Spring 5-13-2014

Evaluation of the Development and Effectiveness of Copper Total Maximum Daily Loads (Tmdls) to Achieve Marine Water Quality Criteria

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This Master's Project

EVALUATION OF THE DEVELOPMENT AND EFFECTIVENESS OF COPPER TOTAL MAXIMUM DAILY LOADS (TMDLS) TO ACHIEVE MARINE WATER QUALITY CRITERIA

by

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is submitted in partial fulfillment of the requirements
for the degree of:

Master of Science
in
Environmental Management

at the

University of San Francisco

Submitted: Received:

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Joanna Florer Date

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Kathleen Jennings, Ph.D. Date

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LIST OF ACRONYMS AND ABBREVIATIONS

µg/L	microgram per liter
AB	Assembly Bill
AFP	antifouling paint
BLM	biotic ligand model
BMP	best management practices
CalEPA	California Environmental Protection Agency
CDPR	California Department of Pesticide Regulation
CPDA	California Professional Divers Association ()
CTR	California Toxics Rule.
CWA	Clean Water Act
GAO	U.S. Government Accountability Office
g/yr	grams per year
LA	load allocation
NPDES	National Pollutant Discharge Elimination System
PCA	Porter-Cologne Water Quality Act
RWQCB	Regional Water Quality Control Board
SIYB	Shelter Island Yacht Basin
SWRCB	State Water Resources Control Board
TMDLs	Total Maximum Daily Loads
USEPA	U.S. Environmental Protection Agency
WER	water effect ratio
WLA	waste load allocation

CHAPTER 1 - INTRODUCTION

Elevated concentrations of certain chemicals in surface water are known to be toxic to aquatic organisms (e.g., barnacles, algae, and fish). For a number of these chemicals (e.g., tributyltin [TBT], copper) federal and state water quality standards exist to protect aquatic organisms. As a means to comply with water quality standards, regulatory agencies establish Total Maximum Daily Loads (TMDLs) to reduce concentrations of toxic chemicals from entering waterways (USEPA 1991). A TMDL determines the maximum amount of pollutant loading a water body can sustain and still achieve water quality standards; they are developed to ensure that surface water concentrations meet applicable criteria. However, there can be uncertainty regarding TMDLs because of the lack of available data and input assumptions used in their development. TMDLs should also be established based on site-specific information, which is not always available or considered when developing TMDLs. Additionally, some studies have indicated that TMDLs, while they do reduce concentrations of toxic chemicals in surface water, are not as effective as anticipated or not feasible as a means to meet water quality criteria (GAO 2013; USEPA 2007b, c; Clean Water Fund 2013). Because the development and implementation of TMDLs vary depending on the pollutant, water body type, and location, this research specifically evaluates the development and effectiveness of a TMDL for copper to achieve marine water quality criteria in California. Additionally, the findings of this research will be used to develop regional water quality policy recommendations.

1.1 The Clean Water Act and TMDLs

The Clean Water Act (CWA) was enacted in 1972 and is administered by the U.S. Environmental Protection Agency (USEPA) to maintain and restore the integrity of the nation's waters. The CWA is the primary federal law concerning water pollution and regulates the discharge of pollutants into the nation's water bodies. The CWA regulates a variety of pollutants including toxic chemicals, physical stressors (e.g., suspended solids, pH), and pathogens (e.g., fecal coliform). Water quality standards were developed under the CWA to protect water quality from pollutants. The water quality standards made it possible to determine if a water body was healthy or impaired and provided as a means to identify how much pollution control would be needed to maintain or restore the integrity of a water body.

The CWA requires each state to adopt or develop water quality standards and identify impaired water bodies in their state, known as the 303(d) list. For waters that do not meet these standards, states must develop TMDLs, which are approved by USEPA and set target limits for pollutants. States implement TMDL programs by identifying pollutants that impair water quality and take actions to reduce them (GAO 2013). States are also required to reduce pollutants by issuing National Pollutant Discharge Elimination System (NPDES) permits for point sources (GAO 2013). However, the focus of this research is on TMDL development.

1.2 Copper in the Aquatic Environment

Some metals are essential nutrients required by plants and animals for basic functions such as growth (Sunda and Huntsman 1998). Copper is an essential nutrient in low doses to nearly all plants and animals, but toxic in high doses (Buck et al. 2007; Sunda and Huntsman 1998). In aquatic environments, elevated levels of copper are toxic and can adversely affect many types of aquatic organisms including amphibians, fish, invertebrates, and plants. Toxic effects from copper include mortality, and reductions in reproduction and growth. In 1980, USEPA established water quality criteria for copper due to its toxicity to aquatic organisms. Over the past 25 years, the USEPA has published a number of guidance documents containing aquatic life criteria recommendations for copper (USEPA 1980, 1985, 1986, 1996, 2007).

Copper is a naturally occurring metal present in the Earth's terrestrial and aquatic environments. In water, copper is most commonly present in the free ion form as cupric ion (Cu^{2+}). Naturally occurring concentrations of copper have been reported from 0.03 to 0.25

microgram per liter (μg/L) in marine water and from 0.20 to 30 μg/L in fresh water (Blossom 2001; USEPA 2007a). Anthropogenically elevated levels of copper are known to occur in in marine environments in marinas, where copper paint is used on the hulls of boats to prevent fouling organisms (Blossom 2001; USEPA 2002a; SDRWQCB 2005; Singhasemanon et al. 2009). In California saltwater marinas, copper concentrations has been reported as high as 18.4 μg/L (Singhasemanon et al. 2009).

Metals can exist in a variety of different forms (i.e., species) that influence their biogeochemical cycle and cellular uptake by organisms in aquatic environments. Dissolved metals can be free ions or bound to inorganic or organic ligands to form complexes. Only metals in the free ion form are bioavailable to aquatic organisms and complexed metals are not bioavailable (Buck et al. 2007; Sunda and Huntsman 1998). Therefore, only the free ion form of the metal is toxic to aquatic organisms.

USEPA's water quality criteria for copper of 4.8 μg/L for acute (i.e., short-term) exposure and 3.1 μg/L for chronic (i.e., long-term) were developed to protect sensitive aquatic microorganisms from toxic levels of the free ion form of copper (Cu^{2+}; USEPA 2007a, Buck et al. 2007). However, the water quality criteria are for total dissolved copper, which consists of both complexed and the free ion species (cupric ion). Cupric ion is highly reactive to complexation with ligands, so its bioavailability is dependent on the type and quantity of ligands in the aquatic environment (Buck et al. 2007). California's coastal waters have an abundant source of organic ligands that complex with the toxic cupric ion. Studies conducted in San Francisco determined that over 99 percent of the cupric ion in the bay are complexed, thus total dissolved copper concentrations in San Francisco Bay exceeding the water quality criteria are not toxic to aquatic organisms (Buck et al. 2007). Therefore, metals speciation and complexation can play a significant role in mitigating copper toxicity. In San Francisco, the local water quality agency (San Francisco Bay Regional Water Quality Control Board

[SFBRWQCB]) used these findings to develop a more appropriate copper water quality standard (i.e., Site-Specific Objective) for San Francisco Bay.

1.3 Copper-Based Antifouling Paints

Effective antifouling paints (AFPs) are important for many reasons, however there can be a disconnect between regulatory activities regarding marine AFPs because they can be toxic in the marine environment, but also have environmental benefits such as improving the fuel efficiency of boat movement and the prevention of invasive species introduction. While some coatings are non-toxic their efficacy can be limited because of boat use patterns and hull niche areas. If regulations focus on only one environmental risk or benefit the result does not integrate all facts, regulations can be in direct contradiction and the best solution for the environment may not be achieved. The risks of AFPs have been particularly well studied since TBT was found to have significant detrimental environmental effects (e.g., snail imposex) and was banned for use in recreational boat paints in 1988 in California and the United States (Blossom 2001, 2009; (SDRWQCB 2005).

Since the banning of TBT concentrations of TBT in water bodies has decreased, however the uses of copper in boat paints and copper concentrations in marinas increased. Copper is currently used in the majority (90 percent) of marine AFPs worldwide and in California (Singhasemanon et al. 2009; Blossom 2009). Elevated levels of copper have been measured at enclosed and low flow marine areas. Toxicity has been measured due to copper in some of these areas when laboratory analysis is performed yet significant marine organism population changes have not been observed (Blossom 2009). The quantification of energy efficiency of boat movement and degree of hull fouling particularly by non-indigenous species is a current focus of the marine hull coatings industry and regulators. Significant reductions in native marine organism populations have been measured in areas where invasive species have been introduced and proliferated (Blossom 2009). No marine AFP has been found to prevent 100 percent of hull born invasive species; however, some are more efficacious than others depending on the application. A call for regulatory flexibility with integration of all risks, benefits and actual measured marine population effects is advocated to best protect the environment (Blossom 2009).

1.4 Problem Formulation

The Santa Ana and Los Angeles Regional Water Quality Control Boards (RWQCBs) have begun development of copper TMDL programs. The proposed copper TMDLs include implementation plan for reducing copper concentrations in Marina del Rey and Newport Bay, since copper exceeds the marine surface water quality criteria (LARWQCB 2013). The proposed copper TMDLs, which will likely be implemented in 2015, is based on a TDML program implemented in San Diego in 2005 where conversion to non-copper based boat paint and hull cleaning are the main implementation strategies being used to reduce surface water copper concentrations (SDRWQCB 2005). This TMDL is referred to as the Shelter Island Yacht Basin (SIYB) TMDL. At all three of these locations there are numerous boats (2000-8000) densely packed into sheltered areas with poor flushing, which greatly contributes to exceedances of the CTR (Singhasemanon et al. 2009)

However, there is some uncertainty regarding the development of the SIYB TMDL because of the limited available data and input assumptions used in 2005. Additionally, site specific copper toxicity effects were not considered for the SIYB. Furthermore, recent results from SIYB TMDL monitoring indicate that although the program has reduced concentrations of copper concentrations in surface water, it was not as effective as anticipated nor a feasible means to achieve water quality criteria.

Because of the uncertainty associated with data assumptions and site specific toxicity, development of an effective TMDL for copper needs to go beyond what has currently been done in California. If a similar approach to the SIYB TMDL development is used by the Santa Ana and Los Angeles RWQCBs, additional research and data evaluation should be conducted. This research identifies key elements of TMDL development that should be considered prior to implementing a TMDL program. The findings of this research could play an important role in developing regional water quality policies for copper and other pollutants.

1.4.1 TMDL available data and input assumptions

For the SIYB TMDL development, the leach rate of copper from boat paint was estimated using an average leach rate from two studies conducted in 2003 (SDRWQCB 2005) that had significantly different leach results. By using an average of two widely variable results, there are inherent increases in the margin of error (i.e., uncertainty) associated with the leach rate input parameter used to estimate copper loadings from boat paint. Since 2005 (after the SIYB TMDL was implemented), additional studies have been conducted on leach rates from copper boat paint (Singh and Turner 2009; Ytreberg et al. 2010; CDPR 2014; Early et al. 2013) that may provide more reliable and defensible data for calculating an average leach rate or determining what leach rate would be required to meet water quality standards.

Additionally, copper loading estimates were re-evaluated in San Diego Bay in 2013, which determined that boat hull cleaning contributed to significantly greater copper loadings than the estimates developed in 2005 for SIYB (Early et al. 2013). Therefore, newer information and potentially more appropriate data should be obtained and evaluated to reduce uncertainty in copper loading estimates described in Chapter 2.

1.4.2 Site specific copper TMDL development

Prior to developing a TMDL program, site-specific information should be considered, particularly for toxicity thresholds to aquatic organisms. USEPA's National Water Quality

Criteria Recommendations are used as the default values for the protection of the Nation's water bodies. However, the USEPA has methods available to develop site-specific water quality criteria for a variety of pollutants, water effects ratio (WER) testing or the use of the biotic ligand model (BLM). These methods allow for adjustments to threshold concentrations for metals in aquatic systems to account for site-specific conditions, such as pH, dissolved organic content or total dissolved solids, which can frequently reduce metal toxicity (USEPA 2007a).

Questions regarding the actual effect of copper and the 3.1 μg/L water quality standard for the chronic protection of aquatic marine organisms have been raised in San Diego (Weston 2012) and San Francisco (Buck et. al 2007). In 2011, water quality studies conducted by the University of San Diego on a TMDL showed elevated levels of copper, but the elevated levels did not affect toxicity levels for aquatic organisms (Neira et al. 2011; Neira et al. 2011; Capolupo et al. 2011).

Studies conducted in San Francisco determined that over 99 percent of the cupric ions in the San Francisco Bay are complexed, thus total dissolved copper concentrations in the bay exceeding the water quality criteria are not toxic to aquatic organisms (Buck et. al 2007). In San Francisco, the local water quality agency (i.e., San Francisco Regional Water Quality Control Board) are using these findings to develop more appropriate copper water quality criteria for San Francisco Bay.

Therefore, since site specific conditions, metals speciation and complexation can play a significant role in mitigating copper toxicity, site specific factors should be considered prior to implementing a TMDL program. Evaluation on the effect of how using site specific water quality criteria would affect TMDL programs for copper is presented in Chapter 2.

1.4.3 Copper TMDL effectiveness

Some studies have also indicated that TMDLs, while they do reduce concentrations of toxic chemicals in surface water, are not as effective as anticipated nor feasible as a means to achieve water quality criteria. The SIYB TMDL reduction program focused on copper loading from boats is being implemented in phases for a reduction of 10 percent in 2012, 40 percent in 2017, and 81 percent in 2022 (SDRWQCB 2005). At SIYB, the 10 percent reduction has been achieved by means of a boat paint conversion grant program, but the next interim target (40 percent reduction in 2017) and final TMDL targets are expected to be more challenging to achieve (Weston 2012). Consequently, more cost effective and efficient strategic approaches will likely be necessary to meet water quality criteria for both currently implemented and proposed copper TMDL programs.

Therefore, the effectiveness of copper TMDL programs should be evaluated. The effectiveness of using copper TMDLs to achieve water quality standards is determined through evaluation of currently implemented TMDL programs identified as part of this research and discussed in Chapter 3. Effectiveness is evaluated based on feasibility and achievement of water quality goals.

Feasibility is a metric used to evaluate effectiveness based on the ability to implement a water pollution control program. The feasibility evaluated based on several key elements including available information and research needs, public and private sector support and the availability of effective alternatives to toxic AFPs. The ultimate goal of the CWA is maintaining and restoring the integrity of the nation's waters by achieving water quality standards. However implementing a TMDL program does not ensure that water quality standards will be achieved. A successful TMDL program should result in achievement of water quality standards.

1.5 Research Summary

The primary objectives of this research are to: evaluate methods used for developing copper TMDLs and identify key elements and uncertainty in TMDL development methods for copper (Chapter 2); evaluate the effectiveness of using copper TMDLs to achieve water quality criteria using case studies and evaluate and compare effectiveness of TMDL programs for achieving water quality criteria (Chapter 3); and present research conclusions and make recommendations for effective approaches to achieve water quality standards for copper in California (Chapter 4).

CHAPTER 2
EVALUATION OF METHODS USED FOR DEVELOPING COPPER TMDL

This chapter evaluates the methods for developing copper TMDLs by providing an overview of the CWA and TMDL regulatory framework, presenting the TMDL development process, discussing copper water quality standards and TMDLs in California, and identifying data gaps and uncertainties.

2.1 Regulatory Overview

Section 303(d) of the Clean Water Act (CWA) enacted in 1972 and administered by U.S. Environmental Protection Agency (USEPA) requires each state to identify impaired waters within their state that exceed water quality standards for a variety of pollutants (e.g., metals, pesticides, nutrients) applicable to that water body's designated use (e.g., recreational activities, drinking water source). The CWA establishes a "rebuttable presumption" that all waters of the United States can attain beneficial aquatic life designations (e.g., fishing, recreation). A rebuttable presumption is a legal assumption that is taken to be true unless someone comes forward to contest it and prove otherwise. Total maximum daily loads (TMDLs) are an approach that is developed and implemented by individual states with USEPA oversight and approval as a means to achieve applicable water quality standards for impaired water bodies to restore them to their designated use (USEPA 1983a, b, 1987, 1994).

A TMDL determines the maximum amount of pollutant loading a water body can sustain and still achieve water quality standards. TMDL programs provide the framework to allow states to establish and implement pollution control and management plans to comply with the CWA. Pollutant loadings are established for both point and nonpoint sources of pollution (USEPA 1991).

The following sections discuss the regulatory process and establishment of water quality standards.

2.1.1 Regulatory process

Under the CWA, each state employs its own process for adopting TMDLs or other remediation plans for their impaired waters. California complies with CWA requirements through implementation of the 1969 state Porter-Cologne Water Quality Act (PCA). The CWA requires the development of a TMDL and the PCA requires the development of detailed planning documents (e.g., watershed basin plans) to achieve the TMDL goals.

Under PCA, the nine Regional Water Quality Control Boards (RWQCBs) in California identify beneficial designated uses and water quality standards for the water bodies in their region of the state and develop watershed basin plans to manage those waters. They also identify impaired water bodies based on pollutants that exceed water quality standards and develop plans to restore the water bodies to their beneficial designated use. In accordance with federal and state laws, the RWQCBs have developed, or are in the process of developing TMDLs for listed water bodies. The RWQCBs comply with the CWA and PCA requirements by developing TMDLs for specific pollutants in an impaired water body. Each RWQCB creates their own TMDL implementation plan that is adopted and approved by the State Water Resources Control Board (SWRCB) and USEPA, and amended into the regional watershed basin plan (CFW 2013).

2.1.2 Water quality standards

Water quality standards are fundamental for a water quality-based approach to pollution control, such as TMDLs and National Pollutant Discharge Elimination System (NPDES) permits, and are integral for watershed management. Water quality standards allow for establishment of water quality goals, monitoring of water quality to provide information on policy decisions, calculation of TMDLs and NPDES discharge limitations for point sources, issuing of certifications or permits for activities that may affect water quality, and development of water quality management plans.

2.1.2.1 National water quality standards

USEPA's first promulgated water quality standards program was initiated in 1975 (USEPA 1986). The water quality standards program was of relatively low priority at that time, which was evident in its minimal requirements. There were few requirements on designating water uses, nor were there procedural guidance documents. Toxic pollutants were not mentioned nor were any specific numeric criteria provided. However, states were required to comply with the national program.

Response to the initial regulation by the states varied and some were deemed by USEPA as inadequate. In the late 1970s, it became apparent that to control pollutants from entering surface water more stringent strategies would be required. The point source discharge permit program for industrial sources, which was the primary pollution control strategy, could not comprehensively address pollution issues to impaired water bodies. Therefore, water quality standards needed to be better developed and USEPA moved to strengthen the water quality program.

In 1983, USEPA revised the Water Quality Standards Regulation for states to include toxic criteria requirements. States may use the criteria developed by USEPA or modified criteria to reflect site-specific conditions or other scientifically defensible methods. USEPA also issued program guidance on the interpretation and implementation of the Water Quality Standards Regulation (USEPA 1983, 1994).

In 1990, to accelerate compliance with the CWA, USEPA began to promulgate numeric water quality criteria for states that had not adopted sufficient water quality standards for toxic pollutants under the National Toxics Rule (USEPA 1992). The National Toxics Rule was revised in 1995 and changed the criteria for metals to be based on the dissolved form instead of the total recoverable amount, which included copper (USEPA 1995). USEPA's water quality standards are still in effect today, known as the National Water Quality Criteria Recommendations, but now include many more specific regulatory and procedural requirements.

2.1.2.2 Site specific water quality standards

The USEPA recognizes that the National Water Quality Criteria Recommendation for total dissolved metals, such as copper, lead, and zinc, may be more or less protective than estimated. The protectiveness of the water quality criteria depends on site specific characteristics, such as diversity and sensitivity of aquatic organisms and water quality measurements (i.e., hardness, pH, dissolved organic matter, total suspended solids, and chemical concentrations; USEPA 1994).

The National Water Quality Criteria Recommendation only takes regulatory effect when it has been promulgated or adopted as a state's water quality standard based on a water body's designated use (USEPA 1983a, b, 1987, 1994). A state's water quality standard may be the same numerical values as the criteria developed by USEPA or states may adjust water quality criteria to reflect local environmental conditions and human, fish, and wildlife exposure patterns. Additionally, states may use different data and assumptions than USEPA to derive criteria that are scientifically defensible and protective of the integrity of a water body's designated use.

In 2000, USEPA found that California's water quality standards did not meet the requirements of the CWA. Therefore, USEPA promulgated federal water quality criteria for toxic pollutants for the state under the regulation of the California Toxics Rule (CTR: USEPA 2002a). In 2003, site specific numeric copper and nickel water quality criteria (referred to as

Site-Specific Objectives in California) for south San Francisco Bay were developed and adopted by California. USEPA determined that these Site-Specific Objectives protected the integrity and designated uses of waters in south San Francisco Bay as required under the CWA. Therefore, USEPA withdrew the promulgated federal aquatic life copper and nickel criteria for south San Francisco Bay (USEPA 2003). In 2007, the copper site specific objective was amended to include additional portions of San Francisco Bay. Using site specific objectives, the copper water quality standards are currently being met in San Francisco Bay, however the quality of the water must be still be maintained to prevent water quality degradation (SFRWQB 2011).

Two commonly used options exist for adjusting site-specific water quality criteria for metals: 1) Water-Effect Ratios (WERs), which recalculate the water quality criteria based on specific aquatic organisms that inhabit the water body, and 2) Biotic Ligand Model (BLM), which is a predictive model that estimates the concentration of a metal that will adversely affect aquatic organisms. Both WER and BLM methods are approved by USEPA and have available national guidance documents (USEPA 1994; Stephan et al. 1985). Both WER and BLM studies are also in accordance with the CTR for dissolved metals (USEPA 2002a).

2.1.2.2.1 Water-effect ratios

WER is one of several procedures that can be used to develop site-specific water quality objectives. In 1994, USEPA developed and recommended WER procedures for determining site-specific values (USEPA 1994). WER studies are used to develop criteria adjustment factors that account for the effects site-specific water characteristics have on pollutant bioavailability and toxicity to aquatic life. WER studies can result in more or less protective criteria, depending on a water body's site-specific conditions. WER testing results are used to determine if differences exist between the toxicity of a pollutant in laboratory water (i.e., control sample) and site water (Carlson et al. 1984; USEPA 1983, 1992, 1994). The WER test results in a ratio of measured toxicity in site water to toxicity in reference or control water where toxicity equals the median effective concentration or EC50 (WER = Site Water EC50/Control of Reference EC50).

Numerous WER studies have been conducted nationally to determine site specific standards for metals. The majority of these studies were focused on copper and several were conducted in California (Carlson et al. 1986; S. R. Hansen & Associates 1992; USEPA 1992; Diamond et al. 1997a; Diamond et al. 1997b; City of San Jose 1998; Rosen et al. 2005; Larry Walker Associates 2006; Earley et al. 2007, Weston 2011). In California, when a final WER value is developed and approval by a Regional Water Quality Control Board (RWQCB) and USEPA, the CTR water quality standard is multiplied by the WER to calculate the Site Specific Objective (SSO) (WER x CTR criterion; SFRWQCB 2007). As shown on Table 1 the results of WER studies and the resultant WER ratio and SSO indicate that the CTR for copper is overprotective (i.e., below the SSO derived toxicity result).

Table 1. Measured and BLM-Predicted Marine WERs (or Toxicity) in California

Site	SSO tests	Result	Calculated SSO (ug/L)	References
San Diego Bay	WER	Measured Average. WER = 1.26 (North Bay) 1.90 (South Bay)	3.91 5.89	Rosen et al. 2005, Chadwick et al. 2008
	BLM-Predicted WER	BLM-Predicted WER = 1.34 (North Bay) 1.76 (South Bay)	4.2 5.5	Rosen et al. 2005, Chadwick et al. 2008
Shelter Island Yacht Basin, San Diego Bay	Measured Toxicity	EC50 (dry, wet season)	8.9 10.2	Capolupo et al. 2011
	BLM- Predicted toxicity	BLM-Predicted Average. EC50 (dry and wet season)	8.8 10.9	
South San Francisco Bay	WER	Measured Average. WER = 4.79	10.8	Tetra Tech et al. 2000
	BLM-predicted toxicity	BLM-Predicted EC50	6.9	
North (of Hayward) San Francisco Bay, San Pablo Bay	WER and Measured Toxicity	EC50	6.0	SFRWQCB 2011
Mugu Lagoon, Ventura County	WER	Measured Average. WER = 1.51 (dry season) 3.58 (wet season)	4.7 11.1	Larry Walker Associates 2005

Notes:
BLM = biotic ligand model
WER = Water Effect Ratio
EC50 = 50 percent effect concentration
SSO = Site-Specific Objective

2.1.2.2.2 Biotic ligand model

The biotic ligand model (BLM) can be used to provide another site specific line-of-evidence that validates the bioavailability and toxicity associated with dissolved metals. The BLM is a model used to predict toxic effects thresholds of metals to aquatic organisms using local water chemistry inputs (e.g., pH, dissolved organic carbon, salinity; Di Toro et al. 2001, Santore et al. 2001). The BLM results in a predicted WER ratio of measured toxicity in site water to toxicity in reference or control water where toxicity equals the median effective concentration or EC50 (BLM-Predicted WER = Site Water EC50/BLM-Predicted Control of Reference EC50).

Numerous BLM studies have been conducted to develop predictive toxicity models for a variety of aquatic organisms and metals, including copper (Santore et al. 2001; De Schamphelaere and Janssen 2002; DeSchamphelaere et al. 2002; Heijerick et al. 2002; HydroQual 2011; Paquin et al. 2002; Weston 2011; Capolupo et al. 2011). The BLM predicted copper toxicity results have been substantiated by studies with results based on aquatic toxicity testing (e.g., WERs) as shown in Table 1, and indicate that the CTR for copper is overprotective when the BLM-Predicted WER is multiplied by the CTR criterion. The advantage of the BLM is that it provides more accurate water quality standard estimates faster and less expensive that deriving a WER. As shown is Table 1, at SIYB toxicity tests were also conducted with site water, which validate the BLM results (Capolupo et al. 2011).

The BLM is the basis of USEPA's 2007 national recommended freshwater water quality criteria for copper (USEPA 2007a). The USEPA is considering revising the marine copper criteria using BLM as a basis (HydroQual 2011). In 2008, a draft marine BLM became available and is anticipated to be included into the next revision of the national recommended marine water quality criteria for copper. USEPA is reviewing the marine copper BLM and its potential for implementation. Despite still being draft, the draft saltwater

BLM is still useful tool to estimate site specific water quality standards for copper, if used cautiously, until it has been further reviewed and formally accepted by the scientific and regulatory communities (CPDP 2014).

2.2 TMDL Development Process

A TMDL stipulates the maximum amount of a pollutant that a water body can receive and still meet applicable water quality standards. The process of developing TMDLs involves several tasks and may require substantial effort and resources. Major tasks involved in the TMDL development process include the following:

- Site specific characterization
  - Characterizing the impaired water body and its watershed
  - Identifying the relevant pollutant sources to the water body
- Applying the appropriate water quality standard
- Calculating the pollutant loading capacity of a water body using appropriate modeling analyses and input assumptions to achieve water quality standards
- Identifying source allocations (e.g., load allocations) required to achieve water quality standards

TMDL program plans typically present the research results and evaluations using the information from the tasks described above to determine a water body's pollutant loading capacity. Each of these tasks (or TMDL program elements) is further discussed in the following sections.

2.2.1 Site specific characterization

Developing a TMDL begins with characterizing an impaired water body and its watershed. This task begins with the collection of vast amounts of data on site specific factors including water quality, point source discharge, spatial extent, precipitation, soils, geology, topography, and land use (e.g., industrial, agricultural, residential) within an impaired water body's watershed. Impaired segments of the water body within the watershed are identified, along with a list of potential pollutants causing the impairment. The source evaluation should include an identification of the point and nonpoint sources of the potential pollutants of concern, including location of the source(s) and the quantity of the pollutant loading (e.g., liters or grams per day).

2.2.2 Applying appropriate water quality standard

As described in Section 2.1.2, an appropriate water quality standard should be established prior to developing a TMDL since the TMDL load allocations are based on achieving the applicable water quality standards. A TMDL program is required to provide a numeric water quality standard for a toxic pollutant, which is used to evaluate whether or not the applicable water quality standard is achieved. The TMDL determines the amount of pollution reduction needed to achieve the water quality standard.

2.2.3 Calculating the TMDL pollutant loading capacity

Once water quality standards are targeted for a water body, the TMDL program determines allowable pollutant loading to achieve the applicable water quality standard. The allowable pollutant loading estimates are then allocated among the identified sources of the pollutant. The pollutant sources must adhere to the specified allocations

2.2.4 Load allocations

TMDL programs allocate allowable pollutant loading between the point sources and the nonpoint and natural sources, with some amount of the total load set aside as a margin of safety (MOS) that accounts for uncertainty in modeling and calculating pollutant loading estimates. The wasteload allocation (WLA) is the total allowable pollutant load from all point sources (e.g., permitted municipal, industrial dischargers). The load allocation (LA) is the allowable pollutant load from nonpoint sources (e.g., agricultural, residential runoff, marinas) and natural sources (e.g., runoff from natural areas or atmospheric deposition). A mathematical equation is used to determine the TMDL allocations, as follows:

$$\text{TMDL} = \Sigma\, WLA + \Sigma LA + MOS$$

Where:

WLA = wasteload allocation. The portion of the TMDL allocated to existing and/or future point sources.

LA = load allocation. The portion of the TMDL allocated to non-point sources and natural background levels

MOS = margin of safety. The portion of the TMDL that accounts for any uncertainty associated with the relationship between pollutant loads and receiving water quality. The MOS can be provided by applying conservative analytical assumptions or by reserving a portion of loading capacity.

2.3 Copper Water Quality Standards and TMDLs in California

In 2000, the USEPA promulgated the California Toxics Rule (CTR) prescribing numeric water quality criteria for priority toxic pollutants. In 2000, the SWRCB adopted the "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California (State Implementation Plan)", which established implementation provisions for priority pollutant criteria promulgated by USEPA under the CTR (SFRWQCB 2007). The State Implementation Plan authorizes the State Board to adopt site specific objectives instead of the CTR criteria when the State Board determines it is appropriate to do so. Site specific objectives are typically determined appropriate if a water quality standard cannot be achieved in an impaired water body, or if a National Pollutant Discharge Elimination System (NPDES) permit holder demonstrates that it does not, or may not in the future, meet an existing or potential effluent limitation based on the water quality standard through reasonable treatment, source control and pollution prevention measures (SFRWQCB 2007).

The leaching of copper from antifouling paints (AFPs) used on recreational boats was determined to be the major source of copper pollution in a large California boat basin known as the Shelter Island Yacht Basin (SIYB) in San Diego Bay (SDRWQCB 2005). Water column levels of dissolved copper at SIYB exceeded the CTR for copper, impairing its beneficial use designation. In the past, monitoring data used in the evaluation of AFP pollution in California have been largely generated from the San Diego Bay region (Singhasemanon 2005). More recently, an increase in the development of copper-related Total Maximum Daily Loads (TMDLs) and additional water bodies in California being placed on the impaired CWA section 303(d) list, challenge the presumption that this issue is only limited to San Diego Bay. AFPs are suspected as being the significant source of copper in two other large boat basins in Southern California, Marina del Rey and Lower Newport Bay (LARWQCB 2013; USEPA 2002b).

2.3.1 Copper Water Quality Studies and Results

2.3.1.1 San Francisco Bay

In San Francisco Bay, SSOs were developed for dissolved copper and amended into the Bay Plan in 2011 (SFRWQCB 2011) on two separate occasions for south San Francisco Bay and north San Francisco Bay. The SSOs were developed because the copper CTR was not being met and because toxicity studies indicated that copper concentrations in San Francisco Bay exceeding the CTR were not toxic to aquatic organisms (Buck et al. 2006; SFRWQCB 2011; Tetra Tech et al 2000). A Bay Area-wide collaborative effort was conducted with the SF RWQCB and scientists to conduct testing, so that defensible data could be used to develop the copper SSOs (Arnold and Hicks 2007). The effort was largely funded by municipalities since water treatment plants were determined to be the dominant copper source. After several years of testing the SFRWQCB adopted the SSOs, thus preventing the need to implement a TMDL program for copper in the Bay Area.

2.3.1.2 CDPR study

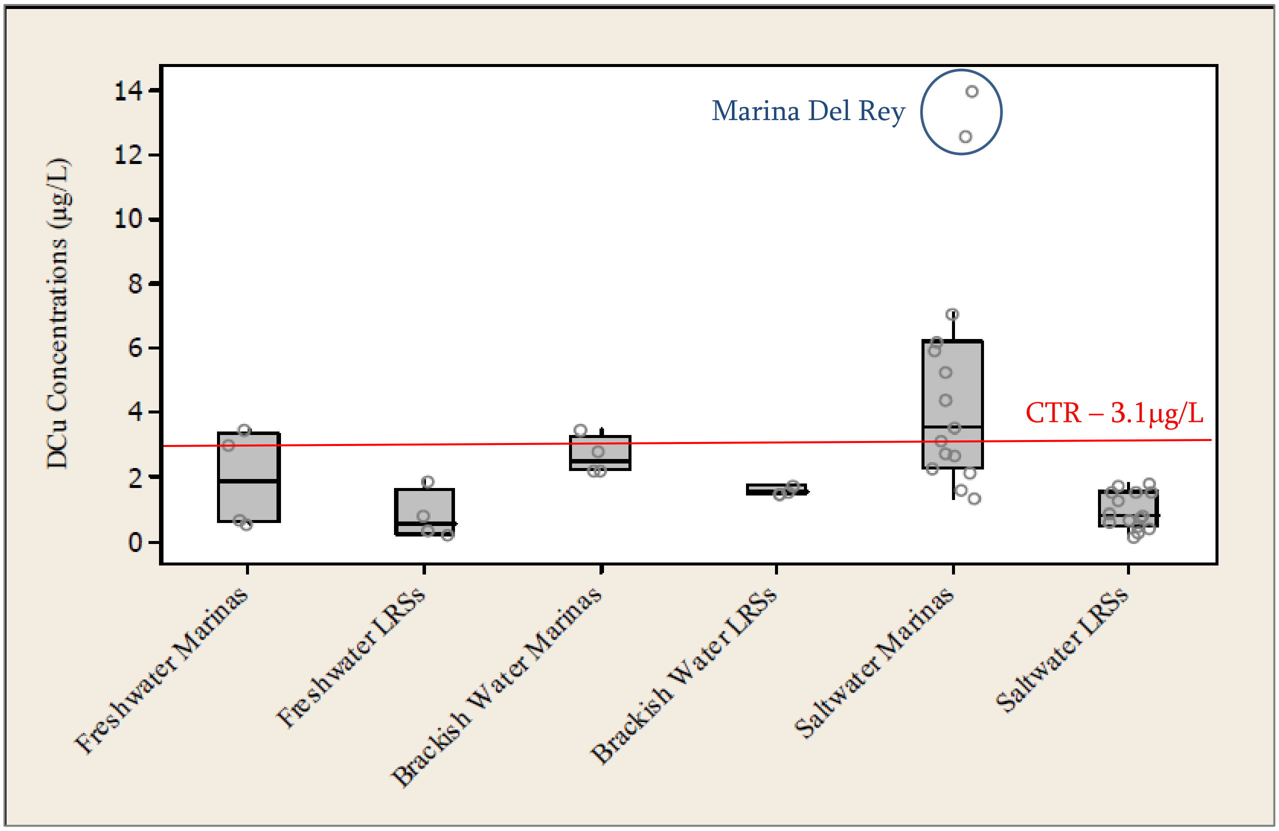
In California, CDPR registers AFPs since they are pesticides. In AFPs, active ingredients are often referred to as biocides, of which copper is a popular biocide frequently used AFPs. Copper is present in more than 90 percent of California' registered AFPs (Singhasemanon et al. 2009). In 2006, the CDPR began to investigate AFP use and water quality in marinas throughout the state. The impetus for this study was due to the popularity of copper-based AFPs, exceedances of copper water quality standards in marinas, and an implemented copper TMDL predominantly for AFPs (See SIYB- Section 2.3.2). This study focused on copper along with other AFP substances (i.e., zinc and Igarol) at 30 marinas throughout California ranging from freshwater to salt-water.

The monitoring study focused specifically on marinas because they are areas densely packed with recreational and commercial boats that are predominantly painted with AFPs. Marinas are also intended to shelter boats from currents and waves, so seawalls or other structures are used to enclose marinas, which results in poor flushing of water in and out of the marina. Therefore, marinas represent the worst-case water quality conditions resulting from the use of AFPs on boats (Singhasemanon et al. 2009).

The CDPR's California marina monitoring studies have shown that high copper concentrations were found mainly in salt and brackish water marinas (Singhasemanon et al. 2009). Copper-based AFPs are not as commonly applied to boats in fresh water areas because hard fouling organisms (e.g., barnacles, mussels) are marine organisms, and are not a major pest of concern to freshwater ecosystems. Non- toxic AFPs are effective against soft fouling organisms (e.g., algae and aquatic weeds) and are often adequate for use in fresh water.

Therefore, copper-based AFP used for boats in salt and brackish water areas tend to be higher than in fresh water areas.

Figure 1 presents the results from California marinas and associated local reference site (LRS) concentrations by water type from fresh water to salt-water (Singhasemanon et al. 2009). The results presented on Figure 1 show that saltwater marinas have the highest copper concentrations. Of the fifteen saltwater marina median dissolved copper results, nine were above the chronic copper CTR of 3.1μg/L. The two highest median dissolved copper concentrations (12.4 and 13.6 μg/L) were from Marina Del Rey (Los Angeles), which is the largest marina in California with approximately 8,000 boats (nearly four times as many as the second largest marina, SIYB with approximately 2,200 boats). Additionally, the LRS (i.e., background) samples collected from just outside of each of the marinas have much lower median concentrations that are well below the CTR, which further indicates that copper from AFPs is the source of elevated copper to marinas (Singhasemanon et al. 2009).



Source: Singhasemanon et al. 2009

Figure 1. Distribution of Marina Median Dissolved Copper Concentrations by Water Type

Of 47 water samples, developmental toxicity tests on the copper-sensitive embryo of the mussel *Mytilus galloprovincialis.* Eight of these samples indicated significant toxicity due to copper elevated copper concentrations. On 517 samples, copper bioavailability toxicity models were conducted to predict toxicity using site-specific water quality data. The models used included the freshwater biotic ligand model (BLM), the saltwater BLM, and the dissolved organic carbon model. Model results indicated that copper sensitive aquatic organisms, particularly *M. galloprovincialis* in saltwater marinas, were only occasionally exposed to toxic levels of copper despite copper concentrations exceeding the CTR (Singhasemanon et al. 2009).

CDPR also recently compiled a list of leach rates for 169 copper AFP products that were actively registered as of December 2013, using data submitted by registrants (CDPR 2014). Leach rates ranged from 1.0 to 29.6 μg/cm^2/day with an average of 11.1 μg/cm^2/day. Nearly 60 percent of these AFPs were determined to exceed CDPR's recommended leach rate (See Section 2.3.3.1), which was developed to allow most marinas in California to achieve the copper CTR. However, the CDPR could not accurately assess the local and regional use of these pesticides since CDPR does not require reporting of use for most AFPs.

Findings from the CDPR monitoring study are being used by the CDPR, SWRCB, RWQCBs, and other interested agencies to more fully evaluate the potential adverse effects of current AFP use on aquatic organisms. These findings will also help CDPR determine if mitigation actions are needed on a local or a statewide scale (CDPR 2014). CDPRs mitigation strategies are discussed in Chapter 4.

2.3.2 Existing copper TMDLs and allocations in California

In 1996, due to high concentrations of dissolved copper in the Shelter Island Yacht Basin (SIYB) the San Diego Regional Water Quality Control Board placed SIYB on the CWA 303(d) list. SIYB is a popular and large recreational marina located in the north end of San Diego Bay. The high density of recreational boats (approximately 2,200) at SIYB, combined with reduced tidal flushing, has resulted in elevated concentrations of dissolved copper that exceed numeric water quality standards for dissolved copper. In 2005, the San Diego Regional Water Quality Control Board developed the "Shelter Island Yacht Basin (SIYB) TMDL for Dissolved Copper" to address water quality impairment in the SIYB (SDRWQCB 2005). The SIYB copper TMDL was the first copper TMDL implemented in California that focused on reducing copper loading from boat paints to achieve water quality standards.

The water quality standard for dissolved copper at SIYB was set to the numeric water quality standards for dissolved copper as defined in the CTR, which are the same as USEPA's National Water Quality Criteria Recommendations (3.1 µg/L for chronic exposure and 4.8 µg/L for acute exposure; SDRWQCB 2005).

Recreational boats are typically painted with copper-based antifouling paints (AFPs) to prevent buildup of marine organisms on the boat's hull. The copper in AFPs is designed to leach into the environment to prevent marine fouling. However, copper is toxic to a variety of aquatic organisms, not just fouling organisms. The SIYB TMDL program determined that approximately 98 percent of all copper loading to SIYB is attributable to copper-based antifouling paints applied to the hulls of recreational boats (SDRWQCB 2005). As shown in Table 2, the passive leaching of copper from AFPs is 93 percent and hull cleaning of AFPs coated boats are 5 percent of the total loading, respectively (SDRWQCB 2005).

Table 2. Summary of Dissolved Copper Sources to SIYB.

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

Source: SDRWQCB 2005

The loading capacity for dissolved copper discharges into SIYB was determined to be 1.6 kilograms/day (kg/day) or 567 kilograms/year (kg/year), which is 76 percent of the overall reduction of copper loading to meet the TMDL of 567 kg/year, as shown Table 3. The percent reduction of dissolved copper from current loading from each source is also presented in Table 3, which shows that loading due to passive leaching must be reduced by 81 percent and boat hull cleaning by 28 percent from current loading estimates, respectively. Overall passive leaching loading needs to be reduced by 75 percent from the total source loading, whereas boat hull cleaning only needs to be reduced by 1 percent (SDRWQCB 2005).

Table 3. SIYB Copper Allocation Summary.

Source	Current Load (kg/year)	Percent Contribution (%)	Allocation (kg/year)	Percent Reduction From Current Source Load (%)	Percent Reduction from Total Loading to SIYB (%)
Passive Boat Paint Leaching	2,000	93	375	81	75
(Active) Boat Hull Cleaning	100	5	72	28	1
Urban Runoff	30	1	30	0	0
Background	30	1	30	0	0
Direct Atmospheric Deposition	3	<1	3	0	0
Sediment	0	0	0	0	0
Total Pollutant Load	2,163	100	--	--	0
Margin of Safety	--	--	57	--	0
TMDL	--	--	567	--	0
Total Load Reduction	--	--	--	--	76

Source: SDRWQCB 2005

When the SIYB was developed in 2005, reported copper concentrations were as high as 12.0 μg/L (SDRWQCB 2005). Water quality monitoring data collected in 2011 to monitor the effectiveness of the TMDL program determined that all sample results exceeded the CTR, however there was little evidence of toxicity with only one sample exhibiting toxicity. No toxicity was evident at concentrations as high as 11.5 μg/L and the one sample that elicited toxicity had a dissolved copper concentration of 8.1 μg/L (Weston 2012). The average copper concentration in SIYB in 2011 was 8.3 μg/L (Weston 2012), which is still above the CTR goal, therefore even though this concentration below toxic levels, SIYB is still considered "impaired". The 2011 results underscore the importance of developing site specific water quality standards when implementing a TMDL, but also indicate that TMDLs do improve water quality, which was needed at SIYB. Therefore, demonstrating that a combination of copper reduction actions and the development of site specific water quality standards could allow a water body to be delisted from the impaired 303d water body list.

The copper reduction for SIYB was developed to occur in stages over a 17 year period. The SIYB TMDL program included the following compliance schedule to achieve water quality standards (Table 4). As of 2012 (7 years after implementation of the TMDL), Stage 2 has been completed and successfully achieved the required copper reduction of 10 percent (Weston 2012). At SIYB, the 10 percent reduction has been achieved by means of a boat paint conversion grant program, but the next interim target (40 percent reduction in 2017) and final TMDL targets are expected to be more challenging to achieve (Weston 2012). Consequently, more cost effective and efficient strategic approaches will likely be necessary to meet water quality criteria for both currently implemented and proposed copper TMDL programs, as described in Chapter 3.

Table 4. SIYB Copper Loading Reduction Schedule

Stage	Time Period (Years)	Reduction to be Attained by End of Year	Percent Reduction from Current Estimated Loading (%)	Estimated Target Loading	Loading Reduction Attained	Percent Reduction Attained
				(kg/year of dissolved Cu)		
1	2	N/A	0	N/A	N/A	N/A
2	7	2012	10	1,900	1,700	17
3	12	2017	40	1,300	TBD	TBD
4	17	2023	76	567 (TMDL)	TBD	TBD

Source: (SDRWRCB 2014)

2.3.3 Proposed copper reduction strategies

2.3.3.1 State-wide marine boat paint leach rate

Based on the findings of their 2009 report, the CDPR initiated the re-evaluation of 212 copper-based AFP products in 2010 to address elevated copper concentrations in salt water marinas that were primarily due to extensive use of copper AFPs on boat hulls (CDPR 2014). In October 2013, Assembly Bill AB 425 was passed requiring the CDPR to determine a leach rate for copper AFPs used on recreational boats. The CDPR objective was to determine the maximum allowable leach rates for AFPs that would reduce copper concentrations to comply with the current chronic marine CTR water quality standard (3.1 ug/L). The CDPR was also required under AB 425 to make recommendations for appropriate mitigation measures that could be implemented to protect aquatic environments from the effects of exposure to AFPs (CDPR 2014), which are discussed in Section 4.2.4.

CDPR's assessment relied on the Marine Antifoulant Model to Predict Environmental Concentration (MAM-PEC) as a reliable modeling tool to simulate the fate of copper in typical California marinas and to evaluate the effects of reducing copper leach rates may have on water quality. The MAM-PEC model was developed by Dutch researchers in 1999, and has been used worldwide, including the United States to predict environmental concentrations of toxic AFP in a variety of marine environments. Additionally, the U.S. Environmental Protection Agency uses MAM-PEC in their registration for copper products.

The MAM-PEC model is normally used to predict copper concentrations in a marina based on input parameters including the leach rate for a copper AFP. For this study, however, CDPR used the California Toxics Rule (CTR) saltwater chronic criterion of 3.1 μg/L dissolved copper as target output to back-calculate the leach rate needed to achieve the desired dissolved copper concentration in a marina. The CDPR used MAM-PEC to generate a maximum allowable copper leach rate for boats painted with copper AFPs.

CDPR selected the CTR chronic criterion as the statewide target for the reduction of copper loading from AFPs in California marinas because the CTR a criteria are currently enforced by the State Water Resources Control Board and the nine Regional Water Quality Control

Boards. CDPR used data on California marina characteristics and the CTR chronic criterion to ultimately produce a matrix of leach rates that represented five risk management scenario levels that could be used in marinas across the state, relying on data for 20 California salt water marinas (See Section 2.3.1.2) to accurately construct marina scenarios that reflected various levels of copper loading. The lowest marina scenario (Scenario 1) represents marinas with 733 boats, which is the median size among the 20 sampled marinas. Scenario 2 represents marinas with 1,270 boats (75th percentile in size); Scenario 3 represents marinas with 1,833 boats (90th percentile in size); Scenario 4 represents marinas with 2,263 boats (95th percentile in size). Scenario 5 represents marinas with 4,754 boats (largest in size among the sampled marinas), which is comparable to Marina del Rey in Los Angeles County.

Based on CDPR's modeling analysis, the maximum allowable leach rates for each of the five scenarios ranged from 1.12 to 24.60 $\mu g/cm^2/day$. The CDPR recommends the establishment of the maximum allowable copper leach rate for AFP products at 9.5 $\mu g/cm^2/day$, under the condition that in-water hull cleaners follow California Professional Divers Association (CPDA) best management practice (BMP) methods of soft-pile carpet and that cleaning cannot be performed more frequently than once per month. For copper AFP products that do not require in-water cleaning, CDPR recommends the establishment of the maximum allowable copper leach rate at 13.4 $\mu g/cm^2/day$, under the condition that in-water hull cleaning is prohibited (CDPR 2014).

2.3.3.2 Regional (TMDLs)

The Santa Ana and Los Angeles Regional Water Quality Control Boards (RWQCBs) have begun development of a copper TMDL program. The proposed copper TMDL includes an implementation plan for reducing copper concentrations in Marina del Rey and Newport Bay, since copper exceeds the marine surface water quality criteria in those areas (LARWQCB 2013). The proposed copper TMDL, which will likely be implemented in 2015, is based the TDML program implemented at SIYB in 2005 where conversion to non-copper based boat paint and hull cleaning are the main implementation strategies being used to reduce surface water copper concentrations (SDRWQCB 2005). The proposed TMDL would focus on reduction of copper AFP, since it is evident that marinas and boats coated with marine AFPs are the predominant source of elevated copper concentrations in a water body (Singhasemanon et al. 2009; SDRWQCB 2005). The proposed TMDL will affect approximately 80 percent of all boats in Newport Bay or Marina Del Rey that would be required to convert to non-copper based AFPs. Site-specific data collected in recent studies indicating exceedances of the CTR support the specified reduction actions in the TMDL. However, the development of SSOs has not yet been conducted or initiated.

By avoiding the need to develop a TMDL, such as was done in San Francisco Bay with the development of copper SSO, the cost of developing and maintaining a TMDL program could also be avoided. A SSO could also eliminate the need for an ineffective TMDL that would not meet the required water quality standard.

2.4 Recent Findings, Data Gaps and Uncertainty

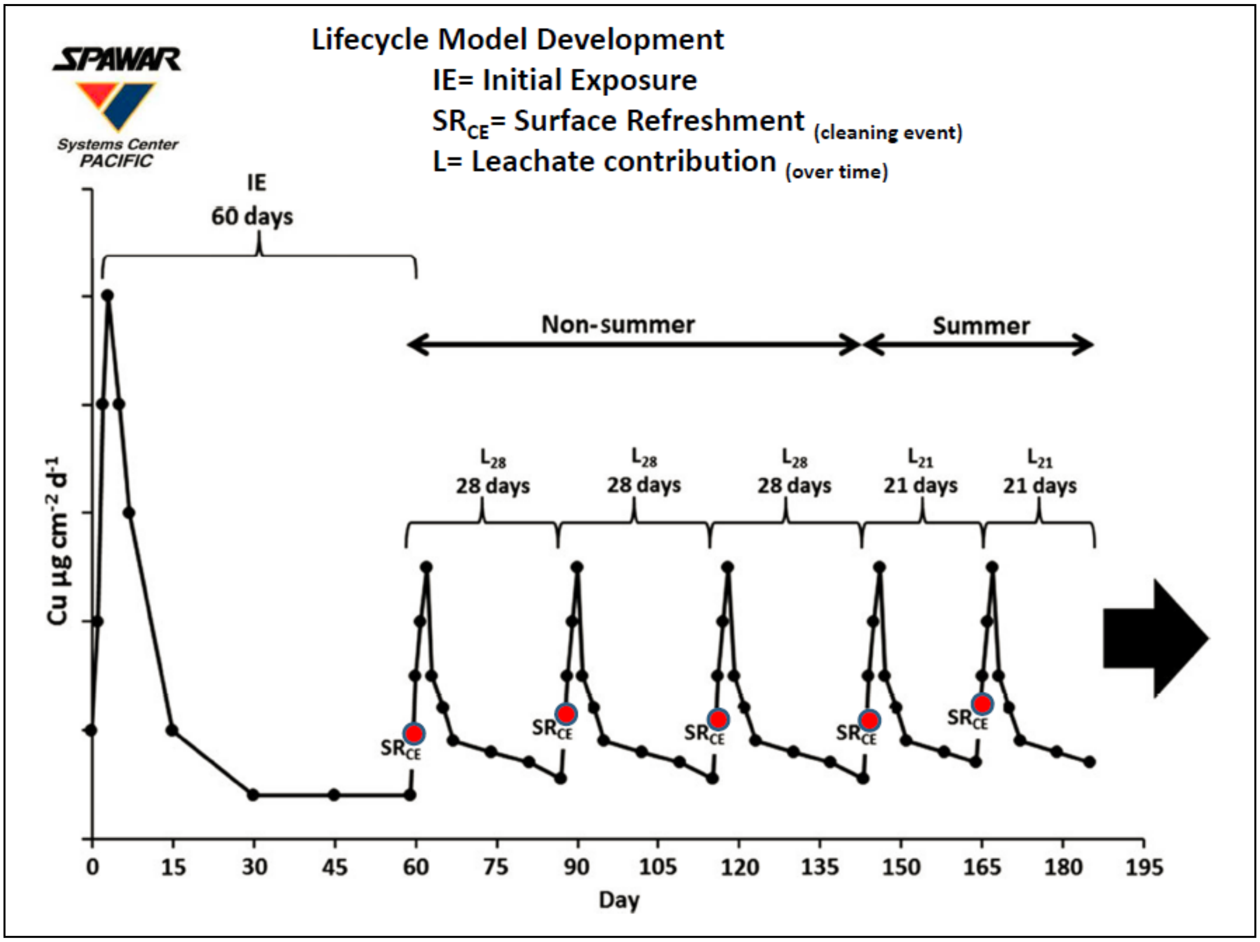
This section presents uncertainties in developing copper TMDLs due to the availability of data at the time of TMDL development or inherent uncertainty associated with modeling.

2.4.1 Recent copper loading estimates

A recent study conducted in San Diego Bay (Early et al. 2013) demonstrated that hull cleaning contributes more to copper loading than previous thought. The Early et al. (2013) study determined that hull cleaning can contribute 40 - 60 percent of the copper loading to a marina. These recent copper loads are remarkably different than the Shelter Island Yacht Basin (SIYB), which estimated passive leaching from boats as 95 percent of the loading, and 5 percent of the loading from hull cleaning.

Early et al. (2013) presented the results from research conducted on the leaching of copper from antifouling paints using two different methods to capture copper released from the paints. One method measured the passive leaching of copper from the paint and the other simulated cleaning of the paint and measured subsequent copper release. The major goal of the study was to accurately establish representative leach rates from two common copper based AFPs types and to measure the impact of underwater hull cleaning activities, which are a common practice in California's coastal marinas, on these leach rates. Panels coated with copper-based epoxy (i.e., hard) and ablative (i.e., soft) antifouling paints applied onto fiberglass panels and exposed in San Diego Bay for several months were used to evaluate environmental loading via continuous passive leaching and underwater cleaning events (Early et al. 2013). Control (i.e., never cleaned) and treatment (i.e., cleaned) panels were deployed concurrently and allowed to foul over the first two months. Passive leach rate measurements were made on all panels throughout the study. On Day 60, treatment panels were then cleaned using one of two methods (BMP or non-BMP). The BMP method was an industry-recommended best management practice using soft-pile carpet. The "non-BMP" method involved a more aggressive procedure using a medium duty abrasive pad for fouling removal (Early et al. 2013).

As shown in Figure 2, there was an initial spike in passive copper leaching following submersion of the panels in seawater for the first 3 days, followed by a rapid decrease in leach rates until day 15 (Early et al. 2013). All the panels reached a steady state flux rate of about 3.0 µg/cm2/day, by day 30. The magnitude of release rates differed between the BMP and non-BMP test treatments for both paint types. Subsequent to the cleaning event, non-BMP treatments had leach rates that were 2.5 times greater than BMP treatments. This result suggests that the BMP (required as part of the California Professional Divers Association's certification program) is effective at reducing copper leach rates compared to non-BMP. Peak leach rates also differed among tested scenarios with the initial exposure being the highest, followed by the non-BMP treatment, and then the BMP treatment. Peak dissolved copper leach rates ranged from approximately 10 to 47 μg/cm² /day for the various leaching scenarios (Early et al. 2013).



Source: Early et al. 2013

Figure 2. Graphical representation of copper leach rates of leach rates over time

These findings indicate that not only does the copper leach rate spike as a result of the cleaning event, the amount of dissolved and particulate copper in the water column increases as well (Early et al. 2013). The release of fouling, biofilm, paint particles, and copper is cumulatively visible as a plume in the water during actual underwater boat hull cleaning episodes. Dissolved copper releases during the cleaning event were more than 3 times higher for non-BMP versus BMP. Using the copper leach rates and emission amounts that were generated, the study researchers were able to calculate the cumulative emissions for key time periods (i.e., 3 weeks and 3 years). Three weeks is a typical summer interval for cleaning events for recreational boats in Southern California. The results also suggest that copper released during cleaning events may be more bioavailable to organisms than copper released during initial exposure from passive leaching (Early et al. 2013).

For a typical 40 foot recreational boat, the average annual loading (based on the three year cumulative loading) ranged from 970 to 1,181 gram per year (g/yr) of dissolved copper for epoxy and ablative paints, respectively, when exclusively using the recommended BMP (Early et al. 2013). For use of non-BMP methods, the average annual loading was 1303 or 1780 g/yr of dissolved copper for epoxy and ablative paints, respectively. Under the no cleaning/no use scenario, a 40 foot recreational boat would release 571 g/yr of dissolved copper for the epoxy and 569 g/yr of dissolved copper for the ablative, representing the minimum loading for this boat (Early et al. 2013).

The recent studies demonstrating that hull cleaning contributes to a greater amount of copper loading than previously thought and that it is a greater contributor than passive leaching, which is an important finding to being able to control copper loading from boats. Active leaching from hull cleaning is more feasible to control and implement through cleaning BMPs than it is to control passive loading, which would require boats to be repainted with paints showing non-copper or low copper leach rates (below CDPRs recommended leach rate of 9.5 $\mu g/cm^2/day$) AFPs.

2.4.2 MAM-PEC model

As with all models, the MAM-PEC model has inherent uncertainties. The MAM-PEC model's uncertainties are primarily from two groups of input variables: the physical dimensions of the modeled marina and the copper emission inputs (CDPR 2014). The important parameters related to physical dimensions include marina width, length and outlet width. These physical dimensions affect water volume, dilution, tidal exchange rates and therefore the estimated concentrations of dissolved copper. MAM-PEC assumes a box shaped (square or rectangle) marina, which is not likely the case for every marina. This inconsistency with reality introduces uncertainties to the modeling results since the modeling was not conducted for a specific marina but a generic marina, and in reality, California marinas vary in shape and there is no specific shape that can be considered as highly representative (CDPR 2014).

In addition to physical dimension inputs, there are uncertainties associated with copper emission inputs including boat size distribution, number of boats moving, number of boats at berth, application factor (percentage of boats applied with copper paint) and the underwater surface area of vessels (CDPR 2014).boats. Information regarding boat sizes in California marinas was based on recent surveys conducted on California marinas, for which its size distribution is likely representative of marinas throughout the state (CDPR 2014). The largest uncertainty is from the estimate of underwater surface areas of boats. Only a rule-of-thumb estimate has been developed; methods for more accurate estimations are currently not available. Underwater surface area is one of the most important input variables for the MAM-PEC model since doubling the values of underwater area would also nearly double the estimated concentrations of dissolved copper. A better method for estimating boat hull surface area would greatly reduce model uncertainties. Therefore, additional studies are needed to obtain better estimations on the on the underwater surface areas of boats in California marinas, as well as marina specific estimates.

2.5 Chapter Summary

This chapter presented an overview of federal and state water quality regulations, including the development of water quality standards and water quality improvement strategies, such as TMDLs and USEPA established National Recommended Water Quality Criteria. However, due to the conservative and nationwide protection of these criteria, USEPA allows for the development of site specific water quality standards based on site specific toxicity. In California, the development of site specific standards for copper have been seldom used, despite exceedances of the national criteria, which could be avoided by the development of SSO, as done in San Francisco Bay.

This chapter also discussed the development of a TMDL, which is a strategy used to achieve water quality standards by reducing loading from the predominant sources. Copped based AFPs were confirmed as the major source of copper loading to saltwater and brackish marinas in California. Therefore existing and proposed copper TMDLs are focused on reducing the copper-based AFPs, and their concentration is water primarily from passive leaching. However, more recent investigation concluded that copper loading from boats is about 50 percent less than previously estimated, and that copper loading from hull cleaning is 50 percent more than previously thought. There is still uncertainty in leach rate estimates, which could be improved upon with additional studies, and allow for more accurate copper loading estimates and more effective source reduction strategies.

CHAPTER 3 - EVALUATION OF THE EFFECTIVENESS OF USING COPPER TMDLS TO ACHIEVE WATER QUALITY CRITERIA

The primary goal of this chapter is to evaluate the effectiveness of existing TMDL programs and recommend improvements to the TDML development process. Recent criticisms of the effectiveness of TMDL implementation, program plans and ability to achieve water quality standards are discussed in this chapter. These recent criticisms were the impetus for this research and are further evaluated using data from TMDL programs that have been implemented for more than five years.

3.1 Criticism of Ability of TMDLs to Achieve Water Quality Criteria

3.1.1 Nationally

The U.S. Government Accountability Office (GAO) is a federal agency that works for the U.S. Congress. The GAO investigates how the federal government spends taxpayer dollars, making the government more efficient and effective, and ensures the accountability and equitability of the government.

In 2011, Congress asked the GAO to evaluate the TMDL program on the following four categories: (1) USEPA's and states' responsibilities in developing and implementing TMDLs, (2) what is known about the status of long-established TMDLs, (3) the extent to which such TMDLs contain features key to attaining water quality standards, and (4) the extent to which TMDLs exhibit factors that facilitate effective implementation (GAO 2013).

After reviewing 191 implemented TMDL programs for various water bodies, the GAO found that pollutants had been reduced in many waters, but few impaired water bodies have achieved water quality standards. A sample of 25 of the long established (more than 10 years) TMDL programs reviewed were further reviewed by GAO water resource experts, who noted that seldom do the TMDL programs contain all the key features identified in TMDL guidance to develop and attain water quality standards (GAO 2013). Key features identified by the National Research Council (NRC) and USEPA include: identifying pollution-causing stressors and showing how addressing them would help attain such standards; specifying how and by whom TMDLs will be implemented; and ensuring periodic revisions, as needed (NRC 2001; USEPA 2007 b, c).

The GAO (2013) reported that 17 of 25 long-established TMDLs they reviewed did not show that addressing identified stressors would help attain water quality standards; 12 contained vague or no information on actions that need to be taken, or by whom, for implementation; and 15 did not contain features to help ensure that TMDLs are revised if need be. GAO's (2013) review showed that USEPA's existing regulations do not explicitly require TMDLs to include these key features, and without such features in TMDL programs, impaired water bodies are unlikely to achieve water quality standards.

State agencies reported that for nonpoint source pollution (e.g., storm water runoff), long-established TMDLs generally do not exhibit factors for achieving water quality standards. This is because the CWA predominantly addresses nonpoint source pollution through voluntary and incentivized means by the public (e.g., rebate programs or tax deductions). Based on surveys from state agencies, the GAO reported that 83 percent of TMDLs have achieved their targets for point source pollution (e.g., industrial discharges) through permits but only 20 percent achieved their targets for nonpoint source pollution (GAO 2013).

More than 40 years after passing the CWA, USEPA reported that many of the nation's waters are still impaired, and the goals of the act are not being met. Without changes to the CWA's approach to nonpoint source pollution, water quality goals are likely to remain unattainable (GAO 2013).

3.1.2 State wide (California)

According to the USEPA, in the 40 years since the CWA was established, none of California's impaired water bodies have been fully restored to meet their designated uses (CWF 2013). The State Regional Board estimates that it will take over 400 TMDLs, developed over 13 years, to address California's impaired waters (CWF 2013). The length of time to implement those plans will vary greatly, but the current established processes for restoring impaired water bodies are not working. Progress has been made in the regulation of point sources, which have reduced discharges of specific pollutants from specific sources. However, other pollutant discharges, such as non-point discharges continue without regulation. Regardless of considerable efforts over the last decade, reducing pollution from non-point sources to achieve water quality standards is a challenge under current regulatory frameworks (CWF 2013).

Although millions of dollars have been spent on the development and implementation of TMDLs or other cleanup strategies, California is failing to adequately restore impaired water bodies and there is uncertainty about whether many of the programs that have been implemented will be effective at achieving water quality standards and a water body's integrity. While some efforts relating to specific water bodies have met with success, overall California has not been effectively addressing water quality problems (CWF 2013).

TMDLs can vary in their clarity, goals, and the aggressiveness of the load allocations and pollution reduction requirements, depending on the pollutant the TMDL addresses, and the particular Regional Water Quality Control Board overseeing its development, implementation, and enforcement. In 2011, a California based TMDL work group identified eleven fundamental issues related to poor outcomes in TMDLs and provided recommended solutions (CWF 2013). Policy recommendations to alleviate ineffective TMDLs are discussed in Chapter 4

3.1.3 Regionally (San Diego)

The TMDL for the Shelter Island Yacht Basin (SIYB) took nearly 10 years to implement after identifying SIYB as an impaired water body. Since the TMDL program was implemented in 2005 annual monitoring has been conducted to evaluate if cooper concentrations are reducing and to determine if water quality standards can be achieved (Weston 2012). The results from the 2011 monitoring event indicate that 10 percent reduction has been achieved by means of a boat paint conversion grant program, but the next interim target (40 percent reduction in 2017) and final TMDL targets are expected to be more challenging to achieve (Weston 2012). Consequently, more cost effective and efficient strategic approaches will likely be necessary to meet water quality criteria for both currently implemented and proposed copper TMDL programs.

The 2011 monitoring study was primarily conducted to determine whether SIYB was coming closer to meeting the 10 percent reduction rate required by the end of 2012 (Weston 2012). The results showed a 27 percent reduction in annual dissolved copper loading from boats in SIYB and a 15 percent overall reduction in the annual dissolved copper concentrations in the basin, which exceeded the 10 percent milestone that the basin was required to meet by the end of 2012. The report also stated that the primary reason for lower copper concentrations is reduced slip occupancy in the basin (Weston 2012). A portion of the 27 percent reduction was achieved due to fewer boats mooring in the marina (i.e., more empty slips).

Several studies water quality studies conducted at SIYB or San Diego Bay indicate that dissolved copper concentrations in the water have decreased as compared to previous studies; and are at concentrations that are not toxic to most of the area's aquatic organisms (Capolupo et al. 2011; Neira et al. 2009, Neira et al. 2011). Results from one study indicated that although water toxicity levels exceeded the chronic CTR at all six of the testing stations, evidence of toxicity to marine life was only found at one of the stations (Neira et al. 2011).

The Department of Defense's study, in coordination with the University of San Diego found a disconnect between the water quality and actual toxicity levels. Samples were collected at 15 locations throughout SIYB at two different depths, with tests conducted in March and July 2011. The results found elevated levels of dissolved copper in SIYB in comparison to San Diego Bay, but the elevated levels did not affect toxicity levels for marine life. The toxicity results showed that in only one of the 62 sample locations was the water deemed "somewhat toxic." In addition, samples with dissolved copper levels as high as 8.8 micrograms per liter (μg/L) were determined to not be toxic to aquatic invertebrates (Capolupo et al. 2011).

There is an increasing body of evidence that the CTR is overly protective in SIYB and San Diego Bay. Although dissolved copper concentrations are still well above the existing water quality standards, further studies are needed to understand how site-specific factors affect copper bioavailability in SIYB and San Diego Bay.

3.2 Effectiveness Evaluation

3.2.1 Re-review of the established TMDL program at SIYB

In SIYB, the original study done in 1996 by SDRWQCB determined 95 percent of the copper came from passive leaching copper-based AFPs in the basin, with 5 percent from hull cleaning. However, as of 2013, hull cleaning may actually contribute to up to ten times more of the copper loading than determined in 2005, which could be used to revise the load allocations determined in the SIYB TMDL.

If SSOs were developed for SIYB, it's likely that the SOO could conservatively be around 8 μg/L and be protective of aquatic organisms throughout the year (wet and dry season). When the SIYB TMDL was implemented average concentrations in surface water were as high as 8.0 to 12.0 μg/L of dissolved copper. However, due to the TMDL as of 2011, the average copper concentration in SIYB in 2011 was 7.11 μg/L (Weston 2012). If 8 μg/L was the SSO for SIYB, then the water quality standard would have already been met based on annual average.

As another estimate of how an SOO could affect a TMDL, Table 5 shows how the SIYB copper TMDL load allocations and reduction requirements could change based on adjusting to SOO to 8 μg/L. Instead of an 81 percent load reduction from passive leaching only a 42 percent load reduction would be necessary, which is a much more attainable reduction goal to achieve.

Table 5. Revised SIYB Copper Allocation Summary

Source	2005 SIYB Estimates		Based on the CTR		Based on a hypothetical SSO of 8 μg/L	
	Load Estimates (kg/year)	Percent Contribution (%)	Allocation (kg/year)	Percent Reduction From Current Source Load (%)	Allocation (kg/year)	Percent Reduction From Current Source Load (%)
Passive Boat Paint Leaching	2,000	93	375	81	1160	42
(Active) Boat Hull Cleaning	100	5	72	28	100	5
Urban Runoff	30	1	30	0	30	1
Background	30	1	30	0	30	1
Direct Atmospheric Deposition	3	<1	3	0	3	<1
Sediment	0	0	0	0	0	0
Margin of Safety	--	--	57	--	147	--
TMDL	**--**	**--**	**567**	**--**	**1469**	**--**

Source: SDRWQCB 2005

3.2.2 Non-toxic AFPs

AFP testing has clearly demonstrated that copper based AFPs are the most effective at preventing marine fouling as shown in Figure 3, which shows test plates painted with four different paint types including copper-based, silicon gel, epoxy, and slick (Culver and Johnson 2012). Therefore, there currently is not an effective alternative to copper-based AFPs, however AFP studies are ongoing and it is expected that non-toxic AFPs will be developed with improved efficacy. Additionally, studies comparing the effectiveness of copper based AFPs based on the various leach rate identified by CDPR will also conducted (CDPR 2014) as part of their recommended AFP reformulation described in Chapter 4.

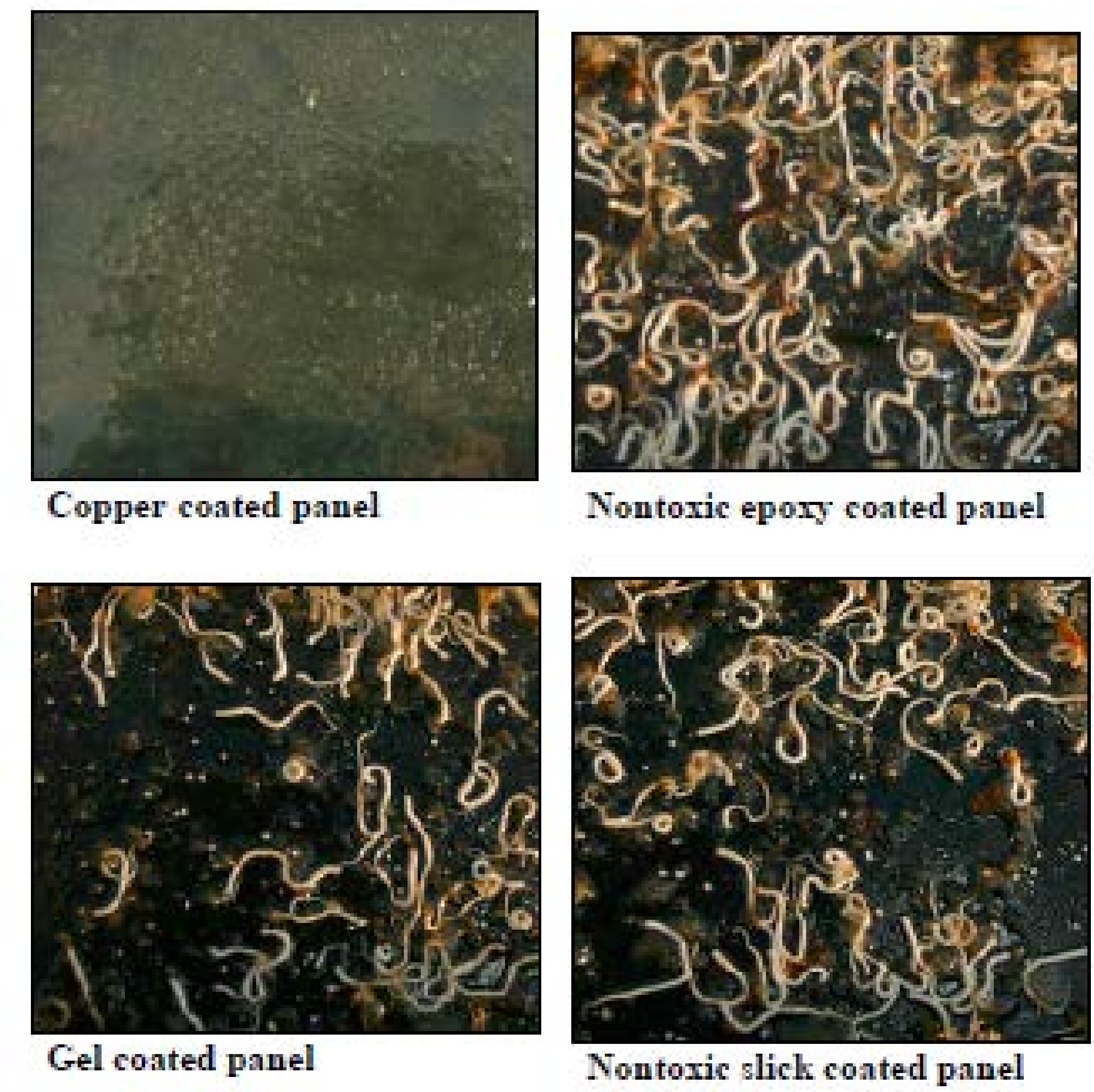


Figure 3. Comparison of Fouling on Four AFPs after 1 Month (Source: Culver and Johnson 2012)

3.3 Chapter Summary

The effectiveness evaluation presented in this chapter determined that on various scales (national, statewide, and regionally), although TMDLs have improved water quality, overall they have not been effective at achieving water quality standards. A re-evaluation of the water quality standards used to develop the TMDL at SIYB indicates that the CTR chronic copper criterion is over protective and could be re-calculated as a SSO. By increasing the water quality standard at SIYB, the water quality standard could already be achieved, thus the copper TMDL would only be required to maintain water quality conditions.

Furthermore, the recent 2013 copper loading study conducted in San Diego Bay (Earley et al. 2013) determined that copper loading from boat hull cleaning may contribute up to 10 times more of the copper loading than estimated in 2005. The increase in copper loading from boat hull cleaning is of importance because TMDL programs can now emphasize multiple reduction strategies and not just the conversion of copper based AFPs. Reducing copper loading from hull cleaning is also a more implementable and less costly strategy than boat paint conversion because best management practices as described in Chapter 4 can be used. This section also presented an evaluation of copper based and non-toxic AFPs to determine the efficacy of AFPs. Copper-based paints are still the most effective AFP on the market.

CHAPTER 4 - CONCLUSIONS AND RECOMMENDATIONS

This section presents the research conclusions and recommendations for development of total maximum daily loads (TMDLs) and evaluation of the effectiveness of TMDL approaches to achieve copper marine water quality criteria in California.

4.1 Conclusions

Based on a review and evaluation of copper TMDLs in California, the California Toxics Rule (CTR) water quality standards are too conservative, which results in overly stringent TMDLs required to meet the water quality standards for the protection of aquatic organisms. These stringent TMDLs may be difficult to achieve. By developing protective site specific water quality objectives, which have been demonstrated to be above the default CTR water quality standards, yet protective of aquatic organisms, a more reasonable TMDL can be developed, which increases the likelihood of meeting water quality standards and is more cost effective. In some cases (e.g., San Francisco Bay) developing site specific water quality objectives allows the impaired water body to meet the water quality standard, thus avoiding the need to implement a TMDL.

4.2 Recommendations

Recommendations are presented as technical recommendations, policy recommendations, and implementation recommendations. Additionally, the California Department of Pesticide Regulation (CDPR) recently released its own recommendations as required under Assemble Bill 425 (CDPR 2014). Recommendations to reduce copper loadings, so that impaired marine water bodies in California can achieve water quality standards are further described in this section.

4.2.1 Technical recommendations

The technical approach to address the pending copper TMDLs includes the following steps:

1. Develop strategy outlining the need to develop a TMDL; and collaborate with the regulators, scientific community, and policy makers.
2. Determine the extent and magnitude of water quality issues in regard to dissolved copper through data review and agree on an approach for calculating a copper toxicity threshold that more accurately reflects site conditions and biological effects.
3. Seek approval of the site specific water quality standards from the State Water Resources Control Board (SWRCB) and U.S. Environmental Protection Agency (USEPA).
4. Develop a monitoring program to assess copper concentrations in surface water relative to the site-specific standard.

4.2.1.1 Site specific water quality standards

Developing site specific water quality standards is the most critical technical aspect for determining if a water body is impaired and needs a TMDL. While copper in the marine system has the potential to be toxic to many aquatic organisms, especially sensitive life stages (e.g., embryo), copper concentrations in several marine water bodies exceeding the CTR have proven not to cause impacts to marine organisms in bays (e.g., San Francisco Bay, San Diego Bay, Newport Bay). There is no doubt that copper in the marine environment can be toxic to many aquatic organisms, but a better linkage between the actual impacts occurring in the water body and the water quality need to be established. Therefore, it is imperative before implementing a TMDL program to develop a scientifically defensible and environmentally protective water quality standard (i.e., SSO) for copper in marine waters. The site specific water quality standard can be used to determine whether the water body should be designated “impaired” for its designated beneficial use. It can also be used to determine if water quality standards are being met, so a program can be developed to monitor and maintain water quality, or if not then can be used as the basis for a TMDL program. Policy makers will greatly benefit from the use of multiple lines of scientific evidence to develop a plan to improve and preserve water quality, thus allowing science to drive the need for meaningful (i.e., useful, effective, implementable) management actions. Governments should establish a task force consisting of members from the scientific community from multiple disciplines that represent both the public and private sectors.

The development of site-specific objectives (SSOs) are supported by the USEPA with methods available to develop SSOs for pollutants. Water effects ratio (WER) testing allows for adjustments to threshold concentrations for metals in aquatic systems to account for site-specific conditions, such as dissolved organic content, and total dissolved solids, which can frequently reduce metal toxicity. WER studies conducted in California marine environments indicate that the CTR is an overly conservative threshold for copper. There is also a draft marine biotic ligand model to predict toxicity using site specific water quality parameters (HydroQual 2011; Singhasemanon et al. 2009). However, the marine BLM has not yet been approved by USEPA, but it is expected to be approved soon and will be a much less expensive and faster means to develop SSOs.

4.2.1.2 Copper source loading uncertainty

Leachate rate studies from various boat paints are a highly discussed topic, of which scientists and regulators have expressed strong and differing opinions. Therefore leach rates may be difficult to reach consensus on, however copper loading from sources have recently been re-evaluated and re-estimated since 2005. Even though one study conducted in 2013 determined copper loading from hull cleaning is significantly more than what was estimated on an annual basis 2005, additional studies should be conducted to confirm the 2013 findings as well as be determined based on site specific conditions, to ensure that the most accurate source loadings are used when developing TMDLs and copper reduction strategies.

4.2.2 Policy Recommendations

Policy approaches include public awareness and education, copper AFP regulation, and TMDL with adaptive management strategies. Each of these policy recommendations are discussed in the following sections.

4.2.2.1 Public awareness and education

Public awareness and education recommendations include:

- Begin a public outreach program to educate boaters of the pending TMDL and address the copper TMDL proactively.
- Begin a public outreach program to educate boaters of copper toxicity and availability of alternative non-biocide boat paint.
- Let boaters know how they can assist in the process.
- Educate the public on converting to alternate hull paints and develop engaged stakeholder group.
- Offer incentives, which can be offered through grant programs for boat paint conversions.

4.2.2.2 Copper AFP regulation and the changing to alternative boat paints

The CDPR, through their pesticide registration process, regulates copper in AFPs. Because the product is legal, the ports, cities, counties, and marinas do not have a way to prevent its use on boats, nor are boat owners violating any laws by using AFPs that are on the market in California. The CDPRs recommendation and copper anti fouling reformulation strategy are discussed in Section 4.2.4.

The changing of boat paint from well-known and effective copper-based AFPs to lesser known and unproven copper-free alternatives will be difficult. There are active grant programs (e.g., Orange County Coastkeeper) that pay for a portion of the costs to boat owners to switch to less toxic alternatives, but there was virtually no interest from the community in making these changes (Orange County Coastkeeper 2013). In Newport Bay a boat paint conversion grant program was implemented. In three years, only six boats participated: two city boats and four private boats. Unfortunately, a bad batch of boat paint required repainting, and three of the private boats switched back to copper-based paints (Orange County Coastkeeper 2013). This lack of participation demonstrates the need for boater education about copper toxicity and a better understanding of the impacts from a copper TMDL program. Additionally, as discussed in Section 3.2.2, copper based AFPs are still the most effective products. Therefore, until effective non-toxic or less toxic AFPs are developed boaters will be reluctant to change boat paints.

4.2.2.3 Adaptive management

A TMDL should include an adaptive management framework, which has been incorporated in other TMDLs (Attachment 2 to Resolution No. R8-2011-0037 Section 4.b.3) as follows:

> *These TMDLs are to be implemented within an adaptive management framework, with compliance monitoring, special studies, and stakeholder interaction to guide the process over time. Information obtained from compliance monitoring will measure progress towards achievement of Waste Load Allocations (WLAs) and Load Allocations (LAs), potentially leading to changes to TMDL allocations; ongoing investigations and recommended special studies, if implemented, may provide information that leads to revisions of the TMDLs, adjustments to the implementation schedule, and/or improved implementation strategies.*

Typically, a justification for an adaptive management framework is required. The developing science of copper-based boat paint impacts, the potential for unknown sources, weather, source control actions and use of best management practices (BMPs), support the need for additional considerations. An adaptive management framework for a copper TMDL could be supported by the following:

- Many copper TMDLs being proposed in California harbors (e.g., Lower Newport Bay, Marina del Rey) are modeled after San Diego's Shelter Island Yacht Basin (SIYB) TMDL. Recent studies from SIYB have demonstrated the following:
    - The amount of copper from passive leaching from boats is much less than what was originally predicted in 2005 for SIYB
    - Hull cleaning contributes more to copper loading than previously estimated in 2005.
    - The copper water quality standard and resulting TMDL are too conservative and overly protective on marine life.
- Evaluations of other source reduction measures (boat paint initiatives, banning/limited use of toxic AFPs, remediation of contaminated sediment, upstream erosion and urban runoff controls) are a data gap. Quantifying those reduction efforts may affect the effectiveness of proposed actions.
- Relative contributions of copper from permitted (e.g., National Pollutant Discharge Elimination System, Municipal Separate Storm Sewer System) and industrial discharges may not have been accurately characterized.
- Unknown sources (e.g., agriculture runoff, undefined sources, boats, and air) may be contributing to current copper loading.
- Seasonal variations
- Changes in boat moorage and maintenance BMP practices

4.2.3 Implementation strategy recommendations

Implementation strategies include:

- Propose an adaptive management TMDL, especially where there is not enough information yet on the feasibility of converting more than 80 percent of boats hulls from copper-based to non-toxic AFPs. This approach would likely involve up-front discussions and could involve the collection of additional data.
- Consider alternate methods of compliance, such as:
    - Water column toxicity must be present with elevated copper to demonstrate need for management actions.
    - Only to the point that is within jurisdiction or authority, since regional copper limitations can only go so far until the state legislates the use of copper-based AFPs.
    - Include use of average copper concentration to define bay-wide copper concentrations, not marina specific
    - Treat each marina as a source that could be permitted for discharges like NPDES permits for boat yards, such that a marina exceeding the CTR could still be in compliance as long as it is not impairing the larger bay or harbor.
- Conduct an economic analysis on boat paint conversion feasibility.
- Convert local government boat fleets (e.g., police, sheriff, Port, State research boats) to alternate boat paints. Keep good records of effectiveness, gas usage, and repainting frequency.
- Look at targeting implementation actions in areas where copper concentrations are highest (e.g., back basins and low flow areas).
    - Consider boat paint conversion only in areas where copper is elevated. The upside is that not all the harbor is impacted. The downside is that it may single out one marina, yacht club, or tenant.

- Consider the feasibility of changing tenant use of an area that has higher copper concentrations to something else (e.g., transient boat docks or sailing center). While it is not possible in the short-term, it could work in the long-term.
- In large marinas with poor flushing (e.g., Marina del Rey or SIYB), consider putting empty slips in the back basins or provide an incentive for this action.
- Consider recommending or requiring hull cleaning only at or near the mouth of the marina or harbor.
- Consider assessing and controlling urban runoff in targeted areas, if appropriate and feasible.

Therefore funding to implement water quality improvement programs would be most effectively spent on:

- Perform analytical and biological testing to support protective SSOs,
- Support technical development of the TMDL,
- Conduct studies to evaluate the effectiveness of BMPs and other source control programs,
- Educate boaters on TMDL issues and AFPs,
- Seek grant funding to assist conversion to alternative non-biocide boat paint.

4.2.4 CDPR mitigation recommendations

In their 2014 report, the CDPR determined the maximum allowable leach rate from boats and made copper mitigation recommendations, which are needed to successfully achieve water quality standards. As part of the CDPR's copper AFP re-evaluation, the CDPR is in current discussion with copper AFP registrants and USEPA regarding reformulation, data requirements (e.g., efficacy), label restrictions and outreach for boaters, boatyards, and marinas. CDPR will also engage with the Water Boards, AFP registrants and key stakeholder groups to further refine and implement the overall mitigation effort. Besides reformulation of copper AFP products, additional recommendations also include:

- Implement maximum allowable leach rates BMPs
- Promote the use of less toxic AFPs or non-toxic paints
- Consider site-specific objectives (SSOs) for copper for certain water bodies

CDPR indicated that the reformulation of copper AFPs is a major undertaking that registrants are willing to work with CDPR on as part of the re-evaluation. This action alone will reduce copper loading to all California coastal marinas. The CDPR's copper reduction recommendations are discussed in greater detail in the following sections.

4.2.4.1 Copper AFP reformulation

Under the AB 425 requirement, the leach rate determined by CDPR was the maximum allowable leach rate that will serve as a limit for California registered copper AFP products. As described in Section 4.2.4.2, this limit would require 58 percent of registered products to be reformulated with less copper. The reformulation to AFP products with leach rates exceeding the CDRP's recommended leach rate will considerably reduce copper loading in marinas (CDRP 2014). However, not only is product reformulation a key component in reducing copper concentrations in marinas, other critical activities need to be implemented to ensure the overall success of this endeavor, as described in the following sections.

According to CDPR (2014), reformulation of AFPs represents a significant reduction of copper loading to all salt water marinas in California. However, the full water quality impact of the paint reformulation mitigation effort may not be realized for many years due to the timeframes involved with reformulation, re-labeling, registration approval, and market distribution. Moreover, the rate at which boatyards can convert boat hulls (i.e., strip existing AFP and apply a new one) is limited. Therefore, the eventual transition to reformulated AFP products is also dependent on these factors. The CDPR expects to see more immediate improvements in water quality from changes to in-water hull cleaning practices.

4.2.4.2 Establish a maximum allowable copper leach rate for AFPs

As recommended by the CDPR (2014), establishing he most conservative maximum allowable leach rate of 9.5 $\mu g/cm^2/day$ (See Section 2.3.3.2) should result in approximately 58 percent of the currently registered copper AFP products, which is approximately 100 of the 169 copper based AFP products, needing to be reformulated. The highest leaching product currently available has a leach rate of 29.6 $\mu g/cm^2/day$, which would require a 68 percent reduction in leach rate. AFP registrants would be required to demonstrate a reduced copper leach rate to CDPR with studies that are conducted in appropriate California marine settings. Although dissolved copper concentrations in larger marinas may still occasionally exceed the chronic CTR criterion, the eventual reduction in copper loading will increase protection of aquatic organisms in all of California's marinas (CDPR 2014).

4.2.4.3 Hull cleaning BMPs

Reformulated copper based AFP products may take several years before entering the marketplace and be used on boat hulls, however anticipated improvements in BMPs for in-water hull cleaning should have a much more immediate impact on copper loading. Earley et al. (2013) tested an in-water hull cleaning BMP that employed soft pile carpet as the scrubbing material. This BMP came directly out of the California Professional Divers Association's (CDPA) hull cleaning BMP certification manual (CPDA, 2008). The BMP material was tested against a more abrasive non-BMP material. Data showed that the BMP cleaning only contributed to 43 percent (average for epoxy and ablative AFPs) of the copper loading over the 3-year lifespan of the paint compared to 59 percent from the non-BMP cleaning (CDPR 2014).

CDPR (2014) also observed that by limiting the frequency of hull cleaning to monthly during the entire year, up to five less passive leaching spikes are eliminated over the 3-year lifespan of the paint. The cleaning schedule used by Earley et al. (2013) was once every three weeks in the summer (June, July, August) and once every four weeks for the rest of the year. Loading comparisons showed that a monthly frequency of cleaning lowers copper loading from 43 percent to 29 percent over the 3-year lifespan of the paint. Implementation of an even lower frequency of cleaning (e.g., every five weeks, bimonthly) could further reduce copper loading; however, reduction in frequency should be carefully weighted with the benefits of cleaning.

Implementation of these two proposed actions to decrease the magnitude of passive leaching of copper allows CDPR to work with a higher range of leach rates that provide greater flexibility in maintaining sufficient product efficacy in reformulated products (CDPR 2014).

4.2.4.4 Promoting use of less toxic AFPs or non-toxic paints

Boaters can gravitate toward products with lower leach rates that are already on the market to accelerate water quality improvements. CDPR expects to see increased adoption of non-toxic AFP alternatives in the future due to the amount of research, development, testing, and demonstration of alternatives paints that has taken place in recent years. The CDPR model estimated that a 12 percent adoption rate of non-copper alternatives will bring additional marinas in compliance with the CTR criterion. A larger adoption rate will bring even larger marinas into compliance. CDPR will continue to work with stakeholder groups to facilitate greater adoption of AFP alternatives, including non-toxic products that are a growing presence in the marketplace. Efficacy of AFPs is critical for the effective control of native fouling species as well as non-native aquatic invasive species.

The CDPR will also work to promote boater awareness and acceptance of lower copper-based AFPs or non-toxic alternatives, promote new incentive programs, and continue support for existing programs for AFP boat hull conversions to safer alternative paints. To reinforce product-specific requirements for in-water hull maintenance for AFPs to boat owners, brochures or other forms of outreach materials will be distributed. Boatyards could provide brochures to boat owners at the time of painting. More general outreach is important as well in the overall mitigation effort. Other points of information distribution (e.g., marinas, AFP retailers, and boating events) will also be explored.

4.2.4.5 Consider site-specific objectives (SSOs)

The CDPR also recommends the development of SSOs for consideration by the Regional Water Quality Control Boards (RWQCBs). However, before undertaking this effort, the various approaches available should be discussed and approved by the RWQCB. The water effects ratio (WER) approach already exists as an option. The biotic ligand model (BLM), which represents a reliable and economical way to calculate site-specific standards in fresh water, is being evaluated by USEPA for use in marine waters. The SWRCB stated its support of the USEPA in pursuing and making it a priority to complete development of marine water copper criteria using the BLM. The SWRCB also stated that if a BLM for marine water copper criteria was completed it would provide another tool that could be used by the RWQCBs for developing SSOs for copper (CDPR 2014).

4.3 Research Summary

Copper AFPs are a significant source of copper to marinas, causing copper concentrations in many California marinas along the coast to exceed the CTR. However, the marine copper CTR is too conservative and overly protective of aquatic organisms in California marinas. Therefore, site-specific water quality standards are key to determining if a water body should be designated as impaired, thus requiring the implementation of a TMDL program.

Although, current methods for developing SSOs in California are costly, they are still less than the cost of implementing a TMDL program. It is also anticipated that USEPA will approve a marine BLM that will be a cost effective and efficient method to develop SSOs.

The use of the latest science is important to better estimate source loading that can be used to develop effective actions to meet TMDL or water quality standards. By using the latest science effective strategies to meet copper water quality standards include: reducing copper AFP use via reformulation of AFPs to lower copper leach rates and educating boat owners on non-toxic alternatives and the use of hull cleaning BMPs. Additionally, best management practices should be implemented when hull cleaning occurs and seasonal and geographic variations should be considered. By developing site specific water quality standards in conjunction with copper reduction strategies, marinas along California's coast should be able to effectively attain water quality standards.

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