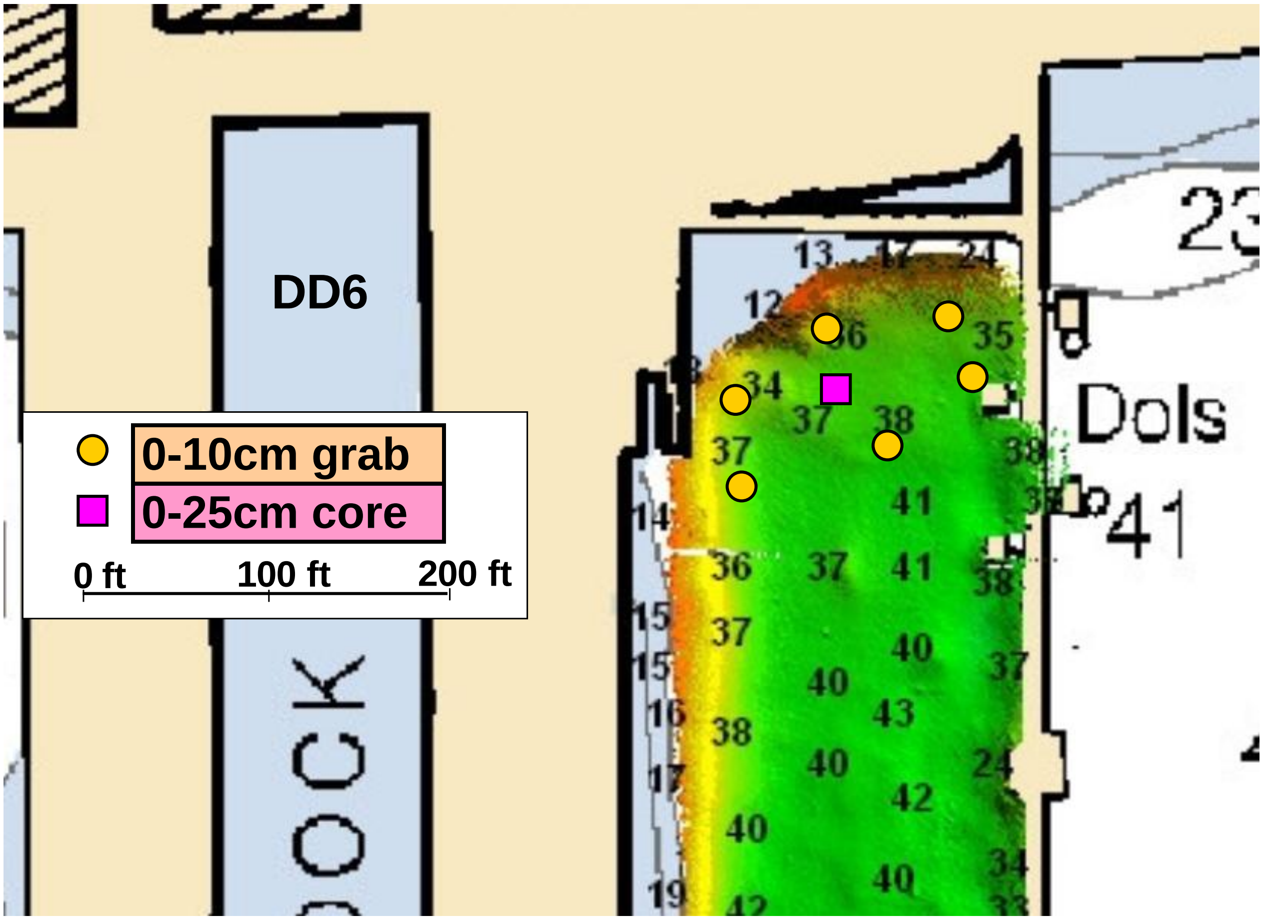


Figure 19. SQVPS07 target sampling locations.

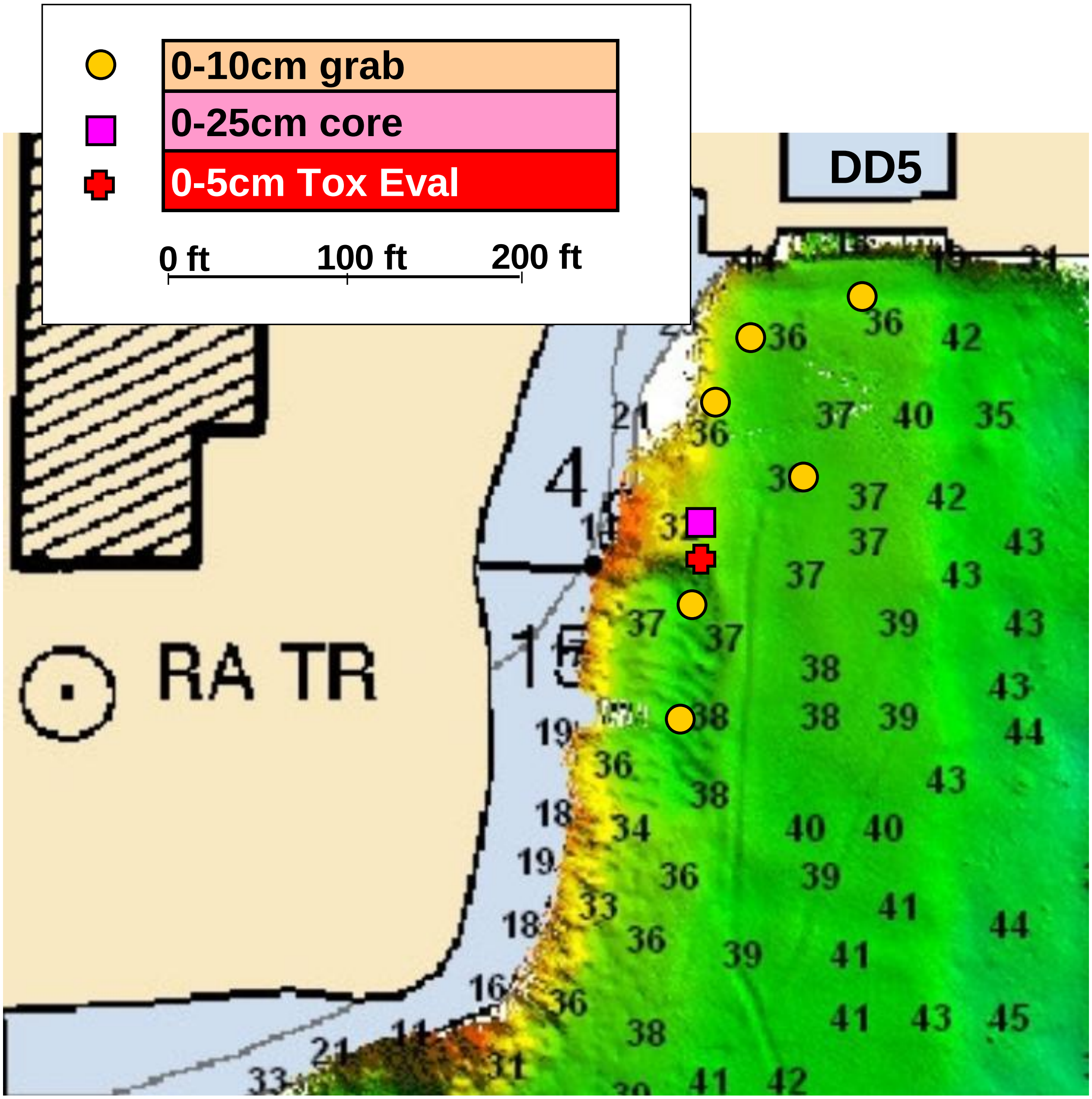


Figure 20. SQVPS08 target sampling locations.

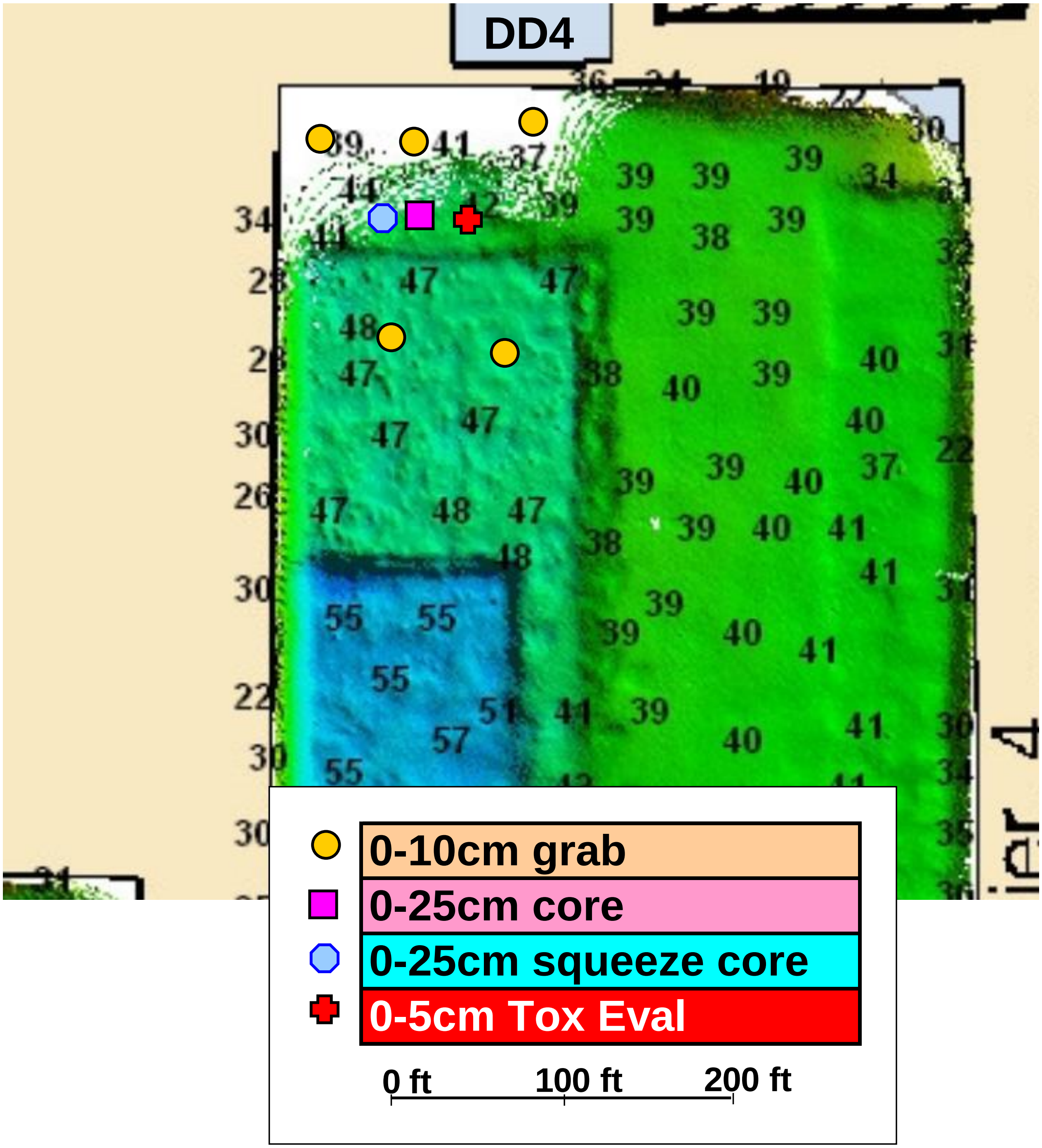


Figure 21. SQVPS09 target sampling locations.

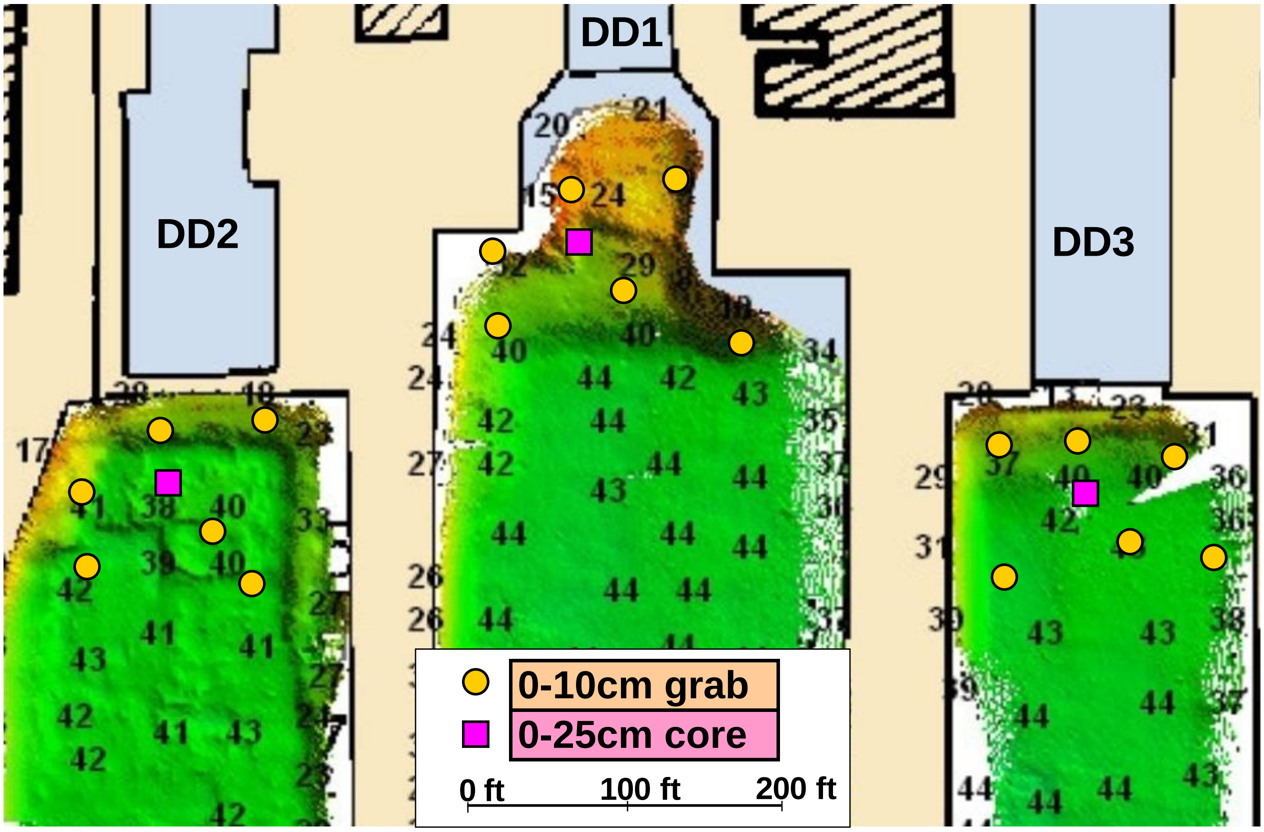
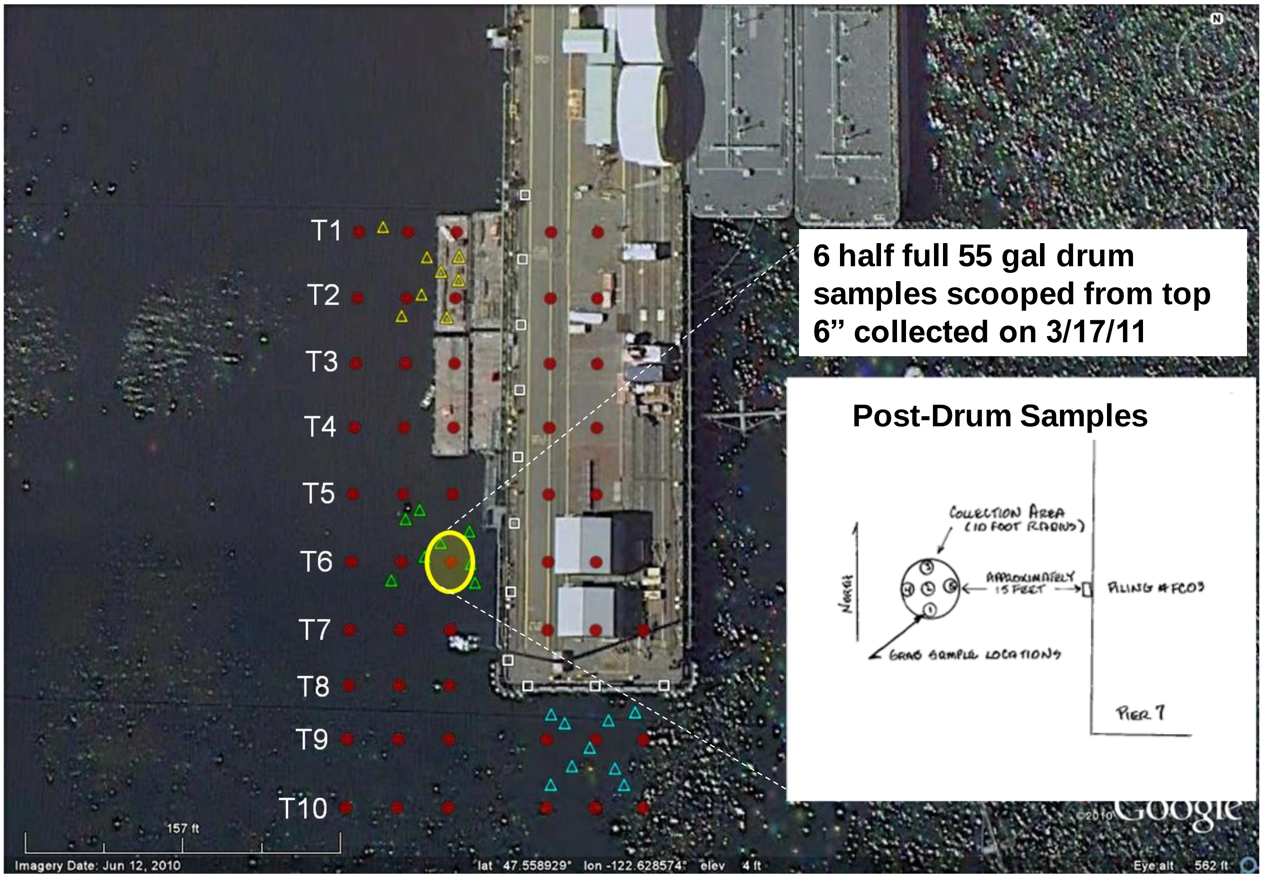


Figure 22. SQVPS10, SQVPS10.1, and SQVPS11 target sampling locations.



6 half full 55 gal drum samples scooped from top 6” collected on 3/17/11

Post-Drum Samples

Figure 23. Pier 7 R&D sampling locations.

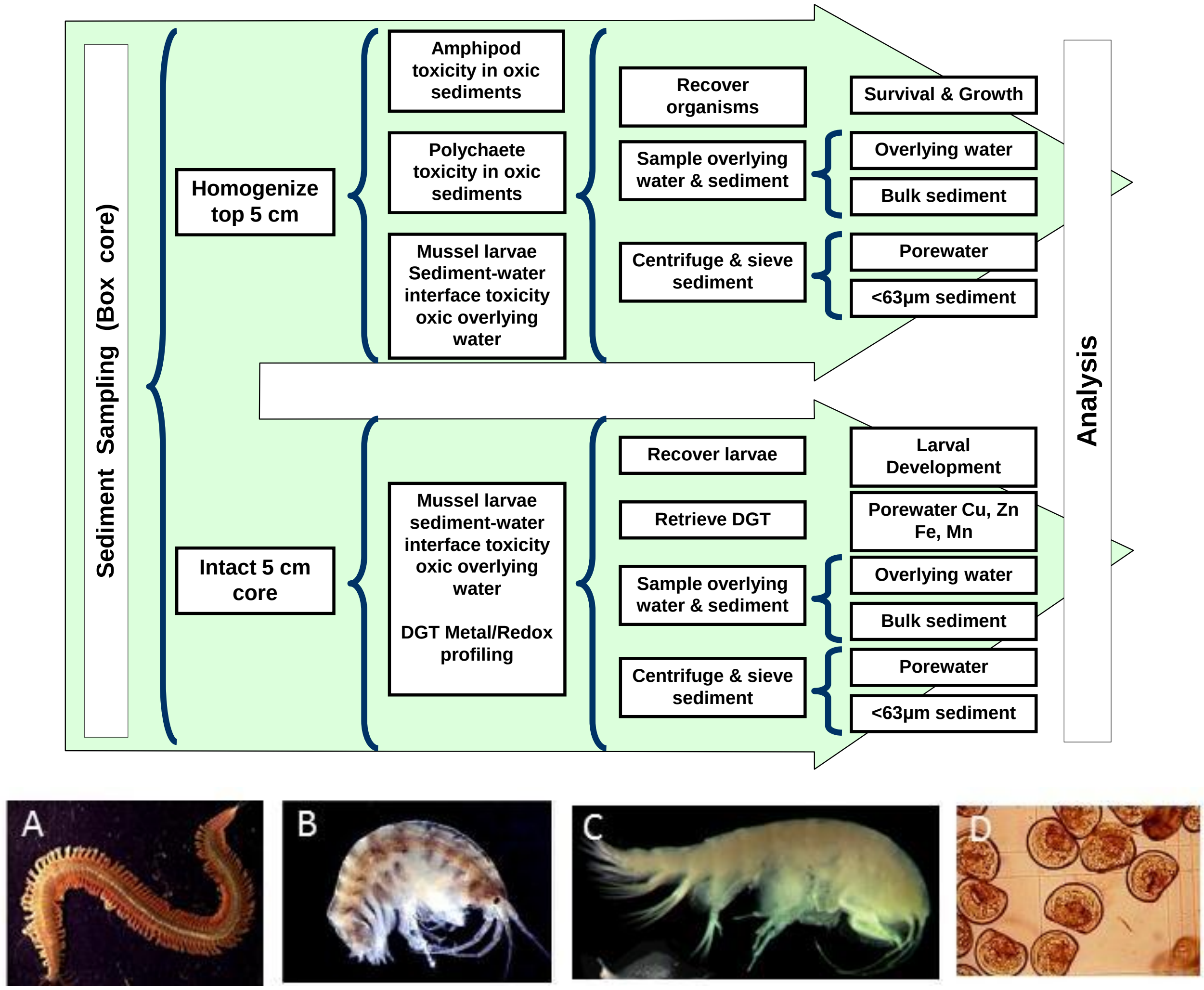


Figure 24. Schematic of toxicity testing experimental design and toxicity endpoints to be evaluated: a) polychaete (*Neanthes arenaceodentata*) survival and growth, b) amphipod (*Leptocheirus plumulosus*) survival, c) amphipod (*Ampelisca abdita*) survival, and d) bivalve (*Mytilus galloprovincialis*) embryo-larval development. Photos are not to scale.

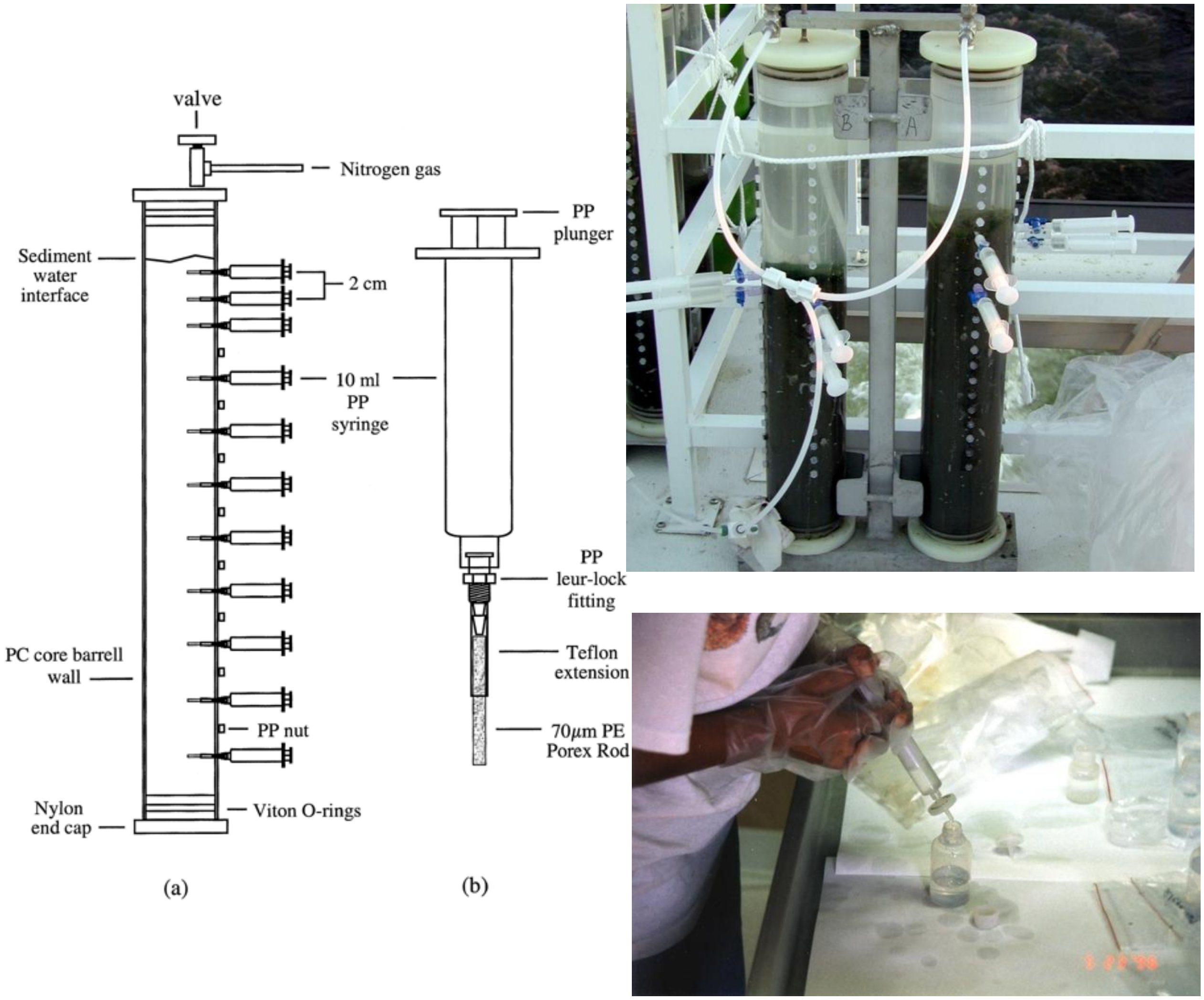


Figure 25. The (a) core squeezer used to extract pore water from a sediment cores with a (b) blow-up of the syringe set-up, consisting of a 10 ml polypropylene syringe, leur lock fitting, Teflon extension, and Porex rod and photos of the sampling device (Warnken et al. 2000).

12.0 Appendices

12.1 A. Screening Results for OUBM Sediment Monitoring Samples

12.1.1 A1. XRF Screening Results for OUBM Sediment Monitoring Samples

AppendixA1_OUBM2010_FPXRF_Metals.xls

Sample Location: Various offshore/inshore sediment sites located inside Sinclair Inlet along Operable Unit B (OU-B), Bremerton Naval Complex (BNC)
(i) Outside [OOUB] 1500 ft grid, (ii) Marine [OUBM] 500 ft grid, (iii) inside Drydock #6 [DD6], & (iv) Pierside - Quaywall [PQ] adjacent to outfall 18,
near/at Naval Shipyard (NSY) Puget Sound, Bremerton, Washington (USA)
Sampling Dates: 4 - 27 May 2010
Sample Type: Sediment (wet), grab, composite
Analysis: Selected Metals (Fe, Cu, Zn, Pb, etc.) by Field Portable X-ray Fluorescence (FPXRF) Spectrometry
FPXRF Application: EPA Method 6200: (Elemental Concentrations) - for soils and sediments
Analysis Dates: 11 - 19 August 2010
Analyst: Joel M. Guerrero, Scientist (Environmental Chemistry), U.S. Navy Space & Naval Warfare Systems Center (SPAWARSYSCEN) Pacific,
Advanced Systems & Applied Sciences Division, Applied Systems & Environmental Sciences Branch (Code 71751), (619) 553-4169
Analysis Location: Building 111, Rapid Sediment Characterization (RSC) Laboratory, Room 122 (Bayside), (619) 553-2765
POCs: ***Dr. James M. Leather***, Scientist (Marine Geochemistry), SPAWARSYSCEN, Pacific [SSC-Pacific], Code 71751: (619) 553-6240
Joel M. Guerrero, Scientist (Environmental Chemistry), SPAWARSYSCEN Pacific [SSC-Pacific], Code 71751: (619) 553-4169

Analytical Technique:

X-Ray Fluorescence spectrometry is an analytical technique that provides rapid, multi-element analysis of metals in soils/sediments.
Samples are exposed to x-ray energy, which liberates electrons in the inner shell of metal atoms.
As the outer electrons cascade towards the inner shells to fill the vacancies, energy is released (fluorescence).
The fluorescing energy spectrum identifies the metals and the intensity is proportional to concentration.

Analytical Instrument:

Sediment samples were analyzed using a X-MET 3000TX Field Portable X-ray Fluorescence (FPXRF) Spectrometer (Oxford Instruments, Elk Grove Village, IL). The X-MET is a field portable elemental analyzer based on energy dispersive X-ray fluorescence technology. This instrument is specifically calibrated for soil/sediment (alloy class) applications and utilizes an integrated personal digital assistance (PDA) computer for data storage. The probe contains a miniature, programmable x-ray tube for primary generation of x-rays (40 kV, 40 µamps) and a Peltier cooled, solid-state Silicone-P-type/intrinsic/N-type detector. The Si-PiN detector provides high spectral resolution which exceeds other solid-state detectors or gas-filled proportional detectors. X-MET data output from each sample analysis includes a broad elemental spectrum display from the K series x-ray lines at the 2.04 - 31.68 keV energy range and their associated dry weight metal concentrations (in mg/Kg or ppm) with error estimates.

Instrument Calibration & Statistically-based Method Detection Limits (note: not field-based detection limits)

The X-MET FPXRF was calibrated using a specific empirical calibration program for soils/sediments in the PDA menu.
Six (6) sediment Standard Reference Materials (SRMs) were analyzed as calibration check standards.
National Institute of Standards & Technology (NIST) 2704, 2709, 2710, & 2711
and Canadian National Reseach Council (CNRC) PACS-1 & PACS-2 were used for standardization.
Method detection limits (MDLs) were calculated using clean blank standards such as Quartz & washed Sea Sand (Fisher Scientific Grade)
Specific MDLs for the following metals: (Fe, Cu, Zn, Pb) were calculated from the standards as follows:

(i) [a]**MDL** = $t_{(n-1,1-\alpha=0.99)}$ (s)

(ii) RDL = 6 σ

where;

MDL = Method Detection Limit (same as LLD, 3 σ) in mg/Kg or (ppm)
RDL **=** Realible Detection Limit in mg/Kg or (ppm)
t = Student's t value for a 99% confidence level & standard deviation estimate
with n-1 degrees of freedom (t = 3.14[b] for 7-10 replicates)
n = number of samples
s = standard deviation (σ)

Analyte	(3 σ) MDL	(6 σ) RDL
Fe	597	3664
Cu	38	74
Zn	19	36
Pb	46	90

Sample Handling:
Sample splits for screening were performed on sediments collected previously at PSNS&IMF Bremerton Naval Complex (BNC) and stored at the Battelle Marine Sciences Laboratory (BMSL), Sequim, Washington. Sediment samples in jars were shipped to Space & Naval Warfare (SPAWAR) Systems Center Pacific [SSC-Pacific] RSC laboratory for further processing/screening.

Sample Processing:
Rapid screening analysis of sediment samples using the FPXRF employed a combination of *ex situ* sample processing with *in situ* sample testing. Samples were mixed thoroughly with clean spoons/wooden sticks. About 20-30 grams were de-watered using a heavy duty filter paper (grade 13 V) and air-dried to reduce moisture content to at least < 30%. Relevant sediment meta-data were also noted and recorded (*i.e*. color, grain size, smell, debris, oil sheen, shell hash, etc.). Dry, homogenized sediments, including standard reference materials (SRMs), were transferred into clean/sterile, pre-labeled ziplock bags.

Sample Analyses:
FPXRF analyses of dried sediments were performed in a controlled area (Class 100 hood) free from dust & temperature extremes. Each sample was analyzed by placing the x-ray window directly into the sediments inside the bags. The operator pushes the analyzer start button and releases it to stop the analysis scan. Each sample was analyzed for approximately 1 minute using the 40kV x-ray source.

Because XRF is a non-destructive technique, the samples were either archived and/or used for other RSC analyses.

Qualitative and quantitative results for each sample were measured, recorded and saved to an iPAQ^{TM} PDA with the appropriate sample label.
Samples were analyzed for a suite of metals (e.g., V, Cr, Fe, Co, Ni, Cu, Zn, As, Se Cd, Mo, Sb, Hg and Pb).
Results were calculated based on empirical assay calibration using standard reference materials.
Samples (at least 1/30 per sample batch) were analyzed in triplicate as an internal quality control check on instrument precision.
Method/instrument blanks and performance calibration checks were routinely performed (1/20 sample batch) as part of RSC QA/QC screening protocols.

Data Handling & Processing:
Screening data stored in the PDA was transferred to a laptop PC via a Windows^{TM} based application ActiveSync^{TM} data acquisition software or a CF flash card. Serial data, with comma separated value (.CSV) formats, were transmitted and copied into a spreadsheet program (Excel^{TM}) for further processing and reduction. Standard reference calibration curves (with $R^2 > 0.9$) are generated for each chemical of potential concern (COPC) (i.e. Cu, Zn, Pb, and Fe).

Data Quality:

<u>Accuracy</u>
Initial/daily method calibration (5 pt) and continuing calibration verification (1/20)
Instrument blank analysis of clean sea sand and quartz (< 5x MDL)
%RPD = comparison of SRMs (≤ 30%)

<u>Precision</u>
%RPD = comparison of field duplicate measurements (< 30%)
%RSD = comparison of three or more sample replicates (≤ 30%)

<u>Data Qualifiers (Q):</u>
U: Analyte was not detected (measured value ≤ MDL)
J: Estimated value (MDL ≤ measured value ≤ RDL)

<u>References:</u>

[a] Title 40 Code of Federal Regulations (CFR), Part 136 Appendix B, Revision 1.11.

[b] US Environmental Protection Agency (EPA), Environmental Monitoring Systems Laboratory, Office of Research and Development (ORD), Methods for the Determination of Metals in Environmental Samples, 1992, Columbus, OH (USA).

FPXRF Metals Results

Field Station/ID	Fe $_{\text{RSC}}$	Q	Stdev	%RSD	Cu $_{\text{RSC}}$	Q	Stdev	%RSD	Zn $_{\text{RSC}}$	Q	Stdev	%RSD	Pb $_{\text{RSC}}$	Q	Stdev	%RSD
OOUB-G 1	**29108**		833	2.86%	**12**	U			**70**	J	19	27.12%	**31**	U		
OOUB-G 2	**21350**		961	4.50%	**25**	U			**47**	U			**29**	U		
OOUB-G 3	**22911**		782	3.41%	**7**	U			**65**	J	10	15.52%	**24**	U		
OOUB-G 4	**23715**		783	3.30%	**25**	U			**66**	J	15	23.22%	**29**	U		
OOUB-G 5	**32484**		526	1.62%	**78**	J	27	34.82%	**136**		17	12.77%	**78**	J	36	45.71%
OOUB-G 6	**36991**		1146	3.10%	**109**		28	25.40%	**159**		4	2.49%	**103**		32	31.09%
OOUB-G 7	**35016**		646	1.84%	**89**	J	15	16.25%	**168**		5	3.27%	**88**	J	11	11.95%
OOUB-G 8	**33979**		458	1.35%	**125**		24	19.12%	**155**		16	10.42%	**104**		8	8.09%
OOUB-G 9	**34531**		1023	2.96%	**110**		19	17.27%	**166**		14	8.59%	**84**	J	15	17.50%
OOUB-G 10	**34905**		700	2.01%	**106**		22	21.01%	**163**		14	8.70%	**117**		22	19.28%
OOUB-G 11	**35059**		610	1.74%	**91**	J	20	22.14%	**156**		18	11.41%	**96**	J	19	19.88%
OOUB-G 12	**19230**		1042	5.42%	**9**	U			**51**	J	11	21.64%	**19**	U	14	
OOUB-G 12dup	**19794**		465	2.35%	**25**	U			**63**	J	12	19.27%	**25**	U	13	
OOUB-G 13	**35692**		1032	2.89%	**76**	J	30	39.92%	**155**		21	13.40%	**79**	J	20	25.07%
OOUB-G 14	**33187**		807	2.43%	**77**	J	34	44.90%	**148**		7	4.88%	**91**	J	13	14.59%
OOUB-G 14dup	**34720**		710	2.04%	**96**	J	11	11.02%	**157**		16	10.31%	**97**	J	14	14.49%
OOUB-G 15	**35899**		1113	3.10%	**75**	J	33	43.38%	**159**		21	12.93%	**93**	J	20	21.18%
OOUB-G 16	**34340**		403	1.17%	**113**		24	21.19%	**201**		28	14.09%	**86**	J	20	22.84%
OOUB-G 17	**36398**		789	2.17%	**94**	J	37	38.91%	**157**		16	10.11%	**87**	J	10	11.68%
OOUB-G 18	**34458**		1737	5.04%	**112**		16	14.46%	**157**		10	6.32%	**73**	J	16	22.20%
OOUB-G 19	**33270**		805	2.42%	**98**	J	35	35.45%	**163**		16	9.84%	**90**	J	13	14.12%
OOUB-G 20	**36255**		995	2.74%	**111**		17	15.09%	**137**		13	9.86%	**94**	J	17	17.70%
OOUB-G 21	**34477**		793	2.30%	**76**	J	24	31.13%	**131**		22	16.56%	**97**	J	27	27.61%
OOUB-G 22	**35295**		990	2.80%	**89**	J	32	36.46%	**155**		7	4.74%	**87**	J	14	15.70%
OOUB-G 23	**26768**		397	1.48%	**44**	U			**126**		12	9.46%	**74**	J	25	34.52%
OOUB-G 23dup	**27379**		678	2.48%	**66**	J	31	46.96%	**154**		50	32.35%	**64**	J	14	21.40%
OOUB-G 24	**34147**		992	2.90%	**89**	J	19	21.00%	**159**		27	16.72%	**75**	J	19	25.25%
OOUB-G 25	**25922**		859	3.32%	**31**	U			**102**		18	17.58%	**53**	J	14	27.07%
OOUB-G 26	**19847**		1124	5.66%	**25**	U			**60**	J	6	9.93%	**11**	U		
OOUB-G 27	**33798**		212	0.63%	**82**	J	35	43.01%	**152**		22	14.52%	**81**	J	31	38.29%
OOUB-G 28	**33937**		1719	5.07%	**42**	U			**134**		7	5.36%	**94**	J	19	20.52%
OOUB-G 29	**28026**		811	2.89%	**18**	U			**113**		23	20.09%	**57**	J	12	20.61%
OOUB-G 30	**18060**		1339	7.42%	**25**	U			**45**	U			**25**	U		
OOUB-G 31	**33356**		1089	3.26%	**51**	J	30	57.91%	**116**		7	6.22%	**91**	J	23	25.61%
OOUB-G 32	**25539**		763	2.99%	**25**	U	20		**107**		17	16.32%	**61**	J	14	23.69%

Definitions:

Stdev *:* Standard Deviation from replicate XRF measurements (n≥3)

% RSD *:* Percent Relative Standard Deviation whereby; [{*stdev/mean}* * *100*]

***Data Qualifier* (Q)**: **U** = not detected, (measured value ≤ MDL); **J** = Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** $_{\text{RSC}}$ = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn $_{\text{RSC}}$ = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb $_{\text{RSC}}$ = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe $_{\text{RSC}}$ = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

OOUB-G = Outside Operable Unit B - Grid **#** (1…32); **dup** = station field duplicate

FPXRF Metals Results

Field Station/ID	Fe $_{RSC}$	Q	Stdev	%RSD	Cu $_{RSC}$	Q	Stdev	%RSD	Zn $_{RSC}$	Q	Stdev	%RSD	Pb $_{RSC}$	Q	Stdev	%RSD
OUBM-G 1	**29822**		1313	4.40%	**95**	J	16	16.81%	**170**		13	7.44%	**77**	J	1	0.68%
OUBM-G 2	**38254**		508	1.33%	**116**		11	9.20%	**164**		24	14.59%	**94**	J	8	7.99%
OUBM-G 3	**29089**		1077	3.70%	**71**	J	5	7.12%	**142**		13	9.24%	**73**	J	21	29.32%
OUBM-G 4	**35879**		727	2.03%	**96**	J	11	11.64%	**162**		4	2.60%	**96**	J	13	13.40%
OUBM-G 5	**36398**		835	2.29%	**96**	J	23	24.26%	**160**		15	9.29%	**83**	J	9	10.55%
OUBM-G 6	**34525**		596	1.72%	**101**		31	30.53%	**168**		5	3.10%	**99**	J	8	8.32%
OUBM-G 7	**35376**		643	1.82%	**89**	J	18	20.73%	**156**		25	16.36%	**101**		39	38.22%
OUBM-G 8	**36093**		529	1.47%	**106**		31	29.37%	**168**		23	13.81%	**115**		33	28.63%
OUBM-G 9	**35458**		598	1.69%	**89**	J	27	29.93%	**147**		17	11.42%	**97**	J	20	20.99%
OUBM-G 10	**27710**		362	1.31%	**34**	U			**128**		37	28.95%	**63**	J	16	25.74%
OUBM-G 11	**32956**		897	2.72%	**70**	J	37	52.96%	**124**		13	10.13%	**75**	J	16	21.65%
OUBM-G 11dup	**35454**		343	0.97%	**63**	J	14	22.67%	**150**		19	12.84%	**94**	J	23	24.28%
OUBM-G 12	**34139**		1222	3.58%	**82**	J	29	34.95%	**154**		17	10.98%	**96**	J	21	22.48%
OUBM-G 13	**36079**		1909	5.29%	**63**	J	20	31.58%	**136**		18	12.96%	**99**	J	41	41.48%
OUBM-G 14	**24675**		817	3.31%	**12**	U			**89**	J	15	16.80%	**36**	U		
OUBM-G 15	**34019**		844	2.48%	**66**	J	34	50.92%	**123**		18	15.06%	**63**	J	5	7.73%
OUBM-G 16	**34962**		735	2.10%	**69**	J	23	33.56%	**152**		29	19.40%	**63**	J	9	13.96%
OUBM-G 17	**36715**		795	2.16%	**88**	J	18	20.30%	**150**		27	18.03%	**89**	J	28	31.09%
OUBM-G 18	**25937**		911	3.51%	**44**	U			**110**		10	9.36%	**68**	J	17	24.37%
OUBM-G 19	**31209**		1691	5.42%	**80**	J	17	21.45%	**150**		14	9.29%	**62**	J	23	37.25%
OUBM-G 20	**36755**		957	2.60%	**69**	J	7	9.50%	**185**		32	17.27%	**85**	J	3	3.76%
OUBM-G 21	**29478**		778	2.64%	**51**	J	19	37.03%	**129**		9	6.98%	**54**	J	13	23.05%
OUBM-G 22	**36398**		923	2.53%	**127**		31	24.40%	**151**		23	15.34%	**94**	J	27	28.73%
OUBM-G 23	**35905**		423	1.18%	**137**		2	1.17%	**176**		27	15.62%	**103**		6	5.37%
OUBM-G 24	**33981**		986	2.90%	**137**		31	22.91%	**178**		14	7.76%	**104**		23	22.54%
OUBM-G 25	**36458**		1055	2.89%	**150**		43	28.45%	**203**		24	11.83%	**85**	J	28	33.26%
OUBM-G 26	**36938**		641	1.73%	**163**		14	8.39%	**261**		81	30.88%	**111**		9	8.26%
OUBM-G 27	**36659**		1393	3.80%	**116**		38	32.55%	**169**		9	5.39%	**101**		22	22.15%
OUBM-G 28	**36553**		841	2.30%	**193**		10	4.96%	**213**		15	6.96%	**102**		8	7.35%
OUBM-G 29	**38459**		1618	4.21%	**206**		7	3.51%	**248**		10	4.13%	**138**		13	9.47%
OUBM-G 30	**35292**		944	2.67%	**119**		23	19.31%	**178**		20	11.45%	**82**	J	38	46.30%
OUBM-G 31	**35409**		485	1.37%	**99**	J	8	7.88%	**169**		7	4.11%	**98**	J	22	22.34%
OUBM-G 32	**36404**		1666	4.58%	**89**	J	16	17.83%	**167**		16	9.34%	**124**		11	9.19%
OUBM-G 33	**34724**		1118	3.22%	**163**		11	7.04%	**204**		5	2.34%	**121**		17	14.22%
OUBM-G 34	**36185**		984	2.72%	**187**		30	16.14%	**206**		35	16.79%	**115**		20	17.62%
OUBM-G 35	**36327**		2006	5.52%	**122**		7	5.58%	**208**		33	15.73%	**116**		10	8.87%
OUBM-G 36	**35648**		1093	3.07%	**148**		31	20.93%	**190**		13	6.82%	**102**		9	9.24%

Definitions:

***Stdev** :* Standard Deviation from replicate XRF measurements (n≥3)

***% RSD** :* Percent Relative Standard Deviation whereby; [*{stdev/mean} * 100*]

***Data Qualifier* (Q)**: **U =** not detected, (measured value ≤ MDL); **J =** Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** $_{RSC}$ = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn $_{RSC}$ = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb $_{RSC}$ = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe $_{RSC}$ = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

OUBM-G = Operable Unit B Marine - Grid # (1…71); **dup** = station field duplicate

FPXRF Metals Results

Field Station/ID	Fe RSC				Cu RSC				Zn RSC				Pb RSC			
		Q	Stdev	%RSD		Q	Stdev	%RSD		Q	Stdev	%RSD		Q	Stdev	%RSD
OUBM-G 37	**36145**		609	1.69%	**135**		41	30.37%	**178**		6	3.42%	**94**	J	26	28.23%
OUBM-G 38	**41095**		2117	5.15%	**203**		21	10.12%	**383**		63	16.46%	**132**		3	2.31%
OUBM-G 39	**27460**		1660	6.04%	**111**		23	20.20%	**385**		56	14.48%	**168**		43	25.64%
OUBM-G 40	**35932**		988	2.75%	**202**		84	41.47%	**210**		20	9.66%	**85**	J	7	7.72%
OUBM-G 41	**36132**		1213	3.36%	**174**		23	13.19%	**239**		10	4.04%	**134**		29	21.63%
OUBM-G 42	**36572**		699	1.91%	**145**		35	24.50%	**209**		28	13.51%	**102**		15	15.01%
OUBM-G 42dup	**37850**		1611	4.26%	**188**		32	16.83%	**208**		8	3.64%	**105**		14	12.98%
OUBM-G 43	**39695**		2615	6.59%	**183**		24	13.04%	**440**		58	13.29%	**138**		33	23.48%
OUBM-G 44	**36020**		760	2.11%	**98**	J	31	31.35%	**181**		30	16.54%	**88**	J	33	37.47%
OUBM-G 45	**37247**		1109	2.98%	**208**		13	6.44%	**223**		12	5.58%	**124**		34	27.48%
OUBM-G 46	**26962**		2232	8.28%	**32**	U			**135**		29	21.40%	**46**	U		
OUBM-G 47	**35571**		220	0.62%	**96**		28	29.35%	**170**		22	12.66%	**99**	J	21	21.74%
OUBM-G 48	**35494**		1546	4.36%	**101**		12	11.51%	**149**		8	5.34%	**72**	J	20	27.65%
OUBM-G 49	**34477**		1122	3.25%	**148**		42	28.21%	**218**		13	6.09%	**111**		9	8.10%
OUBM-G 50	**36272**		1657	4.57%	**106**		28	25.99%	**174**		13	7.67%	**85**	J	23	27.20%
OUBM-G 51	**35316**		938	2.66%	**77**	J	43	56.22%	**162**		17	10.32%	**98**	J	20	20.57%
OUBM-G 52	**37373**		896	2.40%	**180**		28	15.40%	**360**		54	15.02%	**186**		25	13.39%
OUBM-G 53	**36474**		2260	6.20%	**94**	J	22	23.14%	**170**		25	14.51%	**89**	J	26	29.09%
OUBM-G 54	**35278**		1304	3.70%	**78**	J	41	53.37%	**168**		29	16.99%	**111**		60	54.08%
OUBM-G 55	**36280**		1229	3.39%	**157**		33	21.00%	**248**		22	9.00%	**118**		29	24.71%
OUBM-G 56	**39060**		1800	4.61%	**172**		56	32.72%	**300**		18	6.00%	**147**		46	31.04%
OUBM-G 57	**37584**		1787	4.76%	**122**		15	12.66%	**231**		21	9.04%	**118**		25	21.32%
OUBM-G 58	**35835**		1467	4.09%	**81**	J	17	20.44%	**148**		22	14.76%	**80**	J	20	24.97%
OUBM-G 59	**36252**		1209	3.34%	**158**		12	7.54%	**192**		11	5.91%	**105**		21	19.69%
OUBM-G 60	**38807**		1473	3.79%	**211**		26	12.29%	**345**		99	28.61%	**188**		67	35.49%
OUBM-G 61	**41367**		3173	7.67%	**178**		55	30.70%	**337**		65	19.42%	**140**		31	22.29%
OUBM-G 62	**35598**		1180	3.31%	**62**	J	25	40.12%	**147**		16	10.56%	**106**		33	30.79%
OUBM-G 63	**37562**		883	2.35%	**202**		38	18.65%	**221**		19	8.53%	**96**	J	10	10.72%
OUBM-G 64	**37221**		1493	4.01%	**167**		24	14.48%	**286**		35	12.18%	**127**		18	14.02%
OUBM-G 65	**33958**		899	2.65%	**133**		33	25.16%	**348**		66	19.05%	**129**		18	13.92%
OUBM-G 66	**36179**		1350	3.73%	**65**	J	27	41.78%	**185**		17	9.25%	**114**		31	27.09%
OUBM-G 67	**38486**		453	1.18%	**283**		28	9.95%	**382**		30	7.75%	**211**		11	5.32%
OUBM-G 68	**35067**		1145	3.27%	**171**		54	31.83%	**292**		26	8.76%	**125**		22	17.50%
OUBM-G 68dup	**36882**		2013	5.46%	**176**		14	7.78%	**290**		34	11.89%	**122**		15	12.59%
OUBM-G 69	**27942**		1033	3.70%	**79**	J	26	32.50%	**225**		64	28.53%	**85**	J	4	4.42%
OUBM-G 70	**33815**		950	2.81%	**60**	J	12	20.51%	**136**		4	2.74%	**85**	J	16	19.32%
OUBM-G 71	**20633**		1400	6.79%	**25**	U			**84**	J	20	23.18%	**43**	U		

Definitions:

Stdev *:* Standard Deviation from replicate XRF measurements (n≥3)

% RSD *:* Percent Relative Standard Deviation whereby; [*{stdev/mean} * 100*]

Data Qualifiers **(Q)**: **U =** not detected, (measured value ≤ MDL); **J =** Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** RSC = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn RSC = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb RSC = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe RSC = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

OUBM-G = Operable Unit B Marine - Grid # (1…71); **dup** = station field duplicate

FPXRF Metals Results

Field Station/ID	**Fe $_{RSC}$**	**Q**	**Stdev**	**%RSD**	**Cu $_{RSC}$**	**Q**	**Stdev**	**%RSD**	**Zn $_{RSC}$**	**Q**	**Stdev**	**%RSD**	**Pb $_{RSC}$**	**Q**	**Stdev**	**%RSD**
DD6-1	**30089**		1194	3.97%	**112**		34	29.97%	**227**		13	5.93%	**92**	J	20	22.14%
DD6-2	**25006**		1131	4.52%	**81**	J	9	10.66%	**219**		22	10.17%	**226**		55	24.60%
DD6-3	**19061**		766	4.02%	**49**	U			**216**		16	7.55%	**530**		45	8.52%
DD6-4	**31046**		1815	5.85%	**137**		32	23.42%	**220**		16	7.45%	**65**	J	18	27.41%
DD6-5	**24444**		1442	5.90%	**111**		14	12.18%	**248**		20	8.24%	**194**		70	36.22%
DD6-6	**18342**		333	1.81%	**99**	J	35	35.55%	**180**		7	3.61%	**485**		19	3.89%
DD6-7	**32368**		1731	5.35%	**350**		43	12.30%	**526**		76	14.36%	**76**	J	24	32.18%
PQ1	**36642**		1078	2.94%	**357**		71	19.83%	**441**		60	13.71%	**84**		9	11.12%
PQ2	**57559**		2773	4.82%	**1004**		160	15.93%	**1477**		366	24.79%	**393**		62	15.79%
PQ3	**36854**		2281	6.19%	**474**		24	4.99%	**707**		16	2.20%	141		25	17.69%

Definitions:

Stdev *:* Standard Deviation from replicate XRF measurements (n≥3)

% RSD *:* Percent Relative Standard Deviation whereby; [{*stdev/mean}* * *100*]

***Data Qualifier* (Q)**: **U =** not detected, (measured value ≤ MDL); **J =** Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** $_{RSC}$ = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn $_{RSC}$ = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb $_{RSC}$ = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe $_{RSC}$ = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

DD6 = Drydock # 6; **PQ** = Pierside - Quaywall

12.1.2 A2. PAH Screening Results for OUBM Sediment Monitoring Samples

OUB PAH_PCB Results

SAMPLE LABEL	tPCB (µg/Kg)	Q	Stdev	%RSD	tPAH (µg/Kg)	Q	Stdev	%RSD	Fe (mg/Kg)	Q	Stdev	%RSD
OUBM-G 1					3451				29822			
OUBM-G 2					2843				38254			
OUBM-G 3					2432				29089			
OUBM-G 4					2460				35879			
OUBM-G 5					2742				36398			
OUBM-G 6					3167				34525			
OUBM-G 7					2326				35376			
OUBM-G 8					2727				36093			
OUBM-G 9					2524				35458			
OUBM-G 10					2007				27710			
OUBM-G 11					2940				32956			
OUBM-G 11 DUP					2900				35454			
OUBM-G 12					2631				34139			
OUBM-G 13					2651				36079			
OUBM-G 14					2755				24675			
OUBM-G 15					2073				34019			
OUBM-G 16					2333				34962			
OUBM-G 17					2138				36715			
OUBM-G 18					1862				25937			
OUBM-G 19					2199				31209			
OUBM-G 20					2372				36755			
OUBM-G 21					2173				29478			
OUBM-G 22					2539				36398			
OUBM-G 23					3056				35905			
OUBM-G 24					3838				33981			
OUBM-G 25					2958				36458			
OUBM-G 26					2931				36938			
OUBM-G 27					2501				36659			
OUBM-G 28					3882				36553			
OUBM-G 29					3822				38459			
OUBM-G 30					3344				35292			
OUBM-G 31					3198				35409			
OUBM-G 32					3330				36404			
OUBM-G 33					7567				34724			
OUBM-G 34					4392				36185			
OUBM-G 35					3564				36327			
OUBM-G 36					3828				35648			
OUBM-G 37					4317				36145			
OUBM-G 38					2518				41095			
OUBM-G 39					9099				27460			
OUBM-G 40					5147				35932			
OUBM-G 41					9654				36132			

Definitions:

Stdev *:* Standard Deviation from duplicate assay analyses (n=2)

% RSD *:* Percent Relative Standard Deviation whereby; [{stdev/mean} * 100]

Q **:** Data Qualifiers: **U** = None-Detect, **J** = Estimated, **E** = Outside Linear Range, **Blank** = Detect

Label: **OUBM** = Operable Unit B Marine; **OOUB** = Outside Operable Unit B Marine

OUB PAH_PCB Results

SAMPLE	tPCB				tPAH				Fe			
LABEL	(mg/Kg)	Q	Stdev	%RSD	(mg/Kg)	Q	Stdev	%RSD	(mg/Kg)	Q	Stdev	%RSD
OUBM-G 42					4862				36572			
OUBM-G 42 DUP					5237				37850			
OUBM-G 43					4724				39695			
OUBM-G 44					3969				36020			
OUBM-G 45					4965				37247			
OUBM-G 46					2327				26962			
OUBM-G 47					4366				35571			
OUBM-G 48					2949				35494			
OUBM-G 49					2980				34477			
OUBM-G 50					5560				36272			
OUBM-G 51					2514				35316			
OUBM-G 52					5754				37373			
OUBM-G 53					2967				36474			
OUBM-G 54					3620				35278			
OUBM-G 55					5123				36280			
OUBM-G 56					4276				39060			
OUBM-G 57					5776				37584			
OUBM-G 58					4216				35835			
OUBM-G 59					4365				36252			
OUBM-G 60					8415				38807			
OUBM-G 61					11121				41367			
OUBM-G 62					4817				35598			
OUBM-G 63					6131				37562			
OUBM-G 64					8015				37221			
OUBM-G 65					8024				33958			
OUBM-G 66					5030				36179			
OUBM-G 67					9360				38486			
OUBM-G 68					5484				35067			
OUBM-G 68 DUP					6720				36882			
OUBM-G 69					4994				27942			
OUBM-G 70					3685				33815			
OUBM-G 71					2074				20633			

Definitions:

Stdev *:* Standard Deviation from duplicate assay analyses (n=2)

% RSD *:* Percent Relative Standard Deviation whereby; [{stdev/mean} * 100]

Q **:** Data Qualifiers: **U** = None-Detect, **J** = Estimated, **E** = Outside Linear Range, **Blank** = Detect

Label: **OUBM** = Operable Unit B Marine; **OOUB** = Outside Operable Unit B

OUB PAH_PCB Results

SAMPLE LABEL	tPCB (mg/Kg)	Q	Stdev	%RSD	tPAH (mg/Kg)	Q	Stdev	%RSD	Fe (mg/Kg)	Q	Stdev	%RSD
OOUB-G 1					1219				29108			
OOUB-G 2					1127				21350			
OOUB-G 3					1198				22911			
OOUB-G 4					1482				23715			
OOUB-G 5					1847				32484			
OOUB-G 6					2206				36991			
OOUB-G 7					3206				35016			
OOUB-G 8					2117				33979			
OOUB-G 9					2596				34531			
OOUB-G 10					2680				34905			
OOUB-G 11					2478				35059			
OOUB-G 12					2149				19230			
OOUB-G 12 DUP					1318				19794			
OOUB-G 13					2535				35692			
OOUB-G 14					3163				33187			
OOUB-G 14 DUP					2869				34720			
OOUB-G 15					2563				35899			
OOUB-G 16					4807				34340			
OOUB-G 17					3305				36398			
OOUB-G 18					3008				34458			
OOUB-G 19					2552				33270			
OOUB-G 20					2589				36255			
OOUB-G 21					2237				34477			
OOUB-G 22					2361				35295			
OOUB-G 23					1636				26768			
OOUB-G 23 DUP					2187				27379			
OOUB-G 24					2067				34147			
OOUB-G 25					2059				25922			
OOUB-G 26					917				19847			
OOUB-G 27					2825				33798			
OOUB-G 28					2426				33937			
OOUB-G 29					1744				28026			
OOUB-G 30					999				18060			
OOUB-G 31					2748				33356			
OOUB-G 32					2202				25539			

Definitions:

Stdev *:* Standard Deviation from duplicate assay analyses (n=2)

% RSD *:* Percent Relative Standard Deviation whereby; [{stdev/mean} * 100]

Q **:** Data Qualifiers: **U** = None-Detect, **J** = Estimated, **E** = Outside Linear Range, **Blank** = Detect

Label: **OUBM** = Operable Unit B Marine; **OOUB** = Outside Operable Unit B

12.2 B. Stormwater Basin Description Table

APPENDIX B: STORMWATER BASIN DESCRIPTION TABLE

ID		ENVVEST		Total Basin Area				
EPA	PSNS	DSN #	NBK / CIA	Sq. Ft.	Acres	%TIA	Latitude	Longitude
1	126.4	178	CIA	420,576	9.65	94.56%	47 33' 15"	122 39' 17"
2	126.1	178	CIA			94.56%	47 33' 21"	122 39' 2 "
3	124	176	CIA	788,344	18.09	94.56%	47 33' 21"	122 38' 50"
4	122	177	CIA	663,265	15.22	98.50%	47 33' 21"	122 38' 31"
5	117	176	CIA			95.00%	47 33' 28"	122 38' 20"
6	115.1	175	CIA	463,189	10.63	97.00%	47 33' 35"	122 38' 11"
7	106	174	CIA	536,165	12.30	97.00%	47 33' 37"	122 37' 36"
8	096	172	CIA	718,196	16.48	97.00%	47 33' 21"	122 38' 41"
9	099	172	CIA			97.00%	47 33' 30"	122 38' 20"
10	081.1	169	CIA	965,759	22.16	97.00%	47 33' 36"	122 38' 5 "
11	056	PIER D	NBK	19,000	0.44	100.00%	47 33' 39"	122 37' 54"
12	053	168	NBK			97.00%	47 33' 36"	122 37' 47"
13	020.1	168	NBK	1,424,430	32.69	97.00%	47 33' 36"	122 37' 44"
14	015	167	NBK	4,407,826	101.16	91.56%	47 33' 15"	122 39' 20"
15	011	166	NBK	1,304,943	29.95	93.56%	47 33' 15"	122 39' 19"
17	123	176	CIA			94.56%	47 33' 15"	122 39' 18"
22	008	166	NBK			93.56%	47 33' 15"	122 39' 16"
23	126	177	CIA			98.50%	47 33' 15"	122 39' 15"
24	126.2	177	CIA			98.50%	47 33' 15"	122 39' 11"
25	124.1	176	CIA			94.56%	47 33' 17"	122 39' 10"
26	113	PIER	CIA	20,000	0.46	100.00%	47 33' 19"	122 39' 10"
27	108	174	CIA			97.00%	47 33' 20"	122 39' 10"
28	107	174	CIA			97.00%	47 33' 21"	122 39' 8 "
29	085	171	CIA	1,857,726	42.63	97.00%	47 33' 21"	122 39' 5 "
30	082.5	170	CIA	634,570	14.56	97.00%	47 33' 21"	122 39' 1 "
31	082.4	170	CIA	184,000	4.22	100.00%	47 33' 21"	122 38' 59"
32	082.3	170	CIA	224,000	5.14	100.00%	47 33' 21"	122 38' 58"
33	082	170	CIA			97.00%	47 33' 21"	122 38' 56"
34	032	168	NBK			97.00%	47 33' 21"	122 38' 54"
35	031	168	NBK			97.00%	47 33' 21"	122 38' 52"
36	028	168	NBK			97.00%	47 33' 21"	122 38' 48"
37	024	168	NBK			97.00%	47 33' 21"	122 38' 47"
38	017.1	168	NBK			97.00%	47 33' 21"	122 38' 46"
39	017	168	NBK			97.00%	47 33' 21"	122 38' 45"
40	014	166	NBK			93.56%	47 33' 21"	122 38' 43"
41	012	166	NBK			93.56%	47 33' 21"	122 38' 42"
42	122	176	CIA			94.56%	47 33' 21"	122 38' 42"
43	118.2	176	CIA			94.56%	47 33' 21"	122 38' 40"
44	116	175	CIA			97.00%	47 33' 21"	122 38' 39"
45	111	PIER 5	CIA			100.00%	47 33' 20"	122 38' 39"
46	110	PIER 5	CIA			100.00%	47 33' 19"	122 38' 39"
47	108.1	174	CIA			97.00%	47 33' 18"	122 38' 39"
48	104	174	CIA			97.00%	47 33' 17"	122 38' 39"
49	103	174	CIA			97.00%	47 33' 17"	122 38' 39"
50	UNK	168	NBK			97.00%	47 33' 16"	122 38' 39"
51	102	173	CIA	484,387	11.12	97.00%	47 33' 15"	122 38' 39"
52	101	173	CIA			97.00%	47 33' 14"	122 38' 39"
53	099	168	CIA	104,000	2.39	100.00%	47 33' 13"	122 38' 39"
54	090	168	CIA	94,000	2.16	100.00%	47 33' 12"	122 38' 39"
55	084.1	168	CIA	24,000	0.55	100.00%	47 33' 11"	122 38' 39"
56	082.6	170	CIA	15,250	0.35	100.00%	47 33' 12"	122 38' 32"
57	082.2	170	CIA			100.00%	47 33' 13"	122 38' 32"

ID		ENVVEST		Total Basin Area				
EPA	PSNS	DSN #	NBK / CIA	Sq. Ft.	Acres	%TIA	Latitude	Longitude
58	075	PIER D	NBK			100.00%	47 33' 14"	122 38' 32"
59	074	PIER D	NBK			100.00%	47 33' 21"	122 38' 30"
60	072	PIER D	NBK			100.00%	47 33' 22"	122 38' 27"
61	068	PIER D	NBK			100.00%	47 33' 22"	122 38' 26"
62	067	PIER D	NBK			100.00%	47 33' 22"	122 38' 24"
63	066	PIER D	NBK			100.00%	47 33' 29"	122 38' 20"
64	065	PIER D	NBK			100.00%	47 33' 30"	122 38' 19"
65	064	PIER D	NBK			100.00%	47 33' 30"	122 38' 12"
66	063	PIER D	NBK	29,000	0.67	100.00%	47 33' 22"	122 38' 22"
67	061	PIER D	NBK			100.00%	47 33' 36"	122 38' 6 "
68	060	PIER D	NBK			100.00%	47 33' 36"	122 38' 3 "
69	059	PIER D	NBK			100.00%	47 33' 36"	122 38' 3 "
70	058	PIER D	NBK			100.00%	47 33' 36"	122 38' 2 "
71	057	PIER D	NBK			100.00%	47 33' 36"	122 38' 2 "
72	051	168	NBK	59,000	1.35	100.00%	47 33' 37"	122 38' 0 "
73	050	168	NBK			100.00%	47 33' 37"	122 37' 57"
74	049	168	NBK			100.00%	47 33' 37"	122 37' 56"
75	048	168	NBK			100.00%	47 33' 36"	122 37' 54"
76	043	168	NBK	9,000	0.21	100.00%	47 33' 38"	122 37' 54"
77	042	168	NBK	9,000	0.21	100.00%	47 33' 40"	122 37' 54"
78	037	168	NBK	14,000	0.32	100.00%	47 33' 39"	122 37' 54"
79	UNK			6,500	0.15	100.00%	47 33' 41"	122 37' 52"
80	033	168	NBK			100.00%	47 33' 39"	122 37' 52"
82			Gone			100.00%	47 33' 39"	122 37' 50"
83	011.3	166	NBK			100.00%	47 33' 39"	122 37' 49"
84	011.2	166	NBK			100.00%	47 33' 39"	122 37' 50"
85	011.1	166	NBK			100.00%	47 33' 26"	122 37' 48"
87	009	166	NBK	34,000	0.78	100.00%	47 33' 36"	122 37' 40"
88	008.1	166	NBK	64,000	1.47	100.00%	47 33' 36"	122 37' 37"
89	006	166	NBK			100.00%	47 33' 37"	122 37' 37"
90	005	166	NBK			100.00%	47 33' 40"	122 37' 31"
91	003.1	166	NBK	44,000	1.01	100.00%	47 33' 21"	122 39' 9 "
92	UNK	PIER 3	CIA			100.00%	47 33' 23"	122 39' 4 "
93	UNK	PIER 3	CIA	74,000	1.70	25.00%	47 33' 23"	122 39' 3 "
94	UNK	PIER 3	CIA	54,000	1.24	25.00%	47 33' 24"	122 38' 41"
95	125	177	CIA			99.94%	47 33' 23"	122 38' 35"
97	121	176	CIA			80.05%	47 33' 27"	122 38' 23"
10B	081.1B	169	NBK			97.00%	47 33' 44"	122 38' 3 "
12B	053B	169	NBK			97.00%	47 33' 41"	122 37' 59"
14B	015B	167	NBK				47 33' 42"	122 37' 54"
1B	126.4B	178	CIA			94.56%	47 33' 42"	122 37' 44"
25B	124.1B	176	CIA			94.56%	47 33' 37"	122 37' 45"
28B	107B	174	CIA			97.00%	47 33' 43"	122 37' 39"
2B	126.1B	178	CIA			94.56%	47 33' 41"	122 37' 32"
30B	082.5B	170	CIA			97.00%	47 33' 36"	122 38' 4 "
3B	124B	176	CIA			94.56%	47 33' 21"	122 38' 47"
40B	014B	166	NBK			93.56%	47 33' 15"	122 39' 22"
52B	101B	168	CIA	496,586	11.40	107.97%	47 33' 13"	122 39' 27"
6B	115.1B	175	CIA			97.00%	47 33' 8 "	122 39' 38"

12.3 C1. The number of samples and analyses to be conducted.

C2. Supplies required for sampling

12.4 D. Screening Results for Pier 7 samples

12.4.1 D1. Pier 7 Immunoassay Results for PCBs

				Performing Lab	**SSC-Pacific**				**SedTrend**
				Analysis					
Project					Sediment	Sediment	Sediment	Sediment	Sediment
	Site	Location	Sample Type	Samples	metalsXRF	PAH-aa	PCB-aa	Toxicity	GrainSize
OUB Marine Monitoring									
		OUB 500ft grid	0-10cm grab COMP	71	71	71			71
		OOUB 1500 ft grid	0-10cm grab COMP	32	32	32			32
Pier 7 R&D Studies									
	PS16	Surface Cores	0-10cm	50	50		50		50
		Bulk Samples	0-10cm (top 6in)	2					
		Drum Samples	0-10cm (top 6in)	6					
		Post Drum Samples	0-10cm (top 6in)	5	5	5	5		5
		Sediment Amendment R&D SSC-Pacific							
		Sediment Bioavailability R&D ERDC-ERL							
Repair Projects									
	PS05	Pier B (preConstruct	0-10cm grab	11					
	PS12	Pier 8 (post construc	0-10cm grab	7					
		Quay Wall and DDs	0-10cm grab						
		Piers 5&6	0-10cm grab						
	PS06	DD6 Silt Samples	0-2 cm (silt on DD floor)	8	8				
	PS09	Near OF18 (PK sam	0-10cm grab	3	3				
SQV Sampling									
	PS03	Mooring E - Pier D	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
	PS06	DD6 Entrace and Pi	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
	PS07	W. Side DD6 and Fi	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
	PS08	RMTS and DD5	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
			0-25cm Squeeze Core(2)	1	6	6	6		
			0-5cm Tox Eval(3)	1				4	
	PS09	DD4 and Btwn Piers	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
			0-25cm Squeeze Core(2)	1	6	6	6		
			0-5cm Tox Eval(3)	1				4	
	PS10	DD2 and Btwn Piers	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
	PS10.1	DD3 and Btwn Piers	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
	PS11	DD1 and Btwn Piers	0-10cm grab	6	6	6	6		6
			0-25cm core(1)	1	5	5	5		
		Confirmaton Analysis (20%)							
			Total Analysis	255	269	208	155	8	206
			Completed	153	153	103	50	0	0
			Remaining	102	116	105	105	8	206
NOTES									
	🟨	Denotes analysis alteady completed or in progress							
(1)	Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20								
(2)	PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-20								
(3)	Toxicity endpoints								

				Performing Lab	**BMSL**				
				Analysis					
Project					Sediment	Sediment	Sediment	Sediment	Sediment
	Site	Location	Sample Type	Samples	HgDMA	TOC	metal-ICPMS	PAH-GCMS	PCB-GCMS
OUB Marine Monitoring									
		OUB 500ft grid	0-10cm grab COMP	71		22	19	22	
		OOUB 1500 ft grid	0-10cm grab COMP	32		8	11	8	
Pier 7 R&D Studies									
	PS16	Surface Cores	0-10cm	50	50	50	20% of XRF screening samples	20% of PAHaa screening samples	20% of PCBaa screening samples
		Bulk Samples	0-10cm (top 6in)	2					
		Drum Samples	0-10cm (top 6in)	6					
		Post Drum Samples	0-10cm (top 6in)	5	5	5			
		Sediment Amendment R&D SSC-Pacific							
		Sediment Bioavailability R&D ERDC-ERL							
Repair Projects									
	PS05	Pier B (preConstruct	0-10cm grab	11					
	PS12	Pier 8 (post construc	0-10cm grab	7					
		Quay Wall and DDs	0-10cm grab						
		Piers 5&6	0-10cm grab						
	PS06	DD6 Silt Samples	0-2 cm (silt on DD floor)	8	2				
	PS09	Near OF18 (PK sam	0-10cm grab	3	3				
SQV Sampling									
	PS03	Mooring E - Pier D	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
	PS06	DD6 Entrace and Pi	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
	PS07	W. Side DD6 and Fi	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
	PS08	RMTS and DD5	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
			0-25cm Squeeze Core(2)	1	6	6			
			0-5cm Tox Eval(3)	1					
	PS09	DD4 and Btwn Piers	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
			0-25cm Squeeze Core(2)	1	6	6			
			0-5cm Tox Eval(3)	1					
	PS10	DD2 and Btwn Piers	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
	PS10.1	DD3 and Btwn Piers	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
	PS11	DD1 and Btwn Piers	0-10cm grab	6	6	6			
			0-25cm core(1)	1	5	5			
		Confirmaton Analysis (20%)					33	21	31
			Total Analysis	255	160	185	63.2	51	31
			Completed	153	0	0	30	30	0
			Remaining	102	160	185	33.2	21	31
NOTES									
	🟨	Denotes analysis alteady completed or in progress							
(1)	Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20								
(2)	PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-								
(3)	Toxicity endpoints								

				Performing Lab	**BMSL**			
				Analysis				
Project					Sediment	Pore Water	Pore Water	Sediment
	Site	Location	Sample Type	Samples	Met/PAH/PC	metal-ICPMS	DOC etc	AVS/SEM
OUB Marine Monitoring								
		OUB 500ft grid	0-10cm grab COMP	71				
		OOUB 1500 ft grid	0-10cm grab COMP	32				
Pier 7 R&D Studies								
	PS16	Surface Cores	0-10cm	50				
		Bulk Samples	0-10cm (top 6in)	2				
		Drum Samples	0-10cm (top 6in)	6				
		Post Drum Samples	0-10cm (top 6in)	5				
		Sediment Amendment R&D SSC-Pacific						
		Sediment Bioavailability R&D ERDC-ERL						
Repair Projects								
	PS05	Pier B (preConstruct	0-10cm grab	11				
	PS12	Pier 8 (post construc	0-10cm grab	7				
		Quay Wall and DDs	0-10cm grab					
		Piers 5&6	0-10cm grab					
	PS06	DD6 Silt Samples	0-2 cm (silt on DD floor)	8				
	PS09	Near OF18 (PK sam	0-10cm grab	3				
SQV Sampling								
	PS03	Mooring E - Pier D	0-10cm grab	6				6
			0-25cm core(1)	1				4
	PS06	DD6 Entrace and Pi	0-10cm grab	6				6
			0-25cm core(1)	1				4
	PS07	W. Side DD6 and Fi	0-10cm grab	6				6
			0-25cm core(1)	1				4
	PS08	RMTS and DD5	0-10cm grab	6				6
			0-25cm core(1)	1				4
			0-25cm Squeeze Core(2)	1	6	6	6	
			0-5cm Tox Eval(3)	1				
	PS09	DD4 and Btwn Piers	0-10cm grab	6				6
			0-25cm core(1)	1				4
			0-25cm Squeeze Core(2)	1	6	6	6	
			0-5cm Tox Eval(3)	1				
	PS10	DD2 and Btwn Piers	0-10cm grab	6				6
			0-25cm core(1)	1				4
	PS10.1	DD3 and Btwn Piers	0-10cm grab	6				6
			0-25cm core(1)	1				4
	PS11	DD1 and Btwn Piers	0-10cm grab	6				6
			0-25cm core(1)	1				4
		Confirmaton Analysis (20%)						
			Total Analysis	255	12	12	12	80
			Completed	153	0	0	0	0
			Remaining	102	12	12	12	80
NOTES								
	🟨	Denotes analysis altready completed or in progress						
(1)	Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20							
(2)	PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-							
(3)	Toxicity endpoints							

				Performing Lab	**URS**			
				Analysis	As,Cd,Cr,Cu,Pb,Zn			
Project					Sediment	Sediment	Sediment	
	Site	Location	Sample Type	Samples	metal-ICPMS	HgCVAA	TotalArocl	TOC
OUB Marine Monitoring								
		OUB 500ft grid	0-10cm grab COMP	71		71		71
		OOUB 1500 ft grid	0-10cm grab COMP	32		32		32
Pier 7 R&D Studies								
	PS16	Surface Cores	0-10cm	50	15	15	15	15
		Bulk Samples	0-10cm (top 6in)	2				
		Drum Samples	0-10cm (top 6in)	6				
		Post Drum Samples	0-10cm (top 6in)	5				
		Sediment Amendment R&D SSC-Pacific						
		Sediment Bioavailability R&D ERDC-ERL						
Repair Projects								
	PS05	Pier B (preConstruct	0-10cm grab	11	11	11	11	11
	PS12	Pier 8 (post construc	0-10cm grab	7	7	7	7	7
		Quay Wall and DDs	0-10cm grab					
		Piers 5&6	0-10cm grab					
	PS06	DD6 Silt Samples	0-2 cm (silt on DD floor)	8				
	PS09	Near OF18 (PK sam	0-10cm grab	3				
SQV Sampling								
	PS03	Mooring E - Pier D	0-10cm grab	6				
			0-25cm core(1)	1				
	PS06	DD6 Entrace and Pi	0-10cm grab	6	6	6	6	6
			0-25cm core(1)	1				
	PS07	W. Side DD6 and Fi	0-10cm grab	6				
			0-25cm core(1)	1				
	PS08	RMTS and DD5	0-10cm grab	6				
			0-25cm core(1)	1	1	1	1	1
			0-25cm Squeeze Core(2)	1				
			0-5cm Tox Eval(3)	1				
	PS09	DD4 and Btwn Piers	0-10cm grab	6	1	1	1	1
			0-25cm core(1)	1				
			0-25cm Squeeze Core(2)	1				
			0-5cm Tox Eval(3)	1				
	PS10	DD2 and Btwn Piers	0-10cm grab	6	1	1	1	1
			0-25cm core(1)	1				
	PS10.1	DD3 and Btwn Piers	0-10cm grab	6	1	1	1	1
			0-25cm core(1)	1				
	PS11	DD1 and Btwn Piers	0-10cm grab	6	4	4	4	4
			0-25cm core(1)	1				
		Confirmaton Analysis (20%)						
			Total Analysis	255				
			Completed	153				
			Remaining	102				
NOTES								
	🟨	Denotes analysis alteady completed or in progress						
(1)	Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20							
(2)	PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-							
(3)	Toxicity endpoints							

	For Field Study in April														
				Field	**Grab**	**Core**	**Core**	**SSC-Pacific**	**GeoSea**	**BMSL**					
overlap with Repair				**Collection Containers**	16 oz. glass	0-40 cm PP Barrel	40+ cm barrel	8 oz. glass precleaned	2 oz. PP	2 oz. PP (clean)	2 oz. Glass	8 oz. Glass	30 mL Teflon	30mL Glass	from 8oz
# samples Collected				**Matrix:**	Sed	Sed	Sed	Sed	Sed	Sed	Sed	Sed	PW	PW	Sed
	Site	**Location**	**Sample Type**	**Analysis group:**	Field	Field	Field	Screening	GrainSize	Hg + metals conf.	TOC	Org. Conf.	Hg, ICPMS	DOC	AVS/SEM
	PS03	Mooring E - Pier D	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
6	PS06	DD6 Entrace and Pier 9	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
	PS07	W. Side DD6 and Finger Pier	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
1	PS08	RMTS and DD5	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
1	PS09	DD4 and Btwn Piers 3 & 4	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
1	PS10	DD2 and Btwn Piers 4 & 5	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
6	PS10.1	DD3 and Btwn Piers 5 & 6	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
4	PS11	DD1 and Btwn Piers 6 & 7	0-10cm grab	6	6			6	6	6	6	6 (from 16 oz)			
	PS03	Mooring E - Pier D	0-25cm core(1)	1		1		5		5	5	5			5
	PS06	DD6 Entrace and Pier 9	0-25cm core(1)	1		1		5		5	5	5			5
	PS07	W. Side DD6 and Finger Pier	0-25cm core(1)	1		1		5		5	5	5			5
	PS08	RMTS and DD5	0-25cm core(1)	1		1		5		5	5	5			5
	PS09	DD4 and Btwn Piers 3 & 4	0-25cm core(1)	1		1		5		5	5	5			5
	PS10	DD2 and Btwn Piers 4 & 5	0-25cm core(1)	1		1		5		5	5	5			5
	PS10.1	DD3 and Btwn Piers 5 & 6	0-25cm core(1)	1		1		5		5	5	5			5
	PS11	DD1 and Btwn Piers 6 & 7	0-25cm core(1)	1		1		5		5	5	5			5
	PS03	Mooring E - Pier D	0-25cm Squeeze Core(2)	1			1			6	6	6	6	6	
	PS09	DD4 and Btwn Piers 3 & 4	0-25cm Squeeze Core(2)	1			1			6	6	6	6	6	
			Total Jars		**48**	**8**	**2**	**88**	**48**	**100**	**100**	**52**	**12**	**12**	**40**
			25% Confirmation Set							**22**		**22**			
			All ICP/MS and Org. Quantitative Analysis							**34**		**34**			
			Hg Analysis							**100**			**12**		**40**

NOTES

(1) Core sectioned at intervals of 0-2.5, 2.5-5, 5-10, 10-15, 15-20

(2) PW extracted at intervals of 0-2.5, 2.5-5, 5-7.5, 7.5-10, 10-15, 15-20

Summary - PSNS Pier 7 PCB Results

Sample Location: Various offshore/inshore sediment sites located inside Sinclair Inlet along Pier 7 [Operable Unit B (OU-B)] : Naval Shipyard (NSY) Puget Sound, Bremerton, Washington (USA)
Sampling Date: 28 Oct. 2010
Sample Type: Sediment (wet), grab, core
Analysis: Poly-Chlorinated Biphenyls (PCBs) by Enzyme-Linked Immuno Sorbent Assay (ELISA) Methods
ImmunoAssay Application: EPA Methods: 4020 (PCB) For Soils (Modified for Marine Sediments)
Analysis Date: 31 Oct. 2010
Analyst: Joel M. Guerrero, Scientist (Environmental Chemistry), U.S. Navy Space & Naval Warfare Systems Center (SPAWARSYSCEN) Pacific, Advanced Systems & Applied Sciences Division, Applied Systems & Environmental Sciences Branch (Code 71751), (619) 553-4169
Analysis Location: Building 147, PSNS&IMF Foundry Bremerton (WA)
POCs: ***Victoria Kirtay***, Scientist (Marine Geochemistry), SPAWARSYSCEN, Pacific [SSC-Pacific], Code 71751: (619) 553-1395
Joel M. Guerrero, Scientist (Environmental Chemistry), SPAWARSYSCEN Pacific [SSC-Pacific], Code 71751: (619) 553-4169

Method Summary: The ImmunoAssay (IA) test kit used for this method are commercially available (RaPID^{TM} Assay, Stategic Diagnostics Inc., www.sdix.com). In general, the IA method is perfomed using a sample extract. The sample and an enzyme conjugate are added to an antibody. The enzyme conjugate "competes" with the contaminant of interest (PCB) present in the sample for binding to the antibody. The assay test is interpreted by comparing the response produced by the sample test to the response produced by testing a range of kit-supplied standards simultaneously.

Sample Preparation Procedures:
(1) *Pre-processing* : mix wet sediment thoroughly with clean sampler spoons. using filter paper (grade 13V) and heavy-duty lab towels, about 20-30 grams of wet sample are dewatered and/or air-dried to reduce sediment moisture content (at least less than 30%). observe and record other sediment meta data (i.e. color, grain size, smell, oil sheen, debris, shell hash, etc.)
(2) *Sub-sampling:* weigh and record approx. 10 grams of "dry" (at least 70% or more) sediment using top loading balance. transfer into 50 ml centrifuge tubes (pre-cleaned/sterile).
(3) *Extraction:* add 20 ml of methanol (MeOH, Aldrich 99.9+% capillary GC grade). cap centrifuge tube tight. vortex slurry for 1-2 seconds to loosen particles and break-up large sediment clumps. shake the mixture vigorously and continously for at least 1 hour in a rotator/shaker set at maximum amplitude (400 rpm).
(4) *Separation:* check the tube cap again for a tight seal. centrifuge the slurry for at least 10-15 minutes (EIC/Sorvall) at 3000 rpm. transfer/pour MeOH extract into a syringeless filter vial and filter through (GFC/Whatman, 0.45 um pore size) into amber, teflon-lined vial. record extract color. cap and seal the vial, keep dark and cool (2-8 degrees C).
(5) *Dilution:* pipet (using eppendorf) 50 µL of MeOH extract into glass test tube (pre-cleaned with screw cap) containing 5 mL of sample diluent (reagent buffer saline solution having preservatives and stabilizers without any detectable PCBs). cap test tubes and vortex to mix.
(6) *Assay:* pre-label and prepare polystyrene test tubes (allow for field/sample/extract duplicates for each assay run). perform immunoassay (IA) procedures by following SDI standard soil methods for PCBs.

ImmunoAssay (IA) ELISA Protocols: The sample (with the *unknown contaminant concentration* ; ex. PCB) is analyzed by the addition of an enzyme conjugate (labeled PCB).This is followed by addition of paramagnetic particles with anti-bodies specific to "both" PCBs. In relatively proportional concentrations, both the sample PCBs and the "labeled" PCBs (conjugate) compete for the binding sites on the magnetic particles. After an incubation period, a magnetic field is applied to hold (in-place) the magnetic particles having the sample PCB and its "labeled" PCB analog to bind with the antibodies. Any unbound reagents are decanted and washed repeatedly. PCBs in the mixture are detected with the addition of an enzyme substrate (color solution) containing a chromagen which specifically react to the "labelled" PCBs. After another incubation, the reaction is stopped and stabilized by addition of acid (stopping solution). Since the labelled PCBs and sample PCBs are in competition (proportionally) with the binding sites, the color developed at the end of reaction is inversely proportional to the concentration of PCBs in the sample. This color response is measured by a spectrophotometer (set at 450 nm) and compared to the responses taken from a calibrated series of known pcb standards (kit-supplied) to determine the equivalent PCB (as Aroclor 1254) concentration of the sample.

Calculations: The dry-weight corrected organic contaminant (OC) concentration in sediment is calculated (according to eq. 1 and eq. 2) by multiplying the IA result by factors that are introduced by the sample pre-processing procedures (collection, extraction, extract dilution steps above).

$$OC_{conc} = IA \times (V_{MeOH} / W_{drysed}) \times df \qquad (eq.1)$$

$$df = (V_{ext} + V_{dil}) / V_{ext} \qquad (eq.2)$$

where;
OC_{conc}: PCB sediment concentration (mg/kg)
IA: ImmunoAssay result (mg/L)
V_{MeOH}: Volume of methanol (extractant)
W_{drysed}: Weight of dry sediment
df: Dilution factor
V_{ext}: Volume of dilution extract
V_{dil}: Volume of diluent

Colorimetry: Absorbance values at l = 450 nm were measured/recorded using a field-portable/lab benchtop HACH Model DR/2010 direct-reading spectrophotometer (HACH Co., Loveland, CO). This analyzer is a microprocessor-controlled, single-beam instrument with a Littrow Prism monochromator design which uses an ultra-violet (UV) enhanced silicon photodiode for detection. It is manually programmed to display results in raw absorbances. The HACH DR/2010 is calibrated at the start of each assay run. It is zeroed for absorbance measurements and a series of assay method calibrations are performed using a contaminant-free 0 (zero) standard, a range of 3 standard concentration***s*** , and a control. Method/equipment blanks and marine sediment reference materials [NRCC HS-1(PCB)] are also used for standardization. Measurements of raw absorbance data are serially down-loaded to a laptop computer using a Windows^{TM} application HACHLink^{TM} data acquisition software. Serial data, collected as text files, are transferred and copied into a spreadsheet program (Excel^{TM}) for reduction. A calibration curve (with R^2= 0.9) is generated for each assay run

ImmunoAssay (IA) Results

Field ID SAMPLE LABEL	tPCB (µg/Kg)	Q	Stdev	%RSD
P7-T1-1	234			
P7-T1-2	192			
P7-T1-3	91			
P7-T1-4	46	U		
P7-T1-5	152		47	30.74%
P7-T2-1	176			
P7-T2-2	151			
P7-T2-3	28	U		
P7-T2-4	261			
P7-T2-5	58	U		
P7-T3-1	170			
P7-T3-2	96	J		
P7-T3-3	285			
P7-T3-4	74	U		
P7-T3-5	48		25	51.61%
P7-T4-1	341			
P7-T4-2	140	J		
P7-T4-3	113	J		
P7-T4-4	133	J		
P7-T4-5	11	U		
P7-T5-1	111	J		
P7-T5-2	594		76	12.87%
P7-T5-3	159			
P7-T5-4	150			
P7-T5-5	74	U		
P7-T6-1	243			
P7-T6-2	262			
P7-T6-3	6650		1424	21.41%
P7-T6-4	305			
P7-T6-5	439			
P7-T7-1	224			
P7-T7-2	261			
P7-T7-3	129	J		
P7-T7-4	655			
P7-T7-5	193			
P7-T7-6	105	J		
P7-T8-1	227			
P7-T8-2	129	J		
P7-T8-3	163			

<u>Definitions:</u>

Stdev *:* Standard Deviation from duplicate assay analyses (n=2)

% RSD *:* Percent Relative Standard Deviation whereby; [{stdev/mean} * 100]

Q **:** Data Qualifiers: **U** = None-Detect, **J** = Estimated, **E** = Outside Linear Range, **Blank** = Detect

Label: **P7** = Pier 7; **T*x* -*x*** = Transect № (1…10) - Sample № (1…6)

ImmunoAssay (IA) Results

Field ID SAMPLE LABEL	tPCB (µg/Kg)	Q	Stdev	%RSD
P7-T9-1	91	J	53	58.25%
P7-T9-2	74	U		
P7-T9-3	74	U		
P7-T9-4	73	U		
P7-T9-5	84	J		
P7-T9-6	80	J		
P7-T10-1	161			
P7-T10-2	24	U		
P7-T10-3	126	J		
P7-T10-4	92	J		
P7-T10-5	134	J		
P7-T10-6	115	J	9	7.75%

Definitions:

Stdev *:* Standard Deviation from duplicate assay analyses (n=2)
% RSD *:* Percent Relative Standard Deviation whereby; [{stdev/mean} * 100]
Q **:** Data Qualifiers: **U** = None-Detect, **J** = Estimated, **E** = Outside Linear Range, **Blank** = Detect
Label: **P7** = Pier 7; **T*x* -*x*** = Transect № (1…10) - Sample № (1…6)

12.4.2 D2. Pier 7 XRF Results for Metals

2010 Puget Sound Pier 7 Reactive Amendment Study FPXRF Results.xls

Sample Location: Various sediment sites (i.e. offshore, inshore, and underneath) located inside Sinclair Inlet along Pier 7 [Operable Unit B (OU-B)] :
Naval Shipyard (NSY) & Intermediate Maintenance Facility (IMF) Puget Sound, Bremerton, Washington (USA)
Sampling Dates: 28 Oct. - 1 Nov. 2010
Sample Type: Sediment (wet), grab; diver-collected core sample
Analysis: Selected Metals (Fe, Cu, Zn, Pb, etc.) by Field Portable X-ray Fluorescence (FPXRF) Spectrometry
FPXRF Application: EPA Method 6200: (Elemental Concentrations) - for soils and sediments
Analysis Dates: 8 - 13 December 2010
Analyst: Joel M. Guerrero, Scientist (Environmental Chemistry), U.S. Navy Space & Naval Warfare Systems Center (SPAWARSYSCEN) Pacific,
Advanced Systems & Applied Sciences Division, Applied Systems & Environmental Sciences Branch (Code 71751), (619) 553-4169
Analysis Location: Building 111, Rapid Sediment Characterization (RSC) Laboratory, Room 122 (Bayside), (619) 553-2765
POCs: ***Dr. James M. Leather***, Scientist (Marine Geochemistry), SPAWARSYSCEN, Pacific [SSC-Pacific], Code 71751: (619) 553-6240
Joel M. Guerrero, Scientist (Environmental Chemistry), SPAWARSYSCEN Pacific [SSC-Pacific], Code 71751: (619) 553-4169

Analytical Technique:
X-Ray Fluorescence spectrometry is an analytical technique that provides rapid, multi-element analysis of metals in soils/sediments.
Samples are exposed to x-ray energy, which liberates electrons in the inner shell of metal atoms.
As the outer electrons cascade towards the inner shells to fill the vacancies, energy is released (fluorescence).
The fluorescing energy spectrum identifies the metals and the intensity is proportional to concentration.

Analytical Instrument:
Sediment samples were analyzed using a X-MET 3000TX Field Portable X-ray Fluorescence (FPXRF) Spectrometer (Oxford Instruments, Elk Grove Village, IL). The X-MET is a field portable elemental analyzer based on energy dispersive X-ray fluorescence technology. This instrument is specifically calibrated for soil/sediment (alloy class) applications and utilizes an integrated personal digital assistance (PDA) computer for data storage. The probe contains a miniature, programmable x-ray tube for primary generation of x-rays (40 kV, 40 µamps) and a Peltier cooled, solid-state Silicone-P-type/intrinsic/N-type detector. The Si-PiN detector provides high spectral resolution which exceeds other solid-state detectors or gas-filled proportional detectors. X-MET data output from each sample analysis includes a broad elemental spectrum display from the K series x-ray lines at the 2.04 - 31.68 keV energy range and their associated dry weight metal concentrations (in mg/Kg or ppm) with error estimates.

Instrument Calibration & Statistically-based Method Detection Limits (note: not field-based detection limits)
The X-MET FPXRF is calibrated using a specific empirical calibration program for soils/sediments in the PDA menu.
Six (6) sediment Standard Reference Materials (SRMs) were analyzed as calibration check standards.
National Institute of Standards & Technology (NIST) 2704, 2709, 2710, & 2711
and Canadian National Reseach Council (CNRC) PACS-1 & PACS-2 are used for standardization.
Method detection limits (MDLs) were calculated using clean blank standards such as Quartz & washed Sea Sand (Fisher Scientific Grade)
Specific MDLs for the following metals: (Fe, Cu, Zn, Pb) were calculated from the standards as follows:

(i) [a]**MDL** $= t_{(n-1,1-\alpha=0.99)}\,(s)$

(ii) RDL $= 6\,\sigma$

where;

MDL = Method Detection Limit (same as LLD, 3 σ) in mg/Kg or (ppm)
RDL **=** Realible Detection Limit in mg/Kg or (ppm)
t = Student's t value for a 99% confidence level & standard deviation estimate
with n-1 degrees of freedom (t = 3.14[b] for 7-10 replicates)
n = number of samples
s = standard deviation (σ)

Analyte	(3 σ) MDL	(6 σ) RDL
Fe	398	2445
Cu	48	94
Zn	31	61
Pb	50	98

Sample Handling:
Sample splits for screening were performed on sediments collected previously at PSNS&IMF Bremerton Naval Complex (BNC). These screening samples (in jars) were shipped to Space & Naval Warfare (SPAWAR) Systems Center Pacific [SSC-Pacific] RSC laboratory for further sample processing for XRF screening.

Sample Processing:
Rapid screening analysis of sediment samples using the FPXRF employed a combination of *ex situ* sample processing with *in situ* sample testing. Samples are mixed thoroughly with clean spoons/wooden sticks. About 20-30 grams are de-watered using a heavy duty filter paper (grade 13 V) and air-dried to reduce moisture content to at least < 30%. Relevant sediment meta-data were also noted and recorded (*i.e*. color, grain size, smell, debris, oil sheen, shell hash, etc.). Dry, homogenized sediments, including standard reference materials (SRMs), were transferred into clean/sterile, pre-labeled ziplock bags.

Sample Analyses:
FPXRF analyses of dried sediments were performed in a controlled area (Class 100 hood) free from dust & temperature extremes. Each sample was analyzed by placing the x-ray window directly into the sediments inside the bags. The operator pushes the analyzer start button and releases it to stop the analysis scan. Each sample was analyzed for approximately 1 minute using the 40kV x-ray source. Because XRF is a non-destructive technique, the samples were either archived and/or used for other RSC analyses.

Qualitative and quantitative results for each sample were measured, recorded and saved to an iPAQ^{TM} PDA with the appropriate sample label.
Samples were analyzed for a suite of metals (e.g., V, Cr, Fe, Co, Ni, Cu, Zn, As, Se Cd, Mo, Sb, Hg and Pb).
Results were calculated based on empirical assay calibration using standard reference materials.
Samples (at least 1/30 per sample batch) undergo multiple XRF analyses scans as an internal quality control check on instrument precision.
Method/instrument blanks and performance calibration checks were routinely performed (1/20-30 sample batch) as part of RSC QA/QC screening protocols.

Data Handling & Processing:

Screening data stored in the PDA was transferred to a laptop PC via a Windows^{TM} based application ActiveSync^{TM} data acquisition software or a CF flash card. Serial data, with comma separated value (.CSV) formats, were transmitted and copied into a spreadsheet program (Excel^{TM}) for further processing and reduction. Standard reference material calibration curves (with $R^2 > 0.9$) are generated for each chemical of potential concern (COPC) (i.e. Cu, Zn, Pb, and Fe).

Data Quality:

Accuracy

Initial/daily method calibration (5 pt) and continuing calibration verification (1/20)
Instrument blank analysis of clean sea sand and quartz (< 5x MDL)
%RPD = comparison of SRMs (≤ 30%)

Precision

%RPD = comparison of field duplicate measurements (< 30-35%)
%RSD = comparison of three or more sample replicates (≤ 30-35%)

Data Qualifiers (Q):

U: Analyte was not detected (measured value ≤ MDL)
J: Estimated value (MDL ≤ measured value ≤ RDL)

References:

[a] Title 40 Code of Federal Regulations (CFR), Part 136 Appendix B, Revision 1.11.
[b] US Environmental Protection Agency (EPA), Environmental Monitoring Systems Laboratory, Office of Research and Development (ORD), Methods for the Determination of Metals in Environmental Samples, 1992, Columbus, OH (USA).

FPXRF Metals Results

Field Station/ID	Fe $_{RSC}$				Cu $_{RSC}$				Zn $_{RSC}$				Pb $_{RSC}$			
		Q	Stdev	%RSD		Q	Stdev	%RSD		Q	Stdev	%RSD		Q	Stdev	%RSD
P7-T1-1	**22872**		383	1.67%	**73**	J			**228**		16	7.00%	**86**	J		
P7-T1-2	**29996**		2107	7.02%	**113**		29	25.94%	**374**		91	24.28%	**121**		10	7.92%
P7-T1-3	**26798**		239	0.89%	**77**	J			**156**		9	5.67%	**50**	U		
P7-T1-4	**34330**		1194	3.48%	**199**		56	28.28%	**496**		28	5.61%	**224**		20	9.11%
P7-T1-5	**29665**		1461	4.92%	**95**		39	40.83%	**179**		25	13.75%	**83**	J		
P7-T2-1	**26857**		538	2.00%	**95**		25	25.99%	**211**		26	12.54%	**77**	J		
P7-T2-2	**25067**		690	2.75%	**77**	J			**194**		35	18.06%	**50**	U		
P7-T2-3	**21500**		3304	15.37%	**48**	U			**43**	J			**50**	U		
P7-T2-4	**28646**		1825	6.37%	**134**		24	17.81%	**399**		34	8.61%	**138**		8	6.10%
P7-T2-5	**19896**		1587	7.98%	**48**	U			**75**		21	28.30%	**50**	U		
P7-T3-1	**29630**		821	2.77%	**53**	J			**190**		21	10.93%	**91**	J	26	28.71%
P7-T3-2	**28293**		1376	4.86%	**54**	J			**364**		78	21.44%	**58**	J		
P7-T3-3	**30610**		354	1.16%	**104**		10	9.26%	**226**		14	6.26%	**104**		9	8.42%
P7-T3-4	**22061**		973	4.41%	**48**	U			**123**		31	25.62%	**62**	J		
P7-T3-5	**25639**		3399	13.26%	**48**	U			**122**		22	17.93%	**50**	U		
P7-T4-1	**22017**		961	4.37%	**48**	U			**84**		19	22.17%	**50**	U		
P7-T4-2	**20414**		458	2.24%	**54**	J			**159**		17	10.79%	**78**	J	9	11.53%
P7-T4-3	**26868**		1010	3.76%	**51**	J			**265**		20	7.62%	**106**		7	6.83%
P7-T4-4	**29680**		1070	3.61%	**79**	J			**174**		10	5.59%	**88**	J	13	14.45%
P7-T4-5	**24837**		1812	7.29%	**48**	U			**184**		18	9.82%	**59**	J		
P7-T5-1	**26845**		122	0.46%	**66**	J			**279**		77	27.78%	**60**	J		
P7-T5-2	**42415**		3264	7.70%	**333**		63	18.93%	**845**		212	25.13%	**415**		45	10.95%
P7-T5-3	**27014**		1407	5.21%	**2506**		2105	83.97%	**413**		78	18.95%	**85**	J	22	25.90%
P7-T5-4	**25663**		659	2.57%	**70**	J			**154**		36	23.40%	**60**	J		
P7-T5-5	**24507**		1906	7.78%	**48**	U			**112**		21	18.28%	**38**	U		
P7-T6-1	**29509**		413	1.40%	**101**		19	18.94%	**340**		17	4.99%	**147**		13	8.79%
P7-T6-2	**27107**		1144	4.22%	**114**		24	20.76%	**187**		3	1.64%	**75**	J		
P7-T6-3	**28658**		1266	4.42%	**161**		35	21.46%	**272**		22	7.93%	**107**		11	10.60%
P7-T6-4	**29662**		2562	8.64%	**48**	U			**163**		15	9.23%	**138**		34	24.89%
P7-T6-5	**27990**		1338	4.78%	**76**	J			**161**		12	7.32%	**57**	J		
P7-T7-1	**26430**		443	1.67%	**49**	J			**177**		26	14.38%	**115**		5	4.49%
P7-T7-2	**24110**		479	1.99%	**48**	U			**169**		15	8.74%	**73**	J	4	6.10%
P7-T7-3	**23486**		2068	8.81%	**48**	U			**156**		26	16.57%	**52**	J		
P7-T7-4	**31491**		609	1.94%	**120**		38	31.61%	**237**		34	14.35%	**109**		7	6.39%
P7-T7-5	**24433**		1327	5.43%	**48**	U			**143**		34	23.58%	**50**	U		
P7-T7-6	**23335**		1222	5.23%	**48**	U			**117**		15	12.45%	**51**	J		

<u>Definitions:</u>

Stdev *:* Standard Deviation from replicate XRF measurements (n≥3)

% RSD *:* Percent Relative Standard Deviation whereby; [{*stdev/mean*} * *100*]

***Data Qualifier* (Q)**: **U** = not detected, (measured value ≤ MDL); **J** = Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** $_{RSC}$ = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn $_{RSC}$ = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb $_{RSC}$ = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe $_{RSC}$ = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

P7 = Pier 7; **T*x* -*x*** = Transect № (1…10) - Sample № (1….6)

FPXRF Metals Results

Field Station/ID	Fe $_{RSC}$	Q	Stdev	%RSD	Cu $_{RSC}$	Q	Stdev	%RSD	Zn $_{RSC}$	Q	Stdev	%RSD	Pb $_{RSC}$	Q	Stdev	%RSD
P7-T8-1	**20736**		1176	5.67%	**48**	U			**136**		31	22.73%	**66**	J		
P7-T8-2	**20477**		2196	10.73%	**48**	U			**95**		3	3.50%	**50**	U		
P7-T8-3	**23179**		1494	6.45%	**48**	U			**117**		14	12.20%	**53**	J		
P7-T9-1	**22965**		1084	4.72%	**48**	U			**93**		18	18.84%	**52**	J		
P7-T9-2	**21122**		438	2.07%	**48**	U			**170**		58	34.32%	**50**	U		
P7-T9-3	**24705**		2284	9.24%	**48**	U			**136**		19	13.99%	**50**	U		
P7-T9-4	**18154**		672	3.70%	**48**	U			**56**	J			**50**	U		
P7-T9-5	**21648**		2318	10.71%	**48**	U			**91**		20	22.53%	**50**	U		
P7-T9-6	**18677**		954	5.11%	**48**	U			**78**		13	16.23%	**50**	U		
P7-T10-1	**25419**		620	2.44%	**48**	U			**182**		58	31.84%	**64**	J		
P7-T10-2	**25835**		574	2.22%	**48**	U			**81**		7	8.71%	**50**	U		
P7-T10-3	**25280**		1223	4.84%	**52**	J			**139**		19	13.37%	**52**	J		
P7-T10-4	**23247**		1121	4.82%	**48**	U			**106**		6	5.22%	**50**	U		
P7-T10-5	**24726**		982	3.97%	**48**	U			**223**		133	59.61%	**50**	U		
P7-T10-6	**26514**		423	1.59%	**48**	U			**79**		33	41.54%	**50**	U		

Definitions:

Stdev *:* Standard Deviation from replicate XRF measurements (n≥3)

% RSD *:* Percent Relative Standard Deviation whereby; [{*stdev/mean}* * *100*]

***Data Qualifier* (Q)**: **U =** not detected, (measured value ≤ MDL); **J =** Estimated, (MDL ≤ measured value ≤ RDL); **Blank** = detected

Label: **Cu** $_{RSC}$ = SRM (NIST/CNRC) calibrated copper concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Zn $_{RSC}$ = SRM (NIST/CNRC) calibrated zinc concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Pb $_{RSC}$ = SRM (NIST/CNRC) calibrated lead concentration (mg/Kg / *ppm*) - result from FPXRF analysis

Fe $_{RSC}$ = SRM (NIST/CNRC) calibrated iron concentration (mg/Kg / *ppm*) - result from FPXRF analysis

P7 = Pier 7; **T*x* -*x*** = Transect № (1…10) - Sample № (1….6)

12.5 E. Preliminary Evaluation of Tools Towards Improved Assessment of Copper and Zinc Bioavailability and Toxicity at Contaminated Navy Sediment Sites, Space and Naval Warfare Systems Center (SSC) Pacific

Preliminary Evaluation of Tools Towards Improved Assessment of Copper and Zinc Bioavailability and Toxicity at Contaminated Navy Sediment Sites

Space and Naval Warfare Systems Center (SSC) Pacific
Environmental Sciences and Applied Systems, Code 71750
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March 30, 2011

Summary

Copper (Cu) and zinc (Zn) are frequently elevated in marine sediments at coastal U.S. Navy facilities. Although these metals are naturally occurring, and essential for life, there are numerous anthropogenic sources of Cu and Zn that frequently result in elevated potentially harmful sediment concentrations. For the Navy, one of the largest sources of Cu and Zn in coastal embayments is from antifouling paint systems on ship hulls. Assessment and regulation of adverse effects in these sediments typically occurs via co-occurrence-based sediment quality guidelines (SQG) using total metal concentration. The bioavailability and potential toxicity of Cu and Zn, however, is not necessarily related to total concentrations measured in bulk sediments, complicating appropriate application of SQGs for environmental regulation. A biotic ligand model (BLM) to predict Cu toxicity in marine surface waters to sensitive environmental receptors has recently been deemed suitable for use in regulatory programs, and relies heavily on the dissolved organic carbon (DOC) concentration at the site (Arnold et al., 2006; Chadwick et al., 2008). The prediction of metal bioavailability in sediments is considerably more difficult than in surface waters, however, due to the greater range of metal-binding phases and processes influencing metal exposure in sediments (Simpson et al., 2008; Strom et al., in press). These processes include the binding of metals to particulate sulfide, organic carbon, and iron hydroxide phases, in addition to sediment-water partitioning characteristics and the route of uptake (e.g. differences in organism behavior and feeding strategy).

The U.S. Navy has identified several key research areas that are of high priority towards development of an improved understanding of Cu and Zn bioavailability and toxicity in marine sediments. These needs include:

- Field-verification of a promising, recently developed method to improve the prediction of toxicity based on the organic carbon-normalized Cu concentration of the <63 µm sediment fraction (Strom et al., in press) using naturally contaminated sediments from US Navy sites.
- Concurrent measurement of physicochemical parameters in the dissolved and particulate phases to support future improvement of predictive models (e.g. sediment BLM; DiToro et al., 2005). These parameters include organic carbon content, metal concentrations, simultaneously extracted metals (SEM)/acid-volatile sulfide (AVS), salinity, and pH.

- Evaluation of the utility of passive sampling devices, e.g., diffusive gradients in thin films (DGT), for assessing labile Cu and Zn concentrations in sediment porewater.

It is widely recognized that the complexity of sediments and the presence of co-occurring contaminants render definitive identification of Cu or Zn as causal agents in contaminated sediments difficult. The intent of the current study is to support the development of improved tools for assessment of Cu and Zn bioavailability and toxicity in Navy sediments, and to support future advances on the ability to model metal toxicity in contaminated marine sediments. Based on the regulatory and scientific support of using SEM/AVS for prediction of metal toxicity in those cases where AVS>SEM, and assuming that that model does not hold for most oxic and suboxic conditions, in addition to schedule and resource constraints, this study will focus on relatively oxidized sediments exposed to four different benthic receptors commonly used in sediment quality assessment in North America. It is noted, however, that this work is intended to be a precursor to future studies and provide a basis for collaborative efforts to advance the state of the science. As a recent example, SSC Pacific submitted a related Environmental Security Technology Certification Program (ESTCP) pre-proposal with Dr. Stuart Simpson (Commonwealth Scientific and Industrial Research Organisation , CSIRO, Australia) in March 2011.

Background

The DoD has provided support for research towards the development of copper (Cu) and zinc (Zn) bioavailability and toxicity assessment tools for supporting environmental compliance associated with U.S. Navy's use of antifouling paint systems on its ship hulls. This effort was formally titled, "Compliance Tools Development for Metals in Antifouling Paints Program," and included two primary objectives: 1) the publication of a previously derived Biotic Ligand Model (BLM) for Cu in marine waters (marine-BLM) by the U.S. Environmental Protection Agency (USEPA); and 2) support for development of improved tools for assessing the bioavailability and toxicity of Cu and Zn in marine sediments. The first objective is based on the development and application of a Cu BLM to San Diego Bay and Pearl Harbor (Chadwick et al., 2008), and is currently being pursued by HydroQual via the drafting of a guidance document prior to USEPA acceptance and publication. The second objective was initially envisioned as a long-term goal that would evolve based on initial study results and the availability of future funding. Due to time and budgetary constraints, however, this objective is limited to the pursuit of preliminary investigations that address short-term requirements and data gaps identified by the Navy and the program's technical work group (composed of scientific experts in government, industry, and academia). The studies proposed here in response to Objective 2 are intended to address these identified gaps, with longer-term development to be sought through the development of collaborative proposals to DoD environmental programs such as Navy's Environmental Sustainability Development to Integration (NESDI), ESTCP, and the Security Environmental Research Development Program (SERDP), as well as through cooperation with industry and academia. As part of this follow-on effort, an ESTCP pre-proposal was recently submitted in collaboration with Dr. Stuart Simpson (CSIRO, Australia) during the most recent proposal call for that program in March 2011.

Improvement to Empirical SQGs

Recently, Australian researchers have proposed updating Cu SQGs based on the influence of Cu partitioning among the sediment, porewater and overlying water on the Cu exposure pathway and on resulting changes in bioavailability with potential toxic effects (Simpson et al., 2008; Strom et al., in press). One of the most interesting outcomes of that work was the promising potential to enhance SQGs by expressing sediment concentrations based on the <63 µm (silt) sediment size fraction normalized to the TOC concentration associated with that fraction (<63 µm Cu (mg/g OC)). This normalization resulted in much better prediction of toxicity to benthic invertebrates than the more traditional reliance on bulk Cu concentrations (Figure 1). The authors recommended that this relationship, which is based on laboratory tests with spiked sediments, be verified in the field, where dilution of released Cu may occur rapidly. Verification of this approach would be highly significant as it would provide the ability to develop more meaningful SQGs using fairly simple chemical measurements.

Due to the need for advancement in the understanding of metal bioavailability in the oxic and suboxic sediment phases, the current effort will focus on naturally contaminated oxic sediments covering a range of Cu and Zn concentrations and grain size distributions. Laboratory toxicity testing, which involves the presence of oxygenated overlying water required for test organism survival, will be conducted on these sediments. Natural sediments with high concentration of metals and negligible concentrations of other toxicants (e.g., hydrophobic organic compounds, petroleum products, etc.) will be collected from various locations, focusing on Navy installations. Demonstration of the organic carbon normalization of the < 63 µm grain size fraction on naturally contaminated sediments will ensure that the metal concentration is in equilibrium in these oxic sediments, as spiked sediments can pose challenges in adequately representing equilibrium porewater concentrations typical of field sediments, and can over-predict biological exposure (Simpson and King, 2005; Simpson and Batley, 2007; Hutchins et al., 2008).

This study will investigate the above described normalization technique with toxicity testing of four different commonly used North American benthic test organisms, including two amphipods (*Ampelisca abdita* and *Leptocheirus plumulosus*), one polychaete (*Neanthes arenaceodentata*), and bivalve (*Mytilus galloprovincialis*) embryos. The amphipods and polychaete will be exposed in whole sediment tests using standardized protocols (USEPA 1994 and Farrar and Bridges 2011, respectively), while the bivalve embryos will be exposed in sediment-water interface (SWI) toxicity tests described by Anderson et al. (1996).

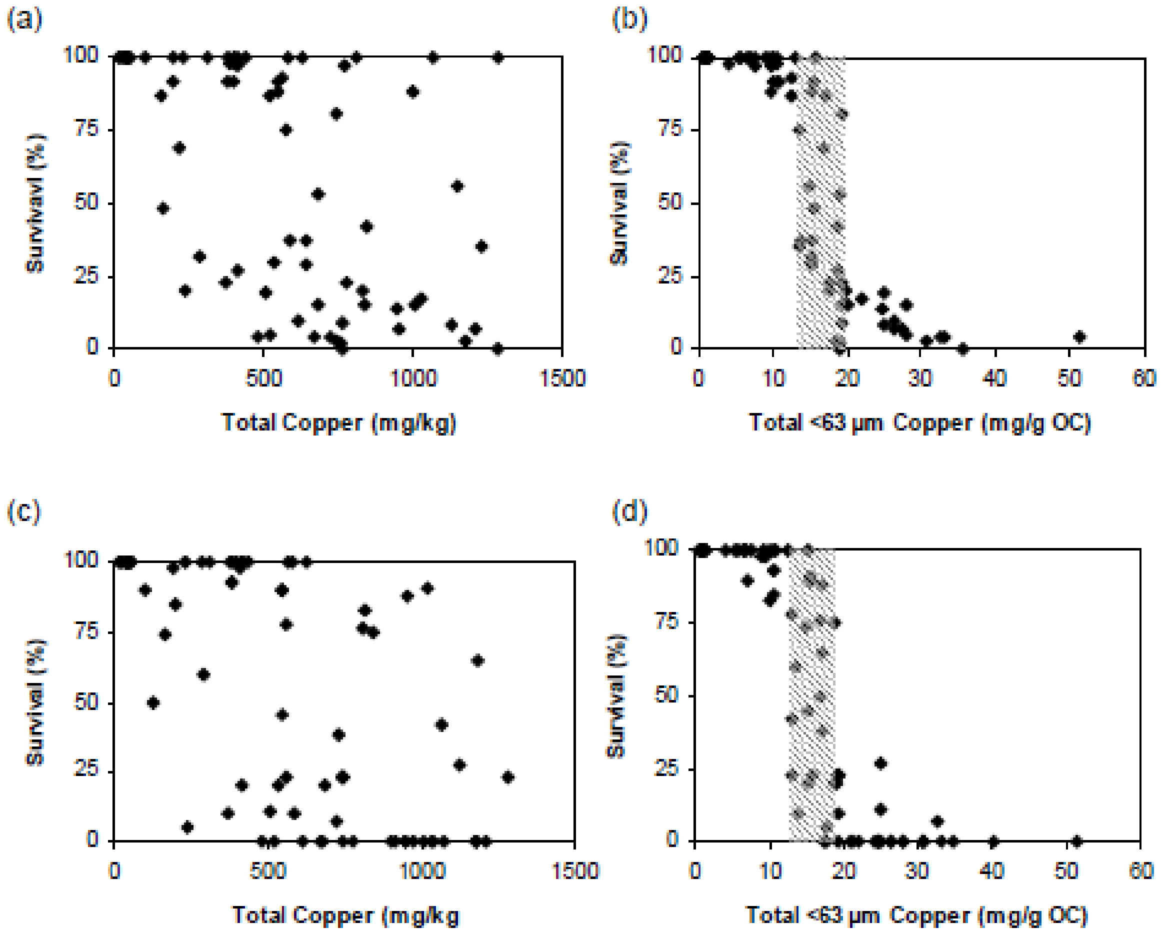

Figure 1. The normalization of total copper to silt (<63 µm sediment fractions) and TOC provided a suitable approach for predicting effects in sediments with varying properties for the Australian benthic invertebrates *Melita plumulosa* (amphipod) (a, b), and *Spisula trigonalla* (clam) (c, d). This method of expressing the data provides narrower ranges that better bracket the toxic effect; for example, while 50% survival spans the full range of total copper concentrations in figures a and c, 50% survival is confined to a narrow range (i.e., 10 to 20 mg Cu/g OC) when the data are expressed as the <63 µm fraction normalized to TOC. Each data point represents the sum of 3 replicates. Figure from Simpson et al. (2008).

Biotic Ligand Model for Metals in Sediment

The marine-BLM for Cu is based on the input of physicochemical parameters (i.e., total and dissolved organic carbon (TOC, DOC), pH, alkalinity, salinity, total and dissolved copper, and total suspended solids) measured in the water column as a means of predicting Cu toxicity to surface water organisms. The model was recently demonstrated to adequately predict Cu toxicity to developing embryos of the bivalve *Mytilus galloprovincialis*, and the purple sea urchin *Strongylocentrotus purpuratus* in marine surface waters (Chadwick et al., 2008). The toxicity endpoint employed in that study was normal larval shell development in short term (48-96 hours, depending on species) exposures, during which effects are presumed to be due to metal in solution (i.e., free copper ion), as the life stage for both species is non-feeding, providing a relatively simple scenario for prediction of toxicity.

In comparison, metal bioavailability and toxicity to infaunal sediment organisms is much more complex. This complexity is due to the close interaction of different sediment phases (i.e., particles, porewater and overlying water), to the various constituents within the sediments and porewaters that may sequester metals (Ankley et al., 1996; USEPA, 2005), which are superimposed on a diagenetic redox sequence (oxic, suboxic and anoxic; Berner, 1980), in addition to varying routes of exposure and uptake, and species-specific physiological characteristics (Simpson and King, 2005, and references therein), including advection and diffusion of metals in porewaters, sediment resuspension, and bioturbation of the sediments by organisms (Berner, 1980; Rivera-Duarte and Flegal, 1997). In spite of this difficulty, single-value sediment quality guidelines (SQGs) based on bulk sediment contaminant concentrations have served as a general indicator of sediment quality since the mid-1990s (e.g. Long et al., 1995). As a first approximation, this proposal addresses the development of site-specific SQGs by comparing the use of bulk sediment metal concentration and metal concentrations normalized to the silt-size fraction in the prediction of toxic effects in naturally contaminated sediments at Navy sites with varying concentrations of Cu and Zn, based on recent encouraging investigations on such an approach with spiked sediments (Strom et al., in press).

A substantial number of studies have shown that the relationship between simultaneously extracted metals (SEM) and acid-volatile sulfides (AVS) is useful in demonstrating the potential for metal toxicity in sediments (DiToro et al., 2005, and references therein). Application of this relationship to anoxic sediments will, in most cases, provide correct assessment of toxicity (i.e. metal toxicity will not occur because AVS exceeds SEM; AVS>SEM). However, the relationship is not as certain for suboxic and oxic sediments, when SEM frequently exceeds AVS (SEM>AVS). Although carbon-normalization of excess SEM reduces uncertainty in those cases, assessment of the potential for biological effects when SEM exceeds AVS is generally not possible (DiToro et al., 2005; USEPA, 2005). Among efforts towards model development when SEM>AVS is the sediment BLM (sBLM; DiToro et al., 2005). This preliminary model is based on the combination of a BLM and a porewater-sediment partitioning model, and is used to predict the metal concentration in the sediment particles that is in equilibrium with the biotic ligand effects concentration in the porewater. However, in order to bypass the effects of porewater chemistry, the authors only consider the partitioning to particulate organic carbon (POC) and the effect of AVS. Under these conditions, they computed that the median lethal concentration (LC50) normalized to POC is essentially unchanged (i.e., constant and within one-order of magnitude) over a wide range of conditions, and is only affected by the porewater pH. The authors concluded that a complete sBLM will require the inclusion of partitioning to other sediment phases to which metal is partitioned (e.g., iron and manganese oxides, and mineral components) as well as consideration of the dietary route of exposure.

Overlying water and organism burrowing activities result in oxygenation of surficial sediments. In these surface sediments, particulate organic carbon (POC) and iron/manganese oxyhydroxides are presumed to be the dominant factors responsible for the reduction of metal toxicity (Simpson et al., 2008). Therefore, there is a need to develop tools that assess/predict metal toxicity in oxic and suboxic sediments. Ideally, such tools should be appropriate for integration with the SEM/AVS model that accurately predicts toxic effects in anoxic sediments to improve the accuracy of prediction of toxicity in natural sediments.

Objectives

In support of the "Compliance Tools Development for Metals in Antifouling Paints Program" for Cu and Zn at Navy sites, the proposed work entails three primary objectives described below. The scope and extent of these efforts is limited to the budgetary and schedule constraints associated with the late distribution of funds for this effort that require completion by the end of fiscal year 2011 (September 2011). Objectives are as follows:

1) Investigate the applicability of the organic carbon normalization of the metal concentration of the silt size fraction (<63 µm) of the sediment as a better predictor of Cu and Zn-associated toxicity at Navy sites, relative to current sediment quality guidelines based on bulk sediment concentrations, in acute and chronic sediment toxicity tests with multiple species and endpoints;
2) Concurrent with testing in Objective 1, measure physicochemical parameters including pH, SEM/AVS, TOC, DOC, grain size, metal concentration in dissolved and particulate fractions to provide context for the results for Objective 1, and to support future development of a mechanistic approach for Cu and Zn toxicity assessment in marine sediments;
3) Concurrent with testing in Objectives 1 and 2, assess the potential for diffusive gradients in thin films (DGTs) to measure labile metal in the test vessels (oxic sediments), and their ability to predict Cu and Zn uptake and toxicity in sediment dwelling invertebrates.

Approach

To meet the defined objectives for the project, this study will include a series of tasks to characterize toxicity, physico-chemical parameters on overlying water, porewater, sediment, and labile metal concentrations using DGTs, in both intact and homogenized sediment samples. An overview of the approach is shown in Figure 2.

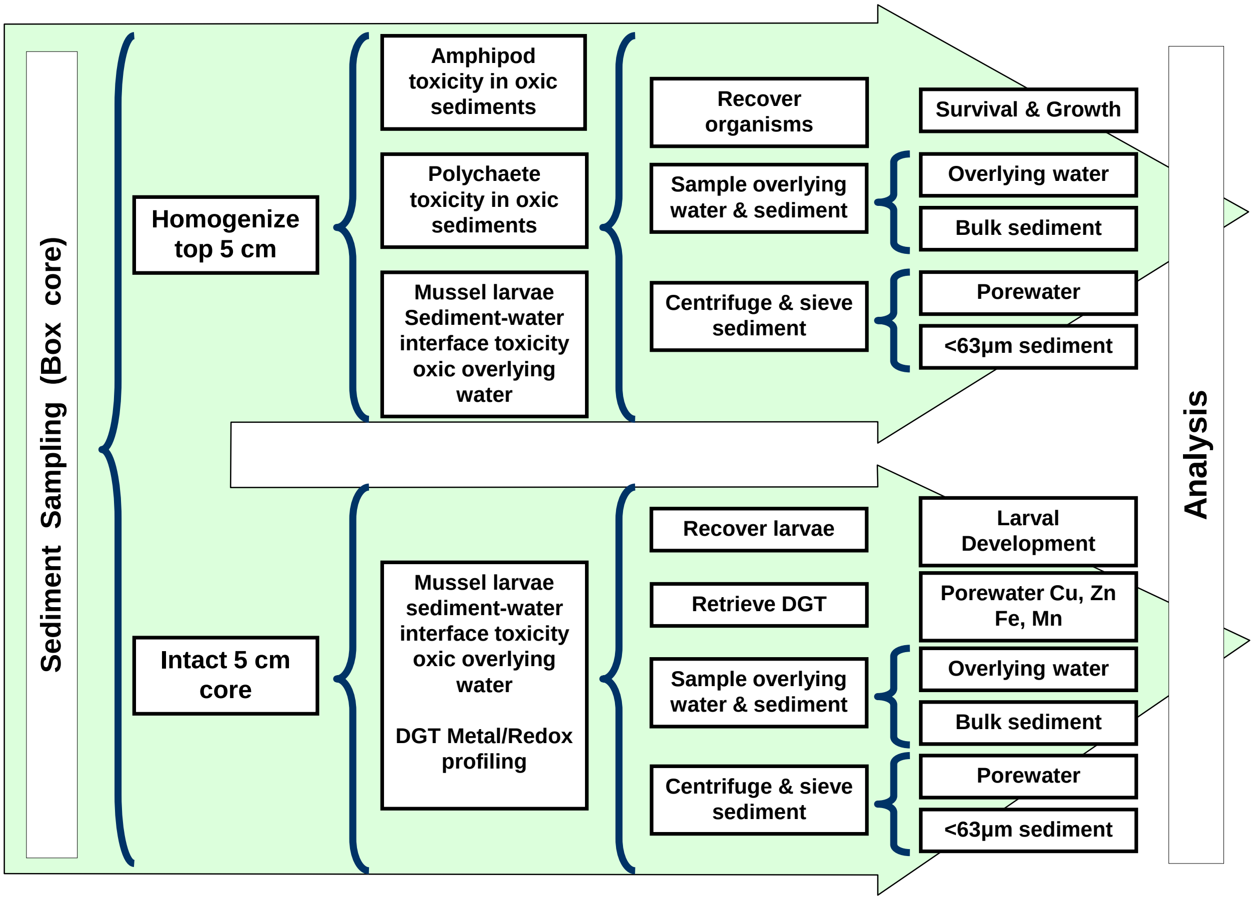

Figure 2. Schematic of overall experimental design.

Objective 1) Normalized (<63 µm/OC) Cu and Zn effects thresholds

This objective will further the development of a promising approach involving post exposure sieving and Cu measurement of the <63 µm (silt) sediment size fraction normalized to the TOC concentration associated with that fraction (<63 µm copper (mg/g OC)(Simpson et al. 2008; Strom et al. in press). In spiked sediment toxicity tests, sediment concentrations expressed in such a manner were much more predictive of toxicity than measurements based on bulk sediment Cu concentrations. However, this measurement has not yet been examined for naturally contaminated sediments. Sediment toxicity tests will be conducted on a range of naturally contaminated marine sediments collected from U.S. Navy (and Navy-adjacent) sites representative of a large Cu and Zn contamination gradient. This objective will be comprehensive in nature, and also supports the measurement of physicochemical parameters and passive samplers necessary to complete Objectives 2 and 3.

Sediment toxicity experiments will be performed on as many samples as practical, and will be divided into two phases, the first targeted for completion in May 2011, and the second targeted for completion in August 2011. The two-phased approach will allow an opportunity to employ lessons learned from the first phase in the latter phase. Sediments evaluated will represent a range of grain sizes, organic carbon contents, and expected Cu and Zn bulk sediment concentrations. San Diego Bay will be the initial focus of this study due to its large

Navy presence, and the wealth of historical knowledge of sediment quality in this water body. In addition, the Shelter Island Yacht Basin (SIYB; a sub-bay of San Diego Harbor) will be sampled, due to presence of elevated Cu concentrations in its water and sediments (Zirino et al., 1998; Neira et al., 2009). Contaminated sediments adjacent to the Puget Sound Naval Shipyard (Bremerton, WA) will also be considered, in addition to other coastal sites in California, Alaska and Maine, and contaminated sediments from Australia and/or Brazil. Some of the foreign sites have reportedly very high metals concentrations (>1500 mg/Kg Cu and/or Zn), which are larger than those typically found in embayments on the west coast of the United States, and may be helpful in establishing potential chemistry-toxicity relationships.

As a positive control, uncontaminated fine-grained sediment (Sequim Bay, WA) spiked with copper, and equilibrated according to methods described by Hutchins et al. (2007, 2008), will be tested concurrently with the naturally contaminated sediments. The positive control will include several concentrations of copper bracketing expected adverse effects concentrations, and provide the opportunity for concurrent comparative assessment of sensitivity among the different test methods. The positive control treatments will undergo the same level of physico-chemical analysis as the naturally contaminated field sediments.

***Sediment sampling**.* Sediment from all sites will be sampled using standard sediment collection, sampling, and storage procedures (ASTM 2008). All samples will be accompanied by chain of custody and sample tracking forms, which will be provided by SSC Pacific. These forms include dates and times of receipt, homogenization (if applicable), and storage conditions. If non-Navy personnel will be collecting sediments from any of the other proposed locations, appropriate communication and training will take place to ensure that sampling procedures are consistent.

Sediment samples will be collected using a box core sampler or Van Veen sampler to preserve the integrity of *in situ* conditions as best as possible. The box corer will be pre-cleaned, and scrubbed and rinsed with site water between grabs, with careful attention not to sample from the sides of the device to avoid cross-contamination. Sampling will occur on the top 5 cm of sediment only, focusing on the oxic and suboxic layers. Intact cores will be removed for the SWI toxicity tests using pre-cleaned polycarbonate core tubes following specifications in Anderson et al. (1996). Core tubes will be marked 5 cm from the bottom, pushed into an acceptable box core sample, capped from beneath, taped, and stored on ice. Remaining sediment from the top 5 cm of the box core will be composited in pre-cleaned 1 gallon HDPE wide-mouth bottles for later homogenization and coarse press-sieving (2 mm) at the laboratory. The decision to homogenize and press-sieve the majority of the sediment for toxicity exposures is based on a multitude of factors that outweigh the benefits of exclusively focusing on intact cores for this study. These factors include, but are not limited to: a) the studies for which the initial OC/grain size normalization measurements were developed with spiked sediments used homogenized sediment (Strom et al., in press); b) toxicity testing in regulatory programs typically involves manipulation of sediments for toxicity testing; and c) some of the toxicity test methods have been designed with coarse sieving in mind (e.g. to prevent artifacts associated with predatory organisms). Intact cores and homogenized cores, however, will be concurrently exposed in the SWI toxicity tests, allowing for comparative analysis of the tools evaluated in this study. As the tools become further developed, future efforts to increase realism should be proposed.

The negative and positive control sediments will be collected from a relatively uncontaminated site in Sequim Bay, WA, that has been successfully used in previous investigations with marine sediment invertebrates including those proposed here (Lotufo et al., 2001).

All sediments will be stored in the dark at 4^{o}C until use, and will be used for experimentation as soon as possible. Test initiation will be targeted for 48 h within collection, with a maximum holding time of two weeks (USEPA, 1994).

Toxicity tests. Toxicity tests proposed include the following (see Figure 3):

- *Ampelisca abdita*: whole sediment 10-day amphipod survival (USEPA, 1994)
- *Leptocheirus plumulosus*: whole sediment 10-day amphipod survival (USEPA, 1994)
- *Neanthes arenaceodentata*: whole sediment 28-day polychaete survival & growth (Farrar and Bridges, 2011)
- *Mytilus galloprovincialis*: sediment-water interface 48-hour survival and embryo-larval development (Anderson et al., 1996; USEPA, 1995b)

The selection of test organisms was based on the desire to assess responses in benthic invertebrates that differ in sensitivity to Cu and Zn, contaminant exposure route, and geographical location. *Ampelisca abdita* (Figure 3) is a suspension feeding, sediment ingesting amphipod that builds tubes out of sand grains (Redmond et al., 1994), while *Leptocheirus plumulosus* is a free burrowing species (USEPA 1994). *Neanthes arenaceodentata* (Figure 3) is a surface deposit feeder/predatory omnivore, and builds mucoid tubes in surficial sediments (Dillon et al., 1993). All three species occur extensively in North America, are exposed to a combination of overlying water and porewater, in addition to sediment particles, detritus, and prey that might be an exposure source for Cu and Zn, and are frequently employed in testing for regulatory programs (USEPA 1994, ASTM 2000, Farrar and Bridges, 2011). These particular species are also sensitive to a variety of divalent metals, with *A. abdita* 96 h LC50s reported as low as 34 µg Cu/L (McPherson and Chapman, 2000) and 80 µg Cu/L (Rosen and Miller, 2011), respectively, in aqueous exposures. Recently, a new protocol was developed using *N. arenaceodentata* (Farrar and Bridges, 2011) that employs an earlier life stage (≤ 7 day old emergent juveniles) than other standard methods with this species (e.g. ASTM 2000). This method was demonstrated to be considerably more sensitive than methods employing 2-3 week old organisms in comparative round robin testing. In addition, the growth endpoint using the new procedure described by Farrar and Bridges (2011) was among the most sensitive in a multi-species comparison of acute and chronic toxicity in marine sediments (Greenstein et al., 2008). Previous studies have also indicated that both *A. abdita* and *N. arenaceodentata* responses in metal-spiked sediments are generally consistent with responses predicted using SEM/AVS ratios and interstitial water toxicity units (IWTU) (e.g. Pesch et al., 1995; Berry et al., 1996; DiToro et al., 2005). Although the acute and chronic test methods for *L. plumulosus* are often considered to be equally sensitive (D. Farrar, pers. comm.), recent range-finding experiments suggest that *L. plumulosus* is relatively sensitive to Cu-spiked sediments (ABC Labs, pers. comm.)

The incorporation of the *M. galloprovincialis* embryo-larval development test endpoint in this study will be via sediment-water interface (SWI) toxicity exposures (Anderson et al. 1996; Anderson et al. 2001). The relevancy of this test in the assessment of sediment bioavailability and toxicity is high; 1) the embryos are negatively buoyant and therefore directly exposed to sediment-associated contaminants during critical phases of cell differentiation; 2) the endpoint plays a major role in the development of saltwater WQC for Cu (USEPA 1995a); 3) the endpoint has served as the primary test for the development of site specific WQC for Cu in water effect ratio (WER) studies (Rosen et al. 2005, 2009; Earley et al. 2007), and for the development of predictive models of Cu toxicity in surface waters (e.g. Arnold et al. 2006; Chadwick et al. 2008); 4) the SWI toxicity test with *M. galloprovincialis* is a recommended test for the assessment of sediment quality as part of recently derived sediment quality objectives (SQOs) for the state of California (Bay et al. 2007); and 5) the lack of feeding during embryogenesis simplifies the interpretation of data towards the dissolved water concentration only. Schematic distributions of metals measured on surface sediments off the California Coast, and from San Francisco Bay, indicate a preference for Cu and Zn to be released from biogenic material and from oxyhydroxides at the oxic and the top of the suboxic layers (Shaw et al., 1990; Rivera-Duarte and Flegal, 1997).

These toxicity tests will be the basis for the assessment of the organic carbon normalization of the silt size fraction for improving the predictability of Cu and Zn associated sediment toxicity. Comprehensive measurement of physicochemical parameters to help interpret and model (in future efforts) toxicity will also be collected, including the deployment of passive samplers (e.g. diffusive gradients in thin films; DGTs) to assess the labile fraction of Cu and Zn in the overlying water and porewater.

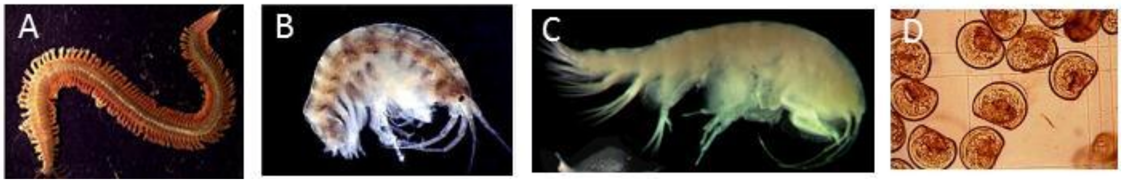

Figure 3. Proposed toxicity endpoints for this project include a) polychaete (*Neanthes arenaceodentata*) survival and growth mussel, b) amphipod (*Leptocheirus plumulosus*) survival, c) amphipod (*Ampelisca abdita*) survival, and d) bivalve (*Mytilus galloprovincialis*) embryo-larval development. Photos are not to scale.

<u>*Whole sediment toxicity tests*</u>*:* The *A. abdita, L. plumulosus,* and *N. arenaceodentata* exposures will be conducted using minor modifications of standard methods (USEPA, 1994; ASTM, 2000; Farrar and Bridges, 2011). Summaries of the test conditions and test acceptability criteria are shown in Tables 1 and 2. Briefly, the amphipod tests will include approximately 150g of homogenized wet sediment in 1 L glass jars, with 700 mL of overlying uncontaminated seawater collected from the research pier at Scripps Institution of Oceanography, located on the coast of La Jolla, California. This water is frequently used by local laboratories, including SSC Pacific, as an uncontaminated source of natural seawater, and will be filtered to 0.45 µm. The polychaete tests will contain 75 g of wet sediment and 175 mL of uncontaminated seawater (Farrar and

Bridges, 2011). Overlying water in all tests will be continuously aerated with filtered laboratory air at a rate of approximately 100 bubbles/minute. A 24-h equilibration period with the overlying water will be allowed prior to addition of test organisms (Day 0). Exposures will be static for *A. abdita* and *L. plumulosus* for 10 days (acute exposure), while weekly renewals of the overlying water will be made in the 28 day exposures with *N. arenaceodentata* (chronic exposure). The organisms will be recovered on 0.5 mm sieves at the end of the test. The overlying water will be decanted, and the sediment will be centrifuged (from surrogate beakers not destructively sampled for toxicity) for separation of porewater and sediment for analyses that are detailed in Objectives 2 and 3. For *N. arenaceodentata,* recovered organisms will be purged overnight in clean seawater prior to drying for growth assessment, and then transferred into microcentrifuge vials for acid digestion (nitric acid under heat) and measurement of Cu and Zn in the tissues (Rosen et al., 2008).

<u>*Sediment-water interface toxicity tests:*</u> The *M. galloprovincialis* embryo-larval development toxicity test will be conducted according to USEPA (1995b) and Anderson et al. (1996). Test conditions and acceptability criteria are summarized in Table 3. In the SWI test, early stage (< 4 hour old) embryos are placed 1 cm above the interface using a screen tube (25 µm mesh) that rests 1 cm above a 5 cm sediment core; Figure 4). Developing larvae will be exposed to metal flux from the sediment in both intact core and homogenized core tubes (2.5 inches in diameter), which are filled with 300 mL of overlying uncontaminated, filtered seawater. The number of surviving normal larvae will be determined on an inverted microscope at the end of the test and used to calculate the percentage normal-alive relative to the negative control (lab seawater).

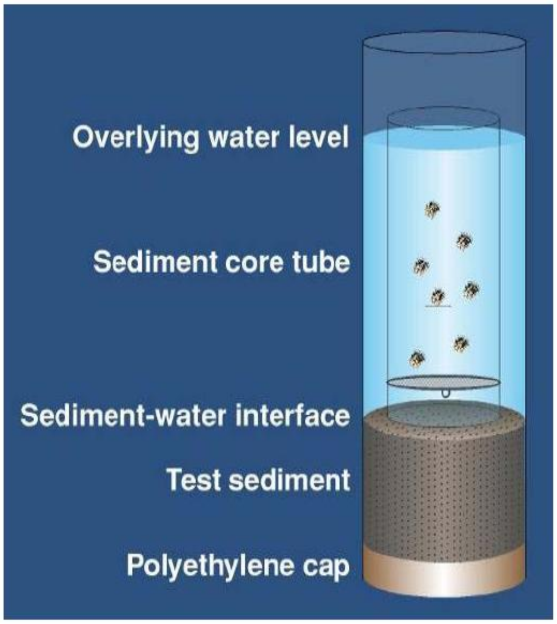

Figure 4. Sediment water interface toxicity test.

Each sample will consist of five replicates, four for organism exposure, and one for placement of a diffusive gradient in thin-film (DGT) to measure the profile of metal (Cu, Zn, Fe and Mn) concentrations in the porewater and overlying water. The mussel embryos do not come into direct contact with the sediment and do not feed, so are exposed primarily to dissolved substances that partition out of the sediment. This test is required in newly established California SQOs, and the embryo-larval development endpoint of this species independently dictates ambient saltwater WQC for Cu (USEPA, 1995a) and was used in marine Cu BLM development (Chadwick et al. 2008), and therefore, provides a nice linkage between water and sediment metal bioavailability assessment. Samples from the overlying water will be collected at the beginning and end of the exposure, while porewater and DGT samplers will be collected and analyzed at the test end only. The measurements made on the overlying water, sediment, and porewater are discussed in the approach for Objectives 2 and 3, and will be used to help interpret to observed responses in the SWI toxicity tests.

Objective 2) Physicochemical characterization of marine sediments

Extensive characterization of the particulate and dissolved fractions will be made on samples collected from the sediment toxicity exposures. These measurements were considered desirable by the project management and technical panels, and will provide a means of interpreting the toxicity data and will provide data that can be integrated into future proposed modeling efforts (not part of the current study).

***Overlying water and pore water**:* Overlying water samples will be collected from the different sediment toxicity exposures from strategically important points in the exposure (i.e. at beginning and end of exposure at a minimum, and prior to and following water changes in static-renewal tests). Porewater samples will be collected by centrifugation (800 g for 5 min) at the beginning and end of the exposures. Samples will be analyzed for the following:

- Dissolved (<0.45 µm) Cu and Zn (ICP-MS)
- Total Cu and Zn (ICP-MS)
- pH (probe)
- Salinity (probe)
- Temperature (thermometer)
- Total organic carbon
- Dissolved organic carbon
- Ammonia (for potential confounding toxic effects)
- Organic contaminants including PAHs, pesticides, PCBs (for potential confounding effects assessment)

Solid phase: Bulk sediment concentrations will be measured on both the unsieved (total) and sieved (<63 µm) fractions for the following:

- Total Cu and Zn (Method 6020, USEPA 1994b)
- Total Cu and Zn in <63 um fraction (following wet sieving of sediment)
- Total organic carbon
- Total organic carbon of the <63 um fraction (following wet sieving of sediment)
- SEM/AVS on bulk sediment
- Organic contaminants including PAHs, pesticides, PCBs (for potential confounding effects assessment).

Assessment of metal concentrations will be made following methodology recommended by USEPA, including use of trace metal clean sampling techniques in the collection, handling and analysis (USEPA, 1996). Water and porewater samples will be collected in 30-mL acid-cleaned low-density polyethylene bottles. Samples will be acidified to pH ≤2 with quartz still-grade nitric acid (Q-HNO_3) in a High Efficiency Particle Air (HEPA) class-100 all polypropylene working area. Metal concentrations will be measured with a Perkin-Elmer SCIEX ELAN DRC II inductively coupled plasma with detection by mass spectrometry (ICP-MS; USEPA, 1994b). If deemed necessary, samples will be diluted with 0.1 N Q-HNO_3 made up in high-purity (18 MΩ cm^{-1}) water in order to minimize matrix related interferences. The diluted or undiluted samples will be injected directly into the ICP-MS via a Perkin-Elmer Autosampler 100. Analytical standards will be made in CASS4 Nearshore Seawater Reference Material for Trace Metals, National Research Council Canada, with Perkin-Elmer multi-element standard solution (PEMES-3) diluted in 1N Q-HNO_3, and will be analyzed at the beginning and end of the run. The analysis will also include measurement of the Standard Reference Material (SRM) 1643e from the National Institute of Standards & Technology (NIST), and analytical blanks made up of 1N Q-HNO_3 after every five samples. A coefficient of variation (CV) of ≤5% for replicate measurements will be observed, as well as a recovery within 15% for direct injection of SRM 1643e. The method limit of detection will be defined as three times the standard deviation of the analytical blanks made of 1N Q-HNO_3.

Objective 3) Diffusive gradient in thin film (DGT) bioavailability assessment

Diffusion gradient in thin films (DGT) are a relatively new approach to the in situ measurement of metal concentration, flux, bioavailability and speciation in water, sediments, soils and porewater (Zhang and Davison, 1995; Zhang et al., 1995; Davison and Hutchinson, 1997). The basic sediment DGT probe design uses three thin layers composed of a gel layer containing a binding resin such as Chelex 100, a diffusive gel layer and a membrane filter. The theory behind the application is that metals must pass through the membrane and diffusive gel layers before contacting and binding to the resin gel layer. The general equation used to calculate the pore water metal concentration is:

$$C = \frac{M\Delta g}{DtA}$$

where Δg is the thickness of the diffusive gel thickness (known), M is the metal accumulated mass (moles)(measured), D is the diffusion coefficient (known), t is the time for deployment, and A is the area of the exposed diffusive layer (cm^2). The ease of deployment of DGTs makes them a suitable tool for assessing the bioavailability of metals. Before field deployment, the sediment DGT probes are deoxygenated in a 0.01M NaCl solution by gently bubbling nitrogen or argon gas through the liquid for 24 hours. After degassing, the probes are deployed by inserting them vertically into the sediment. At the time of deployment and retrieval, the sediment temperature and time is recorded for concentration calculations. To prepare the gel for analysis, the membrane filter and diffusive gel layers are peeled from the probe and the resin gel layer is sliced into segments. The slices are then placed in centrifuge tubes and 200-300 µl of 1M Q-HNO_3 is added to dissolve the gel. The samples are then analyzed for metals by ICP-MS as described above.

The DGTs will be positioned in surrogate test vessels associated with each of the different toxicity test methods, allowing for both DGT determined overlying water and pore water Cu, Zn, Fe and Mn measurements in the oxic and suboxic zones. Suboxic zones are going to be defined as those layers of sediment where either or both Fe and Mn are present in the

(<0.45 µm) porewater. Porewater Cu and Zn concentrations from the DGTs (and from centrifugation) will be compared with toxicity results and uptake by *N. arenaceodentata.*

Key Personnel

The toxicity studies will be led by Navy scientists at SSC Pacific, including Mr. Gunther Rosen (ecotoxicology), Dr. Ignacio Rivera-Duarte (chemistry), and Mr. Patrick Earley (program management). Mr. Brandon Swope will provide internal support for bioassays, analytical, and sample collection. Contract technical support will be provided in house by Master's students employed by the San Diego State University Research Foundation (Ms. Marienne Colvin, Ms. Casey Capolupo). Required ancillary measurements will be made by outside analytical labs, including Columbia Analytical Systems, Battelle, and/or the U.S. Army Corps of Engineers (USACOE) Engineer Research and Development Center (ERDC).

Project Schedule

Description	**Completion Date**
Work plan revision, related proposals, sample location coordination, planning meetings	April 2011
Phase I sediment toxicity tests	May 2011
Phase I chemical analyses	June 2011
Phase II sediment toxicity tests	July 2011
Phase II chemical analyses	August 2011
Data analysis	September 2011
Report Preparation	September 2011

Deliverables

The results of this study will be presented at relevant scientific conferences (e.g. Society of Environmental Toxicology and Chemistry). A final report will be prepared summarizing the study results and conclusions. It is anticipated that the final report will be formally submitted for publication as a SSC Pacific Technical Report. It is also anticipated that one or more journal articles will be generated from this research. In addition, follow-on proposals to DoD programs such as the ESTCP and the Navy's Environmental Sustainability Development to Integration (NESDI) Program have been initiated, and will continue to be pursued to further the development of these tools.

References

American Society for Testing and Materials. 2000. Standard Guide for Conducting Sediment Toxicity Tests with Marine and Estuarine Polychaetous Annelids. E 1611-99. In: *Annual Book of ASTM Standards.* Vol. 11.05. Philadelphia, PA, pp 991-1016.

American Society for Testing and Materials. 2008. Standard Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing and for Selection of Samplers Used to Collect Benthic Invertebrates. ASTM E1391-2008. West Conshohocken, PA. 94 pp.

Anderson BS, Hunt JW, Hester M, Phillips BM. 1996. Assessment of sediment toxicity at the sediment water interface. In: G.K. Ostrander (ed.) *Techniques in Aquatic Toxicology*. Lewis Publishers, Ann Arbor, MI.

Anderson BS, Hunt JW, Phillips BM, Fairey R, Newman J, Puckett HM, 2001. Influence of sample manipulation on contaminant flux and toxicity at the sediment-water interface. *Marine Environmental Research* 15:191–211.

Ankley GT, Di Toro DM, Hansen DJ, Berry WJ. 1996. Technical basis and proposal for deriving sediment quality criteria for metals. *Environmental Toxicology and Chemistry* 15(12):2056-2066.

Arnold WR, Cotsifas JS, Corneillie KM. 2006. Validation and update of a model used to predict Cu toxicity to the marine bivalve Mytilus sp. *Environmental Toxicology* 21: 65–70.

Bay S, Greenstein D, Young D. 2007. Evaluation of methods for measuring sediment toxicity in California bays and estuaries. Southern California Coastal Water Research Project (SCCWRP) Technical Report #503. March 2007. 41 pp. www.sccwrp.org.

Berner RA. 1980. *Early Diagenesis. A Theoretical Approach*. Princeton Series in Geochemistry, Princeton University Press, Princeton, NJ, 241 pp.

Berry WJ, Hansen DJ, Mahony JD, Robson DL, Di Toro DM, Shipley BP, Rogers B, Corbin JM, Boothman WS. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water normalizations. *Environmental Toxicology and Chemistry* 15:2067-2079.

Chadwick DB, Rivera-Duarte I, Rosen G, Wang P-F, Santore RC, Ryan AC, Paquin PR, Hafner SD, Choi WH. 2008. Demonstration of an Integrated Compliance Model for Predicting Copper Fate and Effects in DoD Harbors. Environmental Security Technology Certification Program (ESTCP), Project ER-0523. Technical Report 1973, SPAWAR Systems Center Pacific, 118 pp, http://www.spawar.navy.mil/sti/publications/pubs/tr/1973/tr1973cond.pdf.

Davison W., Hutchinson W. 1997. An assessment of the feasibility of using DGT procedures to measure trace metals and radionuclides in rivers. Environment Agency R&D Technical Report, pp. 92.

Di Toro DM, McGrath JA, Hansen DJ, Berry WJ, Paquin PR, Mathew R, Wu KB, Santore RC. 2005. Predicting sediment metal toxicity using a sediment biotic ligand model: (I) Single metals. *Environmental Toxicology and Chemistry* 24(10): 2410-2427.

Dillon TM, Moore DW, Gibson AB. 1993. Development of a chronic sub lethal bioassay for evaluating contaminated sediment with the marine polychaete worm *Nereis (Neanthes) arenaceodentata*. *Environmental Toxicology and Chemistry* 12:589-605.

Earley PJ, Rosen G, Rivera-Duarte I, Gauthier R, Arias-Thode YM, Thompson J, Swope B. 2007. A comprehensive copper compliance strategy: Implementing regulatory guidance at Pearl Harbor Naval Shipyard & Intermediate Maintenance Facility. Technical Report 1952. SPAWAR Systems Center San Diego. 93 pp.

Farrar D, Bridges TS. 2011. 28-Day Chronic Sublethal Test Method for Evaluating Whole Sediments Using an Early Life Stage of the Marine Polychaete *Neanthes arenaceodentata*. ERDC TN-DOER-R14, February 2011.

Greenstein D, Bay S, Anderson B, Chandler GT, Farrar JD, Keppler C, Phillips B, Ringwood A, Young D, 2008. Comparison of methods for evaluating acute and chronic toxicity in marine sediments. *Environmental Toxicology and Chemistry* 27:933-44.

Hutchins CM, Teasdale, PR, Lee SY, Simpson SL. 2007. The effect of manipulating sediment pH on the porewater chemistry of copper- and zinc-spiked sediments. *Chemosphere* 69: 1089-1099.

Hutchins CM, Teasdale, PR, Lee SY, Simpson SL. 2008. Cu and Zn concentration gradients created by dilution of pH neutral metal-spiked marine sediment: A comparison of sediment geochemistry with direct methods of metal addition. *Environmental Science & Technology* 42(8): 2912-2918.

Long, E.R., D.D. MacDonald, S.L. Smith and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19:81-97.

Lotufo GR, Farrar JD, Inouye LS, Bridges TS, Ringelberg DB. 2001. Toxicity of sediment-associated nitroaromatic and cyclonitramine compounds to benthic invertebrates. *Environmental Toxicology and Chemistry* 20:1762–1771.

McPherson CA, Chapman PM. 2000. Copper effects on potential sediment test organisms: The importance of appropriate sensitivity. *Marine Pollution Bulletin* 40: 656-665.

Neira C, Delgadillo-Hinojosa F, Zirino A, Mendoza G, Levin LA, Porrachia M, Deheyn DD. 2009. Spatial distribution of copper in relation to recreational boating in a California shallow-water basin. *Chemistry and Ecology* 25 (6): 417–433.

Pesch CE, Hansen DJ, Boothman WS, Berry WJ, Mahony JD. 1995. The role of acid-volatile sulfide and interstitial water metal concentrations in determining bioavailability of cadmium and nickel from contaminated sediments to the marine polychaete *Neanthes arenaceodenata*. *Environmental Toxicology and Chemistry* 14: 129-141

Redmond M, Scott KJ, Swartz RC, Jones JKP. 1994. Preliminary Culture and Life-Cycle Experiments with the Benthic Amphipod, *Ampelisca abdita*. *Environmental Toxicology and Chemistry* 13(8): 1355- 1365.

Rivera-Duarte I, Flegal AR. 1997. Porewater gradients and diffusive benthic fluxes from relatively pristine and contaminated sites in San Francisco Bay: Co, Ni, Cu, Zn, and Cd. *Croatica Chemica Acta* 70: 389-417.

Rosen G, Rivera-Duarte I, Kear-Padilla L, Chadwick DB. 2005. Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper in San Diego Bay, California, USA. *Environmental Toxicology and Chemistry* 24: 415–422.

Rosen G, Rivera-Duarte I, Chadwick DB, Ryan A, Santore AC, Paquin PR. 2008. Critical tissue copper residues for marine bivalve (*Mytilus galloprovincialis*) and echinoderm (*Strongylocentrotus purpuratus*) embryonic development: Conceptual, regulatory and environmental implications. *Marine Environmental Research* 66: 327-336.

Rosen G, Miller K. 2011. A post exposure feeding assay using the marine polychaete *Neanthes arenaceodentata* suitable for laboratory and in situ exposures. *Environmental Toxicology and Chemistry* 30: 730-737.

Shaw TJ, Gieskes JM, Jahnke RA. 1990. Early diagenesis in differing depositional environments: The response of transition metals in pore water. *Geochimica et Cosmochimica Acta* 40: 809-816.

Simpson SL, King CK. 2005. Exposure-pathway models explain causality in whole-sediment toxicity tests. *Environmental Science & Technology* 39: 837-843.

Simpson SL, Batley GE. 2007. Predicting metal toxicity in sediments: A critique of current approaches. *Integrated Environmental Assessment and Management*, 3: 18-31.

Simpson SL, Strom D, Batley G. 2008. Development of a sediment quality guideline for copper. CSIRO Land and Water Science Report 51/08. September 2008. Prepared for Rio Tinto Pty Ltd, BHP Billiton Pty Ltd, and Xstrata Copper Pty Ltd. 39 pp.

Strom D, Simpson SL, Batley GE, Jolley DF. In press. Accounting for the influence of sediment particle size and organic carbon on toxicity of copper to benthic invertebrates in oxic/sub-oxic surface sediments. Accepted for publication by *Environmental Toxicology and Chemistry.*

US Environmental Protection Agency. 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA 600/R-94/025. Office of Research and Development, Washington, D.C.

US Environmental Protection Agency. 1994b. Method 6020: Inductively coupled plasma – mass spectrometry. CD-ROM, Revision 0, September / 1994.

US Environmental Protection Agency. 1995a. Ambient water quality criteria—Saltwater copper addendum (Draft). Washington DC: USEPA. (U.S. Environmental Protection Agency. 2003. “Update of Ambient Water Quality Criteria for Copper.” EPA 822-R-03-06. Washington, DC.)

US Environmental Protection Agency. 1995b. Short-term methods for measuring the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. EPA/600/R-95/136. Office of Research and Development, Narragansett, RI.

US Environmental Protection Agency. 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. January / 1996.

US Environmental Protection Agency. 2005. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver, and zinc). EPA-600-R-02- 011. Washington, DC.

Zhang H, Davison W. 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solutions. *Analytical Chemistry* 67: 3391-3400.

Zhang H, Davison W, Miller S, Tych W. 1995. In situ high resolution measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. *Geochimica et Cosmochimica Acta* 59: 4184-4192.

Zirino A, Belli SL, Van der Weele DA. 1998. Copper concentration and Cu activity in San Diego Bay. *Electroanalysis* 10: 423-327.

Table 1. Recommended test conditions and test acceptability requirements for acute (10 day) solid phase sediment toxicity tests with amphipods *Ampelisca abdita* and *Leptocheirus plumulosus.*

Parameter	**Conditions**
Test Type	Solid phase sediment toxicity, static, non-renewal
Test species	*Ampelisca abdita, Leptocheirus plumulosus*
Age at test initiation	Adult 3-5 mm
Salinity	30 ± 1 ppt
Temperature	15 ± 1 ^{o}C
Light quality	Wide-spectrum fluorescent lights
Light intensity	50-1000 lux
Photoperiod	24 hours light: 0 hours dark
Test Chamber type/size	1 L glass jar with ~10 cm I.D.
Test solution volume	2 cm sediment: 700 mL overlying water
No. organisms/chamber	20
No. replicate chambers/concentration	5
Dilution water	Uncontaminated 0.45 µm natural seawater from Scripps Institution of Oceanography
Feeding	None
Aeration	Maintain >90% saturation, ~100 bubbles filtered air per minute
Test Duration	10 days
Endpoint Measured	Survival
Test Acceptability Criteria	Minimum mean control survival ≥ 90%

Table 2. Recommended test conditions for conducting chronic (28-day) sediment toxicity testing with the polychaete *Neanthes arenaceodentata* (adapted from Farrar and Bridges 2011).

Parameter	**Conditions**
Test Type	Solid phase sediment toxicity, static-renewal
Test species	*Neanthes arenaceodentata*
Initial age of test organisms	≤ 7 days post-emergent juveniles
Salinity	30 ± 1 ppt
Temperature	20 ± 1 ^{o}C
Light quality	Wide-spectrum fluorescent lights
Light intensity	50-1000 lux
Photoperiod	12 hours light: 12 hours dark
Test Chamber type/size	1 L glass jar with ~10 cm I.D.
Test chamber sediment volume	2 cm sediment (75 mL)
Overlying water	175 mL
Renewal of overlying water	Once weekly (50 percent)
No. organisms/chamber	1
No. replicate chambers/concentration	10
Dilution water	Uncontaminated 0.45 µm natural seawater from Scripps Institution of Oceanography
Aeration	Trickle-flow; ~100 bubbles filtered air per minute
Feeding	Twice weekly, 2 mg of Tetramarin® per organism
Water quality monitoring	Weekly (pH, DO, salinity, ammonia); Daily (temp.)
Test Duration	28 days
Endpoint Measured	Survival and growth
Test Acceptability Criteria	Minimum mean control survival ≥ 80% and positive growth in control organisms

Table 3. Test conditions for conducting sublethal 48-h sediment-water interface toxicity testing with embryos of the mussel *Mytilus galloprovincialis* (adapted from Anderson et al. 1996 and USEPA 1995b).

Parameter	**Conditions**
Test Type	Sediment-water interface toxicity; static, non-renewal
Test species	*Mytilus galloprovincialis*
Initial age of test organisms	≤ 4 hour old embryos
Salinity	30 ± 2 ppt
Temperature	15 ± 1 ^{o}C
Light quality	Wide-spectrum fluorescent lights
Light intensity	50-1000 lux
Photoperiod	16 hours light: 8 hours dark
Test Chamber type/size	Polycarbonate core tube (outer) Polycarbonate screen tube (inner)
Test chamber sediment volume	5 cm sediment core (intact or homogenized)
Overlying water	300 mL
Renewal of overlying water	None
No. organisms/chamber	150-300
No. replicate chambers/concentration	4
Dilution water	Uncontaminated 0.45 µm natural seawater from Scripps Institution of Oceanography
Aeration	Trickle-flow; ~100 bubbles filtered air per minute
Feeding	None
Water quality monitoring	Daily (pH, DO, salinity, ammonia); Daily (temp.)
Test Duration	48 hours
Endpoint Measured	Survival and normal larval shell development
Test Acceptability Criteria	Minimum normally developed and alive (combined endpoint) ≥ 70% in control organisms

Appendix A- Quality Assurance and Quality Control for Toxicity Tests

Test organism quality. Test organisms will be obtained from established vendors. Individuals selected for testing will be visually inspected to confirm that they are the proper size and in good condition (i.e., no external damage). Holding time prior to testing will not exceed three to five days, depending on species.

Test conditions. Samples for ammonia, pH, dissolved oxygen, temperature, and salinity analysis of each sample will be made prior to introducing test organisms to ensure that concentrations are within those tolerated. All instruments used for water quality measurements will be calibrated daily. Water quality measurements will be made daily in a surrogate chamber.

If water quality measurements are found to fall outside of acceptable ranges, corrective actions will immediately be taken such as increasing air flow (if reduced DO) or change in temperature if it is outside of the acceptable range. Such deviations and corrective actions must be immediately noted on bench sheets and reported in the comments section of the database at the end of the project.

Test acceptability. A reference toxicant test will be run with every batch of test samples in order to document test organism sensitivity and test precision. This test will consist of a 48 or 96-hour exposure to five different concentrations of reagent grade cadmium chloride or copper chloride (species specific) dissolved in uncontaminated seawater (filtered from SIO). Exposure concentrations will be selected to provide an estimate of the LC50. Reference toxicant test results that fall outside of the laboratory's control chart limits (2 s.d. of mean) will trigger a review of test procedures and a possible retest of the corresponding sediment samples. For endpoints where control charts are not available, LC50s will be compared to literature values.

Each of the test methods employed have specific test acceptability requirements based on performance in the controls. Control sediment will be the home sediment from the site of organism collection for solid phase tests. A core tube blank containing filtered SIO seawater will serve as a control for the SWI exposures. Any water quality exceedances will be evaluated for potential impacts they might have had on the test and will be reported in the final report.

Sediment holding time. It is anticipated that toxicity tests will be initiated with 48 hours of sample collection. A sediment holding time of no more than two weeks has been established in order to minimize the potential alteration of the sediment toxicity due to storage; this time period is not a criterion for judging test acceptability. Tests on samples that are stored from greater than two weeks up to four weeks will also be considered valid, but a data qualifier will be attached to the record to indicate that the desired storage time was been exceeded.