Final Conceptual Model for Shelter Island Yacht Basin Total Maximum Daily Load

Prepared for:

Port of San Diego
3165 Pacific Highway
San Diego, CA 92101

May 2011

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ACRONYMS AND ABBREVIATIONS

ACR	acute-to-chronic ratio
APCD	Air Pollution Control District
BLM	biotic ligand model
$BLM_{EC50\text{-}FAV}$	modified biotic ligand model
BRI	Benthic Response Index
CH3D	Curvilinear Hydrodynamics in Three Dimensions
CTR	California Toxics Rule
Cu^{2+}	free copper
CWA	Clean Water Act
DNA	deoxyribonucleic acid
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
EC50	median effective concentration
EMC	event mean concentration
ER-L	effects range-low
ER-M	effects range-median
FACR	final acute chronic ratio
FAV	final acute value
GIS	geographic information system
GMAV	genus mean acute value
ISE	ion selective electrode
LA50	median lethal level accumulation
LC50	median lethal concentration
MAR	marine habitat beneficial use
MOS	margin of safety
MS4	municipal separate storm sewer system
NAVSTA	Naval Station San Diego
pH	hydrogen ion concentration
Port	Port of San Diego
PRC	PRC Environmental Management, Inc.
Regional Board	Regional Water Quality Control Board
RHMP	Regional Harbor Monitoring Program
SCCWRP	Southern California Coastal Water Research Project
SD-1D	steady-state box model
SERDP	Strategic Environmental Research and Development Program
SIYB	Shelter Island Yacht Basin
SMAV	species mean acute value
SP	solid phase
SPAWAR	Space and Naval Warfare Systems Command
SQO	Sediment Quality Objective
SSO	site-specific objective
State Board	State Water Resources Control Board
SWI	surface-water interface
TIE	toxicity identification evaluation

TMDL	total maximum daily load
TSS	total suspended solids
USEPA	U.S. Environmental Protection Agency
WER	water-effect ratio
WESTON	Weston Solutions, Inc.
WILD	wildlife beneficial use
WQC	water quality criteria
WQO	water quality objective

1.0 INTRODUCTION

Investigative Order No. R9-2011-0036, issued by the San Diego Regional Water Quality Control Board (Regional Board) to the Port of San Diego (Port) requires that the Port develop a Conceptual Model for dissolved copper in Shelter Island Yacht Basin (SIYB) as a component of the SIYB Total Maximum Daily Load (TMDL) Monitoring Plan. The Conceptual Model is intended to identify the physical and chemical factors that control the fate and transport of dissolved copper within the basin and the receptors (i.e., biota) that could be exposed to copper in both the water and sediment. The initial Conceptual Model will provide an overview of the state of knowledge for dissolved copper dynamics within SIYB, as detailed in the February 9, 2005 Total Maximum Daily Load for Dissolved Copper in Shelter Island Yacht Basin, San Diego Bay Technical Report (hereafter Technical Report) (Regional Board 2005), as well as other relevant technical reports and scientific literature. The initial Conceptual Model will also identify data gaps and describe any additional required work to complete the model.

1.1 Conceptual Model Overview

The initial Conceptual Model presented as follows describes the inputs of dissolved copper to SIYB, the physical and chemical processes that control the fate and transport of copper within the basin, and the potential biological receptors (Figure 1-1).

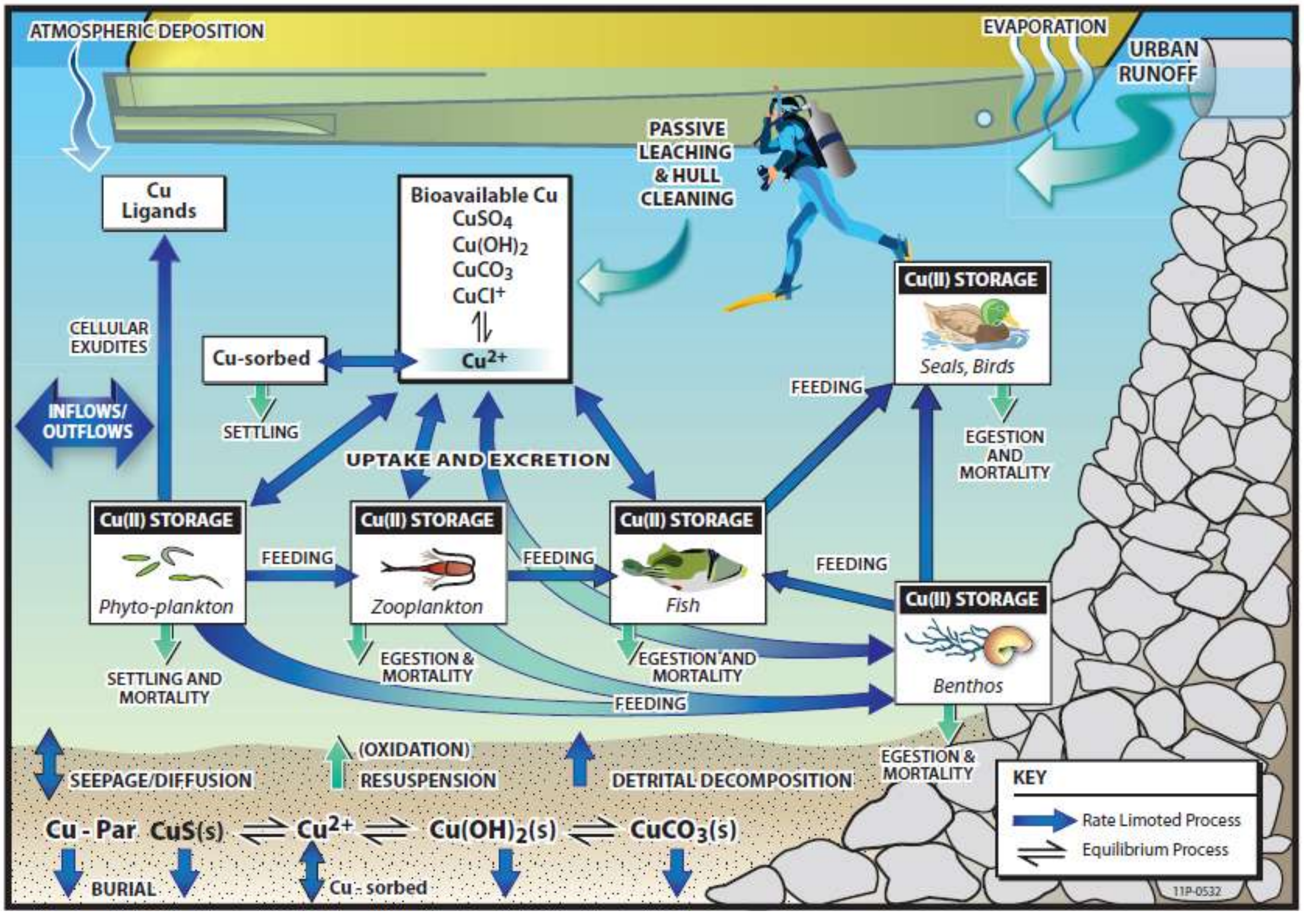

Figure 1-1. Conceptual Model of dissolved copper for Shelter Island Yacht Basin (Adapted from Tetra Tech, Inc., 1999)

The initial Conceptual Model developed for SIYB is based on the Conceptual Model for Copper in Lower South San Francisco Bay (Tetra Tech, Inc., 1999). The SIYB initial Conceptual Model considers three interrelated components, which include dissolved copper sources; fate and transport dynamics (including copper cycling in the water column, tidal forcing, and sediment processes); and biological receptors. The South San Francisco Bay Model was modified to account for site-specific differences in sources of copper, physical and chemical water column and sediment conditions, and hydrodynamics in SIYB.

Copper Sources: Major sources of copper to SIYB include passive leaching from recreational vessel antifouling hull paints, in-water hull cleaning, urban runoff, background inputs from San Diego Bay, atmospheric deposition, and sediment flux. Consistent with the Technical Report, the model considers passive leaching and hull cleaning to be the largest sources of copper to the basin, with inputs from other sources contributing between 2 and 5%. In contrast to the Technical Report, the Conceptual Model also considers loads from sediments in a manner that is more consistent with background inputs from San Diego Bay.

Fate and Transport Dynamics: Once copper enters SIYB waters, there are multiple physical, chemical, and biological factors that control its distribution and bioavailability. Within the water column, copper speciation, complexation, and adsorption regulate the abundance of the most bioavailable form – free copper (Cu^{2+}). Current dynamics affect the eventual fate of copper, with copper entering the sediments in areas of low circulation (e.g., the head of the basin) and copper flushing to the bay in areas closer to the mouth. Currents also affect sediment resuspension, which can lead to desorption and loading of copper back to the water column. Sediment properties, such as grain size, copper concentrations, and oxidation-reduction reactions also affect the potential for copper flux into and out of the sediments.

Biological Receptors: Elevated copper concentrations have been shown to have the greatest potential to impact phytoplankton, zooplankton, benthic invertebrates, as well as larval fish. Additionally, phytoplankton and benthic invertebrates, in particular have the potential to affect the concentration and chemical forms of copper in the water column and sediments due to accumulation in the food web, release of chemicals that bind bioavailable forms of copper, and bioturbation of sediments that can release copper. While these organisms can transfer copper to higher trophic-level species, such as adult fishes, birds, and mammals, there is little or no evidence that copper consumption is adversely affecting higher vertebrate predators.

1.2 Conceptual Model Report Organization

The report on the Conceptual Model report is organized into the following sections.

Shelter Island Yacht Basin Description: A general description of the basin is provided, including nearby land uses and beneficial uses.

Historic or Legacy Conditions: Recent information on the extent and magnitude of copper concentrations in the waters and sediments are reported for SIYB and the vicinity. Surface water and sediment toxicity data for the basin and surrounding portions of San Diego Bay are also provided.

Copper Sources: A discussion of the point and non-point sources of discharges and associated loadings is provided. Uncertainties of loading calculations are noted.

Fate and Transport Dynamics: This section describes the physical and chemical factors that affect the distribution and bioavailability of copper. Physical processes include circulation patterns, sedimentation, sediment resuspension and desorption, and copper flux. The discussion on bioavailability considers speciation and complexation. Lastly, a summary of the results of biotic ligand modeling for San Diego Bay, with particular emphasis on SIYB, is provided.

Evidence for Copper Impacts: Impacts to biota include lethal and sub-lethal effects that can undermine feeding, growth, reproduction, and survival. Evidence for impacts is presented from toxicological experiments and field surveys that report the absence or reduced abundance of copper-sensitive species.

Receptors of Concern: Potential impacts of copper on biological receptors are described as they relate to planktonic and benthic communities.

Revised Copper Box Model: Parameters for the Technical Report copper box model were updated to incorporate recent modeling data on dissolved copper loads from urban runoff, dissolved copper concentrations in the main channel of San Diego Bay, among other factors. Model-predicted dissolved copper concentrations are compared to the average dissolved copper concentration calculated from 2006-2008 monitoring for calibration, and revised loading targets are provided.

Uncertainties and Data Gaps: A summary of the current uncertainties and data gaps for the model is provided, with suggestions for potential studies that may be used to complete the model.

As additional studies are performed and data are gathered, the Conceptual Model will be revised, as needed, to improve its scientific foundation. In doing so, it will facilitate the adaptive approach to reducing copper loading into SIYB and achieving water quality conditions that are protective of SIYB Beneficial Uses.

2.0 SHELTER ISLAND YACHT BASIN

Shelter Island Yacht Basin is a recreational yacht basin that supports marinas, yacht clubs, an anchorage, a fuel dock, and other facilities within the northern portion of San Diego Bay (Regional Board, 2005). This semi-enclosed, constructed yacht basin was developed in the 1950s and now contains approximately 2,363 slips and moorings that support a nearly equivalent number of recreational vessels with copper-based hull paints.

In 1996, SIYB was placed on the Clean Water Act (CWA) section 303(d) list of impaired waters due to elevated levels of dissolved copper in the water column. Existing water quality did not meet numeric water quality standards for dissolved copper or narrative water quality objectives (WQOs) for toxicity and pesticides. As a result, the Regional Board developed a TMDL for SIYB, with the purpose of achieving applicable WQOs as well as the restoration of Marine Habitat (MAR) and Wildlife (WILD) beneficial uses within the basin.

2.1 Nearby Land and Marine Uses

SIYB occurs within the northern portion of San Diego Bay, located immediately southwest of America's Cup Harbor and across the bay main channel from North Island. The northern portion of the bay is characterized by high tidal flushing (Valkirs et al., 1994); however, the semi-enclosed configuration of SIYB limits currents and tidal exchange.

The basin is located within a portion of the Pueblo San Diego sub-watershed, which includes a total drainage area of 2.64 km^2 that contributes wet and dry weather runoff by way of the municipal separate storm sewer system (MS4) outfalls. The watershed is largely comprised of residential and transportation land uses.

2.2 Beneficial Uses

According to the Technical Report (Regional Board, 2005), Beneficial Uses of SIYB are consistent with those of San Diego Bay, and include:

- Industrial service supply (IND);
- Navigation (NAV);
- Water contact recreation (REC1);
- Non-contact water recreation (REC2);
- Commercial and sport fishing (COMM);
- Preservation of biological habitats of special significance (BIOL);
- Estuarine habitat (EST);
- Wildlife habitat (WILD);
- Marine habitat (MAR);
- Migration of aquatic organisms (MIGR);
- Shellfish harvesting (SHELL); and
- Rare, threatened, or endangered species (RARE).

Dissolved copper levels in waters of SIYB exceed numeric WQOs and narrative WQOs for toxicity and pesticides, threatening MAR and WILD Beneficial Uses (Regional Board, 2005). As such, the SIYB TMDL was established to address water quality impairment and restore Beneficial Uses within SIYB through water quality improvements.

3.0 HISTORIC OR LEGACY CONDITIONS

This section describes the spatial distribution of copper within the waters and sediments of SIYB and its vicinity (i.e., San Diego Bay), as well as toxicity based on studies of bay conditions generally performed within the last 20 years.

3.1 Extent and Magnitude of Copper Contamination

Numerous previous studies have documented copper as a contaminant of concern in San Diego Bay (e.g., McPherson and Peters, 1995; Fairey et al., 1998; SDRWQCB, 2005, Schiff et al., 2006a). However, this issue is not unique to the San Diego region alone, as semi-enclosed embayments throughout the state and the nation consistently have copper concentrations both in the waters and sediments that are higher than immediately adjacent open water environments (Schiff et al., 2006b; Zirino et al., 1998; U.S. Environmental Protection Agency [USEPA], 1996). Elevated copper levels in embayments located within urban settings are most commonly attributed to the following inputs: copper-based hull paints (including passive leaching and hull cleaning), discharges from ships, urban runoff, sediment resuspension, atmospheric deposition, and natural background sources. In SIYB, the approximately 2,300 recreational vessels are considered to be the largest source of copper to the basin (Regional Board, 2005). Accordingly, the findings of the 2008 Regional Harbor Monitoring Program (RHMP) (Weston Solutions, Inc. [WESTON], 2010), as well as a number of other studies (Fairey et al., 1998; Schiff et al. 2006a; Neira et al., 2009) have shown that copper concentrations both in the sediments and the water column of SIYB and San Diego Bay as a whole were closely associated with the density of and proximity to vessels. The following sections detail the spatial distribution of copper concentrations in the water column (Section 2.1) and the sediments (Section 2.2) of SIYB.

3.1.1 Copper in the Water Column

Copper exists within the water column in a number of forms, including dissolved, particulate, complexed, and free copper (Cu^{2+}) (Zirino et al., 1998), as discussed in greater detail in Section 5.6. Cu^{2+} is the most bioavailable form of copper and is the form that has been shown to be most closely associated with elevated levels of toxicity (Neira et al., 2009). However, most monitoring programs measure dissolved and total copper, and generally do not assess Cu^{2+}. This is largely due to the fact that the regulatory-established water quality criteria (WQC) is provided for dissolved copper in seawater, rather than its other forms. The WQC for dissolved copper in seawater has been set at 3.1 micrograms per liter (µg/L). This threshold is based on the California Toxics Rule (CTR), which indicates that continuous or chronic exposures may not exceed 3.1 µg/L over a 4-day average, while acute exposures may not exceed 4.8 µg/L over a one-hour average (USEPA, 2000).

Concentrations that exceed these thresholds have been shown to induce toxicity in sensitive species and life history stages, based on laboratory studies; however, recent studies have called into question the relevancy of current dissolved copper WQC due to the site-specific nature of copper bioavailability (Rivera-Duarte et al., 2005; Neira et al., 2009). Prior studies have shown that the potential for adverse effects of copper on biota (e.g., toxicity) is highly site specific, and is influenced by physico-chemical water column parameters, including salinity, dissolved organic matter, and pH (Seligman and Zirino, 1998; Deheyn and Latz, 2005; Rivera-Duarte et al., 2005; Rosen et al., 2005), as discussed in detail in Section 5.6. Although Cu^{2+} may serve to be a better indicator for adverse effects than dissolved copper, this section focuses on the distribution of both dissolved copper and Cu^{2+} throughout SIYB since current regulatory guidelines are based on dissolved copper concentrations.

3.1.1.1 Dissolved Copper

Within SIYB, surface water dissolved copper concentrations ranged from 3.41-16.06 µg/L based on an assessment of RHMP Pilot Study (WESTON, 2008), RHMP 2008 (WESTON, 2010) and Neira et al., (2009) data (Figure 3-1). In assessing the spatial distribution of dissolved copper in SIYB, two patterns were readily apparent. First, dissolved copper concentrations increased from the mouth to the head of the basin (Figure 3-1). In the case of SIYB, the gradient in dissolved copper concentrations from the mouth to the head has persisted for more than 30 years (reviewed by Zirino et al., 1998). Secondly, dissolved copper was found to be higher in surface than in bottom waters (Schiff et al., 2006a; Neira et al., 2009). The average dissolved copper concentration in surface waters was 8.76 ± 0.32 µg/L, which was approximately twice as high as the concentration of water collected just above the sediments (4.34 ± 0.39 µg/L). Neira et al. concluded that both the horizontal and vertical distributions of copper throughout the water column provide evidence that the primary source of copper to marinas is copper-based antifouling paints of vessels, since dissolved copper concentrations consistently declined along both vertical and horizontal axes with distance from vessels. Additionally, the consistent decrease in dissolved copper concentrations with depth provided an indication that sediments serve as a sink for dissolved copper from the water rather than a source.

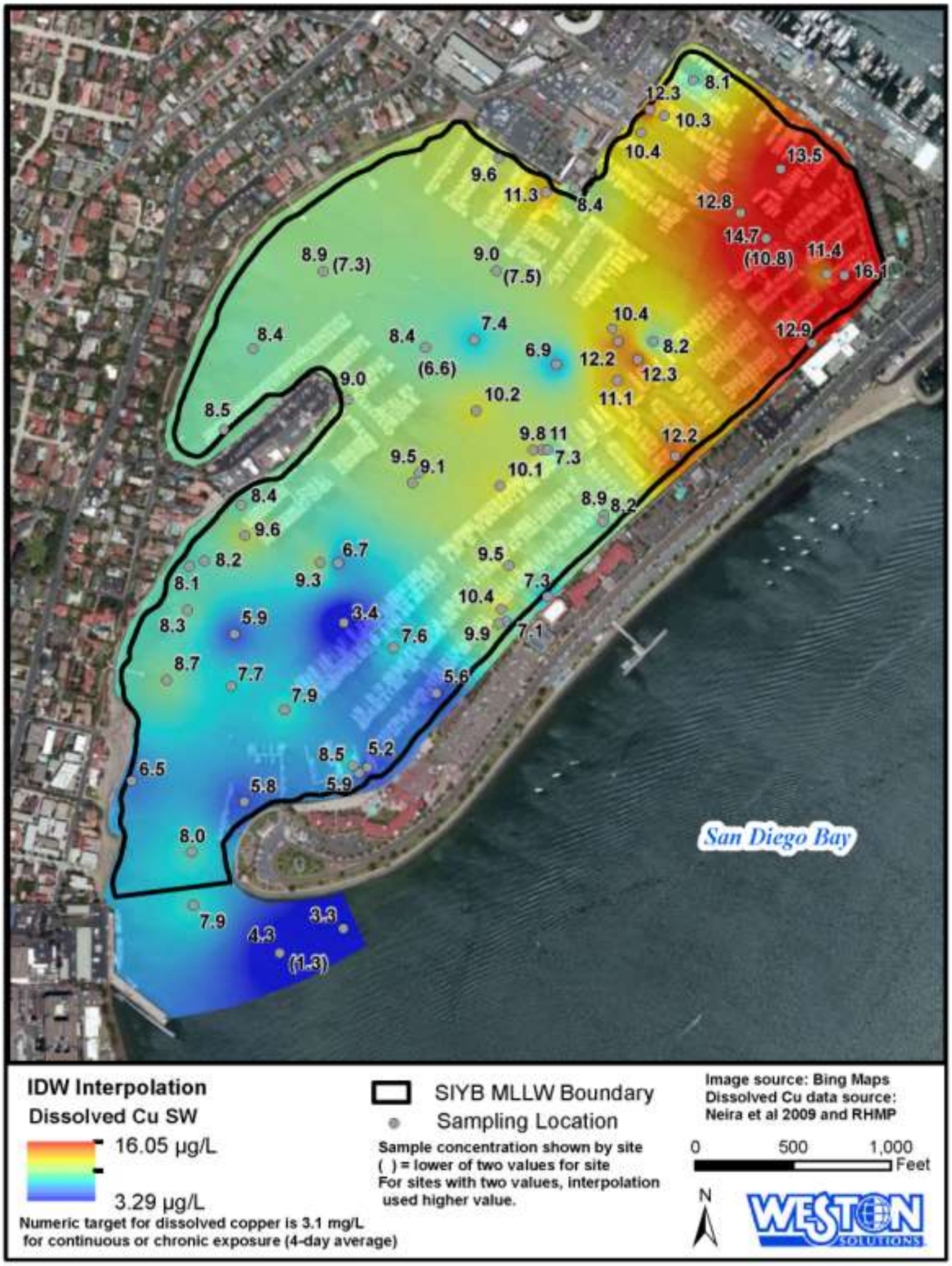

Figure 3-1. Dissolved Copper Levels in Shelter Island Yacht Basin Surface Waters

3.1.1.2 Free Copper (Cu^{2+})

Free copper is considered to be the most bioavailable form of copper to organisms in marine and aquatic systems (Zirino and Seligman, 2002; Rosen et al., 2005; Buck et al., 2007). The concentration of Cu^{2+} can be quantified *in situ* in marine waters using an Orion copper ion selective electrode (ISE), which measures pCu, where pCu = $-\log_{10} Cu^{2+}$; the lower the pCu value the higher the concentration of Cu^{2+} (Rivera-Duarte and Zirino, 2004). In San Diego Bay, studies have shown Cu^{2+} concentrations to range from 12.3-10.4 pCu (Zirino et al. 1998). In a 2000-2001 study that measured Cu^{2+}, dissolved copper and total copper and physical water quality parameters throughout the Bay, Cu^{2+} concentrations in the main channel of San Diego Bay occurred at concentrations considered to be nontoxic to mussel larvae (pCu > 11) (Blake et al. 2004). This was consistent across all four surveys, including the August 2000, May 2001, and September 2001 surveys where the mean concentration was approximately 13.0 pCu and the January 2001 survey where the mean concentration was approximately 12.0 pCu. During the January 2001 survey, Cu^{2+} concentrations were higher than in any of the other surveys, ranging from 12.5-11.9 pCu in the main channel and approaching the threshold for potential toxic effects (11 pCu) in SIYB and America's Cup Harbor. The higher concentrations of Cu^{2+} were not correlated with elevated levels of total or dissolved copper in the main channel; rather, were consistent throughout most of the main channel of the bay until decreasing towards the head, potentially due to increasing levels of dissolved organic carbon (DOC) and total suspended solids (TSS), which bind Cu^{2+}. This study also showed that although there was a temporally persistent trend of increasing dissolved and total copper concentrations moving from the mouth to southern portion of the bay, no such gradient in Cu^{2+} existed due to complexation of copper by ligands, such as DOC and TSS, as reviewed in greater detail in Section 5.6.2. Although there was a relatively high level of temporal variability, concentrations of Cu^{2+} were consistently elevated above the main channel of the bay within SIYB and America's Cup Harbor, with concentrations occurring at levels ten times higher than those of the main channel, which is consistent with the findings of Zirino et al. (1998). Although elevated Cu^{2+} concentrations were associated with vessels, especially within the semi-enclosed basins, the greatest determinant of concentrations was the availability of binding material, which was found to change significantly with time, with Cu^{2+} increasing when there were low levels of DOC and TSS.

In further focusing on the distribution of Cu^{2+} concentrations within SIYB, Neira et al. (2009) found that Cu^{2+} concentrations consistently increased from the mouth of the basin to the head in surface waters (Figure 3-2). As was seen in the bay-wide studies, there was also variability in surface water Cu^{2+} concentrations between surveys, with concentrations in a March 2008 survey ranging from 2.94-6.34 pM (11.53-11.20 pCu) and those of an August 2008 survey ranging from 9.1-13.4 pM (11.04-10.87 pCu). Neira et al. attributed differences to the availability of ligands and/or greater loading of copper during summer months due to elevated temperatures and greater densities and cleaning of vessels. Additionally, Cu^{2+} concentrations were found to be several orders of magnitude higher in surface waters than in porewater. Surface water Cu^{2+} concentrations ranged from 11.3-10.9 pCu, while porewater concentrations ranged from 14.6-11.7 pCu (Figure 3-3). The higher concentration of Cu^{2+} at the surface where vessels occur as compared to concentrations within the porewater of the sediments indicates that vessels are likely a source of Cu^{2+}, while sediments are serving as a sink. These findings substantiate the importance of vessels as a primary source of copper to the bay, and also provide evidence that Cu^{2+} concentrations occur at levels that have the potential to result in toxic effects within SIYB ($pCu \leq 11$).

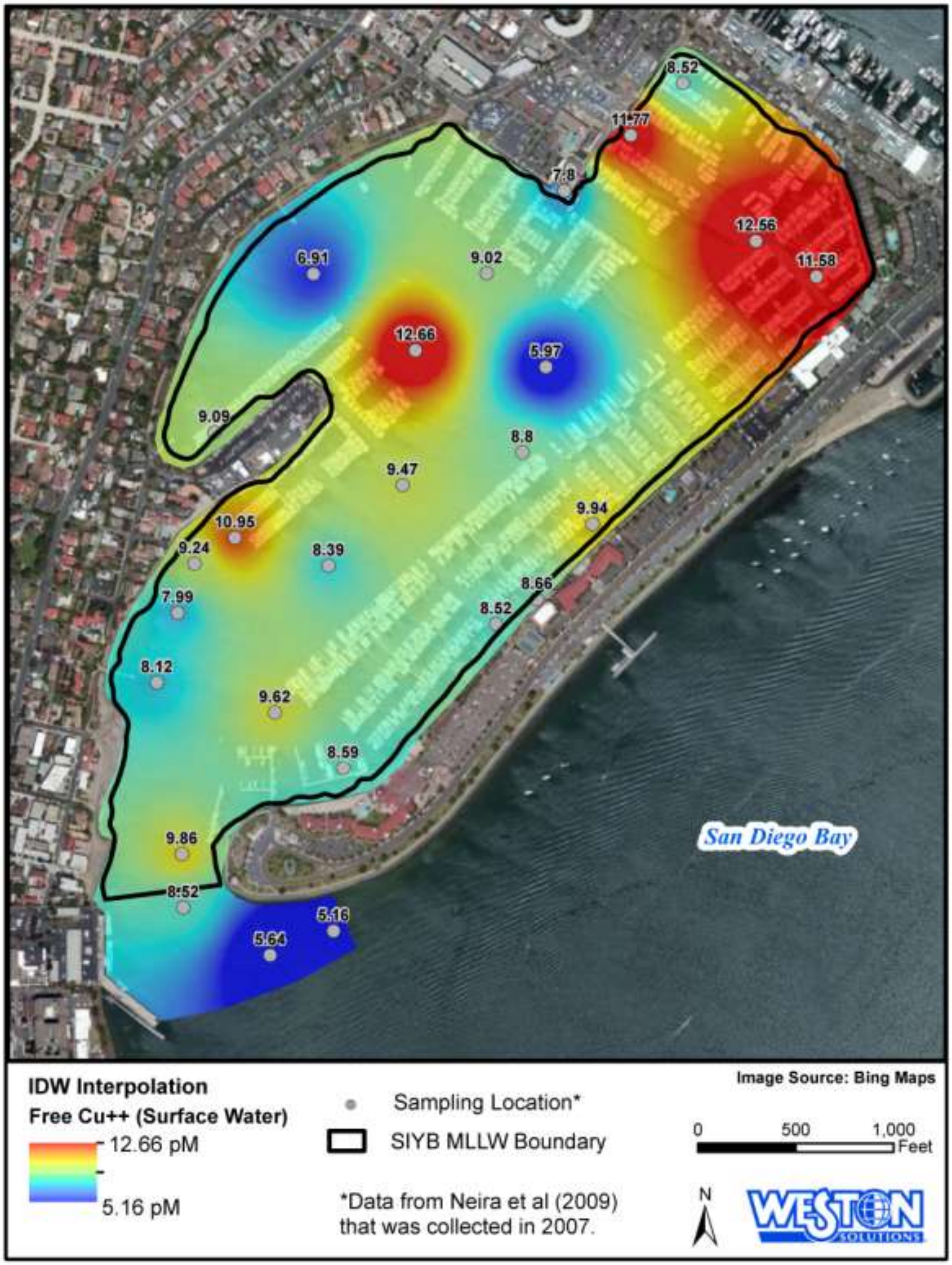

Image Source: Bing Maps

*Data from Neira et al (2009) that was collected in 2007.

Figure 3-2. Free Copper in Shelter Island Yacht Basin Surface Waters

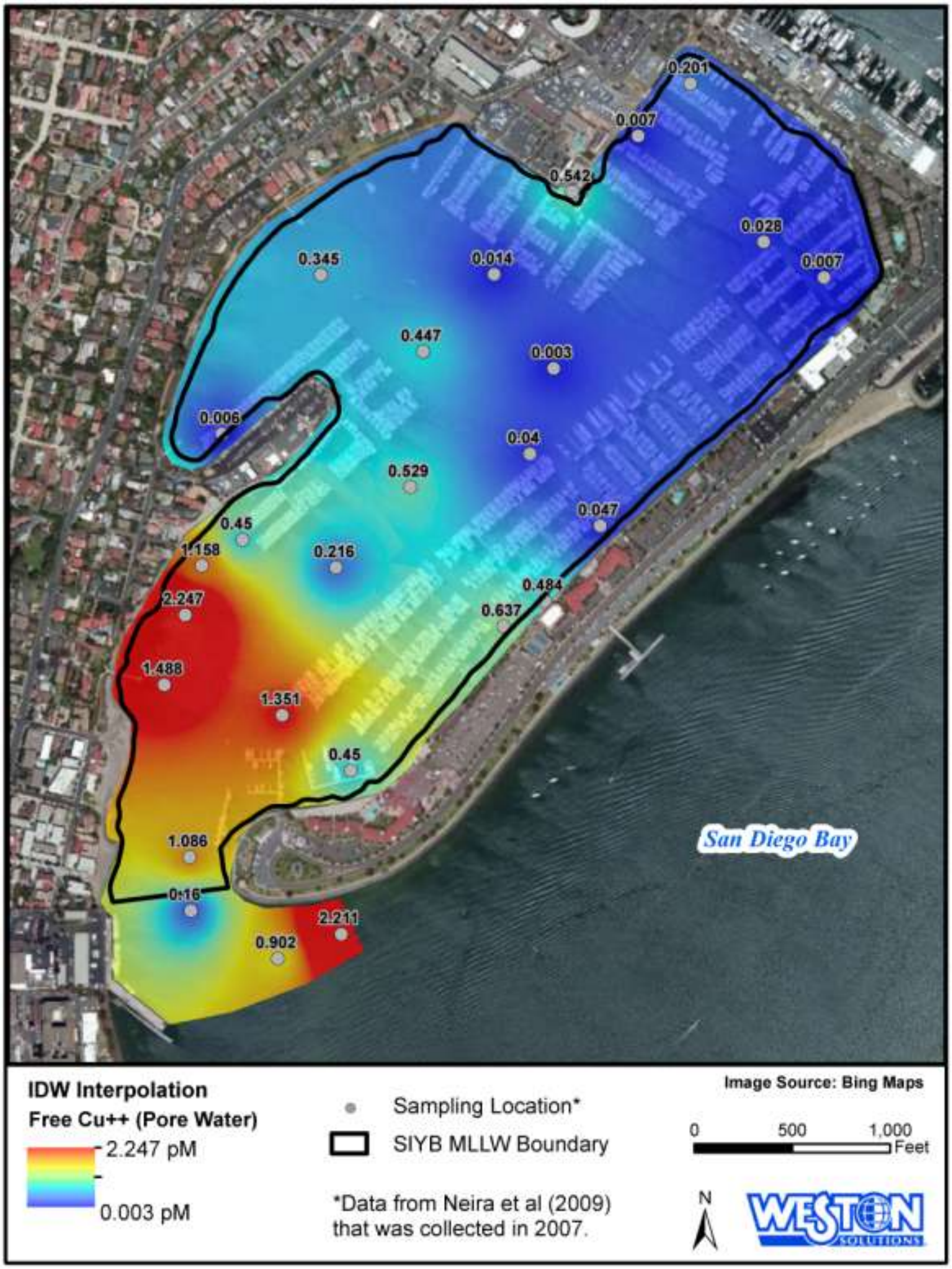

Image Source: Bing Maps

*Data from Neira et al (2009) that was collected in 2007.

Figure 3-3. Free Copper in Shelter Island Yacht Basin Porewater

3.1.2 Copper in Sediment

Copper concentrations in the sediment are commonly compared to sediment quality guidelines, including the effects range-low (ER-L) and effects range-median (ER-M) as a preliminary indicator of whether concentrations have the potential to adversely affect biota. The ER-L and ER-M are two effects-based sediment quality values developed to help interpret sediment chemistry measurements and their potential for causing adverse biological effects (Long et al., 1995). Long et al. developed these parameters from an extensive database of sediment toxicity bioassays and chemistry measurements. The ER-L was calculated as the lower tenth percentile of the observed effects concentrations and the ER-M as the 50th percentile of observed effects concentrations. Concentrations below the ER-L are not likely to result in biological effects, while concentrations above the ER-M are likely to result in biological effects (Long et al., 1995). For copper, the ER-L was determined to be 34 mg/kg and the ER-M was 270 mg/kg. Since copper is a naturally occurring metal within the environment, ambient copper levels within Southern California embayments commonly exceed the ER-L. Therefore, an ambient threshold value of 175 mg/kg was calculated for the RHMP harbors, based on the relationship between copper and iron (WESTON, 2010). San Diego Bay marinas, including SIYB, commonly have sediment copper concentrations that exceeded the ambient threshold value and, at times, the ER-M. These findings are consistent with the 1992-1994 study of San Diego Bay, which found that copper levels exceeded the ER-M primarily within small boat basins and the commercial and military shipping berths (Fairey et al., 1998).

The widespread use of copper-based antifouling paints on boat hulls also has the potential to increase copper in the sediments via passive leaching, followed by diffusion of copper into the sediments, as well as binding of dissolved and free copper to particulates in the water column prior to settlement (Schiff et al., 2003; Valkirs et al., 2003). Additionally, hull cleaning activities can release paint chips and scrapings directly to the sediments, with total copper loads to the sediments estimated to be 2,080 kg/yr (Brown and Schottle, 2006). Therefore, there is a consistent pattern of elevated sediment copper concentrations in portions of the harbors that have the highest surface areas of vessels, similar to what was observed for copper concentrations in the water column.

Within SIYB, copper concentrations in the sediments ranged from 15.4 – 442.3 mg/kg based on data obtained during the RHMP Pilot Study, RHMP 2008, and Neira et al. (2009) studies (Figure 3-4). Similar to the spatial pattern of dissolved copper, sediment concentrations were highest at the head of SIYB and decreased towards the mouth, ranging from 442 mg/kg at the head to 15.4 kg/mg outside the basin (Neira et al., 2009). All stations but four sampled within SIYB exceeded the ER-L, and eight stations exceeded the ER-M. Additionally, sediment copper concentrations increased with proximity to vessels, also similar to the pattern seen for dissolved copper in the water column (Neira et al., 2009).

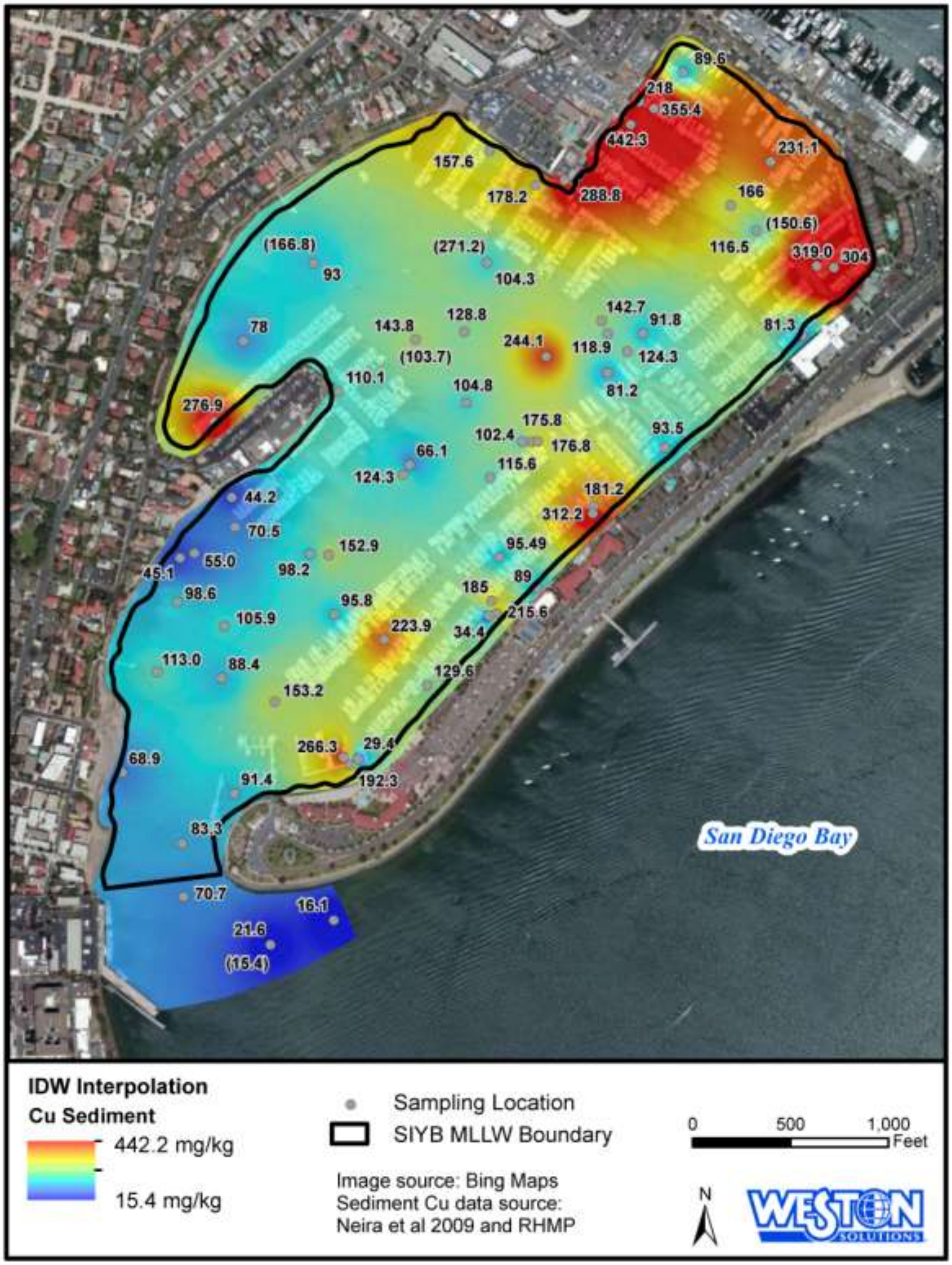

Figure 3-4. Sediment Copper Concentrations in Shelter Island Yacht Basin

3.2 Historical Toxicity

There have been a number of studies that have assessed toxic effects to marine organisms within San Diego Bay (e.g., Fairey et al., 1998; Schiff et al., 2006a; WESTON, 2008; WESTON, 2010). The most common toxicity tests conducted have included mussel development (*Mytilus galloprovinicialis*), including both seawater and sediment-water interface (SWI) tests; urchin fertilization (*Strongylocentrotus purpuratus*) upon exposure to seawater; and amphipod survival (using *Eohaustorius estuarius* and *Rhepoxynius abronius*), which are sediment solid-phase (SP) tests. The results of these studies are presented below.

3.2.1 Surface Water Toxicity

A 2005 study of water column toxicity to mussel development was conducted within SIYB, as well as other marinas in Dana Point Harbor, Oceanside Harbor, Mission Bay and San Diego Bay (Schiff et al., 2006a). Water samples were collected at the surface at randomly selected sites. Toxicity to mussel development (i.e., less than 80% normal alive development and a significant difference between the test and control) was observed in 21% of samples collected from the marinas of the four harbors. Moderate toxicity was found at two of twenty marina sites in San Diego Bay and high toxicity at one site. A total of five marinas were assessed for toxicity in the bay, of which SIYB was the only marina to exhibit toxic effects. TIEs were conducted at sites with the highest levels of toxicity, and the results indicated that metals were the most likely contaminants causing toxicity in the water column. Based on chemical analysis, copper was considered to be the likely causative agent of toxicity, since it was the metal that occurred at elevated concentrations, and mussel embryo normal-alive development was found to be significantly negatively correlated with copper ($r = -0.90$, $p < 0.01$). However, toxic effects were not observed until dissolved copper concentrations were approximately 9 µg/L, or approximately three times higher than the WQC (Schiff et al., 2006a).

A 1999-2002 San Diego Bay-wide study of toxicity in surface waters was performed by Rosen et al. (2005) as a component of the U.S. Navy's Strategic Environmental Research and Development Program (SERDP). Toxicity tests were performed on surface water samples at ambient copper levels as well as under a series of copper additions. Tests were used to assess the level of copper required to induce toxicity to larval development of mussels, urchins, and sand dollar (*Dendraster eccentricus*), from which median effects concentrations (EC50s) were determined. San Diego Bay was divided into 27 segments along boundaries that were perpendicular to the axis of the bay, plus two side basins (SIYB and America's Cup Harbor) where composite water samples were collected along transects. The study concluded that none of the ambient bay water samples showed toxicity to any of the test organisms. Normal development averaged 93% ± 5% (mean ± standard deviation) under ambient conditions where dissolved copper concentrations ranged from 0.09-2.9 µg/L. Using copper additions, Rosen et al. found that EC50s were 1.7-3.4 times higher at the head of the bay as compared to the mouth, providing evidence of an increasing gradient of copper complexation and bioavailability from the mouth to the head. This gradient was apparent for all test organisms, although the mussel was most sensitive to copper additions, with a mean EC50 of 6.4 µg/L as compared to 14.8 µg/L for the sand dollar and 13.1 µg/L for the urchin, based on assessments with filtered coastal seawater collected from Scripps Institute of Oceanography. The gradient of increasing EC50s (i.e., higher concentrations of copper were required to elicit a toxic response) was correlated with increasing levels of DOC and TSS. There were no statistically significant relationships to salinity, pH, and dissolved oxygen (DO), since the latter physico-chemical parameters were largely consistent bay wide.

While toxicity to copper in the water column has been observed in a number of studies, spatial and temporal differences in physico-chemical water column parameters have a tremendous impact on bioavailability of copper and its toxicity, as discussed in greater detail in Section 5.6.

3.2.2 Sediment Toxicity

The most recent and extensive study of sediment toxicity in the San Diego region harbors, RHMP 2008 (WESTON, 2010), has shown that toxicity in the sediments is substantially less common than historically reported (Anderson et al., 1997; Fairey et al., 1998). In the RHMP 2008 study, toxicity was evaluated using the *E. estuarius* SP acute bioassay and the *M. galloprovincialis* SWI chronic bioassays at 60 stations in San Diego Bay. RHMP 2008 found that 92% of stations were classified as either nontoxic or as having low toxicity according to the sediment quality objectives (SQO) toxicity line of evidence. Of the seven stations in SIYB, only one station at the head of the basin was determined to have moderate toxicity. Amphipod toxicity was extremely rare, with 95% of stations being non-toxic (i.e., survival ≥ 80%), and mussel toxicity was also low throughout most areas of the bay, with 85% of stations having ≥ 60% normal-alive development (i.e., the threshold established at 10% below the control acceptability criterion). Toxicity was substantially less prevalent than the findings reported by Fairey et al. (1998) for San Diego Bay. Toxicity results for *E. estuarius* bioassays from 1998 and 2003 Southern California Bight Regional Monitoring Programs, RHMP Pilot Study, and RHMP 2008 and *M. galloprovincialis* bioassays from RHMP 2008 are presented for San Diego Bay and SIYB in Figure 3-5.

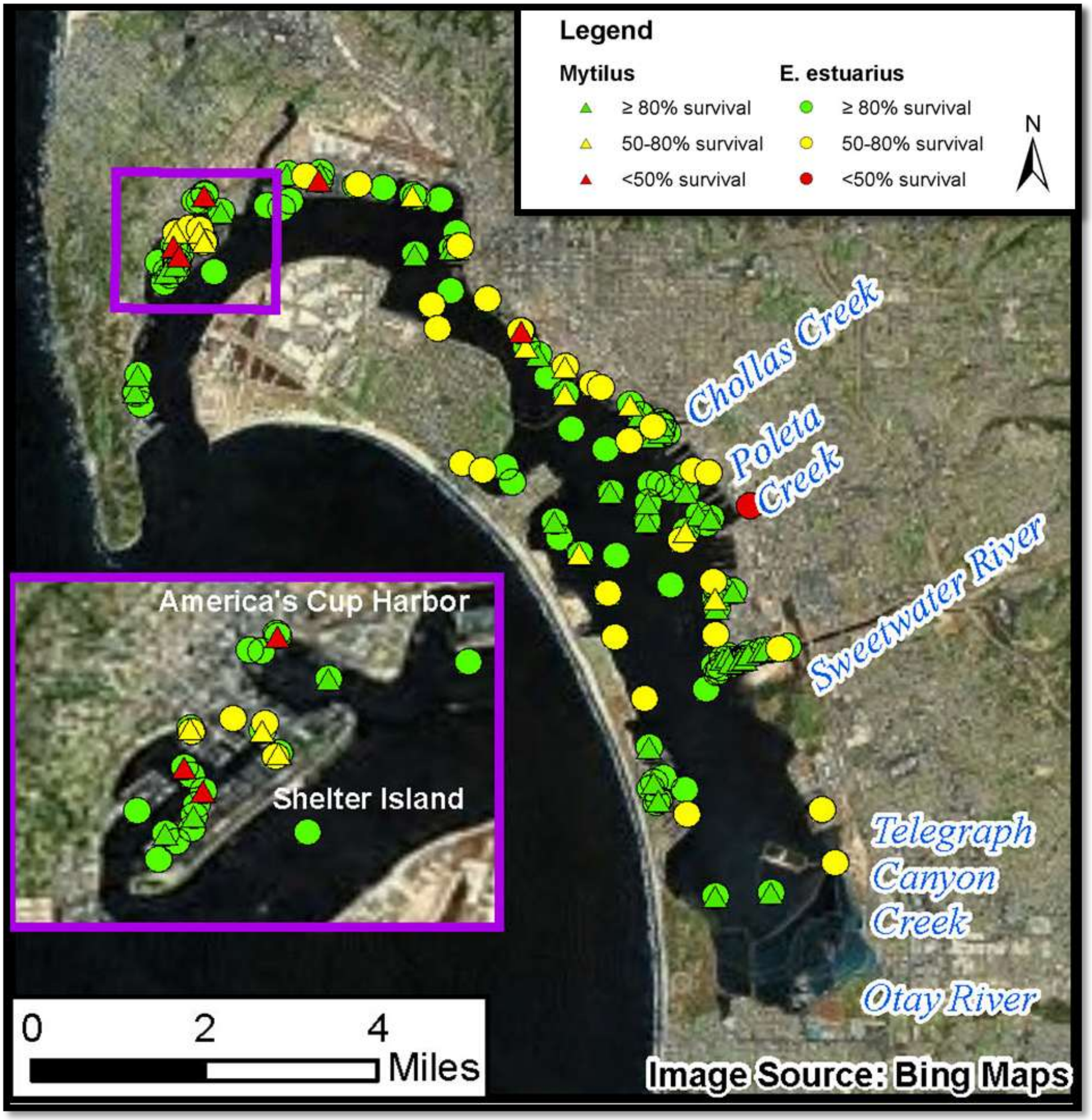

Figure 3-5. Sediment Toxicity in San Diego Bay and Shelter Island Yacht Basin

4.0 SOURCES OF COPPER

There are multiple sources of copper to San Diego Bay, including passive leaching of copper-based antifouling paints of vessels, hull cleaning, discharges from water cooling and treatment systems of vessels, discharges from industrial activities, urban runoff, atmospheric deposition, sediment resuspension and flux (reviewed by Johnson et al., 1998; Regional Board, 2005). Studies have consistently shown that copper-based hull paints are the largest source of dissolved copper to San Diego Bay (PRC Environmental Management, Inc. [PRC], 1997; Johnson et al., 1998; Chadwick et al., 2004; Regional Board, 2005), and may be responsible for up to 98% of the load to semi-enclosed basins, such as SIYB (Regional Board, 2005).

Based on the Regional Board's source analysis, the total mass load of dissolved copper to SIYB was determined to be 2,163 kg/yr, of which 98% of inputs were attributable to copper-based antifouling paints of recreational vessels (Regional Board, 2005). Copper is released from hull paints to the water column through two sources: passive leaching and underwater hull cleaning. Passive leaching is the single largest source of dissolved copper to SIYB resulting in the mass loading of 2,000 kg/yr and representing 93% of the total contribution (Table 4-1). Underwater hull cleaning is the second largest source of dissolved copper resulting in the mass loading of 100 kg/yr and representing 5% of the total contribution. Inputs of dissolved copper from the watershed and upland sources appear to be much less pronounced according to the Regional Board's source analysis. Urban runoff, including dry and wet weather flows, was determined to contribute 1% (30 kg/yr), and atmospheric deposition contributed <1%. Sediments were considered to be a net sink for copper so annual loading was considered to be zero.

Table 4-1. Sources of Dissolved Copper to Shelter Island Yacht Basin

Source	Mass Load (kg/yr)	Contribution (% Dissolved Copper)
Passive Leaching	2,000	93
Hull Cleaning	100	5
Urban Runoff	30	1
Background	30	1
Direct Atmospheric Deposition	3	<1
Sediment	0	0
Total	**2,163**	**100**

The following sections will review the sources of copper to SIYB, and provide annual load estimates based on the Technical Report loading calculations and recent monitoring data. Additionally TMDL-modeled loads were revisited to assess the validity of loading calculations and determine the need for further studies or refinements.

4.1 Passive Leaching

Copper is the most commonly used active ingredient in hull paints applied to recreational vessels. Commercial antifouling paints generally include cuprous oxide along with one or more organic or organometallic biocides. The paints release (or leach) dissolved copper into the water column to inhibit the settlement and growth of fouling organisms, due to its toxic or pesticide effects (Regional Board, 2005). As a consequence, copper concentrations within the waters of harbors, particularly the semi-enclosed, low-flow yacht basins and marinas, build to levels that exceed regulatory standards and potentially impact beneficial uses.

Leaching rates of copper are dependent on the age of the paint applied, the concentration of cuprous oxide, as well as the hardness and type of paint. Copper-based antifouling paints are generally considered to be either ablative or contact leaching (e.g., hard paints such as epoxy), with ablative paints leaching approximately 50% more copper than contact leaching paints over their respective lifetimes (Conway and Lock, 1994). The majority of recreational boats in San Diego Bay have contact leaching epoxy and vinyl hull paints (Johnson and Miller, 2002). Based on the combined leaching studies of Schiff et al. (2003) and Valkirs et al., (2003), the average passive leaching rate was 7.1 µg/cm^2/day for epoxy paints and 5.9 µg/cm^2/day for hard vinyl paints. An average leaching rate of 6.5 µg/cm^2/day was used to estimate passive loading from SIYB vessels since half the vessels were assumed to have epoxy paints and half vinyl paints (Regional Board, 2005).

The Technical Report assumed the following in calculating the dissolved copper loads from passive leaching:

- All 2,363 SIYB slips or buoys were occupied by vessels with copper hull paints.
- The number of vessels is always constant.
- The average size vessel was 40 feet (12.2 m) in length, with an average beam width of 11 feet (3.4 m).
- The passive leaching rate for recreational vessels was 6.5 µg/cm^2/day.
- The hull surface area equals boat length * beam width * 0.85.
- The average annual loading from passive leaching per vessel equals 0.8365 kg/yr.

Based on these assumptions, the total dissolved copper loading from passive leaching was calculated to be 1,962 kg/yr, which was rounded to 2000 kg/yr.

The calculation of loading from passive leaching can be further refined through the vessel tracking program, since the total number of occupied slips/moorings, paint types, sizes of vessels, and the time vessels remain within SIYB will be recorded. Refinements to loading from passive leaching may also benefit from further studies of leaching rates from different brands and varieties of copper paints, such as low copper paints (i.e., less than 40% copper).

4.2 Hull Cleaning

In-water hull cleaning was found to be the second greatest source of dissolved copper to SIYB (Regional Board, 2005). Divers use a variety of mechanical and non-mechanical cleaning techniques to remove fouling organisms and algal slimes that accumulate on the in-water portions of vessels. Cleaning of vessels with copper-based antifouling paints releases dissolved and particulate copper to the waters and sediments at rates that exceed passive leaching alone. Studies have consistently shown that copper concentrations in the water column are markedly increased during hull cleaning; however, elevated copper levels dissipate relatively quickly, often within minutes to hours, once cleaning has been completed (Valkirs et al., 1994; McPherson and Peters, 1995; Schiff et al., 2003). For example, in the study conducted by McPherson and Peters (1995), dissolved copper levels prior to cleaning were found to be 12 µg/L immediately adjacent to a vessel prior to cleaning, concentrations increased to 56 µg/L during cleaning, and dropped to 17 µg/L five minutes after cleaning was completed. Additionally, loads have been found to return to baseline levels within approximately three days following cleaning (Brown and Schottle, 2006).

Although the effects of hull cleaning on copper levels appear to be short lived, most vessels are cleaned on an approximately monthly basis or about 14 times a year (Carson et al., 2002). Schiff et al. (2003) calculated hull cleaning dissolved copper flux rates using one-hour samples corrected for time zero blank samples and passive leaching during the assessment period. Dissolved copper loading rates were quantified to be 8.6 µg/cm^2/event for an epoxy paint with the use of BMPs and 17.4 µg/cm^2/event without BMPs and 3.8 µg/cm^2/event for a hard vinyl paint with BMPs and 4.2 µg/cm^2/event without BMPs. The Technical Report assumed the average of these rates (8.5 µg/cm^2/event) for SIYB loading calculations (Regional Board, 2005). This is largely consistent with the hull cleaning loading rate of 10 µg/cm^2/event empirically quantified more recently by Brown and Schottle (2006).

The Technical Report assumed the following in calculating annual loading from hull cleaning:

- All 2,363 SIYB slips or buoys were occupied by vessels with copper hull paints.
- The number of vessels is always constant.
- The average size vessel was 40 feet (12.2 m) in length, with an average beam width of 11 feet (3.4 m).
- The average leaching rate per hull cleaning event equals 8.5 µg/cm^2/event.
- The hull surface area equals boat length * beam width * 0.85.
- Vessels are cleaned 14 times per year.
- The average annual loading from hull cleaning per vessel equals 0.042 kg/yr.

Based on these assumptions, the total dissolved copper loading from hull cleaning was calculated to be 98.4 kg/yr, which was rounded to 100 kg/yr.

The calculation of dissolved copper from hull cleaning used in the Technical Report may underestimate the load from hull cleaning because elevated leaching rates per hull cleaning event were based on a one-day period. The Schiff et al. (2003) study showed that dissolved copper loading was elevated above the passive leaching rate for both hard vinyl and epoxy paints for approximately three days. For the hard vinyl paint loading ranged from approximately 15 µg/cm^2/day at day one to 5 µg/cm^2/day by day three; therefore, loading over a three-day period totaled approximately 30 µg/cm^2. Using this three-day loading, annual dissolved copper loading from hull cleaning may be as high as 347 kg/yr (i.e., 14% of the total loading to SIYB). Further evaluations of loading from hull cleaning, as well as information garnered from the vessel tracking program, may be used to improve annual load estimates.

4.3 Urban Runoff

Urban runoff transports copper and other pollutants from impervious surfaces into drainages that eventually discharge into receiving waters. Copper metal, compounds, and alloys (i.e., brass and bronze) have the potential to be a significant source of copper to urban runoff, particularly within urban watersheds (TDC Environmental, 2004).

Inputs of dissolved copper from upland sources to SIYB were calculated to be substantially lower than contributions from recreational vessels according to the Regional Board's source analysis. Approximately 846 acres drain into SIYB via the City of San Diego municipal separate sewer system (MS4). Land uses within this area are predominantly residential (64%) and transportation (24%); however, it also consists of military (4.2%), public facility (3.5%), open space/parks (1.9%), and commercial recreation (1.1%). The remaining land uses, each less than 1%, are presented in Table 4-2 and Figure 4-1.

Table 4-2. Summary of Land Uses in the Shelter Island Yacht Basin Drainage Area

Land Use	Acres	Percent (%)
Residential	539	64
Transportation	200	24
Military	35.9	4.2
Public Facility	29.3	3.5
Open Space / Parks & Recreation	15.8	1.9
Commercial Recreation	9.2	1.1
Vacant and Undeveloped Land	8.0	0.9
Commercial	6.8	0.8
Industrial	1.3	0.2
Under Construction	1.0	0.1
Water	0.4	0.1
Total	846	100

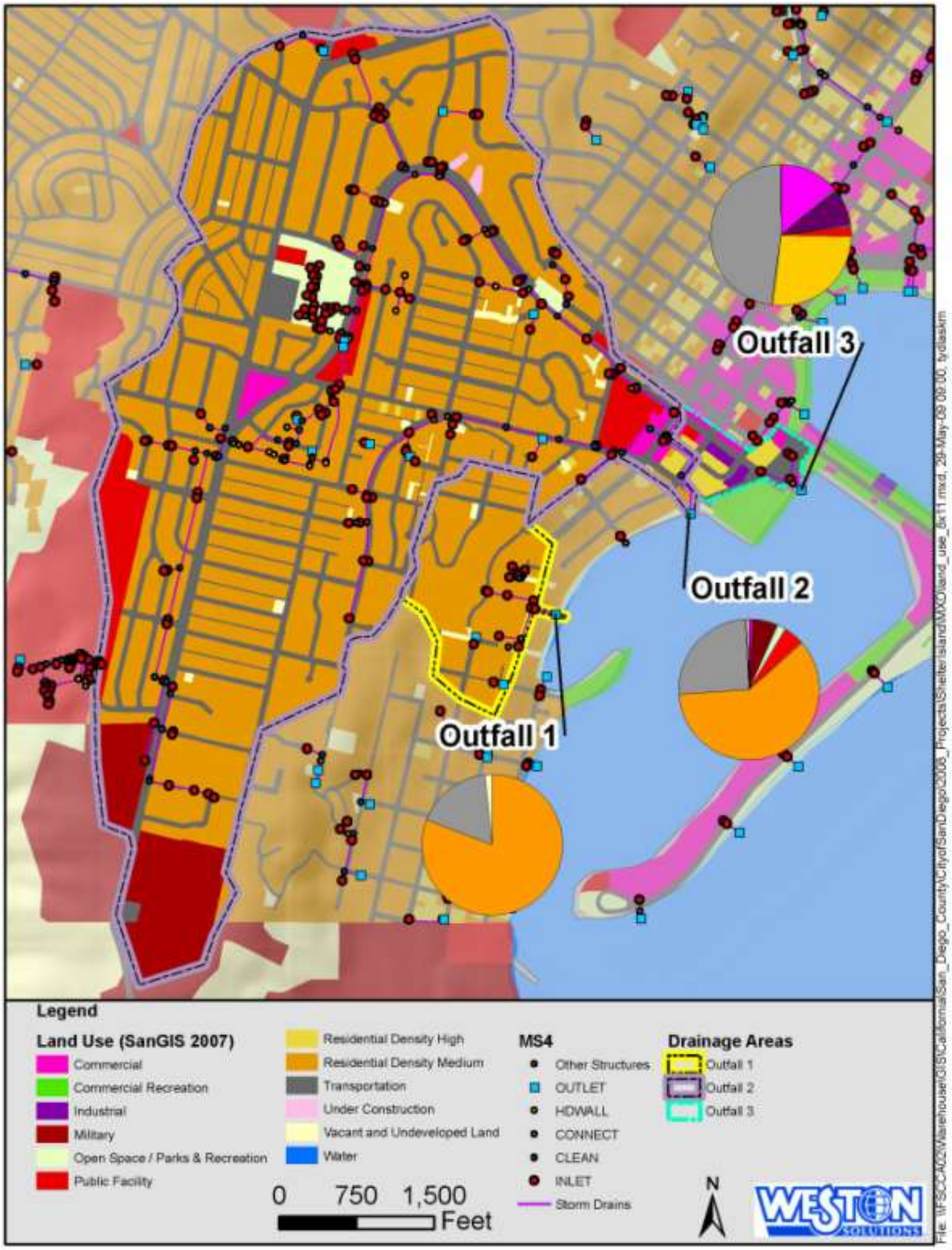

Figure 4-1. Land Use Distribution of Shelter Island Yacht Basin Drainage Area

In the Technical Report, the contribution of urban runoff to SIYB was calculated using the Simple Method (Regional Board, 2005). The Simple Method combines land use information for watersheds that drain to receiving waters, including the area of each land use type, percent of area that is impervious, and event mean concentrations (EMCs), with annual rainfall data to calculate stormwater runoff pollutant loading.

Pollutant Loading = $P*P_j*R_v*C*A$

Where:

P = Average annual rainfall
P_j = Correction factor to account for storms without rainfall (assumed to be 1)
R_v = Runoff coefficient derived from percent impervious land use values
C = Flow-weighted mean pollutant concentration or EMC
A = Area

Using the Simple Method, urban runoff was estimated to contribute 1% (30 kg/yr) of dissolved copper loading to SIYB via urban runoff, which consists of wet weather and dry weather flows (Regional Board, 2005). Empirical data show that the assumptions used in the model may have overestimated loads to the basin, since the urban runoff load predicted in the TMDL Technical Report (30 kg/yr) was over nine times higher than the mean dissolved copper load quantified during three years of monitoring from 2008-2011 (WESTON, 2011a). The mean total annual dissolved copper load from all three outfalls into SIYB was calculated to be 3.67 kg/yr, inclusive of the wet weather and annual dry weather loads. This value was rounded to 4 kg/yr. Thus, it appears that the assumptions of the SIYB TMDL Simple Method are likely to overestimate copper loads from urban runoff.

4.4 Atmospheric Deposition

Direct atmospheric deposition contributes less than 1% (3 kg/yr) of dissolved copper loading to SIYB (Regional Board, 2005). This includes wet and dry deposition directly into SIYB. Indirect deposition is not included in the Technical Report, because it is a component of urban runoff.

Atmospheric deposition is a non-point source of copper that is responsible for a small percentage of copper loading to the region’s bays and harbors, generally found to be less than one percent. Copper in the atmosphere originates from land sources, including brake pads and industrial emissions from shipyards (WESTON, 2007). Copper is used as an additive in brake pads, and copper slag is used by shipyards as an abrasive grain for sandblasting. Particulates can be directly emitted to the atmosphere or resuspended. Wind is the most important factor in mobilizing and transporting particulates, as it controls the direction and distances the particulates travel and ultimately where they will deposit. Copper can be deposited directly or indirectly from the atmosphere into the region’s bays and harbors. Direct deposition occurs on the surface of the waterbody, while indirect deposition occurs within the watershed and the pollutant is transported to the water body by runoff. A summary of atmospheric deposition studies that have been conducted in the vicinity of San Diego Bay to date is provided below.

In 1996, the dissolved copper load into San Diego Bay via atmospheric deposition was calculated as part of a sediment characterization study for Naval Station San Diego (Johnson et al., 1998). The copper load deposited from the atmosphere was estimated to be relatively low, at 7 kg/yr. This equates to less than 1% of the total copper load into San Diego Bay. Also in 1996, PRC calculated wet and dry atmospheric deposition of copper into San Diego Bay. Copper loading due to dry atmospheric deposition was calculated using ambient air concentrations of copper, deposition velocity, and total surface area (PRC, 1997). Based on an average copper concentration collected from the County of San Diego Air Pollution Control District (APCD) from 1990 to 1995, the annual load was estimated to be 41 kg/yr. This equates to only 0.11% of the total copper load to the bay. Copper load contributed from rain falling directly on the surface of the San Diego Bay was calculated using the surface area of the bay, annual rainfall, and concentration of copper in the rain. The wet deposition annual load of copper was estimated to be 21 kg/yr or 0.06% of the total load.

In 2006, the Southern California Coastal Water Research Project (SCCWRP) conducted an atmospheric deposition study assessing dry deposition rates for metals along the coast of California from Santa Barbara to San Diego (Sabin and Schiff, 2007). Eight sites were monitored over a four month period during dry conditions, including San Diego Bay. For all sites, the highest median dry deposition flux rate of copper was measured in San Diego Bay, at a rate of 29 µg/m^2/day. The San Diego monitoring site was located in a highly urbanized area near the naval shipyard, which may account for the higher deposition of copper.

From 2006 to 2009, WESTON conducted a three-phased study to evaluate the contribution of aerial deposition to the loading of copper, lead, and zinc into City of San Diego watersheds facing TMDLs (WESTON, 2007; 2009a; 2009b). An area-wide study assessed regional differences at nine sites, including the mouth of Chollas Creek (adjacent to San Diego Bay). At the mouth of Chollas Creek, the dry deposition flux rate of copper ranged from below the detection limit to 67.7 µg/m^2/day, with a median flux rate of 17.5 µg/m^2/day. Annual deposition rates of copper were also evaluated at high loading areas (WESTON, 2009a). Twenty-four sampling events were conducted from 2007 to 2008. The annual median dry deposition flux rate of copper at the mouth of Chollas Creek was 37.6 µg/m^2/day.

Based on the aforementioned studies, atmospheric deposition is a measureable source of copper; however, it is a relatively small load when compared with other sources. Even if the annual median dry deposition flux rate of copper at the mouth of Chollas (37.6 µg/m^2/day) was used to calculate loading to SIYB, the annual load of total copper would only total 11.0 kg/yr, which is still less than 1% of the total annual load to the basin. Therefore, the Technical Report's calculation of an annual dissolved copper load from atmospheric deposition of approximately 3 kg/yr (i.e., 0.14% of the total annual load) appears to be reasonable in the context of these prior studies.

4.5 Background

Water from San Diego Bay flushes SIYB and contributes to dissolved copper loading. Average copper concentrations in San Diego Bay were used to characterize background conditions and the one-dimensional, steady-state box model (SD-1D) was used to estimate loading. The average total copper concentration in the main channel portion of San Diego Bay adjacent to SIYB was measured to be 0.5 µg/L (Chadwick et al., 2004). Background contributions of dissolved copper from San Diego Bay to SIYB were calculated to be approximately 1% (27 kg/yr) (Regional Board, 2005).

More recent monitoring studies of dissolved copper in the main channel of San Diego Bay have quantified dissolved copper concentrations greater than 1.0 µg/L (Neira et al., 2009; WESTON, 2010). Using an average concentration of 1.0 µg/L, the annual background load of copper was calculated to be 60 kg/yr (i.e., 2.8% of total annual load). As such, the dissolved copper load from the bay to SIYB (30 kg/yr) may have been underestimated in the TMDL copper box model. Additionally, higher dissolved copper concentrations in the bay would also reduce the rate of diffusion between SIYB and the bay, further increasing dissolved copper concentrations in the basin. While San Diego Bay waters may contribute a higher load of dissolved copper to SIYB due to the presence of higher dissolved copper concentrations than previously modeled, bay waters are still serving as a net sink for dissolved copper from SIYB. Given the average residence time of 4.7 days and a settling rate to sediment of 7%/day, approximately 33% of the dissolved copper load to SIYB is predicted to enter the sediment (i.e., 712 kg/yr). That is to say that 67% of the annual dissolved copper load to SIYB (i.e., 1,451 kg/yr) is flushed to San Diego Bay.

4.6 Sediments

Bay sediments are typically considered to be a sink for contaminants (Chadwick et al., 1999), and in the case of San Diego Bay, approximately 48% of the copper within the water column settles into the sediments (Chadwick et al. 2004). Similarly, the Technical Report cites direct evidence that the sediments of SIYB serve as a net sink rather than a net source for copper, since SIYB sediments are comprised of fine particles that bind copper (Valkirs et al., 1994). Assessments of sediment flux using benthic flux chambers performed by the U.S. Navy found that the net loss of dissolved copper to the sediments ranged from approximately 4-7% per day (Regional Board, 2005). As a consequence, the Technical Report assumed that sediments do not contribute a net positive load of dissolved copper to SIYB.

The Navy has conducted benthic flux studies using benthic flux chambers through many areas in San Diego Bay. In an assessment of flux at 11 stations in the NAVSTA area, copper flux rates were found to range from approximately -100 – 300 µg/m^2/day. Seven of the stations had positive fluxes indicating that copper was being released from the sediments, while four had negative fluxes. Using the revised surface area of SIYB of 800,171 m2 and the aforementioned flux rates, dissolved copper loads from sediments were calculated to range from -29 – 87.6 kg/yr. Using these calculations and depending on site-specific conditions in SIYB, dissolved copper loads from sediment flux would be calculated to be as high as 4% of the total annual load to the basin.

The Technical Report noted that sediment resuspension may serve as a source of copper to SIYB; however, no load was attributed to this process either. Using an experiment that simulated sediment resuspension, Chadwick et al., (1999) measured copper concentrations within the water column prior to and following resuspension to quantify desorption. They found that dissolved copper concentrations increased by 0.1% above background levels. In extrapolating the results to the entire NAVSTA area, resuspension and desorption contributed an annual load of copper of 68 kg/yr. Consequently, they concluded that resuspension and desorption do not appear to be an important source of copper to San Diego Bay's water column. At most, SIYB is approximately one fifth the size of NAVSTA; therefore, the annual load from resuspension and desorption would be expected to be approximately 14 kg/yr.

As noted in the peer review of the Technical Report, the potential for sediment to act as a source of copper to the water column was not fully addressed. Dr. Bruland noted that while sediments may act as a net sink, it is unlikely that sediments do not contribute any load to the water column. Similar consideration of dissolved copper loads from sediments as San Diego Bay background inputs is merited. In using the above calculations, based on the NAVSTA data collected by Chadwick et al. (1999), the annual load of dissolved copper from the sediments to SIYB waters would be 82 kg/yr (i.e., 3.6% of the total annual loading to SIYB). As such, sediments would be considered to be the third most important source of dissolved copper to SIYB.

While sediment loading does not appear to be zero, sediments currently appear to be serving as a net sink for copper in SIYB. As discussed in the consideration of background inputs from San Diego Bay, approximately 33% of the total annual load of dissolved copper that enters SIYB settles to the sediments (i.e., 714 kg/yr), while the remainder is flushed to the bay by tidal exchange. Therefore, sediments were calculated to absorb 632 kg/yr more dissolved copper than they release, indicating that they are serving as a net sink.

Sediment release of dissolved copper has the potential to slow progress in obtaining water quality improvements. Both resuspension of historically contaminated sediments that results in desorption of copper and positive copper flux may slow reductions in dissolved copper concentrations within the water column. Additionally, as concentrations of dissolved copper decrease due to load reductions associated with vessel transitions, sediments may increasingly act as a source. Therefore, further studies are needed to assess dissolved copper loading from sediments.

4.7 Other Sources or Discharges in the Immediate Vicinity

No other significant sources of dissolved copper are known to occur within the immediate vicinity of SIYB.

4.8 Summary of Shelter Island Yacht Basin Dissolved Copper Loading

Based on the inclusion of new monitoring data for urban runoff to SIYB and reassessment of dissolved copper loads from hull cleaning and sediments, the total annual load of dissolved was calculated to be 2,496 kg/yr (Table 4-3).

Table 4-3. Revised Annual Dissolved Copper Loading to Shelter Island Yacht Basin

Source	Annual Load (kg/yr)	Percent of Total (%)
Passive Leaching	2000	80
Hull Cleaning	347	14
Sediments	82	3
Background	60	2
Urban Runoff	4	< 1
Atmospheric Deposition	3	< 1
Total	2,496	100

Recreational vessels were still the primary source of dissolved copper to SIYB, contributing 96% of the annual load as compared to 98% in the TMDL. However, in contrast to the TMDL, hull cleaning has the potential to contribute up to 14% of the total annual load to the basin (i.e., 347 kg/yr as compared to 100 kg/yr). Dissolved copper loads from sediments were assessed in a manner that was consistent with background inputs. As such, the dissolved copper loads from sediments and San Diego Bay to SIYB totaled 5% of the total annual load; however, both were determined to be net sinks for dissolved copper. Monitoring data for urban runoff collected at the three MS4s that drain to SIYB showed that loading from this source was far lower than Simple Method predictions, and confirmed that urban runoff is not a substantial source of dissolved copper to SIYB (i.e., < 1%). Similarly, the review of additional monitoring data on atmospheric deposition in the vicinity of SIYB confirmed that direct deposition is a minor source of dissolved copper to SIYB (i.e., < 1%).

4.9 Assessment of Annual Revised Dissolved Copper Loads

A geographic information system (GIS) analysis was performed to determine the surface area of SIYB (A_S) (800,171 m^2) and basin entrance cross sectional area (A_C) (871 m^2), and recent bathymetric data was used to calculate the volume of the basin (V_2) (2,850,000 m^3). Recent RHMP 2008 (WESTON, 2010) salinity data was assessed for San Diego Bay (33.66 ppt) and SIYB (33.82 ppt) were used to calculated the dispersion coefficient (K) (13.6 m^2/sec). Dissolved copper data from 2006 and 2007 Neira et al. study (2009) and the RHMP Pilot Study and RHMP 2008 (WESTON, 2008; 2010) were analyzed using Esri GIS software. Dissolved copper concentrations within SIYB were mapped, and concentrations between sampling locations were extrapolated to determine the average dissolved copper concentration of 9.2 µg/L.

To determine if revisions to the dissolved copper loads were reasonable, the TMDL SD-1D box model was used to solve for the average total copper concentration in the water column (existing value of C_2) by rearranging equation (*q*) in Appendix 3 of the Technical Report. The value of dissolved copper input into SIYB (R_S) was estimated by considering the daily contributions from passive leaching, hull cleaning, ambient seawater, urban runoff, aerial deposition, and sediment flux. The rearranged equation is provided below.

Equation (*q*) from Appendix 3 of the SIYB TMDL (rearranged) (Regional Board, 2005):

$$C_2 = \frac{R_S + A_C\, C_1\left(\frac{e\, A_S}{A_C} + \frac{K}{\Delta x}\right)}{\frac{K\, A_C}{\Delta x} + K_L V_2}$$

Where:
R_S = 2,496 kg/yr
A_C = 871 m2
C_1 = 1 µg/L
e (evaporation rate) = 0.43 cm/day
A_S = 800,171 m^2
K = 13.6 m^2/sec
Δx (salinity gradient mixing length) = 1,512 m
K_L (copper loss to sediment rate constant) = 7%/day
V_2 = 2,850,000 m^3

The SD-1D model value of C_2 was converted to dissolved copper using the 0.83 relationship and compared to the measured area weighted average of dissolved copper (9.2 µg/L). Based on these inputs, the model predicted an average dissolved copper concentration of 7.6 µg/L for SIYB. This predicted SIYB dissolved copper concentration provides a reasonable approximation of the measured area weighted average dissolved copper concentration.

5.0 FATE AND TRANSPORT DYNAMICS

Copper enters San Diego Bay via two primary inputs – copper-based hull paints and urban runoff, as described in Section 4.0. The fate and transport of copper is impacted by a number of processes, including circulation patterns, adsorption and particle deposition, resuspension and desorption, and flux to and from sediments. All of these processes are impacted by both natural and anthropogenic influences, such as the intensity and frequency of storm events, the presence of jetties and other structures that alter currents, boat traffic, bioturbation, as well as the physical properties of the associated waters and sediments. A large number of Navy studies have assessed fate and transport processes in San Diego Bay (e.g., Chadwick et al., 1999; Chadwick et al., 2004; Wang et al., 2006; Chadwick et al., 2008). A review of circulation patterns, particle deposition, resuspension and desorption, and copper sediment flux is provided in the following sections.

5.1 Circulation Pattern

Tidal currents are generally the primary means of water circulation within San Diego Bay and SIYB. Tides in the Southern California Bight are mixed with a tidal range up to approximately 7 feet depending on the bathymetry and shape of the harbor, bottom friction, etc. (Chadwick et al., 2008). The effectiveness of tidal circulation is positively correlated to the distance from the mouth of the embayment or basin. Therefore, areas that are closer to the mouth have greater circulation and reduced residence times as compared to areas closer to the head (Chadwick et al., 2004).

In addition to the tides, the second most important large-scale factor that affects circulation patterns in main channel portions of San Diego Bay is stormwater runoff via creeks, rivers, and streams. For example, winter storm events have the potential to transport urban runoff and fine suspended solids (<12 µm particles) that originated from Chollas and Paleta Creeks and Sweetwater River throughout San Diego Bay (Chadwick et al., 1999). Enclosed water bodies such as harbors and bays are dependent on inputs from local watersheds and tidal currents to circulate water within the embayment and between the embayment and the ocean. In areas within San Diego Bay with little input from the surrounding watershed, tidal currents are often the only means of circulating water and therefore the only natural means of distributing waters and sediments and flushing contaminants. The resulting poor circulation is especially pronounced inside semi-enclosed basins, such as SIYB, where the negatively synergistic interactions of high copper loads and high residence times result in elevated copper concentrations within waters and sediments.

Circulation in SIYB is predominantly due to tidal currents, with occasional flushing by MS4 discharges during winter rain events. Currents weaken from the mouth of the basin towards the interior. The average water residence time in SIYB was calculated to be 4.7 days (Regional Board, 2005).

5.2 Sedimentation

San Diego Bay sediments are typically considered to be a sink for contaminants (Chadwick et al., 1999), with approximately 48% of the copper within the water column estimated to settle into the sediments (Chadwick et al. 2004). Particle deposition (or settlement) in the bay is dependent on natural processes such as flow from rivers and creeks, littoral transport, wave action, and tidal flushing. Additionally, anthropogenic processes such as maintenance dredging, construction of jetties and breakwaters, and runoff due to urbanization, affect deposition. Within SIYB, sedimentation is primarily affected by inputs from MS4s, tidal flushing, and vessel traffic.

Suspended sediments will deposit when there is no longer sufficient energy from waves or tides to allow them to remain in the water column. In contrast, sediment may be suspended when waves, currents, or wind dislodge them from the ocean or bay floor (Parchure and Teeter, 2002). Differing current speeds, bathymetry, and wind conditions, in the bays affect transport and suspension of sediments. Chadwick et al. (2008) measured tidal currents at 15-50 cm/s at the mouth of San Diego Bay, over 65 cm/s in channel bends, and less than 10 cm/s in the interior. Increased current speeds in channel bends result in quicker movement of suspended sediments through those areas.

Freshwater inflow and sediment deposition into San Diego Bay occurs seasonally during winter storm events (Blake et al., 2004). Fine grained, highly organic sediments tend to settle at the mouths of these freshwater inputs, while larger particles settle in areas with increased flushing. In SIYB, poor circulation in the interior of the basin allows fine-grained, highly organic, and often contaminated sediments to settle near the head. In contrast, the outer portions of SIYB, which are well flushed, contain higher concentrations of sandy, inorganic, and less contaminated sediments (WESTON, 2010).

5.3 Resuspension and Desorption

As previously noted, bay sediments are typically considered to be a sink for contaminants; however, transport mechanisms, including resuspension by wind and tidal currents and vessel traffic, can release contaminants back into the water column, potentially increasing bioavailability (Chadwick et al., 1999). Wind and tidal currents have the potential to create bottom shear stresses that result in erosion and increased sediment resuspension and transport. While there are areas of San Diego Bay that are subject to erosion, it appears that large portions of the bay do not achieve minimum bottom shears (~1.0 dynes/cm^2) required to move fine bottom sediments (Chadwick et al., 1999). In relatively shallow areas, such as the low-flow areas of marinas, vessel traffic can play a significant role in the resuspension of sediments. Based on surveys of ship movement within Naval Station San Diego (NAVSTA), which largely encompasses the eastern shoreline of San Diego between Chollas Creek and Sweetwater River, the total mass load of sediments resuspended per ship ranged from 3,800-20,400 kg (Chadwick et al., 1999). Ship resuspension represented 29% of the background mass of suspended solids, which is approximately three times the annual load contributed to NAVSTA by urban runoff inputs.

Once sediments are resuspended within the water column, desorption can result in the release of contaminants into the water. Using an experiment that simulated sediment resuspension, Chadwick et al., (1999) measured copper concentrations, in addition to other metals, within the water column prior to and following resuspension to quantify desorption. They found that dissolved copper concentrations only increased by 0.1% above background levels. In extrapolating the results to the entire NAVSTA area, resuspension and desorption would only contribute an annual load of copper of 68 kg/yr. Consequently, they concluded that resuspension and desorption do not appear to be an important source of copper to San Diego Bay's water column. However, resuspension and tidal current transport of sediments can have important impacts on the movement of contaminants away from sources, increasing the spatial extent of sediment contamination.

In SIYB, ship movements also have the potential to resuspend sediments, potentially resulting in desorption of copper to the water column. If resuspension events resulted in an increase in dissolved copper concentrations of 0.0031 µg/L, as quantified by Chadwick et al. (1999), then water column concentrations of dissolved copper would increase by approximately 0.034%, based on an average dissolved copper concentration of 9.2 µg/L in the basin. If processes are similar in SIYB as NAVSTA, resuspension and desorption may not be an important source of dissolved copper to the water column.

5.4 Copper Flux

Sediments play a major role in the overall fluxes of trace elements in coastal systems, acting as a source or sink to/from the water column. Metals can exist in sediment systems in the aqueous phase, as part of a precipitated mineral, or adsorbed on the surface of a mineral. Similar to overlying water, these processes depend upon several factors including pH, occurrence of complexants, salt concentrations, changing redox conditions, and decomposing organic matter (Carignan and Nriagu, 1985; Jorgensen and Revsbech, 1983). In organic carbon-rich sediments, trapped interstitial or porewater fluids commonly form a strongly reducing, anoxic environment. Low redox potential in this environment can promote sulfate reduction and sulfide mineral deposition. During diagenesis or any chemical, physical, or biological change undergone by sediment, much of the non-silicate-bound fraction of potentially toxic metals, such as copper, can be co-precipitated with pyrite, also known as iron sulfide (FeS_2), to form insoluble sulfides and consequently become unavailable to biota (Morse, 1994). Seasonal variation in flow rates or storms that induce an influx of oxygenated seawater can result in rapid reaction of this anoxic sediment and thereby release significant proportions of these metals. Pyritization and/or de-pyritization of trace metals can be an important process in controlling bioavailability of many trace metals, especially in the marine environment (Morse, 1994).

Given the long history of copper inputs into SIYB, the buildup of copper within sediments has the potential to create a feedback loop where by the sediments re-release dissolved copper back into the water column. As sediment copper concentrations increase, potential for copper flux from the sediments to the overlying waters also increases. Sediment flux can be calculated from the gradient in copper concentrations in pore water, as well as sediment physical parameters (Berner, 1980). Additionally, direct measures of flux can also be obtained *in situ* using benthic flux chambers. Benthic flux chambers are instruments that isolate a volume of water at the sediment-water interface and measures chemical flux (Chadwick et al. 1993). As reported in the SIYB TMDL, the Navy has collected extensive benthic flux data throughout San Diego Bay, which found that the net loss of copper from the water column to the sediments is approximately 4-7% per day (Regional Board, 2005). In the assessment of the NAVSTA area, Chadwick et al. (1999) quantified benthic flux at 11 stations. They found that copper flux was highly site-specific, with flux rates ranging from approximately -100-300 µg/m^2/day. Seven of the 11 stations had positive fluxes indicating that copper was being released (i.e., the sediments were acting as a source). Four had negative fluxes, which was indicative of the sediments serving as a sink. Although there was a wide range of sediment copper concentrations at stations (75.7-485 mg/kg) flux rates were not significantly correlated with copper concentrations ($r = 0.446$, $p = 0.376$). The lack of a significant relationship is likely due to other site parameters, including copper concentrations in the overlying waters, sediment grain size, and organic content. This study showed that although sediments may be serving as a sink bay wide, there are circumstances where sediments will also serve as a source of copper to overlying waters.

The range of dissolved copper flux rates (-100-300 µg/m^2/day) quantified for NAVSTA can be used to predict potential dissolved copper loads to SIYB. Given that the approximate surface area of SIYB is 800,171 m^2 (revised based on recent GIS analysis of SIYB), dissolved copper loads from sediment flux could range from -29 kg/yr to 87.6 kg/yr. Therefore, depending on site-specific parameters of SIYB, it is possible that dissolved copper loading from sediments may contribute up to 4%. However, it is important to note that recent monitoring data support assertions that sediments are currently serving as a sink for dissolved copper in SIYB, since pore water and bottom waters have far lower dissolved copper and free copper concentrations than overlying surface waters (Neira et al., 2009). Further studies are recommended to quantitatively assess copper flux in SIYB.

5.5 Implications for the Distribution of Copper

Copper contamination in SIYB is largely due to its widespread use in antifouling coatings on recreational vessels. The distribution of copper once it enters the basin is often closely associated with the source (i.e., recreational vessels). The spatial distribution of copper is impacted not only by the load to SIYB, but also by transport processes, including current speeds, bathymetry, and vessel activity, as well as the physico-chemical qualities of sediments. As a consequence, the highest copper concentrations in SIYB are associated with areas that receive higher loads of copper, experience low circulation, and have fine sediments, such as the head of the basin. It is in this area in particular, where copper concentrations are elevated in both the water column and the sediments, since the capacity of the sediments to serve as a sink for copper is outpaced by loads from the source. Additionally, low levels of circulation confine the contamination generally within the basin.

5.6 Bioavailability

Bioavailability is the concept that not all forms of a substance are equally assimilated by organisms, since availability is dependent not only on biological parameters, such as the behavior, physiology, and prey of the organism, but also on the physical and chemical environment (Cook et al., 2000; Ho et al., 1999). For trace metals, bioavailability refers to the portion of the total metal in a system that binds to physiologically active surfaces and/or passes across a membrane into an organism. In the case of copper in the marine environment, bioavailability is directly related to its physico-chemical form, also referred to as speciation.

5.6.1 Speciation

Trace metals can be further distinguished from their total elemental composition into different oxidation states, organometallic compounds, complexes, or precipitates and minerals. Every species of an element has distinctive chemical and physical properties, sometimes resulting in profound differences in mobility, bioavailability, and toxicity. Speciation, rather than total concentration, plays a decisive role in metal mobility, bioavailability, and toxicity (Florence, 1986; Hudson, 1998).

Metals can exist in many diverse forms and can also convert rapidly from one species to another. Copper, like many trace metals, interacts in seawater to form free metal positively-charged cations, a variety of soluble complexes, and insoluble particles or precipitates, as well as inorganic complexes depending on the chemical characteristics of the seawater (Santschi et al., 1997). Copper compounds are known in several oxidation states, but in natural waters, it generally occurs in the form of the less stable cuprous or copper(I) state (Cu^{+}) and the more stable cupric or copper(II) state (Cu^{2+}), also known as free copper. Under atypical conditions, a Cu^{3+} state and even an extremely rare Cu^{4+} state can be achieved.

Copper is almost completely bound by organic materials in natural seawater but is strongly ion paired in organic-free seawater (Bruland et al., 2000; Muller et al., 2001). In such a solution, it forms a number of different species listed in Table 5-1 (Holmes-Farley, 2005).

Table 5-1. Copper species found in organic-free seawater.

Species	Percentage of Total
$CuCO_3$	73.8
$Cu(CO_3)_2^{2-}$	14.2
$Cu(OH)^{+}$	4.9
Cu^{2+}	3.9
$Cu(OH)_2$	2.2
$CuSO_4$	1.0
$CuHCO_3^{+}$	0.1

Water chemistry parameters, such as pH, temperature, hardness, alkalinity, salinity, ionic strength, oxidation potential–redox conditions, nature of sorbent phases and their surface areas, or dissolved organic matter (DOM) concentration can influence metal speciation and interaction with biota either directly by lowering free metal ion concentration or indirectly through synergistic or antagonistic effects (Cook et al., 2000; Ho et al., 1999). Hydrogen ion concentration is one of the most important factors governing metal speciation, transport, and bioavailability in aqueous solutions. Additionally, pH has an inverse effect on solubility, with solubility increasing with decreasing pH. Temperature also exerts an important effect on metal speciation, since most chemical reaction rates are highly sensitive to temperature changes (Elder, 1989).

Adsorption, which occurs when dissolved metals are attached to surfaces of particulate matter, is also strongly dependent on pH, the availability of particulate surfaces and total dissolved metal content (Elder, 1989). Particle size and resulting total surface area available for adsorption are both important factors in adsorption processes and can affect metal bioavailability (Luoma, 1989). Small particles with large surface-area-to-mass ratios allow more adsorption than an equivalent mass of large particles with small surface-area-to-mass ratios. Reduced adsorption can increase metal bioavailability by increasing concentrations of dissolved metals in associated water. Adsorption processes typically dominate the association of metals to solid phases such as sediment. In assessing the fate and transport of copper in San Diego Bay waters, Chadwick et al. (2004) noted that adsorption and complexation followed by settlement results in the transfer of approximately 48% of the copper to the sediments. Additionally, assessments of the spatial and temporal distributions of Cu^{2+} in San Diego Bay found that TSS and DOC strongly regulate the concentration of Cu^{2+} in waters (Blake et al., 2004; Rivera-Duarte et al., 2005; Neira et al., 2009).

Alkaline conditions in the sediment and surface water favor precipitation of copper. Precipitation is the process by which dissolved species exceed the solubility limits of their solids, so that some of the species precipitate from solution. When a metal species reaches mineral saturation, addition of further amounts of the species to solution are precipitated, not adsorbed. Precipitation is dependent on copper concentration, presence of other anions and cations, temperature, and time to thermodynamic equilibrium (Jensen, 2003).

It is well established that copper speciation affects toxicity and bioavailability in aquatic organisms. Free copper is readily soluble and is more chemically reactive than complexed forms of the metal, and hence is believed to be the most biologically available form (Sunda and Hanson, 1987). However, there are many other reports that have shown that the toxic response does not always conform to the free-ion model; organic complexing agents and inorganic hydroxyl or carbonate complexes might also exhibit some toxicity to target organisms (Allen and Hansen, 1996; Campbell et al., 2000; Deheyn et al., 2004; Parent et al., 1996).

5.6.2 Complexation

Complexation is the process by which organic compounds affect the mobility and toxicity of dissolved trace metals (Seligman and Zirino, 1998; Zirino and Seligman, 2002). Copper complexation capacity is the ability of the system to convert the bioavailable Cu^{2+} form to a nonreactive or nontoxic state through the combination of Cu^{2+} with ligands (Zirino and Seligman, 2002). Ligands are compounds that have an atom with an unshared pair of electrons, and thus have the potential to readily bind Cu^{2+}. Complexation capacity can be quantified for water samples through titrations to determine the change in the response of a Cu^{2+} ISE to additions of copper (Rivera-Duarte and Zirino, 2004) and differential pulse anodic stripping voltametry, which calculates ligand concentrations based on labile copper concentrations quantified using a series of copper additions to a water sample (Rivera-Duarte et al., 2005).

Copper complexation tends to increase with elevated levels of DOM in the water column, resulting in lower concentrations of Cu^{2+} (Seligman and Zirino, 1998). In San Diego Bay, the concentrations of total and dissolved copper tend to increase from the mouth to the head of the bay, while the concentration of Cu^{2+} has been found to decrease (Blake et al., 2004; Rivera-Duarte et al., 2005). This decrease in Cu^{2+} appears to be largely associated with the increase in copper complexation capacity also from the mouth to the head of San Diego Bay (Rivera-Duarte et al., 2005). The inner waters of the bay tend to have higher concentrations of TSS, DOC, and chlorophyll, all of which can bind with and reduce the availability of Cu^{2+} in the water column, while the concentration of total and dissolved copper are largely unaffected (Blake et al., 2004). These studies show that there can be a large degree of spatial variability in copper complexation capacity based on physical water column parameters. They also showed that temporal variability was also apparent since complexation capacities were found to decrease with seasonal reductions in TSS.

Within SIYB, total, dissolved, and free copper concentrations in surface waters all increase along a gradient from the mouth to the head of the basin, while concentrations of Cu^{2+} in pore water show the opposite trend. Low concentrations of Cu^{2+} in pore water at the head of the basin are likely due to complexation of copper with finer sediments and organic matter. Therefore, complexation appears to play an important role in SIYB, reducing the bioavailability of copper in pore water.

An increasingly large body of scientific literature has shown that it is the concentration of Cu^{2+} rather than total or dissolved copper that relates best to observed toxicity of marine organisms (reviewed by Blake et al., 2004). For example, in testing the relationship between copper complexation capacity and toxicity of San Diego Bay waters to three species of invertebrates, the Mediterranean mussel (*M. galloprovincialis*) the purple sea urchin (*S. purpuratus*), and the sand dollar (*D. excentricus*) through copper additions, Rivera-Duarte et al. (2005) found that moving from the mouth to the head of the bay, more copper was required to elicit toxic responses for the three species. Therefore, as the copper complexation capacity of the bay waters increased, the potential for copper toxicity decreased, assumedly due to the lower concentrations of Cu^{2+}.

These findings have important ramifications to both determinations of bioavailability and toxicity of copper to marine life, since quantifications of dissolved copper concentrations alone may not provide a sufficient indicator of water quality, since both bioavailability and toxicity are much more strongly affected by Cu^{2+}. Therefore, direct quantifications of Cu^{2+} or the use of a model that predicts the availability of Cu^{2+} based on physical water column parameters may provide a more relevant assessment of water quality and its ability to protect beneficial uses than the current water quality standard of dissolved copper alone.

5.7 Biotic Ligand Model

Variations in pH, cations, alkalinity and the presence of organic matter can have a significant effect on the toxicity of metals, as discussed above. As a result, toxicity levels may vary widely for a given metal. This presents an intricate problem for establishing regulatory guidelines because in the absence of a way to forecast these effects, a conservative regulatory limit is usually selected (e.g., the use of the chronic CTR for the SIYB TMDL). The Biotic Ligand Model (BLM) is a predictive tool that integrates the impact of water chemistry on metal speciation using principles in physiology, aquatic geochemistry, and toxicology (Morel, 1983; Pagenkopf, 1983; Di Toro et al., 2001). The model uses known *in situ* water chemistry and experimentally determined binding constants of physiological active receptor sites (biotic ligand) on the receiving surface of the organism, usually the gill of a fish or invertebrate, to forecast the metal concentration that would result in a defined toxic endpoint. The BLM assumes that the free cationic species of trace metals are the source of acute toxicity, triggering toxic damage by binding on or in the gill surface, and that the extent of short-term gill metal binding is directly foretelling of longer-term mortality.

An assortment of water chemistry factors can mitigate metal binding to physiological active receptor sites either by cationic competition (e.g., Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}) or by anionic complexation (e.g., OH^{-}, HCO_3^{-}, CO_3^{2-} Cl^{-}, thiosulfate, sulfide, and DOM) of the cationic metal, thereby averting its binding to the receptor sites. In addition, these naturally occurring cations and anions can interact among themselves in various ways. Based on the concentrations of all moieties *in situ*, the stability constants governing all pertinent reactions, and the experimentally determined relationship between short-term metal binding and longer-term toxicity, the BLM predicts the ultimate outcome for any given metal. The BLM integrates competition, complexation, and concentration into a geochemical modeling framework that includes the organism itself.

The BLM has been successfully validated to predict the toxicity of a variety of dissolved metals to various freshwater organisms and has been used in aquatic quality guidance for copper (Niyogi and Wood, 2004; Arnold et al., 2005; USEPA, 2003). Advantages of BLMs include economy, speed, and the ability to generate site-specific ambient WQC that are cognizant of receiving water chemistry. Biotic ligand models have also been shown to be an efficient substitute to performing bioassays in freshwater environments and may lead to more technically defensible ecological risk assessments. Although the BLM accounts for much of the variation in copper toxicity associated with water chemistry, the model also has limitations. Just as in toxicity testing using indicator species, the BLM cannot account for the considerable variation in sensitivity among species (Grosell et al., 2002). Additionally, there are few investigations of the effectiveness of the BLM to analyze combined toxicity of multiple metals (Playle, 2004). Although all models have limits, the BLM has gained amplified attention in the scientific as well as the regulatory community and is currently considered the most practical procedure to assess the ecotoxicity of metals on a site-specific basis for freshwater systems.

The seawater BLM is a promising construct for predicting metal speciation, complexation, and toxicity to marine organisms using site-specific seawater characteristics. HydroQual, Inc. has recently developed a marine copper BLM (Cu BLM) that is under review by the USEPA. This model was calibrated using toxicity data for *M. galloprovincialis* (mussel), *S. purpuratus* (urchin), *C. gigas* (oyster), *C. virginica* (oyster), and *D. excentricus* (sand dollar) from San Diego Bay, as well as other water bodies of the U.S. The HydroQual Cu BLM is highly pertinent to the region and has the potential to provide more pragmatic assessments of latent adverse effects of copper in the marine environment. In addition, the development of copper toxicity parameters for the implementation of the seawater BLM should provide water quality guidelines that better represent the actual environmental characteristics of the marine environment and potentially reduce requirements for costly empirical studies. The Cu BLM can be used to calculate median lethal concentration (LC_{50}) and EC_{50} values and predict whether copper concentrations are likely to be protective of marine biota based on physical water quality parameters, providing site-specific objectives (SSOs).

5.7.1 Navy Biotic Ligand Model Fate and Transport Analysis

The Navy developed an integrated compliance model for predicting copper fate and effects within harbors, and tested model predictions against measured chemical and toxicity data in Department of Defense harbors, including San Diego Bay (Chadwick et al., 2008). This model combines the seawater BLM with the Curvilinear Hydrodynamics in Three Dimensions (CH3D) fate and transport model to predict the transport, distribution, fate, and toxicity of copper in harbors. Additionally, the integrated model allows for the determination of SSOs, which take into account the physico-chemical water quality parameters that buffer effects of toxic compounds, such as copper.

Within San Diego Bay, including SIYB, the integrated fate and effects model was found to be effective in predicting total and dissolved copper concentrations, explaining 74-93% of the variability of measured total copper values and 68-92% of dissolved copper values. As found in previous studies, the model predicted a gradient of increasing copper concentrations from the mouth to the head of the bay. The model was less effective in predicting Cu^{2+} concentrations, although predicted values generally were within an order of magnitude of measured values, except near the mouth of the bay, where model predictions were more divergent.

The integrated model was also effective in predicting toxicity, with 87% of predicted *M. galloprovincialis* EC50s within a factor of two of measured values. The model combined whole-body lethal-level accumulation (LA50), TSS, DOC, pH, and salinity data to predict water effects ratios (WERs) for 26 segments within San Diego Bay. WERs ranged from approximately 1.4 by the mouth of the bay to approximately 2.0 in the south bay. The geometric mean WER was 1.336 for the north bay, 1.761 for the south bay, and 1.479 for the entire bay, based on toxicity assessments of *M. galloprovincialis*, *D. excentricus*, and *S. purpuratus*. Using the average WER for the entire bay, the model predicts a mean bay-wide WQS of 4.58 µg/L. Using the north bay WER (1.336), the predicted SSO for SIYB would be 4.14 µg/L. In comparing dissolved copper concentrations measured in SIYB by the RHMP and the Neira et al. (2009) study to the predicted SSO, the average dissolved copper concentration (8.76 + 0.32 µg/L) was approximately twice as high as the BLM-predicted SSO. Additionally, all but one of the 69 stations had dissolved copper concentrations that exceeded the SSO.

The integrated model has important regulatory implications for San Diego Bay. While the current WQC for dissolved copper (i.e., the chronic CTR of 3.1 the µg/L) was based on laboratory studies that do not take into account site-specific parameters that affect toxicity, the use of the BLM, as a component of the integrated model, allows for determinations of SSOs for San Diego Bay, including SIYB, at the spatial resolution of approximately 100 m^2. By taking into account the bioavailability of copper within the bay, the chronic SSO for SIYB would be 4.14 µg/L and the acute SSO would be 6.41 µg/L. Therefore, based on the Navy's assessment, dissolved copper concentrations in SIYB currently are not protective of water quality and associated beneficial uses.

5.7.2 Regional Harbor Monitoring Program 2008 Biotic Ligand Model Analysis

A BLM analysis of the RHMP 2008 stations was performed by HydroQual to calculate EC50 values and predicted SSOs for stations based on water quality parameters (WESTON, 2011b). The model used salinity, pH, and DOC to predict the concentration of dissolved copper that would induce a toxic response in 50% of *M. galloprovincialis* larvae (i.e., EC50 values). Salinity, pH, and DOC were used to predict EC50 values. Predictions of EC50 values can be compared to ambient dissolved copper concentrations to determine locations where copper toxicity would be expected in the water column. In a separate analysis, the Cu BLM was calibrated using only those studies that were included in the 1995 marine WQC to determine SSOs for stations. The resulting calibration represented a closer approximation of what the current U.S. marine WQC for copper would be if it had considered bioavailability effects due to the presence of natural organic matter. To develop this calibration, the EC50 values from USEPA (1995), along with associated water chemistry conditions were normalized with the BLM to allow the model to best estimate predicted values ($BLM_{EC50\text{-}FAV}$) comparable to FAV used to develop the marine WQC. Division of the $BLM_{EC50\text{-}FAV}$ by the acute-to-chronic ratio (ACR) of 3.127 was used to produce a value analogous to the current marine WQC. Since the $BLM_{EC50\text{-}FAV}$ also considers site-specific factors that affect copper bioavailability, the $BLM_{EC50\text{-}FAV}$/ACR reflected local conditions in a manner similar to that of a site-specific criterion, or SSO.

Dissolved organic carbon levels were extremely low in San Diego Bay during the RHMP August 2008 survey, ranging from 0.30-1.20 mg/L. In SIYB, DOC concentrations ranged from 0.90-1.20 mg/L. In comparison, during the prior Navy study, which was conducted at multiple times of the year, DOC levels in San Diego Bay ranged from 1.3-2.8 mg/L. The parameter that provided the greatest predictive power of toxicity was DOC (Figure 5-1). Dissolved organic carbon explained 95.5% of the variability in predicted EC50 values according to the BLM (r^2 = 99.5, p = 0.000, EC50 = 0.487 + 6.30·DOC. Based on the BLM calculations toxic effects to mussels were predicted to occur at concentrations below the chronic CTR (3.1 µg/L) when DOC levels were low (~0.4 mg/L). The low DOC concentrations encountered during the RHMP 2008 survey greatly affected toxicity predictions.

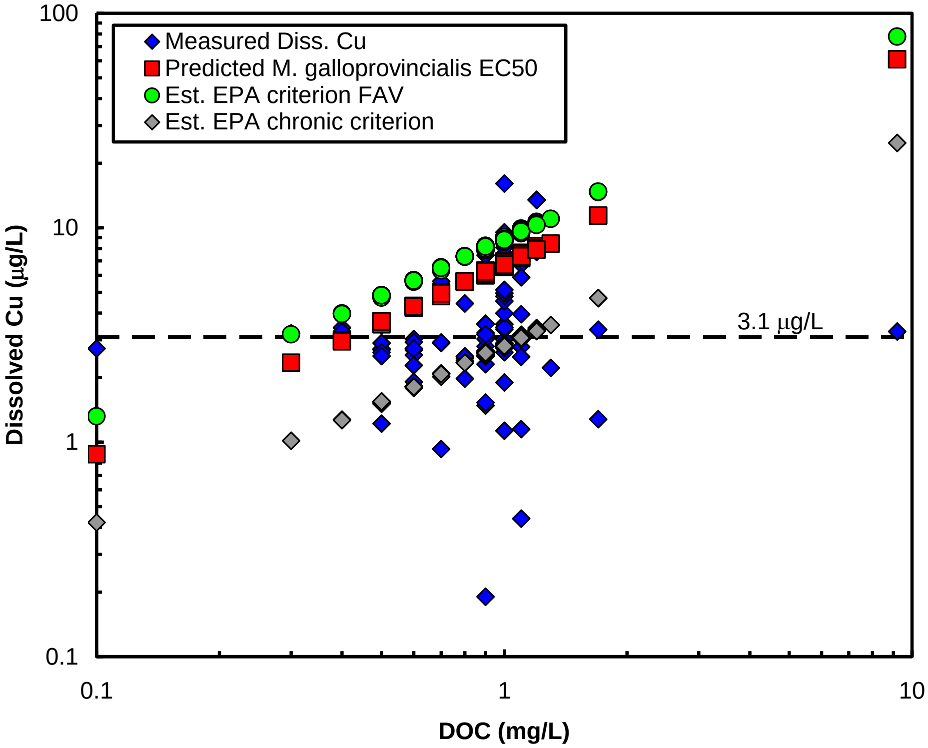

Figure 5-1. Comparison of measured dissolved copper concentrations to predicted *M. galloprovincialis* EC50 values

Predicted *M. galloprovincialis* EC50s ranged from 2.35-8.20 µg/L in San Diego Bay. The average EC50 for the bay was 5.67 ± 0.19 µg/L (mean ± standard error). In examining predicted EC50s for SIYB, there was a slight gradient of increasing EC50s from 6.6 µg/L at the mouth to 8.0 µg/L at the head. However, the slight increases in the predicted EC50s were not sufficient to counterbalance the substantial gradient of increasing dissolved copper concentrations in surface waters, as shown in the margin of safety (MOS) assessment below.

In comparing measured dissolved copper concentrations to predicted EC50s in San Diego Bay, 79% of stations (i.e., 46 stations) had measured dissolved copper concentrations that were below predicted station-specific EC50s (i.e., MOS > 1; Figure 5-2). All seven of the SIYB stations had dissolved copper concentrations greater than the predicted station-specific EC50s (i.e., MOS < 1). The low MOS within SIYB was primarily due to the presence of higher levels of dissolved copper within the water column, since the average DOC concentration in SIYB (1.03 ± 0.04 mg/L) was slightly greater than the San Diego Bay-wide average of 0.89 ± 0.03 mg/L.

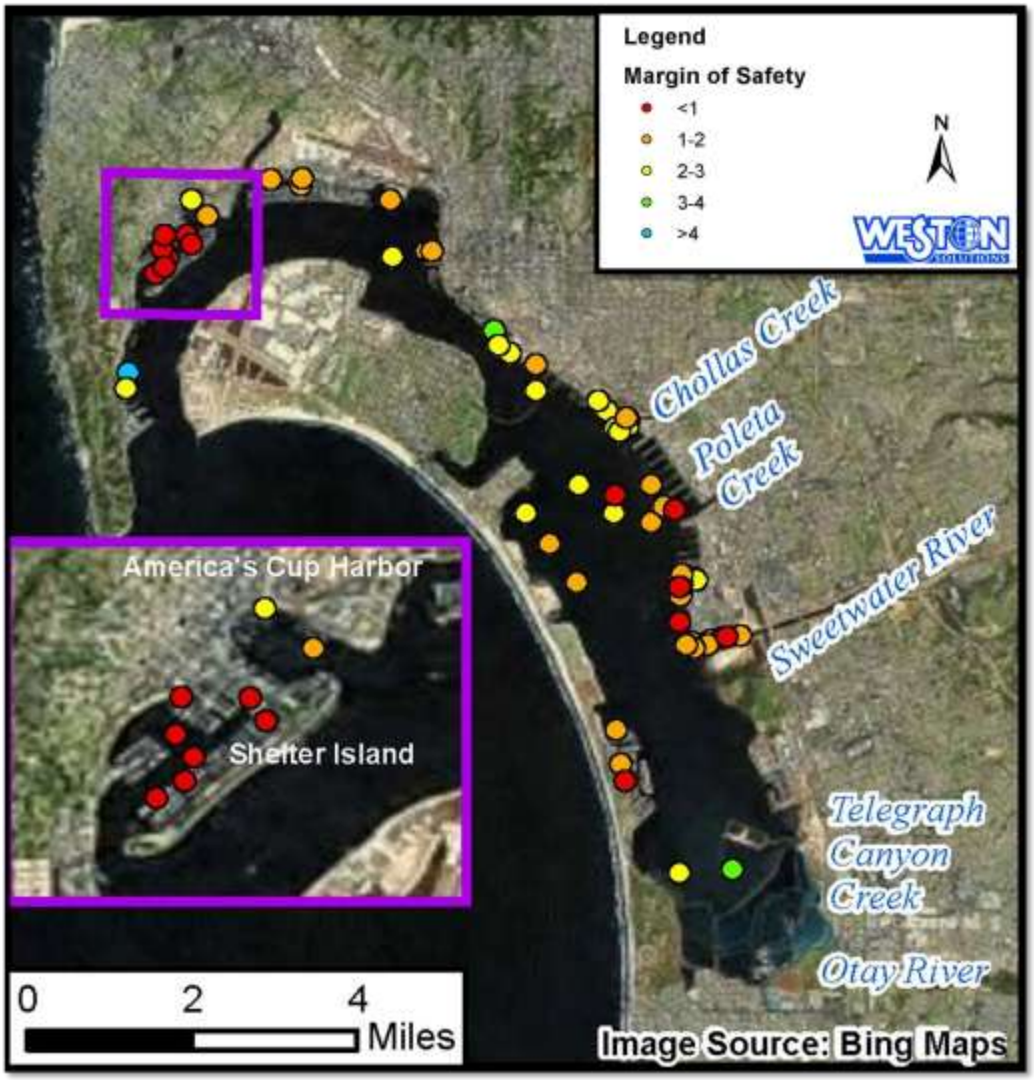

Figure 5-2. Spatial distribution of the margin of safety values (i.e., the ratio of predicted EC50s to measured dissolved copper concentrations) within San Diego Bay

Predicted $\mathrm{BLM}_{\mathrm{EC50\text{-}FAV}}$/ACR values, or SSOs, for 95% of San Diego Bay stations were lower than the ambient marine WQO of 3.1 µg/L (WESTON, 2011b). Additionally, all but one station in SIYB had predicted SSOs that were below the WQO, ranging from 2.45-3.22 µg/L (Figure 5-3). As described for the predicted EC50s, DOC levels measured during the RHMP 2008 survey were not sufficiently high to substantially limit the bioavailability of copper to levels that would result in SSOs that were greater than the WQC.

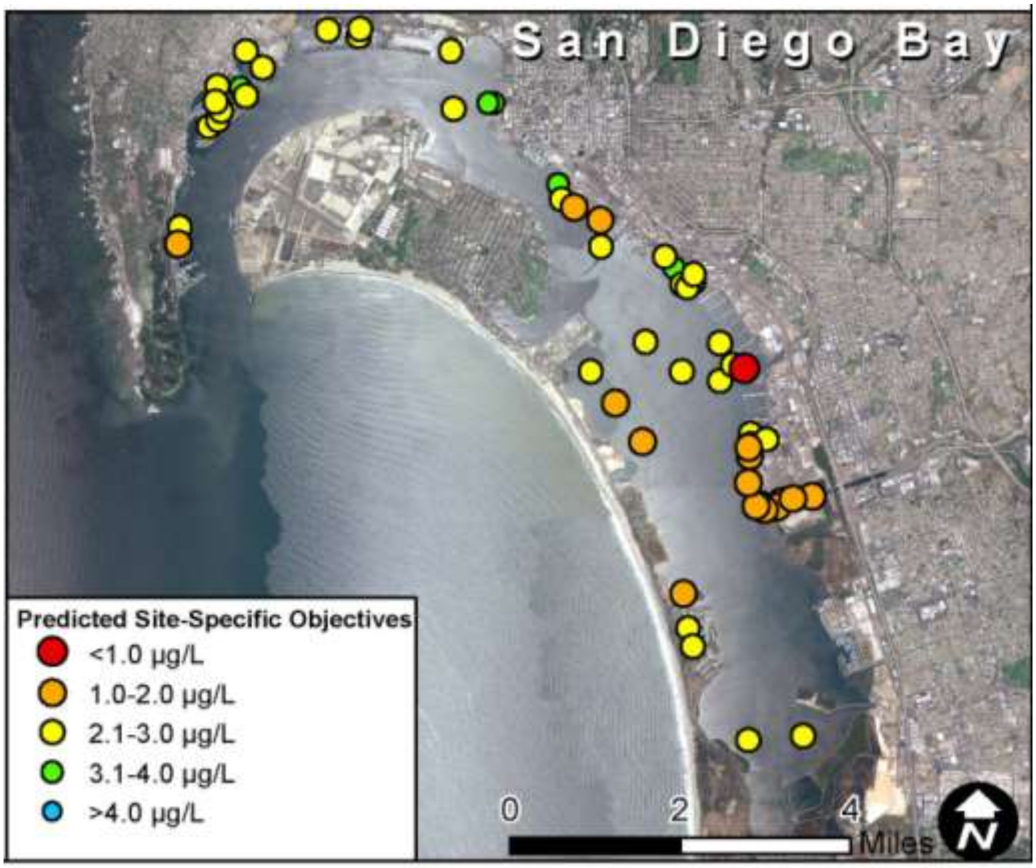

Figure 5-3. BLM-predicted site-specific objectives for San Diego Bay

Based on the results of the BLM, the areas of San Diego Bay predicted to exhibit the highest levels of toxicity occurred within the marinas, as well as along the eastern shoreline of San Diego Bay. Shelter Island Yacht Basin, in particular, had dissolved copper concentrations that exceeded predicted EC50s, indicating that water column toxicity would be expected, at least for *M. galloprovincialis*. Taking into account physical water quality parameters that limit the bioavailability of copper has the potential to establish SSOs that are protective of water quality and beneficial uses, but are not overly restrictive. The most important influence on the bioavailability of copper is the content of DOM within the water column; therefore, in areas where DOC and TSS levels are elevated, Cu^{2+} concentrations are reduced even at higher dissolved copper concentrations. Substantial temporal variability in DOC levels present a challenge for using the BLM to predict SSOs, since the potential for toxic effects at the same dissolved copper concentration will also change substantially based on DOC concentrations. For example, concentrations of DOC measured in San Diego Bay during the Navy study (Chadwick et al., 2008) ranged from 1.3-2.8 mg/L, while those of RHMP ranged from 0.3-1.2 mg/L. As a consequence, BLM-predicted WERs from the Navy study ranged from 1.2-2.4, which equates to SSOs of 3.72-7.44 µg/L in San Diego Bay as compared to 0.99-3.30 µg/L based on RHMP 2008 water quality conditions. Further studies are needed to compare the BLM predictions to the empirical results of a WER study. These studies would help validate the model and test whether BLM-predicted SSOs are equivalent to those of a WER study, potentially reducing the cost for future SSO assessments.

6.0 EVIDENCE FOR COPPER IMPACTS TO BIOTA

While copper serves as a nutrient to plants and animals at low concentrations, an extensive body of literature has shown that copper can be toxic to aquatic organisms, resulting in both sub-lethal (i.e., chronic) and lethal (i.e., acute) effects (USEPA, 2003). Copper's effectiveness in inhibiting recruitment and growth of fouling organisms to vessels is evidence of its toxic effects, even at relatively low concentrations. Copper has been found to be especially toxic to early life history stages of marine organisms, including fish, bivalves, and echinoderms (reviewed by Seligman and Zirino, 1998). Additionally, the potential for adverse effects of copper, such as acute and chronic toxicity to marine life, is dependent on the concentrations and chemical forms in which copper occurs in the marine environment. This section provides a review of toxic effects of copper in aquatic habitats, assessing relationships of copper concentration with toxicity and benthic community condition.

6.1 Toxic Effects of Copper

The accumulation of copper in many aquatic organisms is typically associated with oxidative stress and subsequent macromolecular damage. In times of increased abiotic pressure, electron transport mechanisms (e.g., mitochondrial transport chains) become less efficient, ultimately resulting in a series of reactive oxygen species that can in turn denature proteins, mutate deoxyribonucleic acid (DNA), and damage cells (Richier et al., 2005). The observed adverse effects of copper toxicity in marine organisms include damage to gills, liver, kidneys and the nervous system (reviewed by Seligman and Zirino, 1998).

Although present in water in numerous forms, toxicity of copper to aquatic life is principally related to the activity of Cu^{2+}, and possibly some hydroxy complexes (Allen and Hansen, 1996; Borgmann and Ralph, 1983; Pagenkopg, 1983). Consequently, any modifications in water and sediment quality that could decrease cupric ion activity would also be projected to decrease the bioavailability of copper. Due to the influence of parameters such as pH, alkalinity, and organic matter on the formation of compounds that affect the amount of cupric ion present, not all of the copper in the marine environment contributes directly to toxicity.

6.2 Relationships between Copper Concentrations and Toxicity

Upon detection of toxicity using bioassays, one of the first steps is to assess the presence of chemical contaminants that may occur at levels that have been reported to induce toxicity. Additionally, evidence that a chemical of concern may or may not be affecting toxicity can be assessed using correlation analyses, where by the results of toxicity tests (e.g., percent normal-alive development or survival) are compared to chemical concentrations. While causation cannot be inferred from correlations alone, relationships between elevated chemical concentrations and toxicity can be used to focus follow-up experimental studies. The following sections assess the relationship between water and sediment copper concentrations and toxicity, as well as sediment copper concentrations and benthic infaunal disturbance.

6.2.1 Dissolved Copper

The relationship between dissolved copper concentrations and toxicity appears to be highly variable both spatially and temporally. While some studies have found significant correlations between dissolved copper concentrations and toxicity within RHMP marinas (e.g., Schiff et al., 2006a), other studies conducted in San Diego Bay have encountered completely opposite findings (e.g., Rosen et al., 2005). This high degree of variability in the toxic effects of dissolved copper to marine invertebrates is thought to be the result of processes that bind the bioavailable form of copper, Cu^{2+}, such as complexation (Rivera-Duarte et al., 2005 and discussed in further detail in Section 5.6.2). In certain instances, organic material may complex more than 99.9% of the dissolved copper in marine environments (Bruland et al., 2000). Therefore, the availability of ligands, such as TSS and DOC, greatly impact toxicity, as do the presence of other contaminants.

A 2005 study that compared surface water dissolved copper concentrations to mussel development toxicity was conducted within marinas of Dana Point Harbor, Oceanside Harbor, Mission Bay, and San Diego Bay (Schiff et al., 2006a). Dissolved copper concentrations in surface waters ranged from nondetectable to 21 µg/L and normal-alive development in surface waters ranged from 0-104%. This study found a strong positive relationship between copper concentrations and mussel toxicity. Stations with higher copper concentrations had lower normal-alive mussel development, resulting in a statistically significant correlation ($r = -0.90$, $p < 0.01$). Although there was a significant negative relationship, toxicity in surface waters was not apparent until a dissolved copper concentration of approximately 9 µg/L. Additionally, there were approximately 17 stations that had dissolved copper concentrations that ranged from approximately 3-10 µg/L that did not meet the threshold for toxicity (i.e., <80% normal-alive development). Therefore, it appears that dissolved copper did not begin to have a detectable toxic effect until concentrations were approximately three times the chronic CTR threshold of 3.1 µg/L in the RHMP marinas.

In a 2000-2001 study of San Diego Bay, dissolved copper concentrations were found to increase from the mouth to near the head of the bay, ranging from 0.3-2.9 µg/L, and normal-alive mussel development averaged 93 ± 5% (Rosen et al., 2005). Since dissolved copper concentrations did not exceed the chronic CTR threshold, the finding of limited toxicity is reasonably expected. Through copper spiking experiments, the researchers were able to determine the concentrations of copper required to elicit a toxic response in 50% of the organisms (referred to as the EC50). The study found that EC50s for mussel normal-alive development increased from 7.1 µg/L near the mouth of the bay to 24.3 µg/L at the head. The increase in EC50s from the mouth to the head of the bay by a factor of 2.5 indicated that although dissolved copper concentrations also increased from the mouth to the head of the bay, the potential for toxic effects decreased along the same gradient. Therefore, any relationships between dissolved copper concentrations and toxicity would be expected to be highly site specific.

6.2.2 Free Copper

An increasing body of scientific evidence has shown that Cu^{2+} provides the best prediction of copper-induced toxicity to marine organisms (reviewed by Blake et al., 2004). Free copper is far less abundant in aquatic systems than either total or dissolved copper. In a study of the relative concentrations of free and total copper in San Diego Bay, Cu^{2+} concentrations were less than

0.01% of the total copper measured (Zirino et al., 1998). Studies conducted in San Diego Bay have shown that Cu^{2+} varies substantially both spatially and temporally due to the availability of ligands and the copper complexation capacity (Zirino et al., 1998; Deheyn and Latz, 2005; Rivera-Duarte, 2005). Although variability in concentrations is high, the Cu^{2+} threshold for toxicity has been consistently found to be 1 x 10^{-11} mol/L or 11 pCu (Rivera-Duarte et al., 2005). While the current water quality thresholds are based on dissolved copper concentrations, a Cu^{2+} threshold may provide a WQC that assesses the bioavailable form of copper and therefore reduces the need to use costly analyses, such as WER studies, to determine SSOs.

6.2.3 Sediment Copper

In the case of RHMP 2008, sediment toxicity was assessed using the *E. estuarius* SP bioassay and the *M. galloprovincialis* SWI bioassay. Since toxicity to the amphipod was extremely rare, correlation analysis was only used to examine the relationship between mussel normal-alive development bioassay results and sediment copper concentrations. There was a significant negative relationship between normal-alive development and copper concentration (r = -0.315, p = 0.006), indicating that copper concentrations explained just over 31% of the variability in toxicity results. When copper concentrations were normalized by the percentage of fines in the sediments, the correlation was even stronger (r = -0.418, p = 0.000). Based on the RHMP 2008 findings, it appears that higher copper concentrations are associated with higher levels of mussel chronic toxicity (Figure 6-1). Although the relationship is significant, the high degree of variability in mussel toxicity provides evidence that there are other physico-chemical parameters and/or contaminants that are affecting toxicity.

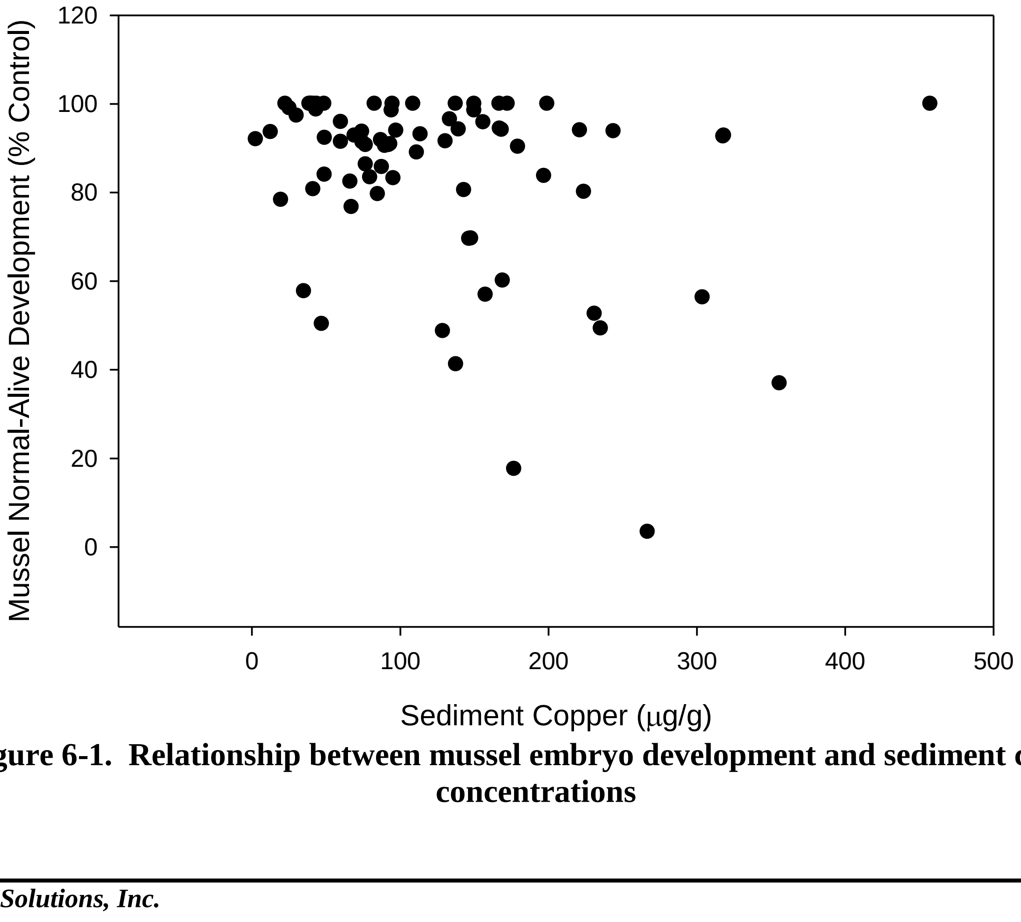

Figure 6-1. Relationship between mussel embryo development and sediment copper concentrations

7.0 RECEPTORS OF CONCERN

Copper has the potential to adversely affect marine organisms that inhabit the waters and sediments of SIYB. Effects of copper are species specific and also dependent on the life history stage of organisms (reviewed by Regional Board, 2005). Early life stages of fish, bivalves, and echinoderms are most vulnerable to copper contamination, as evidenced both acute and chronic effects of copper in marine waters and sediments (Seligman and Zirino, 1998). This section describes the primary receptors of concern, including planktonic and benthic communities.

7.1 Planktonic Community

Phytoplankton and zooplankton are the most sensitive organisms to copper contamination (reviewed by Regional Board, 2005). Phytoplankton taxa known to be sensitive to copper were absent from SIYB, while copper tolerant species were present (Krett, 1980). Similarly, Johnston (1990) measured a decrease in species diversity of plankton from the mouth to the head of SIYB, paralleling the trend of increasing copper concentrations. In addition to community level impacts of copper to the plankton community, experimental bioassays have shown evidence for both acute and chronic toxicity of plankton, including larvae, to copper (USEPA, 1986). Copper has been demonstrated to reduce phytoplankton reproduction rates (Brand et al., 1986) and inhibit the production of naturally-occurring bacteria in marine environments (Boyd et al., 2005).

The planktonic community plays an important role in marine systems. Phytoplankton are important primary producers that serve as the base of the food chain and zooplankton serve as important food sources for many animals, including benthic invertebrates, fishes, marine birds, and mammals. Additionally, zooplankton are comprised of organisms, such as copepods that spend their entire life history in the water column as plankton; fish larvae; and larvae of benthic organisms, which settle to soft and hard bottom areas. Therefore, copper impacts to plankton have ramifications to food availability, population dynamics, and community structure.

7.2 Benthic Community

Shelter Island Yacht Basin is largely comprised of soft-bottom habitat that supports benthic demersal fish and invertebrate species, as well as infaunal invertebrate species. Hard substrates, such as rock riprap and pylons, also provide habitat for benthic animals. Benthic organisms of SIYB are exposed to copper in the water column, pore water, and within the sediments. The interactions of the organisms with copper is dependent on multiple factors, including life history stage, motility, feeding strategies, and physiology.

Copper has been demonstrated to bioaccumulate in the tissues of benthic organisms in San Diego Bay. Results from the State Mussel Watch Program have documented elevated copper concentrations in mussels transplanted to SIYB (State Water Resource Control Board [State Board], 1995). In a 2001 study conducted in San Diego Bay, brittlestars, *Ophiothrix spiculata*, were collected from outside the bay and transplanted to four locations in the bay (Deheyn and Latz, 2006). The study found that although copper, as well as other metal, concentrations increased moving from the mouth to the head of the bay, bioaccumulation to brittlestars was uniform throughout the bay. Copper tissue concentrations of transplanted organisms were 1 to 10 times greater than those of organisms maintained in aquaria. While bioaccumulation alone is not evidence of adverse impacts, these studies provide evidence that copper is bioavailable to organisms in the sediments and water column.

Copper contamination has been demonstrated to result in stress to marine invertebrates, including limitations to the ability to feed and acquire resources, as well as reduced growth and reproduction (Luoma and Carter, 1991; Krang and Ekerholm, 2006; Roberts et al., 2006; Hollows et al., 2007). Additionally, experimentally elevated copper levels in the sediments have resulted in reduced abundances of amphipods (Morrisey et al., 1996). Assessments of the relationships between benthic community structure and copper in San Diego Bay (WESTON, 2011b) and SIYB (Neira et al., 2011) have shown increased community degradation with higher copper contamination, as described in greater detail below.

The relationship between RHMP 2008 sediment copper contamination and benthic community condition was assessed using the benthic response index (BRI). The BRI provides a measure of benthic infaunal community structure, using a four-category scale of disturbance to classify the infaunal assemblages. Categories include:

- Reference (BRI < 39.96),
- Low disturbance (39.96-49.14),
- Moderate disturbance (49.15-79.26), and
- High disturbance (≥ 79.27).

During RHMP 2008, benthic infaunal communities ranged from reference to moderately disturbed. Communities occurring in sediments with higher copper concentrations were increasingly categorized as being moderately disturbed (Figure 7-1). This resulted in a significant positive correlation between BRI and sediment copper concentrations ($r = 0.501$, $p = 0.000$). Sediments in San Diego Bay have been shown to serve as an important sink for copper from the water column (Chadwick et al., 2004), and while they may reduce the impact of copper to species that reside within the water column, the community structure of species that live and feed within the sediments appears to be impacted by increases in sediment copper concentrations. While the relationship between copper concentrations and benthic infaunal community disturbance was significant, it is important to note that only 8 of 75 stations were categorized as moderately disturbed (WESTON, 2010).

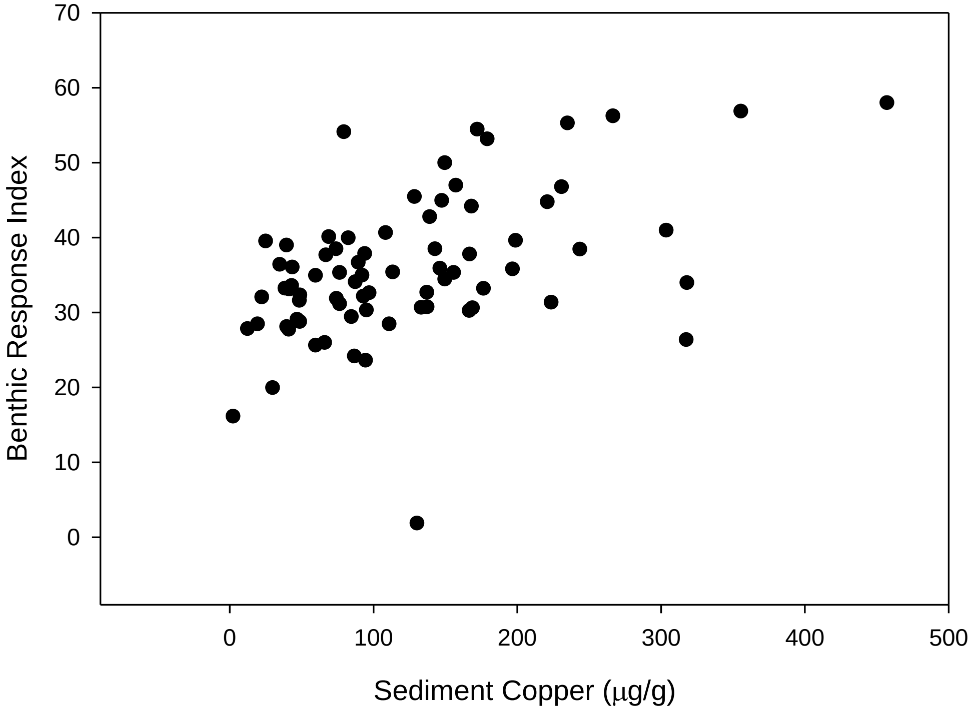

Figure 7-1. Relationship between benthic community condition and sediment copper concentrations

In 2007, Neira et al. conducted sediment sampling at SIYB sites previously determined to have high, medium, and low sediment copper concentrations (Neira et al., 2011). Sediments were analyzed for copper concentration, and benthic infauna were collected and identified to the lowest practical taxa. Copper concentrations within infauna also were quantified. The study found that the benthic infaunal communities at sites with elevated copper concentrations were less diverse and were comprised of individuals of lower body size and weight as compared to sites with lower copper contamination. Copper was detected in invertebrate tissues, indicating that copper is bioavailable. For certain species tissue concentrations increased with increasing copper concentrations, while for others it did not. Differences in tissue concentrations among species were attributed to variations in feeding strategies, physiology, and assimilation between species, as well as site-specific differences in organic matter that bind copper.

8.0 UNCERTAINTIES AND DATA GAPS

Throughout the conceptual model report, a number of data gaps and uncertainties were noted relating to the bioavailability of copper in SIYB, transport and release of copper from sediments, and loads of copper from sources. These areas should be the focus of additional study, since they can greatly affect the approach to implementing the TMDL.

Is the numeric WQO (3.1 µg/L) overprotective of water quality and Beneficial Uses in SIYB? – An increasing wealth of scientific evidence now indicates that the bioavailability of copper and potential for toxic effects is strongly controlled by physical and chemical processes that control the availability of Cu^{2+}. One of the most important factors that regulate Cu^{2+} is the abundance of ligands within the water column and sediments, such as DOM, DOC, and TSS, as well as physical properties of the site, such as pH, salinity, temperature, and grain size of sediments. The current numeric WQO, based on the chronic CTR threshold of 3.1 µg/L, was derived from laboratory experiments performed using filtered laboratory seawater, which consequently does not take into account site-specific parameters that control copper toxicity. Therefore, it is recommended that a combination of monitoring, modeling, and laboratory studies be performed to better understand the site-specific copper concentrations that will still be protective of water quality and SIYB Beneficial Uses. These studies would include monthly monitoring of DOC at multiple stations in SIYB, since DOC is the factor that is most predictive of copper bioavailability and toxicity according to the BLM. Based on the results of this study, a WER may be performed to validate the predictions of the BLM and calculated an SSO that is not overly protective of water quality and Beneficial Uses in SIYB.

What is the actual load of copper from vessels? – While the evidence is overwhelming that the largest source of copper to SIYB is copper-based hull paints of recreational vessels, there is a high level of uncertainty as to the loading rate from vessels and the percentages of the loads due to passive leaching and hull cleaning. By instituting a monitoring program that tracks the number, size, paint type, and percentage of time that vessels remain in SIYB, we will begin to get a more accurate picture of the combined loading of copper from passive leaching and hull cleaning combined.

How does paint type and age affect loading? – Both paint type and age can have affect leach rates and loading, since copper-based antifouling paints contain varying amounts of cuprous oxide, ranging from less than 30% to greater than 75%. Additionally, the age of paints also can have an important impact on loading, since newer paints have higher copper concentrations initially and potentially leach copper at higher rates. Ongoing and future studies being performed by the Department of Pesticide Regulation assessing leach rates from antifouling paints will help develop better estimates of loading.

What is the relative importance of passive leaching and hull cleaning to copper loading in SIYB? – Hull cleaning has been reported to increase leaching of dissolved copper during cleaning, suspend particulates (i.e., total copper), and increase passive leaching rates following cleaning. Additionally, hull cleaning events have been shown to increase copper leaching rates above baseline passive leaching rates for at least three days, which indicates that there may be a need to revise the definition of a hull cleaning event from a one-day period to a three-day period following cleaning. Additionally, hull cleaning, particularly without the use of BMPs, releases particulates, including total copper to the sediments. Once in the sediments, the copper is largely bound; however, increasing concentrations can increase the potential for sediments to serve as a source to the overlying waters. Therefore, further studies are needed to assess the impact of hull cleaning on passive leaching rates and dissolved copper loading. Experimental studies that compare copper concentrations over time for vessels that are cleaned and uncleaned may be useful in determining the influence of hull cleaning on loading, both during and after cleaning events.

Is the dissolved copper load from sediments actually zero? – The independent reviewers questioned the validity of the determination that sediments do not contribute dissolved copper to the water column. While the Technical Report's conclusion that sediments are likely to serve as a net sink for dissolved copper from the water column similar to main channel waters of San Diego Bay (i.e., background), similar consideration of dissolved copper loading from the sediments as background loading from the bay appears to be merited. If potential inputs from both copper flux and resuspension/desorption, the maximum expected load of dissolved copper to SIYB would be approximately 82 kg/yr. While sediment loads are anticipated to be substantially less than passive leaching and hull cleaning, loading from sediments may be the third most important source of dissolved copper to the basin. Assessments of copper flux and resuspension studies will help determine whether sediments are serving as a net source or sink in SIYB.

Laboratory and field studies are scheduled in 2012-2013 through the RHMP to assess the potential for copper-laden sediments to serve as a net source or sink for copper into and from the water column depending on the concentration of copper within the overlying water. Performing such a study may be crucial to understanding and predicting the effectiveness of converting vessel hull paints from copper-based to non-copper-based products as a means of reducing dissolved copper concentrations in the water column to levels below the WQC. Although sediments in the harbors appear to be serving as a sink for copper at current copper levels, it has yet to be tested if reductions in water column copper concentrations to levels approaching the WQC will shift sediments from a net sink to a source.

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